SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF NIOBIUM(V)ARYLOXIDES

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Dedicated
To
My Loving Parents
&
Supervisor

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CERTIFICATE

Certified that **Ms. MALA SHARMA** carried out the research work on "SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF NIOBIUM(V)ARYLOXIDES" under my supervision. This work is original and has not been submitted in any part or any other degree of this or any other university and is worthy of the degree of Doctor of Philosophy

Neeraj Sharma
(NEERAJ SHARMA)

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(Mala Sharma)

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INTRODUCTION

The alkoxo(OR) and aryloxo(OPh/OAr) groups are a class of versatile ancillary ligands in metal-organic chemistry which can be used to tune steric and electronic properties in complexes of intermediate to high oxidation state metal centres (1). In this context, the family of closely-related compounds well recognized as metal alkoxides and phenoxides has been a subject of continuing research interest over the last many years. The use of these π-donor ligands towards main group elements, transition metals, lanthanides and actinides now covers a full gamut of areas (2) ranging from the general considerations of not only the metal-oxygen bonding and electron delocalization in metal complexes but also to a detailed understanding of the properties of complexes viz. the determination of crystal structures, magnetic properties, thermochemical measurements and dramatic spectroscopic manifestations. The chemistry of metal alkoxides and metal phenoxides in recent years is experiencing a renaissance due to the wide applications of these compounds as polymerization catalysts, surfactants and molecular precursors in the synthesis of advanced technological materials based on simple and complex metal oxides.

1.1. Metal alkoxides and their applications

The chemistry of metal alkoxides has extensively been reviewed by Bradley and Mehrotra (3). The chemistry of the C—O bond in alkoxide and related ligands has also been reviewed by Meyer (4). The importance of the alkoxo group in the transition metal alkoxides stems from its ability to act as either a terminal, doubly or triply bridging group (5). The bridging gives rise to coordination polymerization with the formation of oligomeric species wherein the metal achieves preferred coordination geometry (3). However, oligomerization may be suppressed by the use of sterically bulky alkoxo ligands and unusual geometries may be offered. The alkoxo groups are also associated with metal–metal bonds while both theoretical and synthetic studies have shown that these groups are essential for certain organometallic reactions such as olefin and acetylene–metathesis reactions. The alkoxide derivatives of the late transition elements have aroused considerable interest due to their involvement in several catalytic processes e.g. C—O bond formation, cleavage, olefin and alkyne alkoxycarboxylation and olefin polymerization (6). The metal alkoxides also display high reactivity (7), which is sometimes reminiscent of that of metal alkyls (8). Likewise, related low-valent siloxide derivatives are known. The isolation of $(Bu^tSiO)_3Ta$ (9) a highly unsaturated and reactive tantalum(III) compound, is known to engage in a variety of bond activation processes; most notable of which is the facile scission of carbon monoxide into dicarbide and oxo groups.

Metal alkoxides are the most interesting and versatile precursors to obtain oxide-based networks (10) by sol-gel process. The sol-gel chemistry of metal alkoxide precursors has been of immense research interest (11) whereby different factors viz. nature of the metal catalyst, hydrolysis ratio etc. affecting the evolution of the system from the solution upto the gel formation are described (12-14). Furthermore, metal alkoxides [$M(OR)_n$] appear as versatile potential candidates that can meet the requirements for both sol-gel and MOCVD (15) (metal-organic chemical vapour-phase decomposition) conversion of the precursor to the final material.

Owing to the increasing global demand for better systems in chemical industry, the synthesis and development of catalysts has engendered a phenomenal interest. The successful exploitation of a material as a catalyst may afford value-added products with better yields. Many new catalysts have been discovered which can be broadly classified either as homogeneous or heterogeneous catalysts. Though homogenous systems possess several advantages such as better selectivity, activity and reproducibility, however these are associated with several drawbacks like low thermal stability and short catalyst life time, which amplify the cost of production. Hence the synthesis of new heterogeneous catalysts to replace the existing homogeneous systems has been a challenging task in the catalysis field. The potential of metal alkoxides as catalysts is well-recognised. The oxovanadium trialkoxide and functionalized oxovanadium alkoxides find use as a component of homogeneous Ziegler-Natta type catalysts for olefin polymerization and as potential triggers for the production of abzymes with phosphatase activity (16). Compared to lanthanide isopropoxide catalysts reported by Okano (17), alkali metal alkoxides are known to exhibit remarkable catalytic activity for ester metathesis reactions. Bismuth is an important component of oxide ion conductors (18), ferroelectric materials (19), catalysts (20), superconductors (21) and other advanced materials (22). The bismuth alkoxides have been exploited as promising precursors for bismuth oxide containing materials (22), in propene/propane oxidation and ammoxidation. The polymerization of ε-caprolactone has been reported using bulky alkoxo-titanium complexes (23). The multicomponent Ziegler-Natta systems implicating rare-earth alkoxides and organoaluminium compounds display efficient polymerization catalysts in diene and styrene polymerization (24).

Compounds of type [$(M(\mu\text{—}O)_2Al_2(OR)_4)_m$] (M = Co, Zn; R = alkyl) are highly active catalysts for the oxiranes, thiranes, lactones and isocyanides (25), wherein polymerization proceeds by insertion in M—OR bond. The activity of the well defined compound [Ti_2-$(OEt)_8Cl]_2Mg_2(\mu\text{-}Cl)_2$] estimated for the polymerization of polyethylene or 1,3-butadiene in the

presence of $AlEt_3$ and that of the heterometallic catalyst surface formed from $MgCl_2$ and $Ti(OR)_4$ has been compared. A similarity in the microstructure of the high molecular weight polyethylene produced by the two systems has been observed and it has been suggested that the electron donation from the metal chloride to the titanium centre promotes the propagation rate constant as well as the concomitant absence of chain-transfer reaction and thus increases the length of the macromolecular chain. The dimer of composition $[\{Al_3Nd_6(\mu\text{-}Cl)_6(\mu\text{-}Cl)_6(\mu\text{-}Et)_9Et_5(O^iPr)\}_2]$ has been reported to display high activity and stereospecificity for the polymerization of butadiene. The heterometallic alkoxides, involving alkali metals find use in organic synthesis (26).

1.2. Metal aryloxides and their applications

The phenoxide ion finds an important place as ligand in inorganic chemistry because it provides not only a strong metal-oxygen bond but also a flexible organic moiety having advantages over analogous alkoxide ligands in that its electronic properties can easily be varied by changing the substituents in the phenyl ring and steric effects in close proximity to metal can be modified by varying the bulk of the substituents at ortho- and para- positions of the ring. A large number of metal phenoxides containing t-butyl, phenyl, isopropyl, methyl, methoxy, chloro, nitro groups etc. as substituents are well-documented. The ortho substituted phenols draw special attention, as this ring position has the largest effect on the steric "cone" around each metal ion. Of a variety of alkyl/aryl group substituted phenols, 2,6-disubstituted aryloxides, viz. dimethylphenoxide (DMP), di-iso-propylphenoxide (DPP) and di-phenyl phenoxide derivatives have been the subject of intensive research interest. Literature abounds with examples of the synthesis, structural, characterization and reactivity of transition metal phenoxides (27) of industrial importance. Rothwell and co-workers (28-30) have utilized sterically demanding aryloxide ligands to favour monomeric complexes with resultant well-behaved reactivity. The sterically hindered phenols bearing tert-butyl substituents at 2- and 6-positions viz. $2,6\text{-}Bu^t_2\text{-}4\text{-}RC_6H_2OH$ (R = H, Me or Bu^t) which find use as antioxidants have proved to be the source of interesting metal aryloxides which, in general, are hydrocarbon soluble, available in unusually low metal oxidation state and/or coordination number and have a low degree of molecular aggregation. A series of mononuclear niobium(V) and tantalum(V) complexes derived from 2,6-diphenyl-3,5-di-tert-butylphenol $HOC_6HPh_2\text{-}2,6\text{-}Bu^t_2\text{-}3,5$ have been reported (31).

The another reason that why such aryloxide ligands have proved to be of interest is that a methyl group of one or more of the $-Bu^t$ substituents is capable of participating in

cyclometallation reactions (32). The actual pathways leading to C–H bond activation have been established by careful labelling studies (33). The early transition metal chemistry is known to involve the cyclometallation of 2,6-di-t-butyl phenoxide ligands (butylated hydroxybenzene referred as H-BHB, BHB implies the deprotonated anion) (34). A series of mechanistic studies of the reactions at cyclometallated compounds $[Ta(OC_6H_3Bu^t\text{-}CMe_2CH_2)(OPh)_2]$ have shown that these reactions may proceed via indirect and sometimes competing reaction pathways (32). The cyclometallation chemistry of 2,6-diphenylphenoxide ligand (abbreviated as H-DPP; DPP = deprotonated anion) at various p- and d-block metal centres, has been reported (35). The dimethyl derivatives of the type $[M(DPP)_3(CH_3)_2]$ (M = Nb, Ta) are known to generate the monocyclometallated compounds of composition $[M(OC_6H_3Ph\text{-}C_6H_4)(DPP)_2(CH_3)]$ (36). The high-valent early d-block element, lanthanide and actinide metal-hydride bond has been described to be an extremely important functional group implicated in a wide range of stoichiometric and catalytic activity (37). The intramolecular arene hydrogenation has been reported by niobium aryloxides (38).

Malhotra and Martin (2) have reviewed the chemistry of metal phenoxides with regard to their synthesis, structural characterization and applications. The phenol derivatives find use for generating coloured smoke signals in aerospace industry. The organolead phenoxides and copper phenoxides are especially effective fungicides and insecticides. The fungicidal properties of organotin compounds have been reported (39). The coating of plastic mouldings with alkali metal phenolates and hydrolyzates of $[R_nSi(OR)_{4-n}]$ (n = 1→3) find use for improved surface hardness. The cobalt(II) and tin(II) phenoxides find use to inhibit oxidative deterioration of mineral lubricating oils. The multivalent metal salts of substituted phenols have been reported to find use to stabilize vinyl resins, which become effective against high temperature, decolouration and blooming. The polymerization of acrolein is known to be effective in the presence of phosphorus(III) phenoxide as a catalyst (40-49).

The metal aryloxides are also key intermediates in metal-catalyzed C—O bond formations of phenols (50). The titanium alkoxides and aryloxides are extensively used as procatalysts for olefin polymerization (51), oxidation (52), epoxidation (53) and enantioselective carbon-carbon bond formation (54). The titanium aryloxides are able to stabilize unusual coordination polyhedron (55) and also find use to synthesize covalent 2-D and 3-D metal-organic frameworks (56). Titanium(IV) bis aryloxide complexes have been reported to find use as Lewis acid catalysts for processes such as Diels-Alder reactions (57) and a series of monomeric Lewis acid-

base adducts of Diels-Alder catalyst $[Ti(O\text{-}2,6\text{-}Me_2C_6H_3)_2Cl_2]$ with bidentate diphosphines and diamines of composition $[Ti(O\text{-}2,6\text{-}Me_2C_6H_3)_2Cl_2L_2]$ (where L_2 ; dmpe = dimethylphosphinoethane, depe = diethylphosphinoethane, dpeda = diphenylethylenediamine, dmeda = N,N'-dimethylethylenediamine) have been reported. The free radical incorporation of a titanium(IV) aryloxide into a rigid and porous polystyrene/divinylbenzene-based matrix is reported to yield a yellow-orange insoluble polymer. The titanium(IV) aryloxide catalysed cyclization reactions of 1,6 and 1,7 dienes have been reported (58). The dimerization/oligomerization and cross coupling of 1,3-cyclohexadiene with α-olefins has been reported to be achieved using a variety of titanium aryloxide catalysts (28). The ring-opening polymerization of ε-caprolactone (CL) has been reported by scandium tris(2,6-di-tert-butyl-4-methylphenolate) (59). The aluminium(III), samarium(II) and samarium(III) aryloxides have been reported to find use as catalysts for ethylene polymerization (60). The low-valent samarium aryloxides are known to display one of the most remarkable and unpredictable chemical reactivities, with most diversified substrates (61). The aryloxides ligands are important component of many tungsten metathesis catalysts (62). Complexes of composition $[MCl_{6-n}(OPh)_n]$ (M = W or Mo) and monooxo complexes $[WOCl_{4-n}(OPh)_n]$ have been shown to act as catalyst precursors in either the presence or absence of main group cocatalyst such as alkylaluminium complexes or organotin hydrides (63).

The success of group 4 metallocene olefin polymerization catalysts has stimulated interest in the development of related homogeneous catalysts supported by non-Cp ancillary ligation (64). Mannich-type reactions of imines synthesized from aldehydes and 2-aminophenol using a chiral zirconium complex of zirconium(IV) tert-butoxide and (R)-6,6-disubstituted-1,1'-bi-2-naphthols have been reported (65,66). The oligomerization of butadiene to cyclic or linear products is catalyzed by transition metal complexes (67). In recent years, multidentate BINOL derivatives (where BINOL = 1,1'-bi-2-naphthol) have been designed for the establishment of precise asymmetric environments to achieve high enantioselectivity (68-74).

The synthesis of bismuth aryloxide, $[Bi(O\text{-}2,6\text{-}Me_2C_6H_3)_3]$ has been reported by the reaction of bismuth amide $[Bi[N(SiMe_3)_2]_3]$ with 2,6-dimethylphenol (75). Several bismuth oxo aryloxide clusters (76) and bismuth catechols have been reported (77). The more exotic bismuth aryloxides include bismuth calixarenes (78) and a tripodal bismuth aryloxide that forms an inverted sandwich structure with toluene as the π-donating ligand. The aryloxide-based multidentate ligands (79) have been reported to stabilize the chemistry of early transition metal

and f-element complexes. There is currently a great deal of interest in the synthesis and characterization of metal-organic frameworks and coordination polymers (80). A common strategy for the synthesis of these materials is the building-block approach, in which isolated metal atoms or metal clusters are linked by bridging organic ligands (81).

A new class of bis(-aryloxy) bridged dimers with first row transition metals of composition $[(Et_4N)_2[M_2Cl_4(OC_6H_4CH_3\text{-}p)]$ (M = Mn(II), Fe(II), Co(II), Zn (II) and Cd(II)) have been reported by anaerobic reaction of equimolar amounts of Et_4NCl, $NaC_6H_4CH_3$-p and appropriate anhydrous bivalent metal chlorides (82). The binuclear cobalt(II), nickel(II), copper(II) and zinc(II) complexes of composition $[M_2L^{1,2}(\mu\text{-}Cl)Cl_2].nH_2O$ with Schiff-base ligands (where L^1H and L^2H are the potential pentadendate ligands derived by condensing 2,6-diformyl-4-methylphenol with 4-amino-3-antipyrine and 2-hydroxy-3-hydrazinoquinoxiline, respectively) have been reported (83). The dinuclear titanium(IV) complexes bearing phenoxide-tethered N-heterocyclic carbene ligands with cisoid conformation through control of hydrolysis (84) have been reported. A phenol based novel macrocyclic binucleating compartmental ligand N,N-bis(2,6-diiminomethyl-4-methyl-1-hydroxyphenyl)malonoyldicarboxamide has been reported. A series of dinuclear complexes by the reaction of Cu(II), Ni(II), Co(II), Cd(II), Zn(II) and Hg(II) chlorides with 2,6-diformyl-4-methylphenol malonoyl dihydrazide have been reported (85). The synthesis of a binuclear nickel(II) complex of composition $[Ni_2C_{26}H_{22}N_4O_{10}Cl_2]$ with Hsalamp (2-[(4-methylpyridin-2-ylimino)-methyl]-phenol has been reported (86).

The reactions of $[TiCl_3(thf)_3]$ and $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with 2,6-$Bu^t_2C_6H_3ONa$ and 2,6-$Me_2C_6H_3ONa$, have been reported to yield the corresponding monophenoxo derivatives (87). The mononuclear aryloxides of titanium, zirconium and hafnium of composition $[MCl(OC_6H_3\text{-}2,6\text{-}Bu^t_2)_3]$ have been reported (88). A blue mononuclear paramagnetic complex $[Ti(OC_6H_3Bu^t_2)_3]$ has been reported. A series of cis and trans-mer-$[MCl_3(OC_6H_3Pr^i_2\text{-}2,6)_2(L)]$ adducts have been reported by the reactions of chloro-aryloxides $[M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]_2$ and $[M(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2]_2$ (M = Nb, Ta) with pyridine and PMe_2Ph (L) (43).

The chelating aryloxides represent a useful class of ancillary ligands in postmetallocene R-olefin polymerization catalysis (89). Miyatake and Kakugo (90) have reported good activities for ethylene polymerization using X_2Tidiphenolate/MAO (X = Cl, Pr^i) systems. Extensive alkylation

studies have also been reported using Cl_2Mdiphenolate (or binaphtholate) type complexes (M = Ti, Zr) with lithium alkyls or via reaction of the tetrabenzyls $M(CH_2Ph)_4$ with the appropriate biphenol or binaphthol by Schaverian and co-workers (91). Okuda and coworkers (92), have reported the nature of the bridging group ($-CH_2-$, $-CH_2CH_2-$, -S-, -SO-) in diphenolate ancillary ligands upon the resulting catalytic activity in the copolymerization of styrene with ethylene. The bridging groups, including -Te- and $-SO_2-$, have also been successfully used in ethylene polymerization (93). Such studies led to the development and use of more functionalized bridges in bis(phenolate)-type ligands, typified by amine bis(phenolate) ligands with a $-CH_2N(R)CH_2-$ bridge (R = $CH_2CH_2CH_3$, $CH_2CH_2NMe_2$) primarily for 1-hexene polymerization (94). The chelating trisphenol ligands tris(2-hydroxyphenyl)amine and tris(2-hydroxy-4,6dimethylbenzyl)amine proved to be the excellent precursors for the chelating phenoxides, and the latter has been used to prepare a series of cyclopentadienylmetal derivatives of early transition metals (95).

The coordination chemistry of model phenolic ligands (pyrocatechol, salicylic acid and 2,2′-biphenol) able to form five-, six-, or seven-membered rings respectively with titanium(IV) aryloxides has been reported (96). The coordination chemistry of main-group and transition metals involving o-phenylene derived hybrid chelating ligands containing both soft and hard donors has been described (97). The chelating (poly)phenolate ligands such as $(OPO)^{2-}$ are currently receiving considerable attention, particular for group 4 chemistry, due at least in part, to their potential use as homogeneous catalyst precursors for polymerization of terminal olefins and ring-opening polymerization of heterocyclic molecules (98). The catechol (1,2-dihydroxybenzene) is a potent bidentate ligand with high affinity for metals in high oxidation state (99). The chelating 3,3′-R^1-5,5′-R^2-2,2′-dithiophenyl ligands ($R^1 = R^2$=Cl, $R^1 = R^2 = Bu^t$, R^1 = allyl R^2 = H) and the 2,2′-methylenedibenzenethiol ligand (4d) has been reported to be synthesized from the corresponding diols via a three-step procedure involving Miyazaki-Newman-Kwart rearrangement (100). The thiophenolate-based ligand systems coordinated to transition metals have been successfully applied in homogeneous catalysis and bioinorganic model chemistry (101). The particular classes of chelating dithiolate ligands studied extensively are the1,1-dithiolates (such as dithiocarbonate, xanthate, etc.) (102), 1,2-dithiolates (mainly dithiolene type ligands and related systems such as 1,2-benzenedithiol (103), 2,3-dimercaptomaleonitrile (104), 4,5-dimercapto-1,3-dithiole-2-thione, etc. (105)).

The chemistry of tungsten aryloxides has been an area of intense interest (106). Complexes of tungsten(IV) and (VI) containing 2,6-diphenyl phenoxide ligands have been described by Kerschner and coworkers (107). The oxotungsten(VI) complexes of the type $[WOCl_2(OPh)_2]$ (OPh = $OC_6H_3Bu^t$-2-Me-6 and $OC_6H_2Bu^t$-2-Br-6-Me-6) have been reported to be synthesized by the reaction of $WOCl_4$ with phenolic ligands in toluene (108). The sodium amalgam reduction (2 Na per W) of hydrocarbon solutions of $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_4]$ in the presence of pyridine or 4-tert-butylpyridine has been reported to afford tungsten(IV) compounds $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(py)_2]$ and $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2$(4-tert-butylpyridine)$_2]$ (109).

The synthesis of $[MoO_2(OPh)_2]$ from MoO_2Cl_2 and the formation of four, five and six-coordinate analogues by manipulation of the steric environment of the aryloxy ligand has been described (110). The monooxo compounds of composition $[MoOCl_{4-n}(OPh)_n]$ (n = 0-2, Ph = 2,6-$Me_2C_6H_3$ or 2,6-$Pr^i_2C_6H_3$) have been reported to be synthesized from the dioxo precursor MoO_2Cl_2 (111). The likely mechanism involves phenol precoordination followed by addition across the Mo=O bond. The reaction of $Mo_2(OPr^i)_6$ and $Mo_2(NMe_2)_6$ with 2,6-dimethyl and 2,6-diphenylphenol have been reported to yield the mixed ligand complexes of composition [1,2-$Mo(NMe_2)(OPh)_2$] and [1,2-$Mo_2(NMe_2)_3(OPh)_3$]. On the other hand, the sterically less demanding ligands 4-methylphenol, 3,5-dimethylphenol and 2-tert-butyl-6-methyl-phenol have been found to give salt complexes $[Me_2NH]_2[Mo_2(OPh)_7(HNMe_2)]$ and $[Mo(OPh)_2(NMe_2)_4]$ respectively. The reactions of Mo(alkyne)Cl_4(ether) with 2,6-diisopropylphenol (DIPP) salts is known to yield complexes [Mo(alkyne)$(DIPP)_2Cl_2$], [Mo(alkyne)$(DIPP)_3Cl$] and [Mo(alkyne)$(DIPP)_4$] (alkyl = EtC≡CEt or PhC≡CPh) (112).

The reactions of trans-Ti$(TMEDA)_2Cl_2$ (TMEDA = N,N,N′,N′-tetramethylethylenediamine) with two equivalents of RONa [R = Ph and 3,5-$(Bu^t)_2C_6H_3$] have been reported to yield paramagnetic linear trimeric Ti(III) derivative $[Ti_3(OPh)_9(TMEDA)_2]$ and the pink dimeric complex $[Ti(RO)Cl(TMEDA)]_2(\mu\text{-}OR)_2]$ (R = 3,5-$(Bu^t)_2C_6H_3$) respectively (113). The formation of $[PdCl[N(SiMe_3)_2](TMEDA)]$ has been reported by the reaction of $PdCl_2$(TMEDA) with $NaN(SiMe_3)_2$ (114). The homoleptic phenoxides $[Re(DIPP)_4]$ and $[Re(DMP)_4]$ have been reported to be synthesized by the reaction of $ReCl_4(THF)_2$ with Li(DIPP).OEt_2 and Li(DMP).THF respectively (115).

The titanium(IV) complexes supported by (2,2′-phenylphosphino)bis(4,6-di-tert-butylphenolate) $(OPO)^{2-}$ have been reported (116). The dibenzyl compounds $(PhO)_2M(CH_2Ph)_2$

(PhO = 2,6-diphenyl-3,5-dimethylphenoxide, M = Ti, Zr; PhO = 2,6-diphenylphenoxide, M = Ti) react with $B(C_6F_5)_3$ to afford the corresponding zwitterionic species $[(PhO)_2M^+(CH_2Ph)(\eta^6\text{-}C_6H_5CH_2B^-(C_6F_5)_3)]$. The addition of $B(C_6F_5)_3$ to titanium dimethyl compounds $(PhO)_2TiMe_2$ yield unstable species capable of polymerizing ethene and propene (117). A number of mononuclear homoleptic aryloxides of titanium(IV) and zirconium(IV) of composition $[Ti(OC_6H_3Pr^i_2\text{-}2,6)_4]$, $[Ti(OC_6H_3Me_2\text{-}2,6)_4]$, $[Zr(OC_6H_3Pr^i_2\text{-}2,6)_4]$ have been described and their chemical and electrochemical reduction behaviour has been investigated (118). The transformation of H_2 and CO with zirconium complexes supported by 2,6-bis(3-tert-butyl-5-methyl-2-oxybenzyl)-4-R-anisole ligands has been reported (119). Compounds of composition $[Ta(OC_6H_3Me_2\text{-}2,6)_3Cl_2]$ and $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2]$ (120) and their corresponding diphenyl compounds have been reported. A family of tantalum compounds derived from triaryloxide $(R\text{-}L)^{3-}$ ligands ($H_3(R\text{-}L)$ = 2,6-bis(4-methyl-6-R-salicyl)-4-tert-butylphenol, where R = Me or Bu^t) has been reported (121). The synthesis of sterically hindered trisphenoxide complexes of tantalum(V) of composition $[TaCl_2(OC_6H_3Bu^t_2\text{-}2,6)_3]$ and $[Ta_2Cl(\mu\text{-}Cl)_2(OC_6H_3Pr^i_2\text{-}2,6)_5(\mu\text{-}O)]$ by the reaction of tantalum(V) chloride with lithium salts of 2,6-di-t-butylphenol and 2,6-di-isopropyl phenol, has been reported by Clark and coworkers (122). The degree of substitution by –OPh for chlorine has been reported to depend upon the alkyl substituents e.g. in case of 2,6-dimethylphenol, total substitution occurs to yield $[Ta(OC_6H_3Me_2\text{-}2,6)_5]$ while for the sterically demanding 2,6-di-t-butylphenoxide, the disubstituted mononuclear $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$ is formed (123). Compounds of composition $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(CH_3)_3]$ and $[Ta(OC_6H_2Bu^t_2\text{-}2,6\text{-}OMe\text{-}4)_2(CH_3)_3]$ containing sterically demanding aryloxide ligands have been reported. The protonolysis reactions between $Ge[N(SiMe_3)_2]_2$ and substituted phenols have been reported to yield new germanium(II) aryloxide complexes $[Ge(OPh)_2]_n$ (n = 2, OPh = $OC_6H_2Me_3$-2,4,6 or $OC_6H_3Pr^i_2$-2,6; n = 1, OPh = $OC_6H_3Ph_2$-2,6 or OC_6HPh_4-2,3,5,6 (124). The reactions of alkaline-earth diiodides with potassium salts of alcohols and phenols have been reported to yield soluble alkoxides and aryloxides of calcium and barium. The formation of hydrocarbon-soluble $[Ca(OPh)_2(THF)_3]$ has been reported by the reactions of CaI_2 with bulky 2,6-di-tert-butyl-4-methylphenol aryloxide ligand $(OC_6H_2\text{-}t\text{-}Bu_2\text{-}2,6\text{-}Me\text{-}4)^-$ in THF (125).

The homoleptic group 10 aryloxides consisting of discrete molecules have been reported to be formed from the reaction of $NiBr_2(dme)$ (dme = ethylene glycol dimethyl ether) or $PdCl_2(MeCN)_2$ with sodium salts of bulky phenols. The nickel 2,6-diisopropylphenolate has been described to be a trimer, displaying σ-coordinated aryloxide ligands, while the nickel and

palladium derivatives of 2,6-di-tert-butylphenol are monomers exhibiting unprecedented π-allylic, sandwich-like structure (126). The formation of two related phosphonium aryloxides, $[Ph_3PCH_3]_2^+$ $[CH_2(C_6H_2\text{-}3,5\text{-tert-butyl-4-}O)_2]^{2-}$ and $[Ph_3PC_2H_5]_2^+[CH_2(C_6H_2\text{-}3,5\text{-tert-butyl-4-}O)_2]^{2-}$ has been reported by protonation of nonstabilized phosphorus ylides with 4,4′-methylenebis(2,6-di-tert-butylphenol) (127).

The knowledge about chemical, structural and applied aspects of alkoxo and aryloxo chemistry of lanthanoids, yttrium and scandium has progressed quickly during the last decade (128). The reactions of various highly substituted lanthanide(III) and (II) aryloxide complexes with trimethylaluminium (TMA) have been investigated (129). The solvent-free, π-arene-bridged dimers $[La(OPh^{i\text{-}Pr,H})_3]_2$, derived from aryloxide ligand $OC_6H_3Pr^i_2$-2,6, form bis-trimethyl aluminium adducts, $[La(OPh^{i\text{-}Pr,H})_3(AlMe_3)_2]$, for the metal centres yttrium, samarium and lanthanum. The homoleptic monomeric $Ln(OPh)_3$, featuring a large lanthanum centre and sterically bulkier ortho-Bu^t_2-substituted aryloxide ligands, afford the mono-TMA adducts $[La(OPh^{t\text{-}Bu,R})_3(AlMe_3)]$ (R = H, Me). Evans and coworkers have reported the utility of 2,6-dimethylphenoxide ligand to provide halide and oxide free complexes of composition $[Y(OR)_3(solvent)_a]_6$ with enough steric flexibility to achieve five and six-coordination viz. $[Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3]$ and to form bridged bimetallic species $[Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2]$ (130). A fully characterized homoleptic complex of composition $[Y(OC_6H_3{}^tBu_2\text{-}2,6)_3]$ with an unusually low coordination number of three has been described (131).

Several synthetic procedures have been developed for the preparation of early actinide aryloxide complexes. The simple alcoholysis of actinide metallacycle $\{[(Me_3Si)_2N]_2An(CH_2SiMe_2NSiMe_3)\}$ [An = Th and U] with one equivalent of 2,6-disubstituted phenol is known to result in the protonation of An–C bond to form mono(aryloxide) complexes $An(O\text{-}2,6\text{-}R_2C_6H_3)[N(SiMe_3)_2]_3$ [An = U; R = Bu^t and Pr^i; An = Th; R = Bu^t and Me] in essentially quantitative yield (132). Compound of composition $U(BHB)_4$ has been reported to be synthesized by the reaction of $[(Me_3Si)_2N]_2UN(SiMe_3)SiMe_2CH_2$ with 2,6-di-t-butylphenol by William and coworkers (133). The formation of 1:1 and 1:2 addition compounds of $U(BHB)_3$ with t-butylisocyanide have been reported (134).

1.3. Niobium alkoxides and their applications

Like other transition metals, much interest has been shown in the coordination chemistry of niobium with the related classes of oxygen-containing ligands such as alkoxide, siloxide and

aryloxide derived from alcohols, silanols and phenols because of their immense potential applications. Interestingly, niobium alkoxide and aryloxide complexes have been the subject for numerous studies due to their significant applications in materials science.

The pentaalkoxy compounds of niobium and tantalum of composition $M(OR)_5$ [R = Me, Et, n-Pr, n-Bu, n-pentyl] have been reported to be synthesized by the reaction of metal pentachlorides with the respective alcohols in ammonical benzene. The $Nb(OMe)_5$ and $Ta(OMe)_5$ are solids at room temperature while other normal penta-alkoxides are liquids (135). The reactions of niobium pentachloride with ROH (where R = Me or Et) are known to provide interesting studies. Complexes of composition $[NbCl_{5-n}(OMe)_n]$ have been characterized using ^{93}Nb and ^{1}H NMR spectroscopy (136). A report by Kolditz and Schönherr (137), that only $[NbCl_2(OMe)_3]$ is formed in non-polar solvents on adding excess of MeOH to $NbCl_5$ has also been confirmed by Crayston and coworkers (138) indicating $[NbCl_3(OMe)_2]$ to be unstable, disproportionating to $[NbCl_4(OMe)]$ and $[NbCl_2(OMe)_3]$ (139). The addition of $NbCl_5$ or $NbBr_5$ to a series of magnesium, lithium or potassium allylic or propargylic alkoxides has been reported to provide allylic or allenic halides (140). The preparation of alkoxides of composition $[(CH_2{=}CH\text{-}CH_2O)_5M]_2$ (M = Nb or Ta) has been reported by the reaction of the corresponding metal isopropoxides with allyl alcohol (141). The exchange of the alkoxy group of $M(OR)_5$ by other alcohols has been reported to result in the formation of a number of compounds containing different alkoxy groups (142). The formation of a new series of niobium oxychloride cluster compounds, $[A_2Ti_2Nb_6Cl_{14}O_5]$ (A = K, Rb, Cs) has been reported from stoichiometric amounts of ACl (A = K, Rb, Cs), Ti, Nb_2O_5, $NbCl_5$ and Nb heated at 750°C (143). The reactions of dimeric alkoxo complexes $[Nb(OR)_5]_2$ with CO_2 have been reported to yield $[Nb(OR)_4(OC(O)OR)]$ (R = Me, Et, allyl) (144). Thermal decomposition of oxomethoxo compounds $[Nb_4O_2(OMe)_{14}(ReO_4)_2]$ and $[Ta_4O_2(OMe)_{14}(ReO_4)_2]$ has been reported (145). The trialkoxydichloride niobium(V) complexes of composition $[Nb(OR)_3Cl_2]$ (where R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9) have been reported (146). The preparation of alkoxy halides of composition $[MX_{5-n}(OR)_n]$ (X = F, Cl, Br); (n = 1→5) has been reported by the interaction of stoichiometric amounts of alcohol with niobium and tantalum pentahalides in CCl_4, CH_3CN or by the halogenation of the alkoxides with acetyl halides (147). The halogen alkoxides are known to dimerize in non-polar solvents such as benzene but polar solvents offer transfer of the alkoxy group or halide with the formation of cations and anions as

$$2NbCl_4(OC_2H_5) \quad \rightarrow \quad (NbCl_3OC_2H_5)^+ \quad + \quad (NbCl_5OC_2H_5)^-$$

The metal chloride alkoxides with higher halogen content are known to show an increased tendency to form solvates (148). Compound of composition $[NbCl_4(OC_2H_5)]$ is known to precipitate from CH_3CN as 1:1 adduct while $[NbCl(OC_2H_5)_4]$ crystallizes from CH_3CN without a solvate molecule. A solvate free compound can be prepared simply by using a nonpolar solvent such as carbon tetrachloride. Gibson (149) has reported the preparation of complexes of composition $[Nb(OR)Cl_4]_2$ (where R = Me, Et, $SiMe_3$) from the reactions of niobium pentachloride with appropriate trimethylsilylethers Me_3SiOR. The niobium(V) complex of composition $[Nb(OPr^i)_3(diket)(NCS)]$ (diket = $PhCO(CH)COPh)^-$ has been reported to exhibit a fac-octahedral structure (150-152). The reactions of $[Nb(OPr^i)_5]$ with acetic acid has been reported to yield $[Nb_4O_4(OAc)_4(OPr^i)_8]$ (153).

The formation of niobium(III) and niobium(IV) alkoxides of composition $[Nb_2Cl_5(OR)(HOR)_4]$ (R = Me, Et, Pr^i), $[NbOCl_4(OR)_2(THF)_2]$ (R = Et, Pr^i) (154), $[Nb_2Cl_4(OMe)_4(CH_3CN)_2]$, $[Nb_2Cl_4(OR)_4(HOR)_2]$ (R = Me, Et, Pr^i) (155), $[Nb_2Cl_2(OEt)(O_2CMe)_5]$ (156) and $[Nb_2(OMe)_9]$ (157) has been described. The niobium (IV) dichloride dimethoxide complexes of composition $[Nb_2(\mu\text{-}OMe)_2(OMe)_2Cl_4(L)]$ (L = MeOH, MeCN) also display the edge-shared bi-octahedral structure (158). A similar structure has been reported for Nb(III) complex $[Nb_2(\mu\text{-}OPr^i)(\mu\text{-}Cl)(Pr^i(OH)_4Cl_4]$ having $[Nb(\mu\text{-}OPr^i)(\mu\text{-}Cl)Nb]$ double bridge (159). The $[Nb_2(\mu\text{-}OMe)_3(OMe)_6]$ anion has been reported to exhibit confacial bi-octahedral structure in three related salts $\{[Mg(MeOH)_6][Nb_2(OMe)_9]Cl_3\}$, $\{[Mg(MeOH)_6][Nb_2(OMe)_9]1.2MeOH\}$ and $\{[Na(MeOH)_6][Nb_2(OMe)_9]\}$ (160). The hexanuclear niobium and tantalum cluster units of composition $\{[M_6X_{12}][OMe]_{24}MeOH\}$ and $\{M[Ta_6C_{12}][OMe]_6.6MeOH\}$ (M = Nb, Ta, X = Cl, Br, M = alkali metal) have been reported (161).

The metal alkoxides $[M(OR)_n]$ are excellent precursors for the preparation of metal oxides and the current interest in using metal oxides in optoelectronics, high-T, superconductors and ceramics has led to a resurgence of interest in the chemistry of these compounds. The formation of binary organic-inorganic gels has been reported by mixing a carbonaceous hydrosol and Nb_2O_5 or Ta_2O_5 sol derived by hydrolysis of alkoxides (162). The formation of ultrafine Nb_2O_5 doped $SrTiO_3$ powders by sol-gel precipitation process from precursor titanyl acylates using acetic acid and chelating titanium alkoxides in strong alkaline solution has been reported. The manufacture of composite alkoxides as precursor of bismuth containing layered pervoskite type compounds by the reaction of double alkoxide $Sr(Bi(OR)_4)_2$ with $Ta(OR)_5$ or $Nb(OR)_5$ for the

preparation of ferroelectric thin films in memory devices has been reported. A number of functional eletroceramics incorporate niobium as one of the elemental constituents, including many important materials such as lead magnesium niobate, $[Pb(Mg_{1/3}Nb_{2/3})O_3]$ (PMN) (163) which is one of the most important niobate ceramics with potential applications in capacitors and transducers. Several niobium precursors have been utilized for the preparation of PMN including niobium ethoxide, niobium pentachloride and potassium orthoniobate (164). Niobium is also an important dopand in ferroelectric oxides such as lead zirconium titanate $[Pb(Zr,Ti)O_3]$ (PZT) (163), niobia-silica (NS) mixed-oxide sols (165) and lithium niobate $[LiNbO_3]$ ceramics to provide numerous performance enhancement (166). Lithium niobate powders have been reported to be prepared from LiCl and a water-soluble complex synthesized from DL-malic acid (MA) and $NbCl_5$ (167). The modification in bulk PZT with a small amount of niobium has been reported to increase dramatically the piezoelectric coefficient by up to 80% and the electromechanical coupling factor by 30% (168). The niobium doping is known to enhance significantly the displacement without increasing the hysteresis loss (169), desirable for thin-film microelectromechanical systems (MEMS). The niobium doping has been reported to reduce the electrical leakage and to provide improved electrical breakdown strength (170). The niobium doping also minimizes imprint (171) and coercivity for ferroelectric memory applications.

The reactive sputtering, sol-gel, laser ablation and metal-organic chemical vapour deposition (MOCVD) (172) processes find use to deposit high-quality, thin-film Nb doped PZT (PNZT). The modification of PZT has been described using liquid-delivery MOCVD (173) which requires to identify a set of precursors with well-matched chemical and thermal stability and transport, vaporization and decomposition properties (174). The good quality PZT thin films have been reported to be prepared using the set of Pb-Zr-Ti precursors (175). The niobium tetrakis(isopropoxide)-2,2,6,6-tetramethyl-3,5-heptanedionate, $[Nb(OPr^i)_4(thd)]$ find use as precursor for doping of PZT thin films (163). A number of unique niobium alkoxides find use into novel solution processes for the production of lead magnesium niobate oxide (PMN) and niobium-doped lead zirconate tiatanate oxide (PNZT) materials (176). The multicomponent niobates, belonging to the pervioskite and tungsten bronze crystal families, possess useful electrical and electro-optic properties (177).

The addition of niobium oxides, in small amounts to known catalyst, is known to enhance markedly catalytic activity and selectivity and prolong catalyst life for various reactions. Layer compounds containing niobium combined with metal show peculiar photocatalytic activity

(178). Niobium compounds and materials such as niobium pentoxide (Nb_2O_5), niobic acid ($Nb_2O_5.nH_2O$), niobium phosphate ($NbOPO_4$), niobium layer compounds ($K_4Nb_6O_{17}$,$HCa_2Nb_3O_{10}$, etc.) and mixed oxides containing niobia (Nb_2O_5–SiO_2, Nb_2O_5–Al_2O_5, Nb_2O_5–TiO_2, Nb_2O_5–V_2O_5, etc.) have been found to be useful as promoters and supports of catalysts and as unique solid acid catalysts, selective oxidation catalysts and photosensitive catalysts. Recently, several mesoporous metal oxides synthesized by neutral templating and ligand-assisted templating methods have been reported (179). Metal oxides for mesoporous materials are often more susceptible to hydrolysis, redox reactions or phase transitions accompanied by thermal damage of the structural integrity, while silica and aluminosilicates are typically stable materials (180). The formation of highly ordered mesoporous materials has been reported with titanium (181), vanadium (182), zirconium, tungsten, niobium and tantalum oxides (183), while the most mesoporous metal oxides show non-ordered pores originated from the void among the particles (184). One–pot synthesis of Pt and Pt-Pb nanoparticles incorporated into the pores of mesoporous niobium oxide-carbon composites find use as fuel cell electrodes (185). The influence of niobium source on the structural properties and the incorporation of niobium species into the walls of FDU-1 molecular sieves has been reported (186). The mesoporous niobium-tantalum mixed oxide with a wormhole like structure has been reported (187). The synthesis of microporous transition metal oxide molecular sieves by a supramolecular templating mechanism from niobium alkoxides has been reported (188).

A partial hydrolysis of niobium or tantalum alkoxides containing iron, calcium, strontium, sodium and uranium as impurities in solution state, is known to provide high purity niobium and tantalum oxides for electronic parts. Niobium pentoxide materials find use as effective catalysts for a variety of acid and redox reactions (e.g. dehydration of alcohols, esterifications etc.). The catalysts of Nb_2O_5/SiO_2-Al_2O_3 have been reported with 2, 5, 10, 15, 20 and 25 wt % of Nb_2O_5 by aqueous solution impregnation using ammonium niobium oxalate on silica-alumina (189). Niobium pentoxide is an interesting catalyst because of its acidity and water-tolerant properties (190). There are many roles for this oxide acting in catalysis, such as promoter, support, acid catalyst and redox materials (191). The high catalytic activities, selectivities and stabilities of niobium compounds and materials and metals (Rh, Pd, Ni, Co, etc.) supported on Nb_2O_5 have been demonstrated for various reactions (192). Propylene has been reported to be oxidized by air to acrylic acid over catalysts containing oxides of arsenic, niobium or tantalum and molybdenum (193).

One of the major applications of niobium-based catalysts which possess good Lewis acidity has been in the area of oxidation catalysis. The molecular structures and redox properties of different niobia-containing catalysts have been investigated for several different oxidation reactions (194). The application of niobium pentachloride as Lewis acid in organic synthesis has been recently reviewed. Since then the use of niobium catalysts in organic reactions such as Biginelli reactions, Friedel-Crafts acylation and Sakurai-Hosomi reactions of acetals, Knoevenagel condensation, acetylation of alcohols and phenols is well established. The chiral niobium complexes have been reported to give high enantiomeric excesses in asymmetric Mannich-type reactions (195). The catalytic behaviour of niobium materials has recently been reviewed (196).

The compounds derived from transition metals and group III, IV or V elements containing polyfluoroalkoxide ligands and early transition metal dichalcogenides constitute promising cathode materials for lithium batteries (197). The layered metal disulfide films (MS_2) because of their applications as cathode materials for lithium batteries and as solid lubricants have drawn an immense research interest (198,199). The thio "sol-gel" reaction of titanium alkoxides or thiolates with H_2S has been yielded bulk TiS_2 (200). The preparation of TiS_2 thin films via dual and single source chemical vapour deposition (CVD) has been reported (201). The alkanethiol adducts of composition $[TiCl_4(HSR)_2]$ function as molecular precursors to high quality titanium disulfide films (198). The titanium thiolate complexes $[Ti(S\text{-}t\text{-}Bu)_4]_{12}$ and $[Ti(S\text{-}t\text{-}Bu)_3\text{-}(NEt_2)]_{14}$ function as molecular precursors to TiS_2 thin films. The CVD routes for niobium disulfide(NbS_2) films are limited (202). The single source precursor $[NbCl_4(S_2\{CH(CH_3)_2\}_2)][NbCl_6]$ has been reported to afford the formation of mixed $[Nb_2O_5/NbS_2]$ films via CVD. The homoleptic thiolate derivative of niobium (203) of the type $[Nb(SR)_5]$, might function as precursors to NbS_2 thin films. The adducts derived from niobium pentachloride with organosulphides afford complexes of composition $[NbCl_5(R_2S)]$ (204). The polymeric precursors prepared from the reaction of niobium alkoxide, tantalum alkoxide and molybdenum ethylene glycolate with a chelating reagent (acetylacetone) and organic compounds having two or more reactive –OH groups such as ethylene glycol, saccarose, tartaric acid and dihydrobenzene find use for the preparation of NbC, TaC and Mo_2C fibres and films (205).

The aqueous solution chemistry of niobium is although unexplored yet a new niobium aqua ion is formed upon treatment of zinc-reduced ethanolic solutions of $NbCl_5$ with HCl in the presence of a sulphide source (206). The homogeneous hydrogenation of a variety of arene

substrates has been reported to be catalyzed by hydride derivatives of niobium and tantalum containing bulky ancillary aryloxide ligation. Niobium compounds possess an ability to rapidly hydrogenate arylphosphine ligands providing a new procedure for the synthesis of cyclohexylphosphine ligands (207). The gelation behaviour of niobiumchloroalkoxides in alcoholic solutions has been interpreted from Flary, Stockmeyer theory of gelation and particle charge model (208).

1.4. Niobium aryloxides and their applications

The chloroaryloxides and pentaphenoxides of niobium and tantalum of composition $[MCl_{5-x}(OPh)_x]$ (M = Nb or Ta) have been reported (209-210), to be dimeric through phenoxy bridging both as solids and in coordinating solvents (211-212). The preparation and characterization of napthoxides of niobium(V) and tantalum(V) has been reported (213-215). The monomeric homoleptic aryloxides of composition $[Nb(OC_6H_3Me_2\text{-}2,6)_5]$ (216) and edge–shared bi-octahedral $[Ta_2(\mu\text{-}OC_6H_4Me\text{-}4)_2(OC_6H_4Me\text{-}4)_8]$ (217) exhibiting trigonal bipyramidal geometry have been reported to find utility as precursors for low valent derivatives. The structural studies have shown a square-pyramidal geometry for bulky aryloxides e.g. $[Ta(OC_6H_3B^tu_2\text{-}2,6)_xCl_{5-x}]$ [x = 2,3; axial OPh] while complexes of composition $[M(\mu\text{-}Cl)_2(OC_6H_3Pr^i_2\text{-}2,6)_3]$ (M = Nb, Ta) have been described to be dimeric with chloro bridges. The tribromide complex $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2Br_3]$ has been reported to exhibit square pyramid geometry while the triiodide complex $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2I_3]$ has been described to display trigonal bipyramidal environment around niobium with axial OPh groups.

The three homoleptic aryloxides $[Nb(OPh)_5]$ (OPh = OPh-4-Me, OPh-3, 5-Me_2 and OPh-2, 6-Me_2) have been reported by Chamberlain and co-workers (218). The sodium amalgam reduction of hydrocarbon solutions of $M(OPh)_3Cl_2$ (M = niobium and tantalum) or $[Nb(OPh)_2Cl_3]_2$ (OPh = 2,6-di-isopropylphenoxide) in the presence of either 1,3 or 1,4-cyclohexadiene is known to yield complexes $[M(OPh)_3Cl(\eta^4\text{-}C_6H_8)]$ and $[Nb(OPh)_2Cl(\eta^4\text{-}C_6H_8)]$ respectively, which upon hydrolysis, yield 2,6-di-isopropylphenol and one equivalent of cyclohexane (219). The synthesis and characterization of niobium(V) complexes of 4-tert-butyl and 4-methoxyphenol has been reported (220-222). The preparation of 4-methylbenzyl derivatives of composition $[M(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4Me\text{-}4)_3]$ and $[M(OC_6H_2Ph_3\text{-}$

2,4,6)$_2$($CH_2C_6H_4Me$-4)] (where M = Nb, Ta) by the reaction of [M($OC_6H_3Ph_2$-2,6)$_2Cl_3$] or [M($OC_6H_2Ph_3$-2,4,6)$_2Cl_3$] with [Mg($CH_2C_6H_4Me$-4)$_2$], bis(4-methylbenzyl)-magnesium has been reported (223). The solid state structures of mixed aryloxide phenyl compounds of tantalum and correlation with alkylaryloxides of niobium has also been reported (224).

The synthesis and characterization of two four coordinate niobium oxophenoxides of composition [Nb(O)($OC_6H_3R_2$-2,6)$_3$] (R = Me, Bu^t) via the reaction of [$NbOCl_3(CH_3CN)_2$] with bulky dimethyl and di-t-butyl phenoxide ligands has been reported. The Nb–O bond lengths and Nb–O–C angles in tetrahedral [NbO($OC_6H_3Ph_2$-2)$_3$] have been reported to be a typical of the mono-oxoniobium(V) compound, however, these adopt a distorted octahedral form. The synthesis and structural characterization of monomeric lithium niobium(V) oxoaryloxide, [LiNbO($OC_6H_3Me_2$-2,6)$_4$.3THF] and a dimeric lithium niobium(IV) chloroaryloxide [LiNbCl($C_6H_3Me_2$-2,6)$_4$] has been reported.

The synthesis of a series of niobium(V) complexes derived from linear linked aryloxide trimers 2,6-bis(4,6-dimethylsalicyl)-4-tert-butylphenol[H_3(Me-L)] and 2,6-bis(4-methyl-6-tert-butylsalicyl)-4-tert-butylphenol(H_3^{t}Bu-L) has been reported (225). The use of linear linked aryloxide trimers (H_3R-L) as new ancillary ligands in which aryloxide units are connected at the ortho positions through methylene linkers has offered a very useful concept in coordination chemistry to afford the isolation of transition metal complexes in unstable oxidation states or in unusual coordination geometries and many with diverse highly reactive functionalities. A new Lewis acid system based on a complex formed from niobium(V) methoxide and (R)-3,3′-bis(2-hydroxy-3-isopropylbenzyl)-1,1′-binahthelene-2,2′-diol has been reported to find use as catalyst for the stereoselective ring opening of meso-epoxides and meso-aziridines (226).

1.5. Aim of Present Work

A careful survey of literature on the chemistry of metals alkoxides and aryloxides in general, and niobium analogues, in particular, has revealed that the chemistry of niobium complexes derived from alcohols and phenols continues to be the fascinating and fruitful area of study for chemists of several generations. Of numerous substituted phenols utilized as π-donors towards niobium, 2- and 4-isopropylphenols compared to well explored iso-propylalcohol and 2,6-di-isopropylphenol have not so far been studied as ligands. It is, therefore, of interest to investigate the potential of

these phenols to extend niobium(V) chemistry, with an aim to have an insight into structural assessment of the variation of niobium-aryloxide bonding i.e. oxygen pπ to metal dπ bonding. The whole work has been presented into three chapters:

Chapter-I

The niobium(V) aryloxides of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2/4)_n]$ have been synthesized using $NbCl_5$ and 2- and 4-isopropylphenol as starting materials. The complexes have been characterized by elemental analysis (metal, carbon, hydrogen and chlorine), molar conductance measurements, molecular weight determinations and IR, ^1H and ^{13}C NMR, UV-VIS, mass spectral and XRD studies. The likely structures of the complexes have also been computed by molecular modelling. The thermal behaviour of niobium(V) aryloxides has been studied using TG-DTA techniques. The kinetic parameters namely activation energy [E], frequency factor [A], entropy of activation [S] etc. have been evaluated from TG-DTA data using Coats–Redfern equation. Based upon these studies, the tentative structures of the complexes have been proposed. The bimetallic aryloxides of composition $[MNb(OC_6H_4CH(CH_3)_2\text{-}2/4)_6]$ have been synthesized by the reaction of niobium pentaaryloxides of composition $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ with respective alkali metal aryloxides (M = Li, Na). The mixed-metal acetatoaryloxides of composition $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ and $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$, have been synthesized by the reactions of $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ with anhydrous metal acetates $M(OAc)_2$ (M = Cd, Pb). The isolated compounds have been characterized by physico-chemical, IR and ^1H NMR spectral studies.

Chapter – II

Lewis acid character of complexes of composition $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ has been studied by carrying out their reactions with nitrogenous bases viz. 2,2′–bipyridyl and 1,10–phenanthroline. The reactions of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ with oxygenous bases viz. triphenylphosphine oxide, triphenylarsine oxide and phosphorus and arsenic donors viz. triphenylphosphine, triphenylarsine and arsenic trithiophenoxide have established their Lewis acid character. The isolated complexes have been characterized by usual physicochemical and spectral studies. The results have been incorporated in the second chapter.

Chapter – III

The reactivity of niobium(V) aryloxides of composition $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ towards chelating ligands viz. acetylacetone, benzoin and salicylaldehyde; hydroxamate ligands viz. potassiumbenzohydroxamate and 4–chlorobenzohydroxamate has been investigated. The reactivity of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4]$ towards sodium alkoxides viz. MeONa, EtONa, Bu^tONa has also been studied. The isolated complexes have been characterized by the usual physico-chemical and IR and ^1H NMR spectral studies. This work has been incorporated in third chapter.

CHAPTER – I

Synthesis, Characterization, and Thermal Behaviour of Niobium(V) Complexes of 2- and 4-Isopropylphenols.

2.1. Introduction

Niobium (formerly called columbium) and tantalum, second and third member of vanadium group VA elements have virtually identical atomic radii (1.47Å) and close ionization energies (Niobium, 6.67 and Tantalum, 7.30 eV). Owing to lanthanide contraction, the chemistry of niobium and tantalum is more comparable to those of titanium and zirconium in their higher oxidation states, but closer to molybdenum and tungsten in their lower oxidation states and usually display quite similar chemical behaviour. A comparison of niobium and tantalum with titanium and zirconium shows similarity in an affinity for dioxygen and a reluctance to be reduced but differ from them in their stronger tendency to form metal-metal bonds and to exhibit rich cluster chemistry. Likewise, with molybdenum and tungsten, these metals share a propensity to yield oxo species and an ability to give multiple bonds with non metals. The relatively large atomic radii also account for the less tight coordination sphere, and hence for the stereodynamic character often encountered in complexes. The chemistry of niobium as well as tantalum has mainly been focussed on +5 oxidation state since most chemical studies have inevitably been dealt with this state. Nevertheless, the chemical reduction of pentavalent derivatives to tetravalent under strictly controlled conditions has been able to provide convenient starting materials for developing the chemistry of niobium and tantalum in their low oxidation states. The powerful reductants such as sodium amalgam or naphthalenide are required for access to oxidation states lower than +3. The least documented chemistry of the formally positive oxidation states of these metals is that of oxidation state +2.

The chemistry of niobium has been a fascinating area of study owing to its significant applications in material science. The alloys of niobium particularly niobium-titanium alloys are the most common examples of superconducting materials, which can be transformed into wires and can be handled with ease (227). Niobium-titanium alloys find use as the primary material in the construction of coils for magnetic resonance imagery (MRI) equipment utilized in medicine for the detection of anomalies in soft tissue. Niobium is a component of some phosphate optical glasses and has been incorporated into thermocouples to increase their stability at elevated temperatures. Several metal niobates find use in piezoelectric ceramics and dielectrics (227). Niobium chemicals, primarily niobium oxides possess a variety of applications including high-refractive index lenses, high-dielectric, multilayer ceramic capacitor formulations and in the manufacture of lithium niobate for surface acoustic wave (SAW) filters, commonly used in electronic circuitry. The major market for SAW filters is in cell phones. A new application for

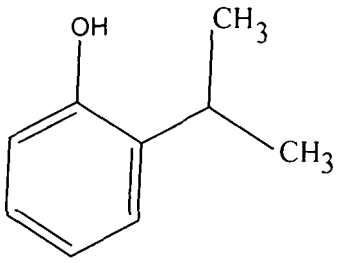
niobium chemicals is in catalytic conversion of palm oil into biodiesel fuel, which is environmental friendly as it reduces the emission of carbon dioxide from combustion engines. Niobium carbide finds utility in the manufacture of cutting tools and in wear-resistant applications. Niobium carbide clusters, Nb_nC_m (n = 3-10, m = 0-7), in the gas phase has been reported to be prepared by double laser ablation technique (228). Niobium is of interest in metal carbonyl chemistry because of its oxophilicity relative to other metals forming stable carbonyls, even its lighter congener vanadium (229).

Niobium and Tantalum display a typical tendency to form complex compounds. These are known to form so called adsorption complexes which are products of complex formation reactions taking place on the surface of colloid particles and of chelate compounds with many organic reagents. Niobium and tantalum complexes find importance in analytical chemistry. The halides and oxyhalides probably the most extensively studied compounds for the synthesis of a large variety of complexes and have been excellently reviewed by Fairbrother (230-231) and Cotton and Canterford (232).

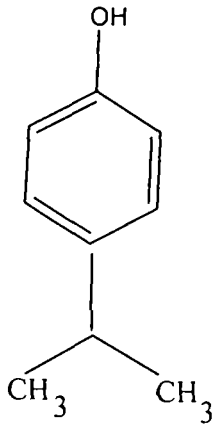
The non-integral valence state halides which are known to contain trimeric or hexameric metal clusters have also received much attention. Over the years, an interest has mainly been centered on the characterization of halide complexes of these elements with oxygen, sulphur and nitrogen donors. The very reactive pentahalides are known to provide the most convenient entry to the molecular chemistry of these metals and their activity as Friedal-Crafts catalysts is another manifestation of their Lewis acidity (233). The strong acceptor capacity of the highvalent metal compounds tends to favour the formation of dimers and sometimes of higher condensation products which compete for coordination with other donor molecules. The metal pentahalides find applications in the alkylation of aromatic compounds (234) and of alkenes (235). The synthesis of high polymers with simple niobium(V) and tantalum(V) halides as catalysts has also been reported (236-239). The disubstituted alkynes which owing to steric hindrance cannot be polymerized by Ziegler-Natta type catalysts get polymerized in the presence of these pentahalides, whereas monosubstituted alkynes selectively are known to give cyclotrimers.

A detailed survey of literature on niobium alkoxides and aryloxides has shown that niobium(V) chloride is most often used as the starting material to obtain solvolytic products. This is perhaps due to the fact that the degree of substitution of chlorine by –OPh/OAr group for the synthesis of niobium aryloxides is determined by the steric and electronic factors of the

phenols (240). In the present work, a series of new niobium(V) aryloxides have been synthesized by the reactions of niobium(V) chloride with two substituted phenols viz. 2-isopropylphenol and 4-isopropylphenol.



2-Isopropylphenol



4-Isopropylphenol

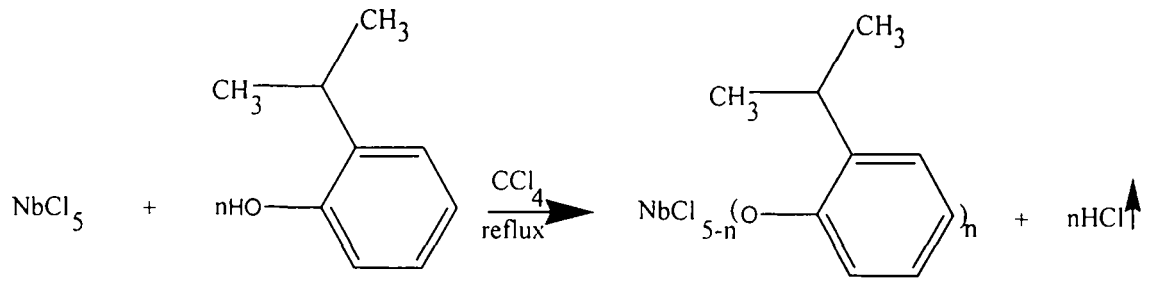
As, a pre-requisite for the synthesis of complexes is the proper choice of the solvent and since niobium is quite electrophilic, the selection of suitable solvent for the synthesis of niobium complexes is very important. Literature survey reveals that tetrahydrofuran and diethylether, though, of these, the former is less bulky and also a stronger Brönsted base, both are known to form adducts with niobium pentachloride. The formation of $[NbCl_5(CH_3CN)]$ has also been reported (241). The NbX_5 species, usually the fluorides or the chlorides are also known to polymerize tetrahydrofuran and can catalyze the hydrolysis of acetonitrile (242). The donor capacity of the solvents towards niobium pentachloride has been reported to follow the order:

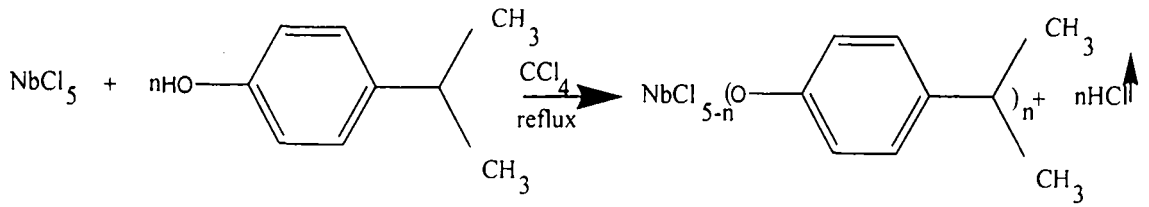
$$HCONMe_2 > CH_3CN > RCOOR > RCOR > R_2O > C_4H_8O > C_6H_6$$

Hence, the solvent has been observed to play an important role in niobium chemistry. The synthesis of niobium oxychloride is known to involve the pyrolysis of niobium pentachloride diethylether adduct (243). The tetrachloro-monoalkoxoniobium(V) complexes $[NbCl_4(OR)]_2$ (R = Me, Et and $SiMe_3$) in 1,2-dichloroethane constitute precursors for the preparation of niobium oxytrichloride in good yield. The reaction of niobium pentachloride with $(Me_3Si)_2O$ in acetonitrile is known to proceed smoothly to yield $[NbOCl_3(CH_3CN)_2]$ which is readily converted to $[NbOCl_3(THF)_2]$ upon dissolution in tetrahydrofuran (244). Another interesting aspect of solvent behaviour has been suggested wherein the alkoxy halide with higher halogen content e.g. $[NbCl_4(OC_2H_5)]$ has been found to show an increased tendency of association

towards acetonitrile and precipitates out as 1:1 adduct of composition $[NbCl_4(OC_2H_5).CH_3CN]$ while $[NbCl(OC_2H_5)_4]$ crystallizes from acetonitrile without a solvent molecule. The interactions between niobium pentachloride and aromatic hydrocarbons have also been indicated by the intermolecular charge transfer spectra, however, the equilibrium constants showed these interactions to be very weak (245). The solvate free materials have generally been prepared by using non-polar solvents such as carbon tetrachloride, toluene and dichloromethane. The utmost importance of dry and suitable solvents in niobium(V) chemistry has been described by Lee and Crayston (246). Apart from the Lewis acid behaviour of MX_5 or MOX_3 and anionic or neutral complexes, there is an extensive chemistry of niobium complexes formed by the replacement of halogen by alkoxide (OR), aryloxide (OPh), dialkylamide (NR_2) and alkyl (CR_3) groups.

In cognizance of the previous reports, in the present work niobium(V) complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2/4)_n]$ (where n = 1→5) have been synthesized in good yields by the direct reaction of niobium pentachloride with stoichiometric amounts of the respective substituted phenols in carbon tetrachloride under reflux as:





(where n = 1→5)

The elemental analyses (niobium, chlorine, carbon and hydrogen) of complexes established their stoichiometric formulations (Tables 1 and 2). The complexes are moisture sensitive yellow to brown coloured solids and change their colour upon exposure to atmosphere. The complexes have poor solubility in carbon tetrachloride and dichloroethane but are fairly soluble in C_6H_6,

Table 1. Analytical data of niobium(V) 2-isopropylphenoxides

Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %				Molar Cond. in $PhNO_2$ (Scm^2 $mole^{-1}$)
		Nb	C	H	Cl	
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$	Brown	25.10	29.15	2.95	38.33	0.62
$C_9H_{11}OCl_4Nb$ (370)		(25.12)	(29.17)	(2.97)	(38.36)	
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$	Maroon	19.80	46.01	4.65	22.65	0.55
$C_{18}H_{22}O_2Cl_3Nb$ (469.50)		(19.81)	(46.00)	(4.69)	(22.68)	
$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3$	Brown	16.31	56.92	5.79	12.45	0.50
$C_{27}H_{33}O_3Cl_2Nb$ (569)		(16.34)	(56.94)	(5.80)	(12.48)	
$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$	Maroon	13.90	64.60	6.55	5.30	0.44
$C_{36}H_{44}O_4ClNb$ (668.50)		(13.91)	(64.62)	(6.58)	(5.31)	
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_5$	Brown	12.10	70.30	7.15	-----	0.37
$C_{45}H_{55}O_5Nb$ (768)		(12.11)	(70.31)	(7.16)		

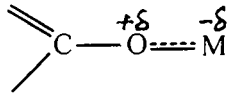
Table 2. Analytical data of niobium(V) 4-isopropylphenoxides

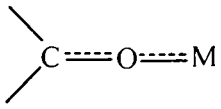
Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %				Molar Cond. in $PhNO_2$ (Scm^2 $mole^{-1}$)
		Nb	C	H	Cl	
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$	Brown	25.11	29.16	2.96	38.35	0.79
$C_9H_{11}OCl_4Nb$ (370)		(25.12)	(29.17)	(2.97)	(38.36)	
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$	Dark	19.82	46.03	4.67	22.67	0.78
$C_{18}H_{22}O_2Cl_3Nb$ (469.50)	Brown	(19.81)	(46.00)	(4.69)	(22.68)	
$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3$	Yellow	16.33	56.93	5.82	12.47	0.77
$C_{27}H_{33}O_3Cl_2Nb$ (569)		(16.34)	(56.94)	(5.80)	(12.48)	
$NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$	Yellow	13.92	64.61	6.56	5.32	0.76
$C_{36}H_{44}O_4ClNb$ (668.50)		(13.91)	(64.62)	(6.58)	(5.31)	
$Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$	Yellow	12.08	70.29	7.17	-----	0.53
$C_{45}H_{55}O_5Nb$ (768)		(12.11)	(70.31)	(7.16)		

$CHCl_3$, CH_3OH and $C_6H_5NO_2$. The molar conductance values of millimolar solutions of complexes in nitrobenzene are too low to be attributed to 1:1 electrolyte (247,248). The cyroscopic molecular weight determinations of complexes in nitrobenzene are suggestive of their dimeric nature.

The structural analysis of newly synthesized complexes is of importance in view of the reports met in literature on the structures of earlier synthesized niobium pentaphenoxides (249) and mixed chlorophenoxides (250), wherein it has been described that these complexes as solids as well as in non-coordinating solvents dimerize through phenoxy groups (251). A common feature observed for the few structurally characterized early transition-metal chloride phenoxides is the presence of μ-phenoxo rather than μ-chloro linkages (252,253). Of complexes of composition $[NbCl_4(OR)]$ (R = Me, 1; Et, 2; $SiMe_3$, 3) complexes 1 and 2 have been formulated as dimeric species. The ability of alkoxide ligands for π-donation to metal centres is most dramatically shown in structural studies of high valent electron-deficient alkoxide compounds (254-256) wherein short M—O distances and large M—O—R angles are normally found. The structural impact of the π-donation of alkoxide ligands has also been shown to have some dramatic spectroscopic manifestations (257-259). Unlike their alkoxide counterparts, aryloxide and siloxide (260) ligands have the ability for their oxygen atoms to π-interact with their substituents as well as the metal atom to which they are bound. This feature has been used to rationalize the very large, sometimes linear M—O—Ph and M—O—SiR_3 angles typically found for high valent, electron-deficient metal aryloxides (261) and siloxides (256,257). If one considers the case of a linear M—O—X function (X = Ph, SiR_3) the sp hybridized oxygen atom has two mutually perpendicular p-orbitals which can π-donate to empty d-orbitals of the correct symmetry on the metal. In the case of an aryloxide ligand, one of the p-orbitals can overlap with the arene ring, reducing its availability for interaction with the metal. Hence one might rationalize from this simple picture that the strongest π-donation from aryloxide ligands should occur into metal d-orbitals which are coplanar with the aryl ring. If this is indeed the case then the orientation of the aryl rings in the absence of dominating steric effect may give some insight into the oxygen p to metal dπ bonding (262).

The C—O stretching vibrations for p-monosubstituted phenols are known to increase in frequency with the electron withdrawing ability of the substituent and vice-versa. The υ(C–O) mode, in general, gets significantly lowered on complextion suggesting a considerable

contribution from the structure of type  from a bonding through oxygen to metal atom, thereby, weakening the carbon oxygen bond. On the other hand, the electron release by the substituent at the aromatic ring may help to stabilize the metal-oxygen double bond by reducing the formal positive charge on oxygen. The extent to which the metal-oxygen double bond formation would vary, can in turn be predicted from the nature of the substituent at the aromatic ring. The possibility of a considerable contribution from the structure of the type



resulting from delocalisation of aryloxide ring electrons to the metal via (L→M) л interactions is also likely.

Of the three homoleptic aryloxides of composition $[Nb(OPh)_5]$ derived from 4-methyl, 3,5-dimethyl and 2,6-dimethylphenol, the complex from the latter, bulky phenol has only been found to be monomer with perfectly trigonal bipyramidal arrangement around metal atom. In case of $[Nb(NMe_2)_5]$, for niobium a geometry much closer to a square-pyramid has been described (263). The exact, prediction and even rationalization as to which of these two extreme geometries are formed, is not straight-forward.

2.1.1. IR spectra

The formation of newly synthesized niobium(V) 2-/4-isopropylphenoxides has been inferred from a comparison of their IR spectra with that of respective substituted phenols scanned in 4000–200 cm^{-1} range. The broad band occurring in 3500–3400 cm^{-1} region in parent phenols ascribed to intermolecular hydrogen bonded phenolic –OH group (264), has been found to be missing in the IR spectra of complexes suggesting the deprotonation of the phenolic proton. This observation is further supported by the fact that hydrogen chloride gas was evolved during the course of the reaction. The sharp bands occurring at 3067, 3037 and 3016 cm^{-1} due to υ(CH) vibrations of the aromatic ring in 2-isopropyl and 4-isopropylphenol respectively have been found to move to higher wave numbers upon complexation. The absorption bands in 1600–1400 cm^{-1} region due to υ(C=C) vibrations in the phenolic ring have been observed to suffer a slight shift towards higher wave numbers possibly due to increasing ring conjugation brought about by bonding to niobium metal.

The most important and strong bands due to υ(C–O) mode occur in free phenols in 1260–1180 cm^{-1} and 1300–1200 cm^{-1} and 1410–1310 cm^{-1} regions (265,266). The bands appeared in 1364–1236 cm^{-1} and 1362–1221 cm^{-1} regions may be ascribed to υ(C–O) mode in free 2- and 4-isopropylphenol respectively. The absorption bands observed in 1286–1235 cm^{-1} region in infrared spectra of complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n]$ (n = 1→5), are characteristic of υ(C–O)Nb mode while in case of analogous niobium(V) complexes derived from 4-isopropylphenol these bands appeared in 1260–1218 cm^{-1} and 1172–1097 cm^{-1} regions. These observations are suggestive of Nb⟸OPh π-bonding in these complexes. The appearance of entirely new bands in 580–570 cm^{-1} region which were not present in free phenols have been assigned to infrared active υ(Nb—O) mode in agreement with previous reports on niobium alkoxides and phenoxides (267,268).

Intense and sharp absorption bands observed in 550–530 cm^{-1} region in complexes have been attributed to bridging Nb<O>Nb mode (269). This observation is quite in agreement with previous reports that if polymerization takes place through halogen or oxygen, the bridging modes appear at lower wave numbers than for terminals ones. All important IR bands for niobium(V) complexes are given in Tables 3 and 4.

A number of controversial reports concerning the assignments of υ(Nb–Cl) vibrational modes have appeared in literature. A sharp band at 420 cm^{-1} as υ_3 in niobium compounds has been reported for υ(Nb–Cl) mode by Carlson (270) while Djordjevic (271) has assigned a vibrational band at 333 cm^{-1} due to υ(Nb–Cl) for octahedral complexes. In niobium(V) chloride 2-/4-isopropylphenoxides the sharp intense bands observed at ~ 370 cm^{-1} have been attributed to υ(Nb–Cl) stretching vibrations which are in agreement with the reported υ(M–Cl) vibrations for octahedral complexes. No band that could be assigned to bridging Nb<Cl>Nb mode expected to lie in the lower region than those of terminal υ(Nb–Cl) mode has been observed in these complexes thereby suggesting that bridging takes place through phenoxy group rather than through chlorine in complexes under study.

2.1.2. ^{1}H NMR Spectra

The room temperature proton NMR spectra recorded in $CDCl_3$ of newly synthesized niobium(V) complexes has further supported their formation. The disappearance or change in the characteristic

Table 3. IR spectral data (cm^{-1}) of niobium(V) 2-isopropylphenoxides

Ligand/Complex	Bands (cm^{-1})
$HOC_6H_4CH(CH_3)_2$-2	3067, 3037, 2964, 2871, 2728, 2577, 2479, 2415, 2080, 1935, 1900, 1783, 1606, 1609, 1503, 1588, 1491, 1452, 1449, 1384, 1449, 1384, 1364, 1335, 1288, 1236, 1181, 1151, 1113, 1081, 1034, 933, 893, 854, 825, 753, 720.
$NbCl_4(OC_6H_4CH(CH_3)_2$-2)	2963, 2923 w, 2870w, 1619s, 1499m, 1451s, 1385w, 1342s, 1286s, 1235vs, 1185s, 1149w, 1111m, 1083s, 1036s, 879m, 827s, 753vs, 589 b, 420w, 365.
$NbCl_3(OC_6H_4CH(CH_3)_2$-2)$_2$	3375b, 3240b, 3150b, 2961m, 2913m, 2855, 2362, 1640m, 1614s, 1559, 1482s, 1448s, 1403s, 1334m, 1287m, 1244b, 1190s, 1154s, 1086m, 1027, 829m, 754s, 674s, 645, 600, 564, 420m, 327m, 281m.
$NbCl_2(OC_6H_4CH(CH_3)_2$-2)$_3$	3404, 2962s, 2918s, 2843b, 2074, 1631s, 1646s, 1559s, 1484s, 1443s, 1374b, 1339b, 1293, 1239vs, 1189s, 1154s, 1085s, 825s, 750s, 715s, 680, 651, 611s, 589s, 553s, 534s, 507s, 478s, 420s, 391s, 361s, 310s.
$NbCl(OC_6H_4CH(CH_3)_2$-2)$_4$	3754, 3696, 3062, 2960, 2867, 2363, 1580s, 1481s, 1443s, 1339s, 1237s, 1190s, 1111s, 1082s, 907s, 822, 752s, 639, 524, 426s, 359, 322s.
$Nb(OC_6H_4CH(CH_3)_2$-2)$_5$	3863s, 3754s, 3674s, 3389s, 3161b, 2963vs, 2930s, 2918s, 2872s, 2362vs, 2337s, 1739s, 1704, 1613s, 1553m, 1507m, 1482s, 1451s, 1536, 1380m, 1337s, 1286s, 1253s, 1187s, 1154s, 1110s, 1083s, 1033s, 822m, 752vs, 721m, 638s, 588m, 460s, 429s, 399s, 365s, 333m, 300m.

Table 4. IR spectral data (cm^{-1}) of niobium(V) 4-isopropylphenoxides

Ligand/Complex	Bands (cm^{-1})
$HOC_6H_4CH(CH_3)_2$-4	3313, 3016s, 2951s, 2864s, 2682, 2566, 2459, 1893s, 1655s, 1612s, 1598s, 1514s,1446s, 1362s, 1333s, 1221s, 1104s, 1051s, 1013s, 959s, 892s, 829s, 704s, 657.
$NbCl_4(OC_6H_4CH(CH_3)_2$-4)	3754m, 3378b, 2959s, 2926s, 2855s, 1756, 1721, 1620b, 1511vs, 1458s, 1374s, 1322w, 1260s, 1218m, 1172m, 1097m, 1050m, 1016s, 900m, 832s, 582ms, 368m.
$NbCl_3(OC_6H_4CH(CH_3)_2$-4)$_2$	3377b, 2960s, 2918m, 2861m, 2364m, 1715, 1603m, 1496vs, 1449s, 1416s, 1382s, 1351s, 1328s, 1229vs, 1190vs, 1163vs, 1097s, 1053s, 1014s, 923vs, 836vs, 778s, 755s, 703s, 634s, 586s, 517s, 483s, 443vs, 391.
$NbCl_2(OC_6H_4CH(CH_3)_2$-4)$_3$	3025m, 2958vs, 2926s, 2868s, 2361s, 2345m, 1600s, 1555s, 1498vs, 1459s, 1419s, 1382s, 1363s, 1232vs, 1190vs, 1167vs, 1099s, 1053s, 1013s, 919vs, 899s, 834vs, 776s, 748s, 718s, 669s, 640s, 610s, 590s, 546s, 518vs, 453s, 423s, 387s, 358vs, 302s.
$NbCl(OC_6H_4CH(CH_3)_2$-4)$_4$	3320s, 3028s, 2957s, 2866s, 2363s, 1890s, 1600s, 1499s, 1418s, 1382s, 1361s, 1238s, 1200s, 1166s, 1053s, 1011s, 900s, 835s, 746s, 640s, 583s, 514s, 447s, 357s, 300s, 242s.
$Nb(OC_6H_4CH(CH_3)_2$-4)$_5$	3240, 2958s, 2668s, 1605s, 1503s, 1383s, 1363s, 1258s, 1170s, 1099s, 1055s, 1016s, 835s, 581s, 489, 260s, 235s.

signals of free 2/4-isopropyl phenols on complexation has been carefully examined. The uncoordinated 2-isopropylphenol exhibited signals due to phenolic –OH at δ 5.42 ppm, two doublets centered at δ 6.85 and δ 7.37 ppm due to H–6 and H–3 respectively and two triplets centered at δ 7.08 and δ 7.20 ppm ascribed to H–4 and H–5 respectively. The resonances due to methine and methyl substituents appeared as heptet and doublet at δ 3.39 and δ 1.42 ppm respectively (Fig. 1). In none of the complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n]$ (n = 1→5) signal due to the phenolic proton was observed which confirmed deprotonation during the course of the reactions between niobium(V) chloride and 2-isopropylphenol. The complexes showed two distinct doublets in δ 7.12–7.28 ppm and δ 6.75–6.78 ppm range due to aromatic protons H–3 and H–6 respectively and two triplets at δ 6.96–7.12 and δ 6.80–6.96 ppm due to aromatic protons H–5 and H–4 respectively. The observed upfield by (-0.08)–(-0.10) ppm in aromatic signals of 2-isopropylphenolic ligand can be explained by considering the shielding effect exerted on aromatic protons by the electron releasing isopropyl substituent present at ortho position to phenolic group. The proton resonances due to methine and methyl groups also shifted slightly upfield upon complexation (Figs. 2-5).

The ^{1}H NMR spectra of free 4-isopropylphenol is reported to display signals due to phenolic –OH, H-2,6 and H-3,5 aromatic ring protons and aliphatic methine and methyl protons at δ 4.91, δ 6.75, δ 7.23 and at δ 3.20 and δ 1.24 ppm respectively. The absence of the signal at δ 4.91 ppm in $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)_n]$ (n = 1→5) is indicative of its participation in reactions with niobium(V) chloride which is lost in the form of HCl gas during the reaction. The complexes displayed two signals due to ortho (H-2,6) and meta (H-3,5) aromatic protons in δ 6.79–7.29 ppm range. The downfield shifts by + 0.04 to 0.06 ppm observed in aromatic ring proton resonances may be ascribed to the deshielding of these protons due to transfer of electron density from aromatic nucleus to niobium metal as (PhO ⟶ Nb) (272,273). These observations are substantiated by a similar explanation advanced by Clark and coworkers (272) and Chisholm (273) for the downfield shifts observed in titanium(IV) complexes with different substituted phenols. The proton resonances due to methine and methyl groups insignificantly shifted upfield upon complexation. The integration of protons supported the formation of complexes (Figs. 6-10). The ^{1}H NMR spectral data are given in Tables 5 and 6.

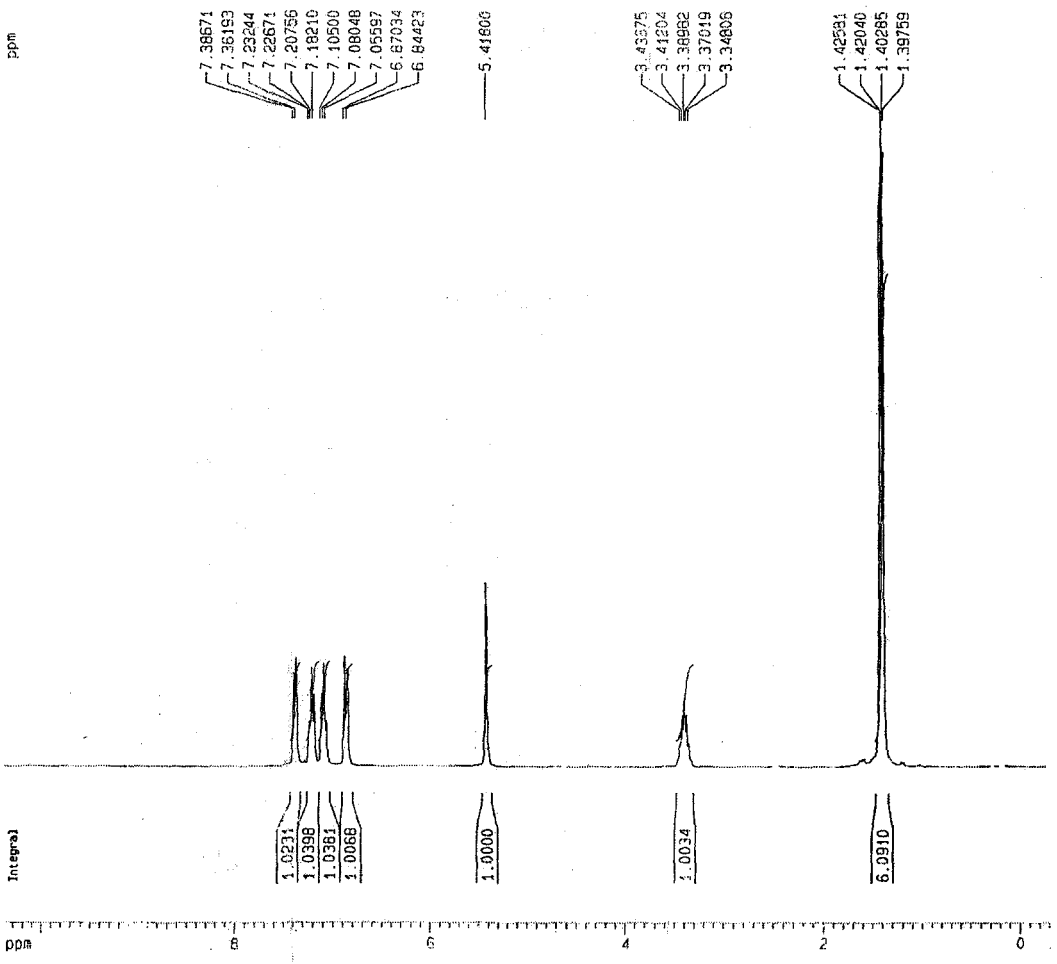


Fig. 1 ^{1}H NMR spectrum of $HOC_6H_4CH(CH_3)_2$-2

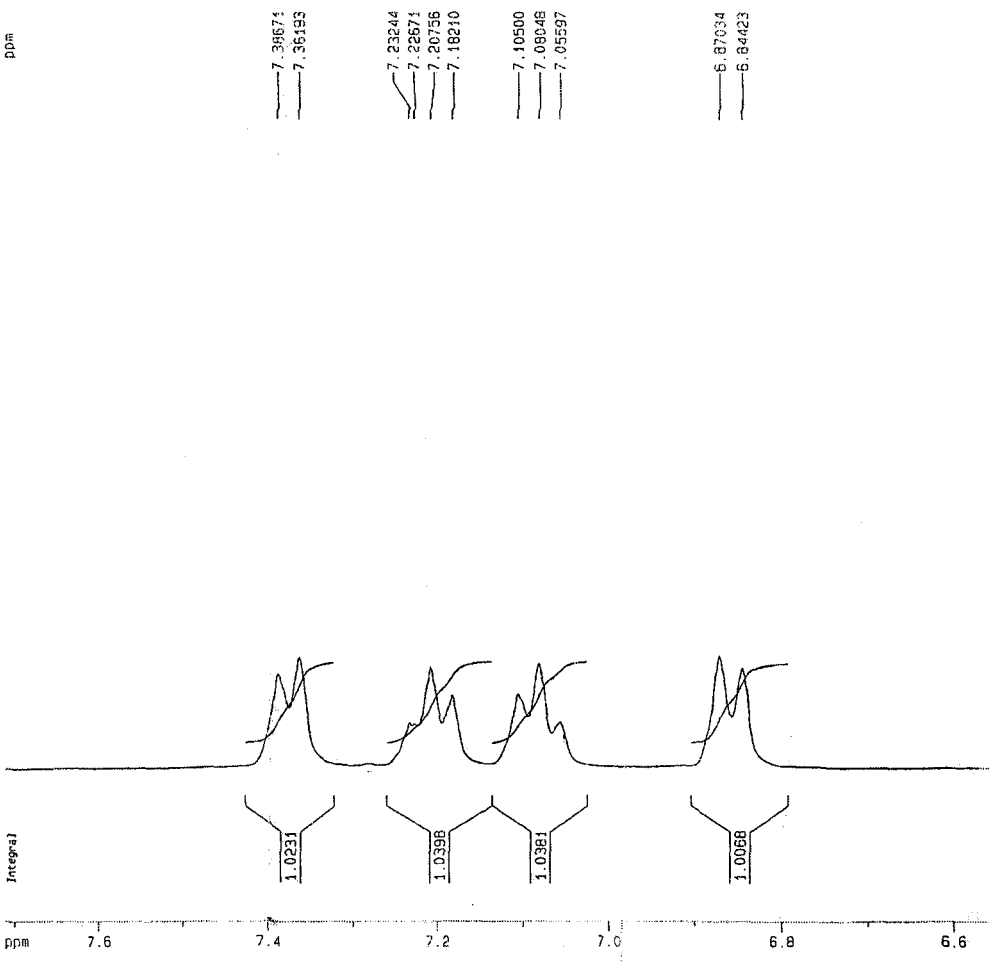


Fig. 1 ^{1}H NMR spectrum of $HOC_6H_4CH(CH_3)_2$-2

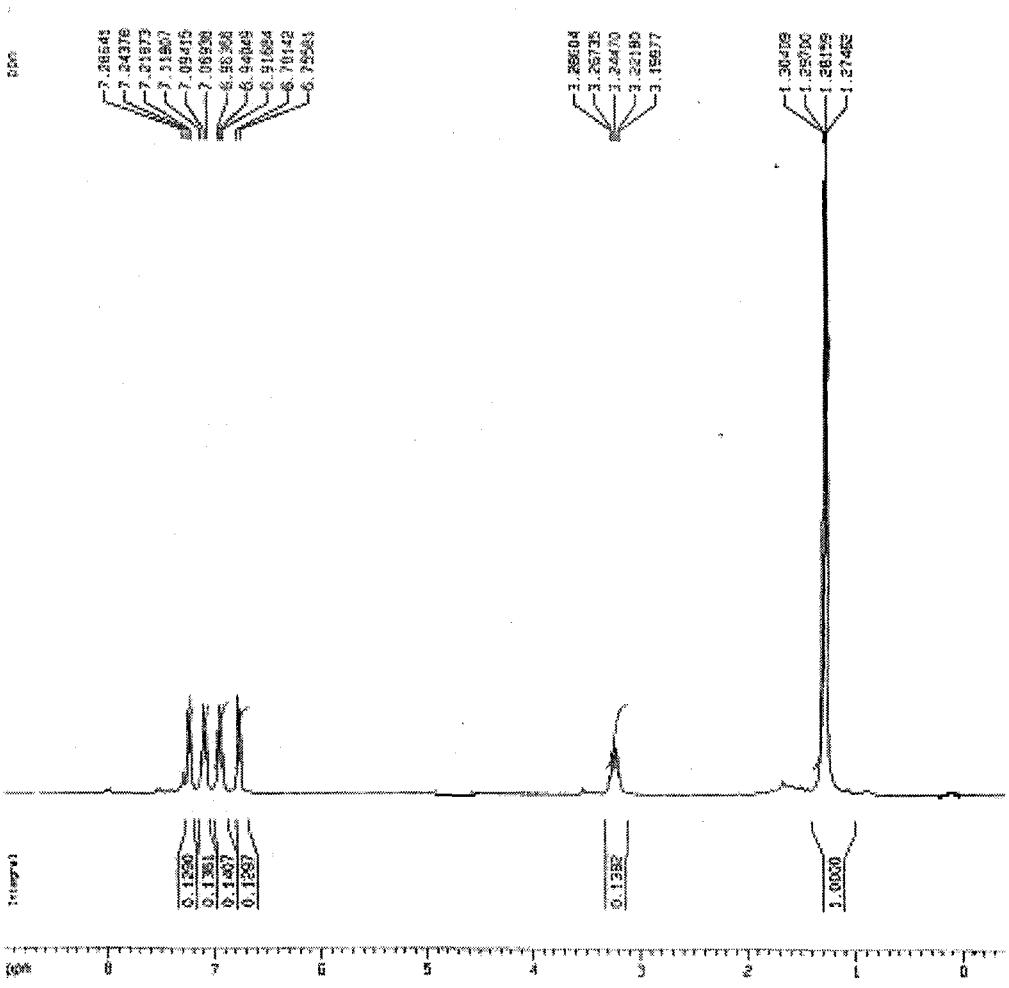


Fig. 2 ^{1}H NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$

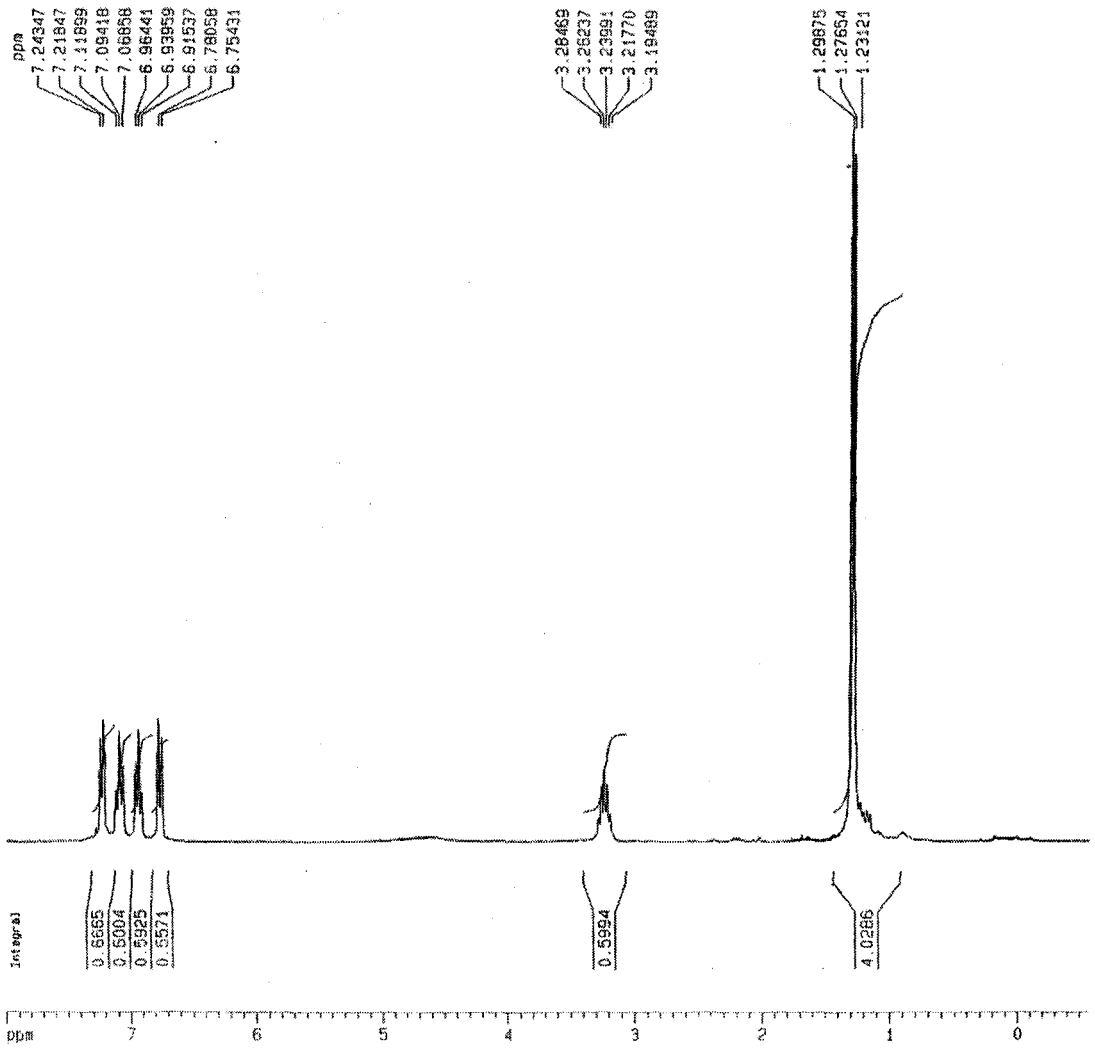


Fig 3.^{1}H NMR spectrum of $NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$

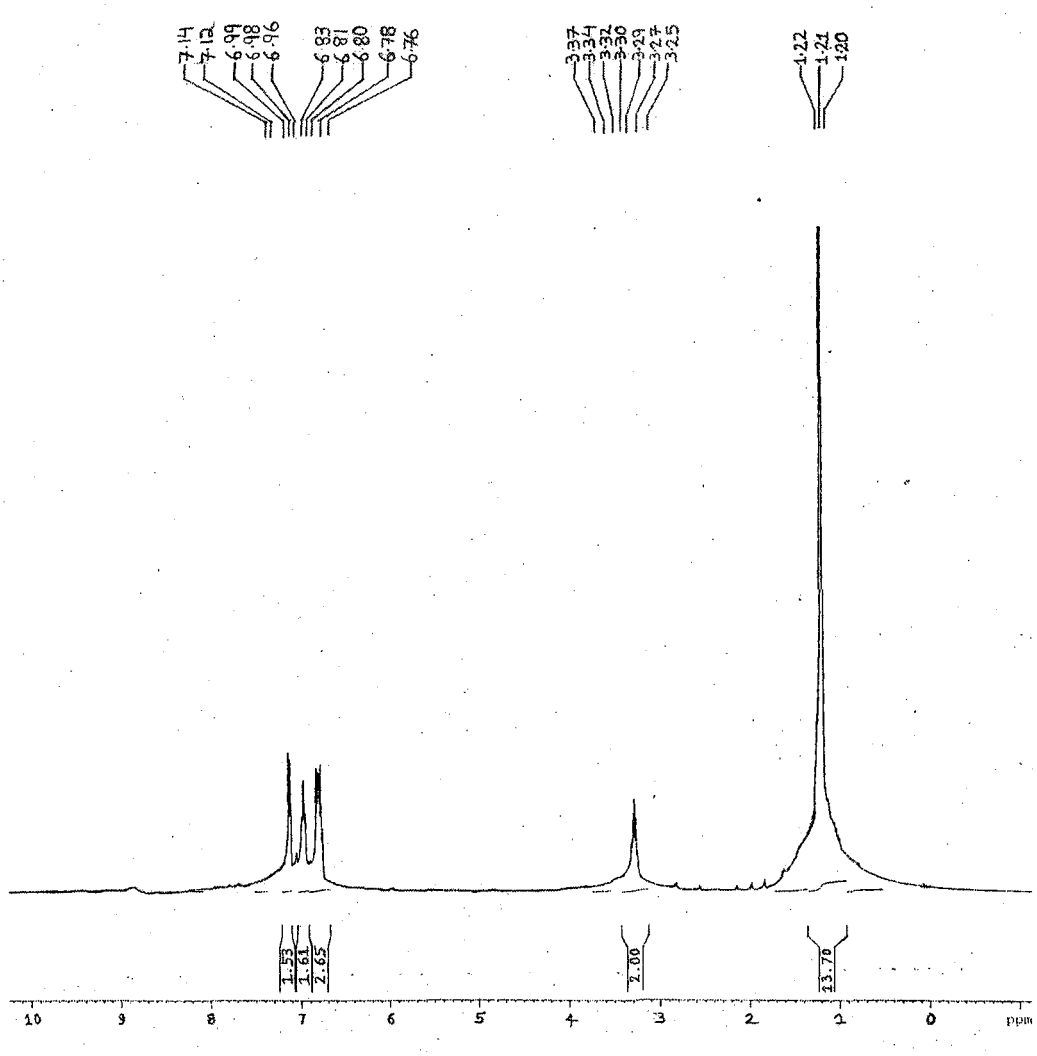


Fig 4.^{1}H NMR spectrum of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$

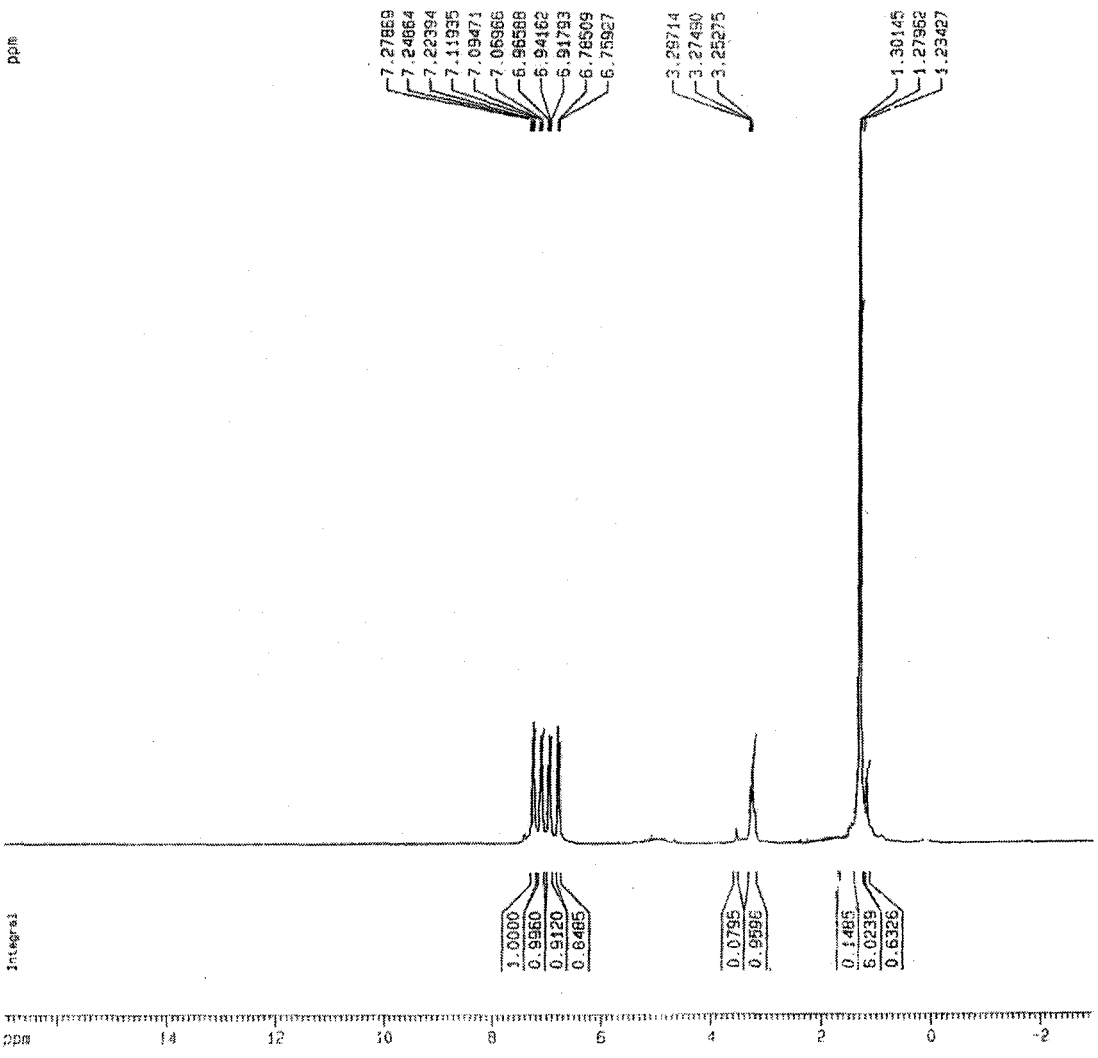


Fig 5.^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_5$

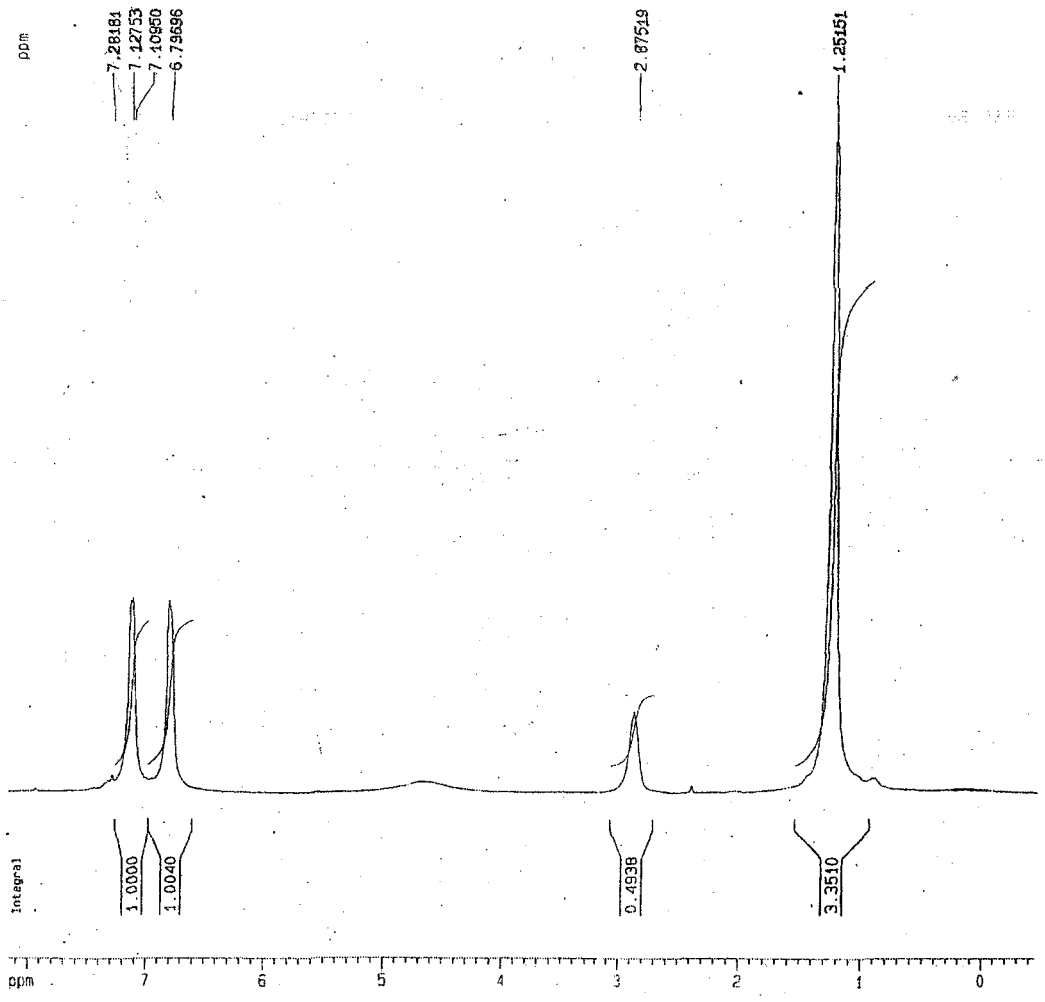


Fig 6 ^{1}H NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$

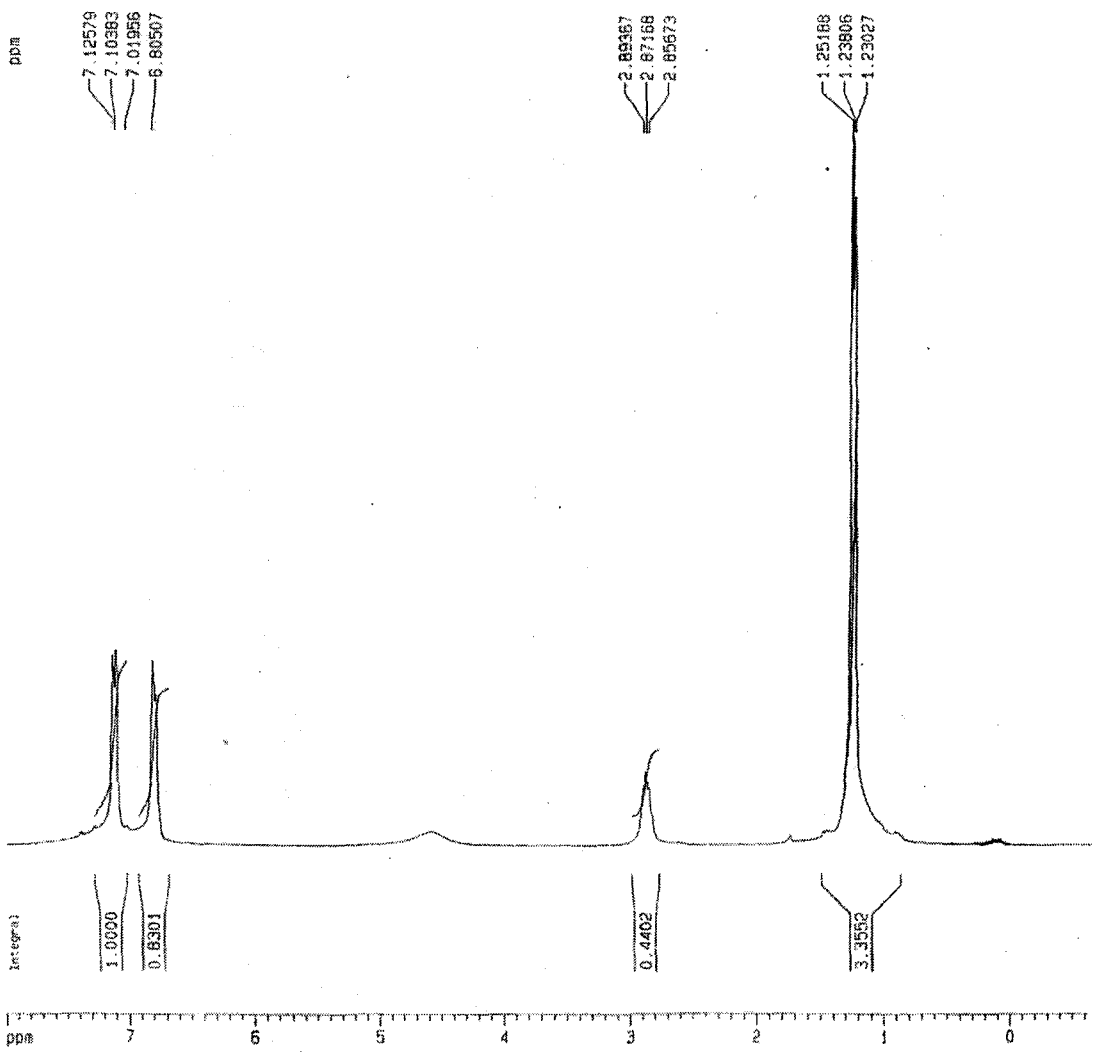


Fig 7 ^{1}H NMR spectrum of $NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$

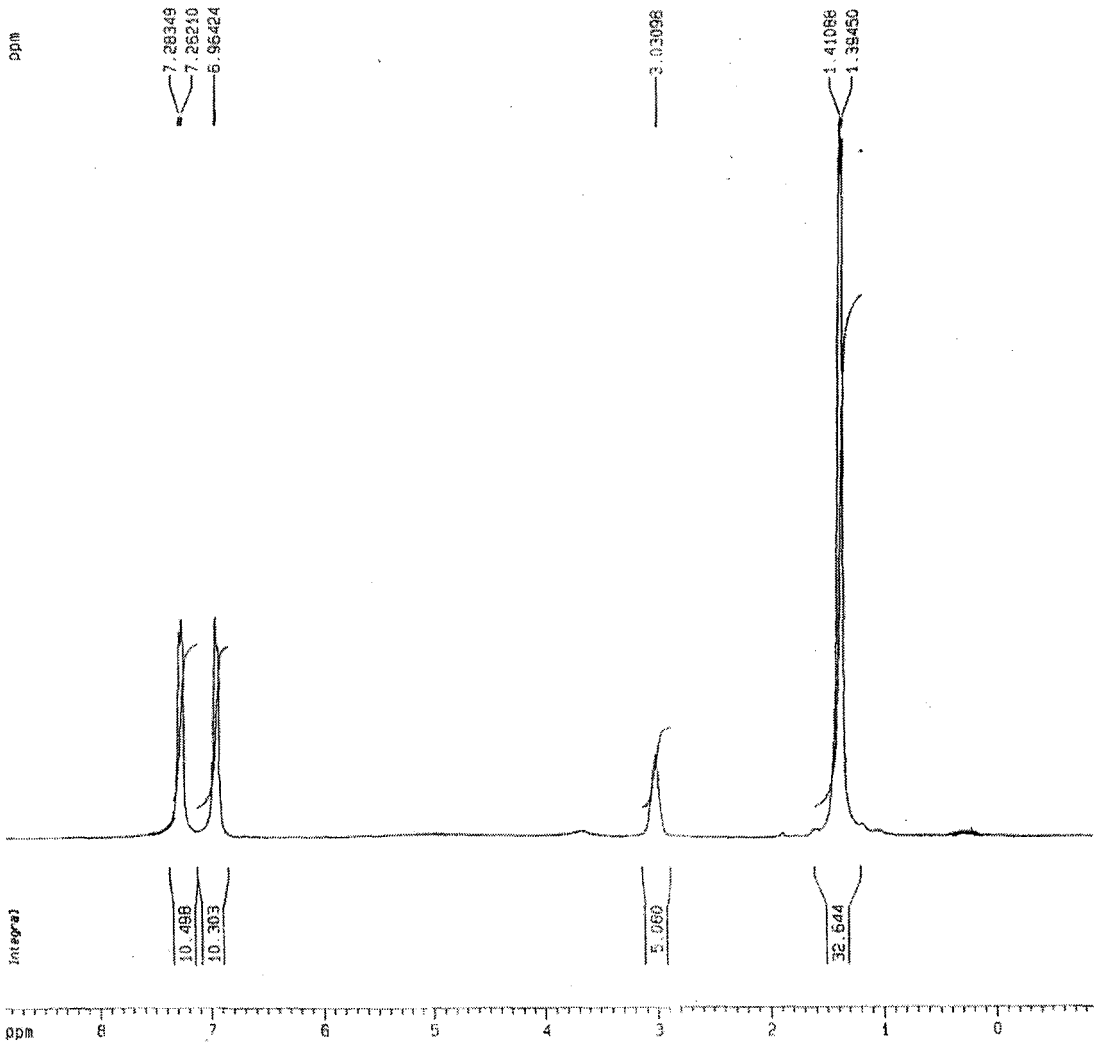


Fig 8 ^{1}H NMR spectrum of $NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3$

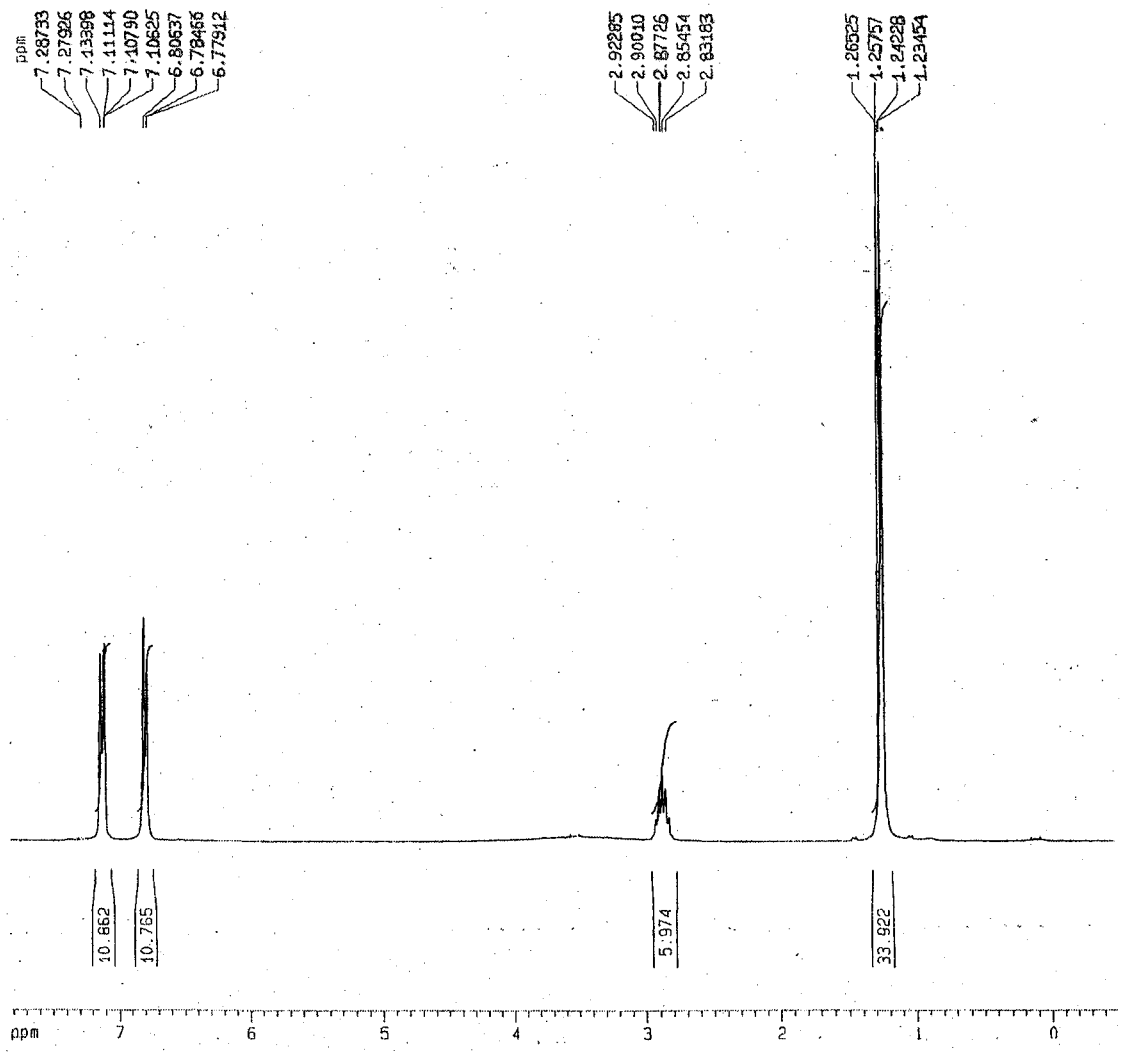


Fig 9. ^{1}H NMR spectrum of $NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$

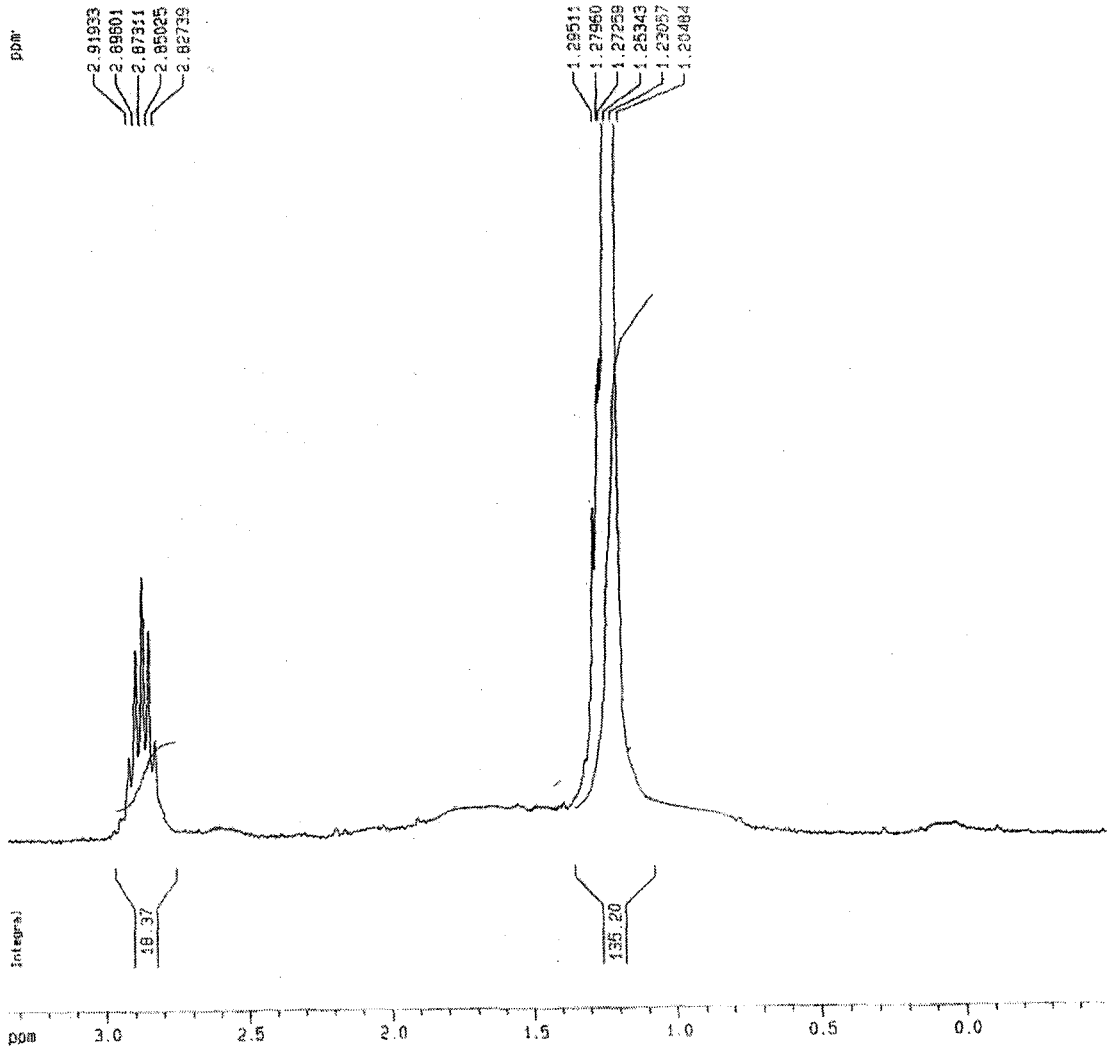


Fig 10. ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

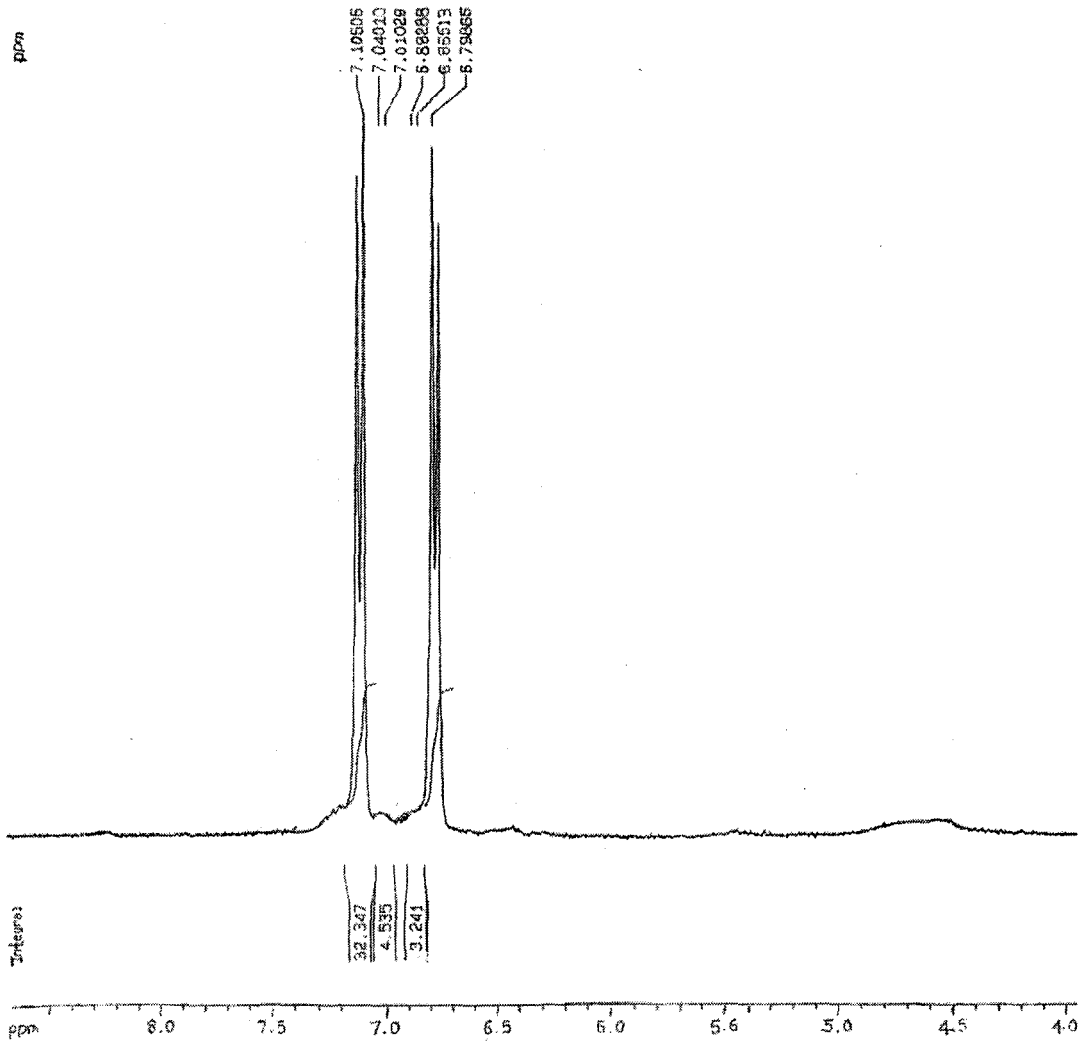


Fig 10. ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

Table 5. ^{1}H-NMR data of niobium(V) 2-isopropylphenoxides (ppm).

Ligand/Complex	Phenolic proton (−OH)	Substituent (Isopropyl protons)		Aromatic phenolic ring protons			
		$-(CH_3)_2$	-CH	H-3	H-4	H-5	H-6
$HOC_6H_4CH(CH_3)_2$-2	5.42	1.42(d)	3.39(h)	7.37(d)	7.08(t)	7.20(t)	6.85(d)
$NbCl_4(OC_6H_4CH(CH_3)_2$-2)	---	1.28(d)	3.24(h)	7.24(d)	6.94(t)	7.09(t)	6.76(d)
$NbCl_3(OC_6H_4CH(CH_3)_2$-2)$_2$	---	1.27(d)	3.23(h)	7.23(d)	6.93(t)	7.09(t)	6.76(d)
$NbCl_2(OC_6H_4CH(CH_3)_2$-2)$_3$	---	1.27(d)	3.24(h)	7.24(d)	6.93(t)	7.09(t)	6.76(d)
$NbCl(OC_6H_4CH(CH_3)_2$-2)$_4$	---	1.21(d)	3.30(h)	7.13(d)	6.81(t)	6.98(t)	6.77(d)
$Nb(OC_6H_4CH(CH_3)_2$-2)$_5$	---	1.27(d)	3.27(h)	7.24(d)	6.94(t)	7.09(t)	6.76(d)

where d = doublet, t = triplet and h = heptet

2.1.3. ^{13}C NMR Spectra

A comparison of ^{13}C NMR spectra of niobium(V)2-/4-isopropylphenoxides with that of respective 2- and 4-isopropylphenols has further substantiated their formation. The ^{13}C NMR spectral data are given in Tables 7 and 8. The ^{13}C NMR spectra of 2-isopropylphenol exhibited six signals in δ 115.94–153.14 ppm range ascribed to phenolic ring carbons and two signals at δ 23.12 and δ 27.45 ppm due to methyl and methine carbons of isopropyl substituent (Fig. 11). The carbon resonances due to C–1 showed downfield shifts by δ 0.77–1.59 ppm while other aromatic ring carbons and that of isopropyl substituent showed moderate upfield shifts. The carbon resonance C–6 of complex $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ showed downfield shifts by δ 1.44 ppm (Figs. 12-15).

The ^{13}C NMR spectra of 4-isopropylphenol exhibited four signals in δ 115.40–154.50 ppm range ascribed to C–1, C–4, C–2,6 and C–3,5 phenolic ring carbons and two signals at δ 24.40 and δ 31.70 ppm due to methyl and methine carbons of isopropyl substituent. A downfield shift for ipso-carbon by δ 1.13 ppm suggested bonding through phenolic oxygen to niobium metal. On the other hand C–4 showed an appreciable upfield shift by δ 2.36 ppm while rest of carbon resonances remained unaltered upon complexation. Of methine & methyl carbon resonances, only methine carbon showed downfield shift (Figs. 16-20).

2.1.4. Electronic Spectra

The electronic spectral studies of metal complexes provide useful information about the stereochemistry, oxidation state of the central metal ion and in suitable circumstances, the nature of metal-ligand bond. The niobium(V) 2-/4-isopropylphenoxides synthesized in the present work are orange to rust to maroon coloured solids, apparently the d^0 species and no d–d bands are thus expected to be observed for such complexes. However, absorption bands displayed by these complexes may be assigned as ligand to metal charge transfer (LMCT) transitions from the phenolate oxygen to empty d-orbitals on niobium metal or the $\pi \rightarrow \pi^*$ intra-ligand transitions. Such transitions are characteristics of phenolate or catecholate coordination to easily reducible metal ions (274,275).

The UV-visible spectra of free 2- and 4-isopropylphenols and the respective niobium(V) complexes have been examined in 200–800 nm range, in methanol/acetonitrile in order to have an insight into the oxidation state of the metal and to know how the absorption bands of the ligands are perturbed on complexation with niobium metal. The absorption bands observed at ~ 285 and ~ 280 nm in 2-isopropylphenol and 4-isopropylphenol respectively have been attributed to $\pi \rightarrow \pi^*$ transition of the phenolic aromatic ring.

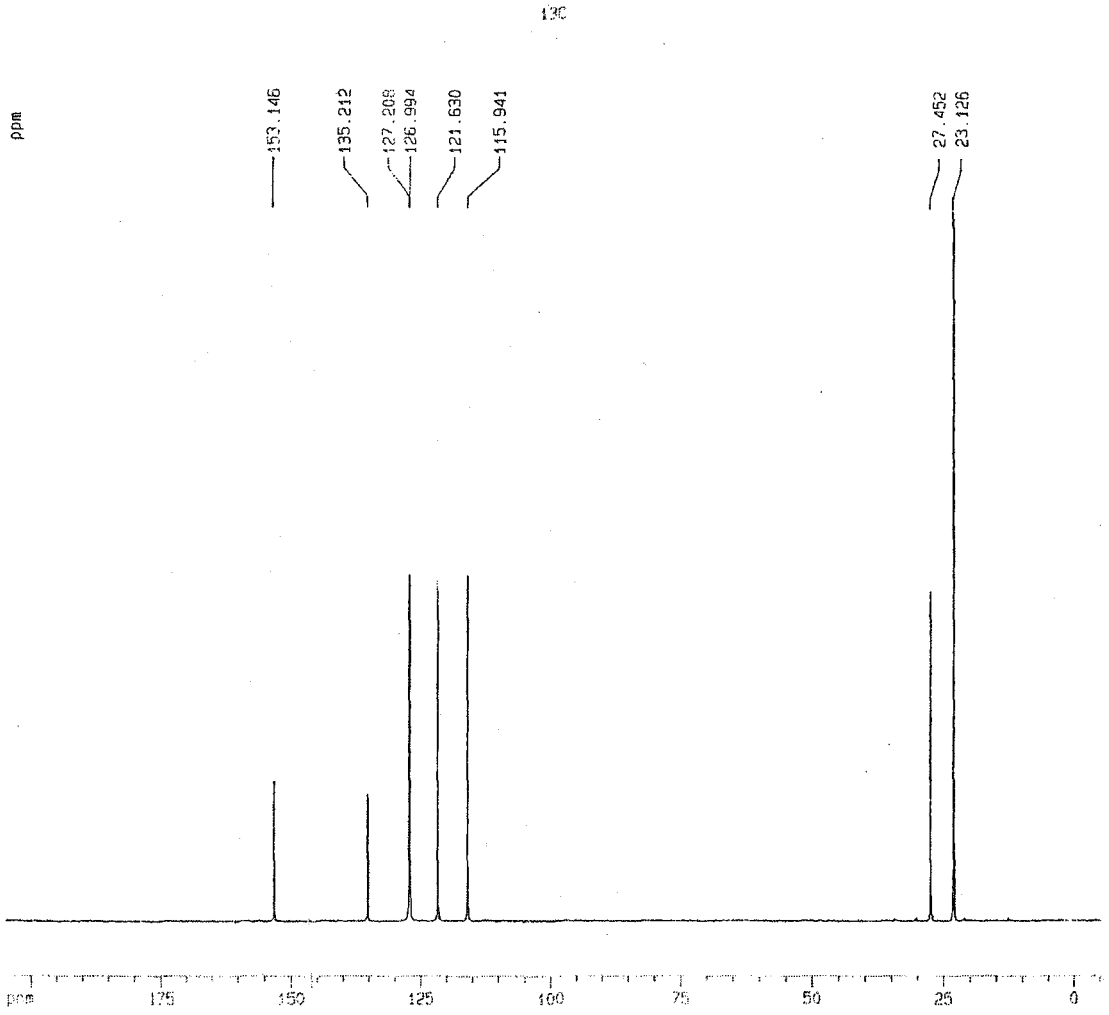


Fig 11. ^{13}C NMR spectrum of $HOC_6H_4CH(CH_3)_2$-2

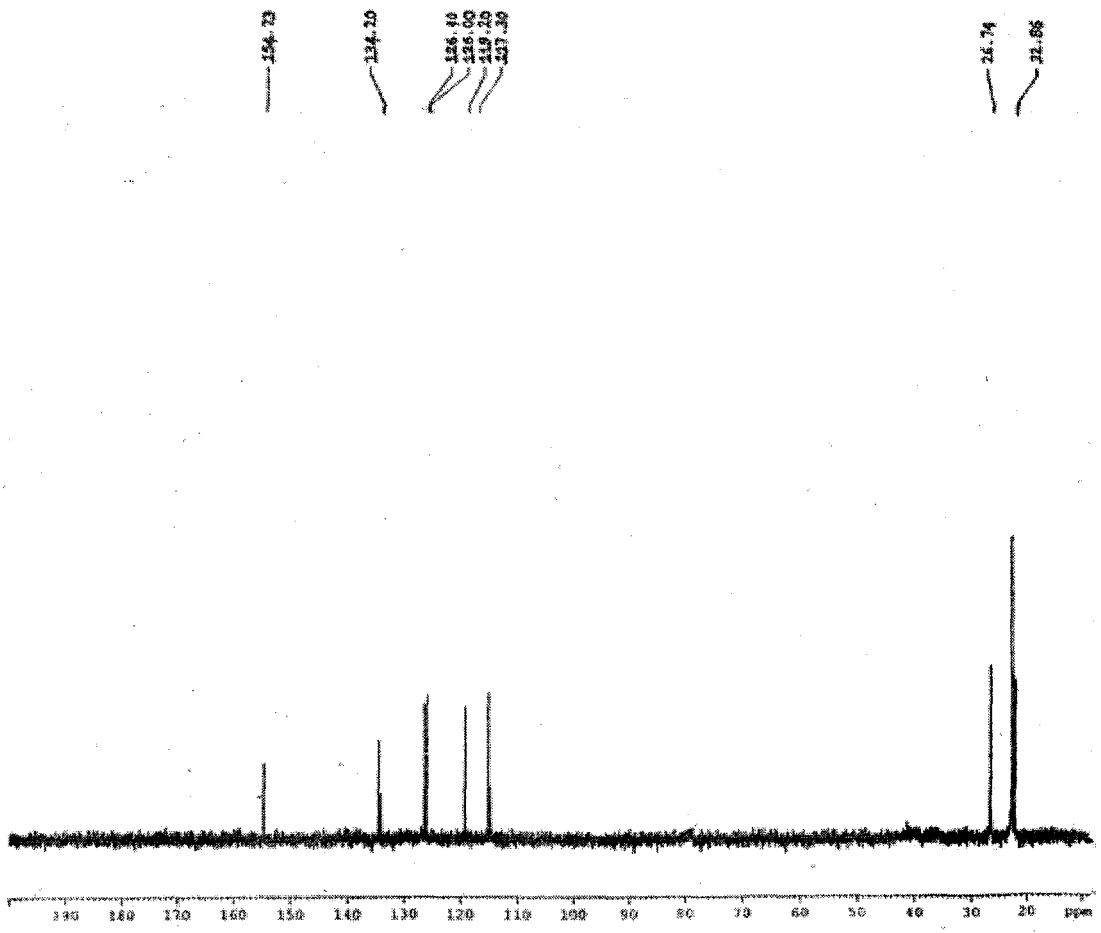


Fig 12. ^{13}C NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$

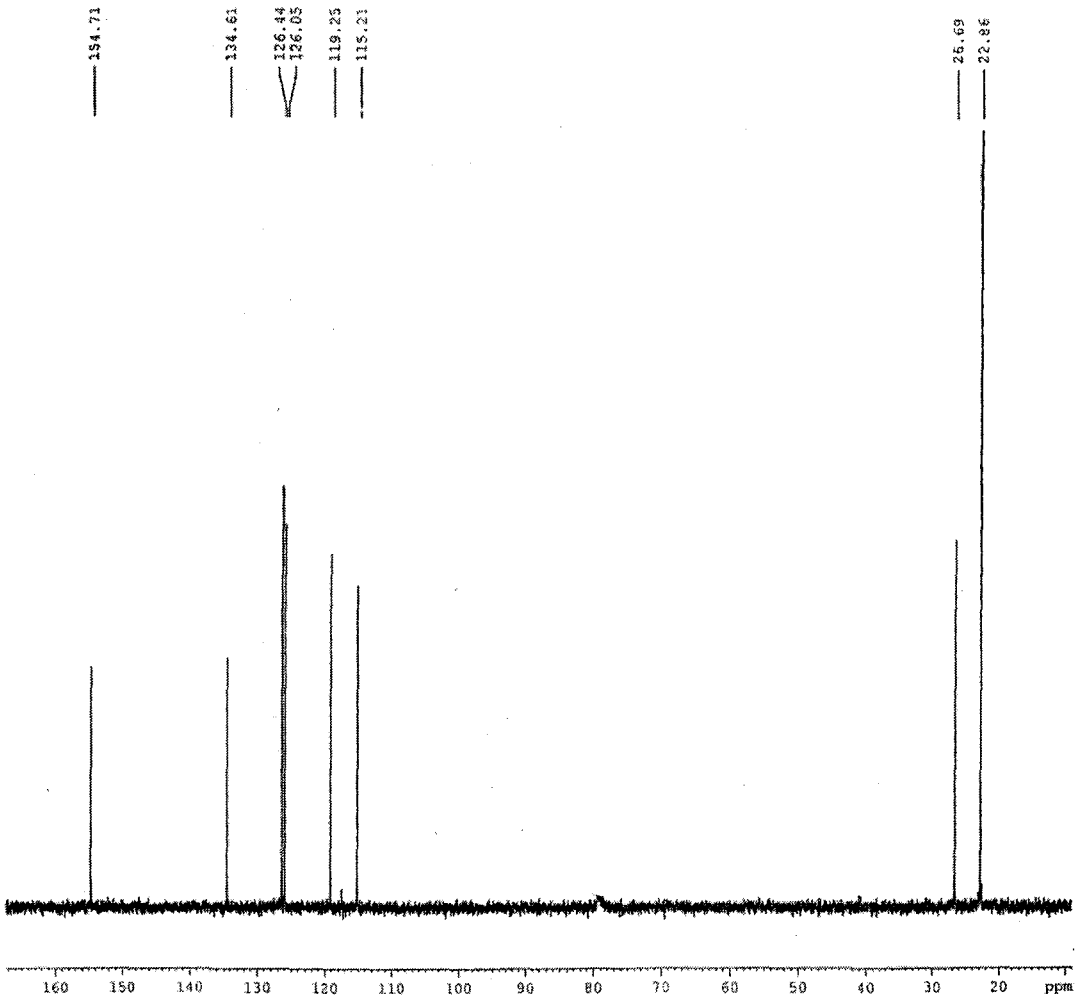


Fig 13. ^{13}C NMR spectrum of $NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$

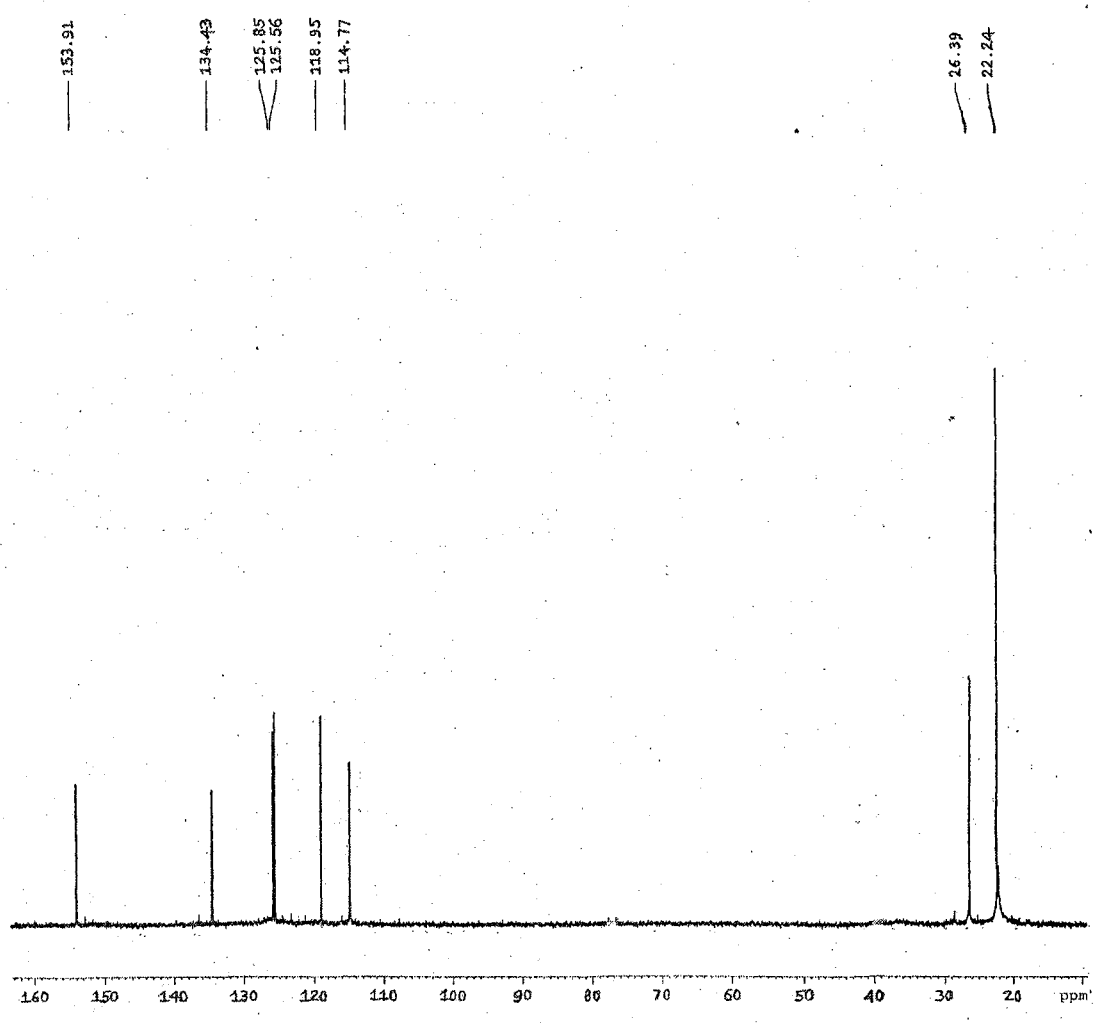


Fig 14. ^{13}C NMR spectrum of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$

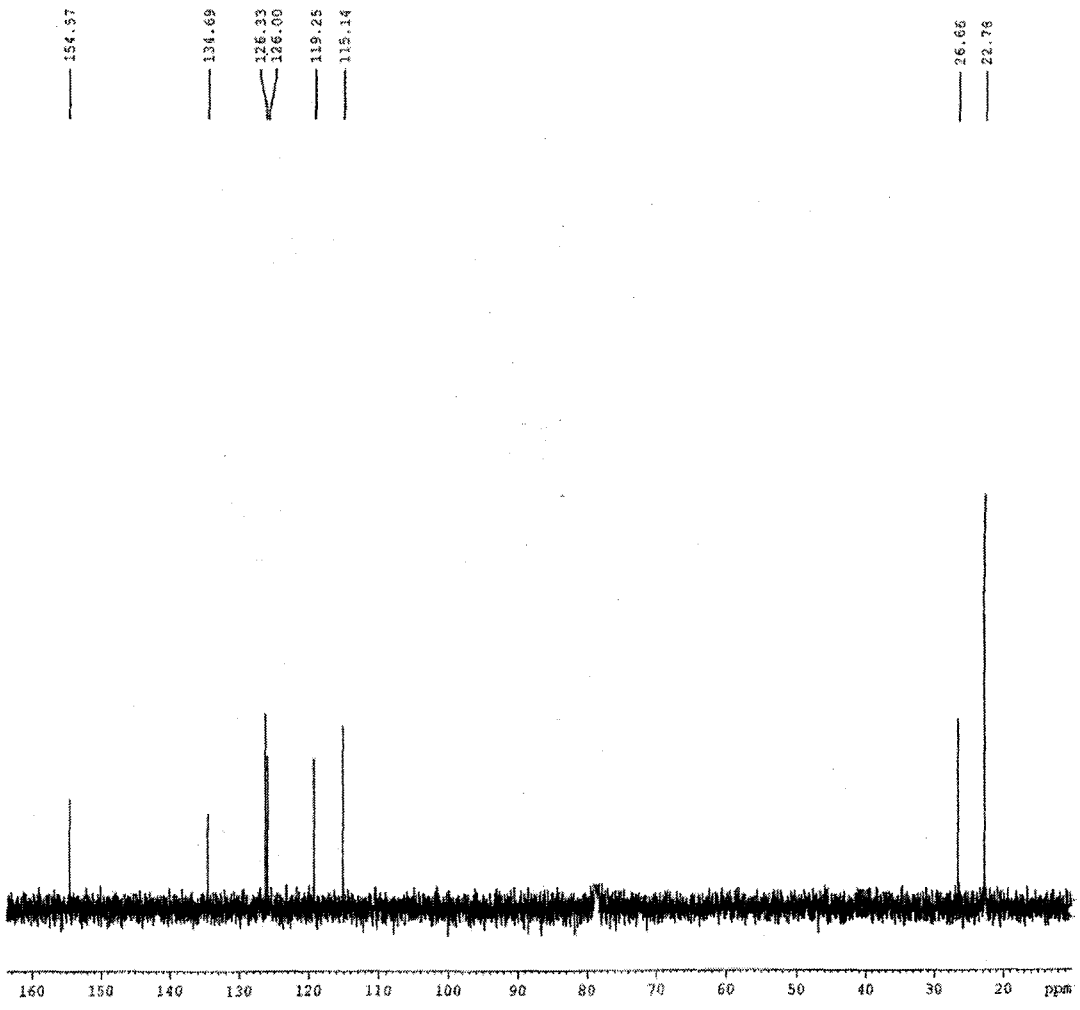


Fig 15. ^{13}C NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_5$

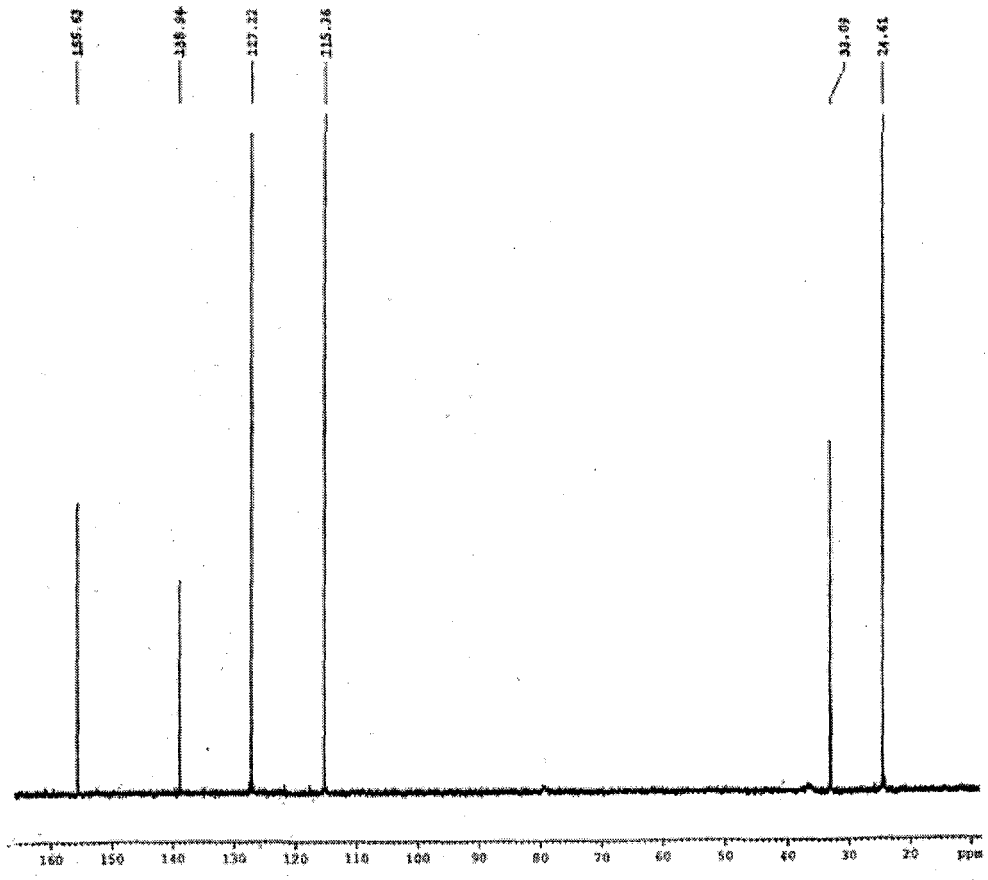


Fig 16. ^{13}C NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$

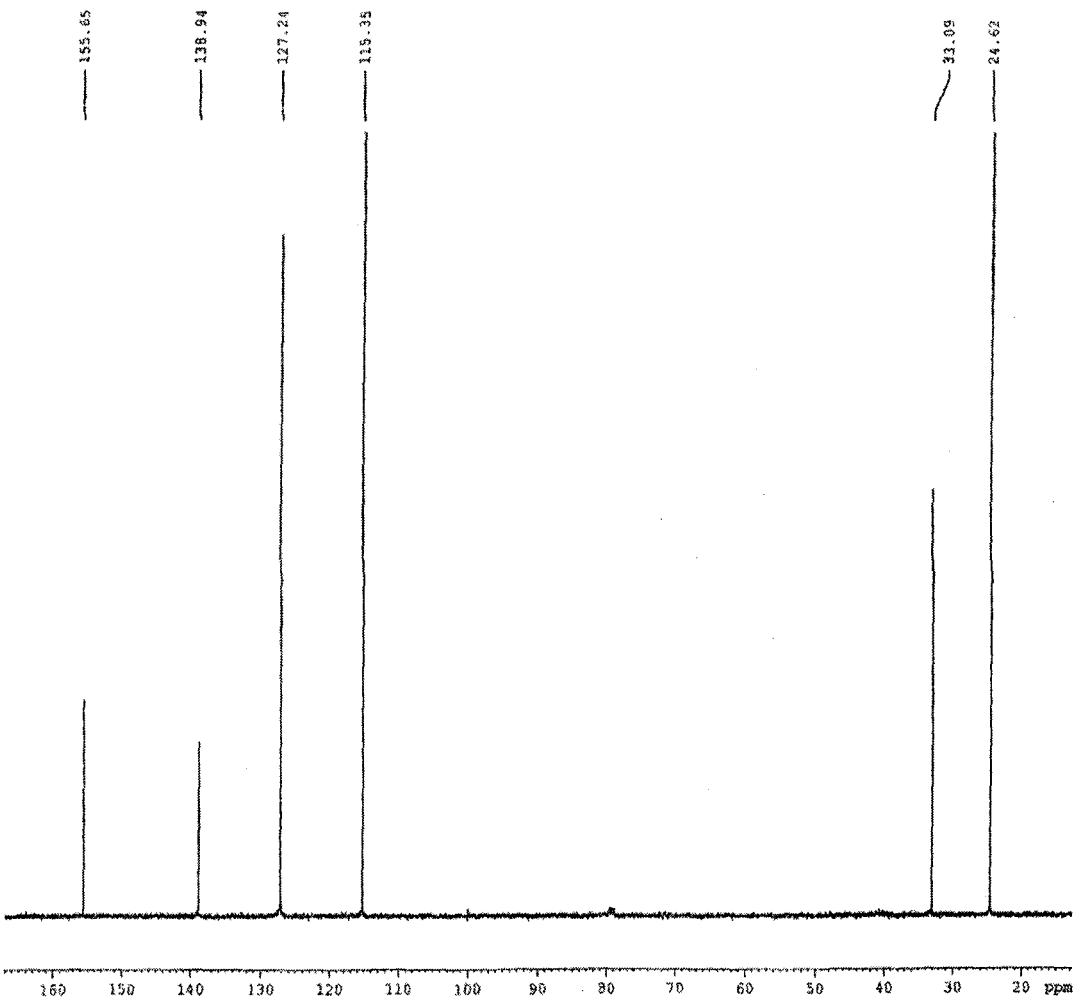


Fig 17. ^{13}C NMR spectrum of $NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$

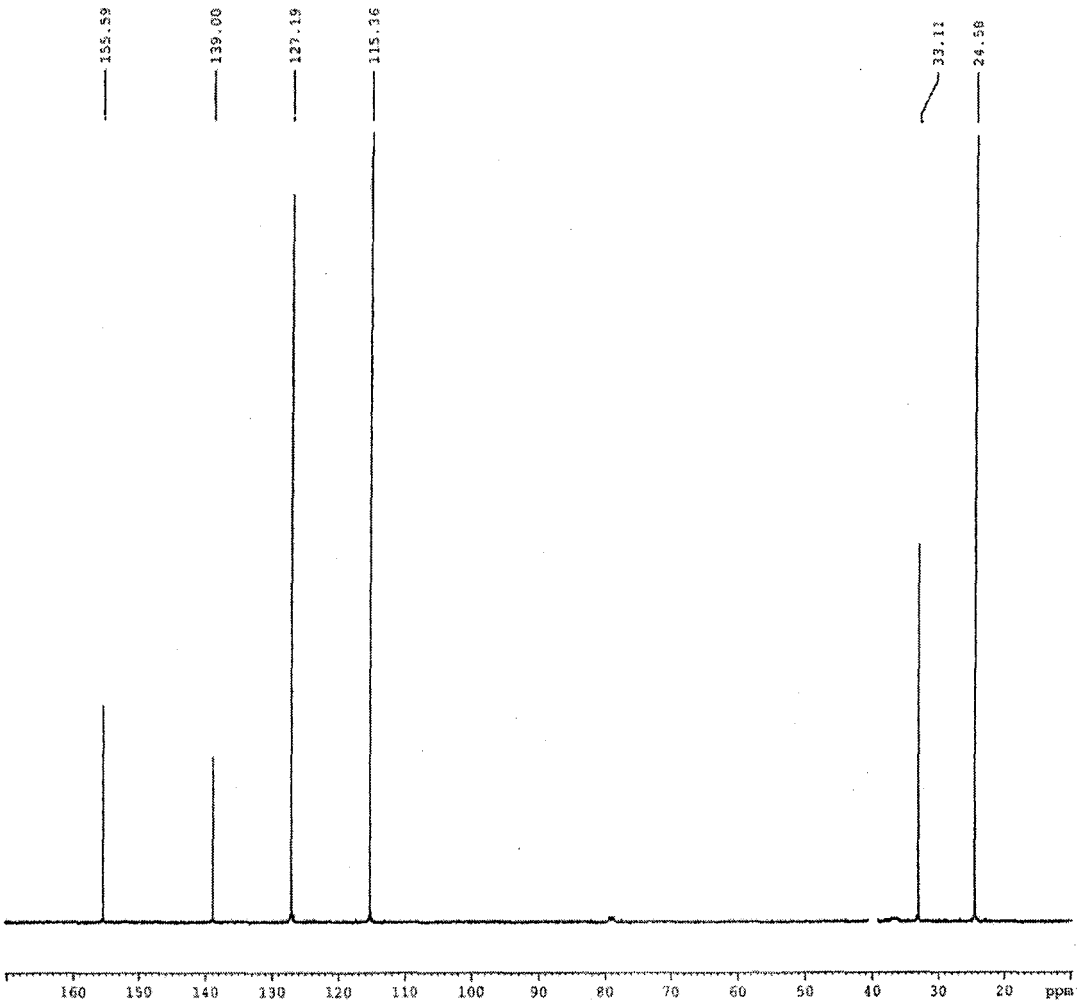


Fig 18. ^{13}C NMR spectrum of $NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3$

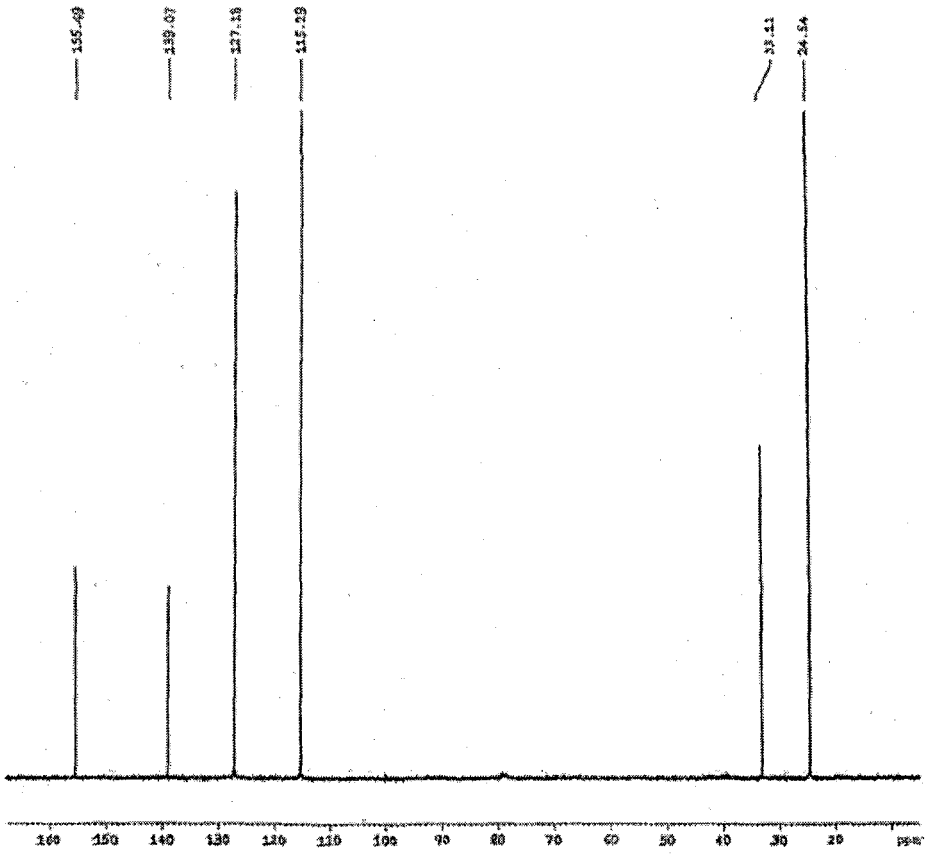


Fig 19. ^{13}C NMR spectrum of $NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$

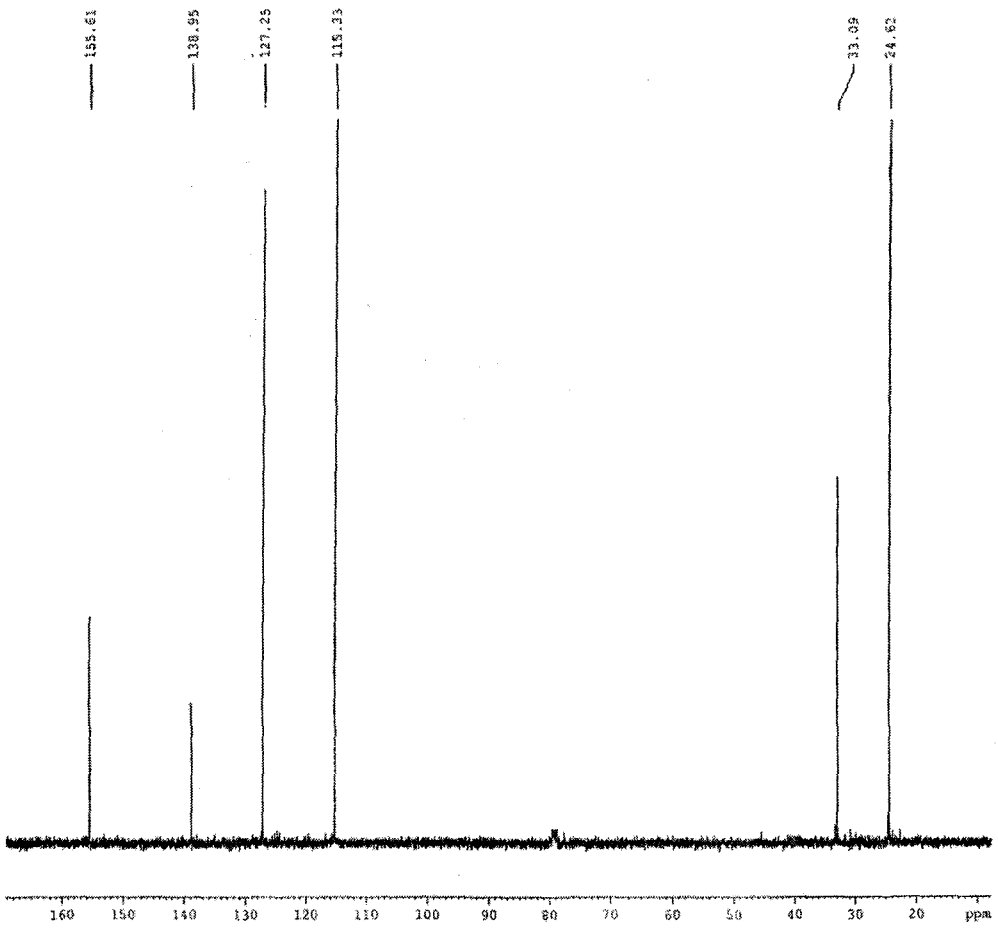


Fig 20. ^{13}C NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

Table 8. ^{13}C-NMR data of 4-isopropylphenol and niobium(V) 4-isopropylphenoxides (ppm)

Ligand/Complex	Aromatic phenolic ring carbons						Substituent (Isopropyl carbons)	
	C-1	C-2	C-3	C-4	C-5	C-6	-CH	$-(CH_3)_2$
$HOC_6H_4CH(CH_3)_2$-4	154.50	115.40	127.70	141.30	127.70	115.40	31.70	24.40
$NbCl_4(OC_6H_4CH(CH_3)_2$-4)	155.63	115.36	127.22	138.94	127.22	115.36	33.09	24.61
$NbCl_3(OC_6H_4CH(CH_3)_2$-4)$_2$	155.59	115.36	127.19	139.00	127.19	115.36	33.11	24.58
$NbCl_2(OC_6H_4CH(CH_3)_2$-4)$_3$	155.65	115.35	127.24	138.94	127.24	115.35	33.09	24.62
$NbCl(OC_6H_4CH(CH_3)_2$-4)$_4$	155.49	115.29	127.18	139.07	127.18	115.29	33.11	24.59
$Nb(OC_6H_4CH(CH_3)_2$-4)$_5$	155.61	115.33	127.25	138.95	127.25	115.33	33.09	24.62

The UV-visible spectra of complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n]$ (n = 1→5) displayed intense bands at ~ 240 nm and ~ 300 nm while complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)_n]$ (n = 1→5) exhibited an intense band at ~ 240 nm and low intense band at ~ 320 nm. These bands may be assigned to ligand to metal charge transfer transition (LMCT) involving the oxygen lone pair (2p) electrons. It may be presumed as an electronic transition from a bonding π-molecular orbital formed by the overlap of d_{xz} or d_{yz} atomic orbitals of niobium with the filled π-orbitals of phenoxide ion to a non-bonding orbital say d_{xy} on niobium. A change in the position of the absorption band of the ligand has been observed upon complexation.

2.1.5. Mass Spectra

There has been a continuous advancement in mass spectrometry (MS) not only owing to its broad applicability in chemical sciences, life sciences, public safety screening, industrial hygiene and environmental monitoring but also due to the innovations in both instrumentation and methodology with regards to speed, sensitivity and specificity over other methods of chemical analysis. The emergence of several revolutionary ionization techniques such as desorption electrospray ionization (DESI) and several of its variants viz. desorption atmospheric pressure chemical ionization (DAPCI), atmospheric pressure thermo desorption ionization (APTDI), desorption sonic spray ionization (DSSI) renamed ambient sonic spray ionization (EASI), desorption atmospheric pressure photo-ionization (DAPPI), neutral desorption extractive electrospray ionization (ND-EESI), plasma-assisted desorption ionization (PADI) and electrospray-assisted laser desorption/ionization (ELDI) and its variants viz. matrix-assisted laser desorption/ionization (MALDI), atmospheric pressure MALDI (APMALDI), matrix-assisted laser desorption electrospray ionization (MALDESI), laser ablation electrospray ionization (LAESI), IR laser-assisted desorption electrospray ionization (IR LADESI) and impact desolution of electrosprayed microdroplets (IDEM), electrosprayed droplet impact ionization (EDI), extractive electrospray ionization (EESI) etc. have played a significant role in recent developments in mass spectrometry. The utility of these techniques has been well demonstrated for all sorts of small and large molecules, including drugs, explosives, proteins and chemical warfare agents and various other living and non-living objects. The modern instruments often have the facility to perform more than one mass analysis on a single sample i.e. ES/MS (the earlier term used is Tandem mass spectrometry) or even MS^n (where n = number of stages of mass spectrometry). The inductively coupled plasma mass spectrometry (ICP-MS), liquid

secondary ion mass spectrometry (LSIMS) and fast atom bombardment (FAB) techniques have also attracted the attention of scientists. The discrimination between ions of different mass-to-charge ratio (m/z) is carried out by many types of mass analysers viz. sector, quadrupole, ion trap, TOF, Q-TOF and FTICR (Fourier Transform Ion Cyclotron Resonance). Of these, Time-of-Flight (TOF) mass analyzer is perhaps the simplest means of mass analysis. The orthogonal TOF (Oa-TOF), quadrupole TOF (Q-TOF) and TOF-TOF instruments are known to be fast, highly efficient, sensitive and capable of high resolution. Mass spectrometry has been used successfully of assigning structures to various complex molecules (276).

In the past, mass spectrometry of either inorganic or organometallic compounds was dominated by the ionisation techniques of electron impact (E1) or fast atom bombardment (FAB). Electron impact technique is largely limited to the analysis of neutral volatile species which for many reasons were also required to be stable. On the other hand, Fast Atom Bombardment is more successful and works extremely well for both polar compounds and salts which promote the formation of either a protonated molecular ion $[MH]^+$ or the radical cationic species $[M]^+$ (277), but was still disadvantaged by the relatively high degree of fragmentation making identification of molecular ions difficult. FABMS and tandem mass spectrometry (MS/MS and MS/MS/MS) have been used to obtain molecular information of a variety of 4[t-butylcalix [8] arene$(MOR)_2]^-$ [M′ or $RNH_3]^+$ (M = Ti, Zr, V, Sn, M′ = Li, Na, K) complexes (278).

The soft ionization technique of electrospray (ES) which has proven particularly beneficial to biochemists for the characterization of large organic molecules, e.g. proteins (279) has recently found favour among inorganic and organometallic chemists (280-286). In general, ESMS gives considerable control over the degree of fragmentation by varying the skimmer cone voltage. In principle, the technique is applicable to any pre-existing cation, anion or neutral compound that can be modified by the addition of a suitable reagent to form an ion, provided that the ion is stable to the solution environment used in the mass spectrometer. ESMS analysis of a variety of hydroxymethylphosphines and their derivatives including phosphines, sulphides and phosphonium salts have been described (287). Only weak ions are observed in the positive ion ES mass spectra of many phosphines because they are weak bases, however, it was demonstrated that addition of a suitable reagent (either aqueous $AgNO_3$, or a mixture of 40% formaldehyde and concentrated HCl) could aid in the formation of cations for positive ion

ESMS. Colton and coworkers (285) have described the use of iodomethane as an alternative ionisation agent for the analysis of tertiary phosphines by ESMS (286).

There are scattered reports in literature concerning the mass spectra of polymeric/dimeric alkoxides such as $[Ti_4(OMe)_{16}]$, $[Zr_4(OEt)_{16}]$, $[Nb_2(OEt)_{10}]$, $[Ta_2(OEt)_{10}]$ and double alkoxides of aluminium $[MAl_3(OPr^i)_{12}]$ (M = lanthanide element). No parent ion peak has been reported in these compounds except for m/z ion peak at 928 in fairly large abundance in $[LaAl_3(OPr^i)_{12}]$ (288). The mass spectrum of thallous phenoxide by Lee (289) has been reported to contain both monomeric and dimeric species as well as the ions $[Ti_2O]^+$ and $[Ti_2OH]^+$. Despite the fact that TiC_5H_5 is a stable compound, no formation of ions of the type $[C_5H_5Ti]^+$ was observed. The mass spectra of aryloxythionyltrifluorides showed parent ion peak along with strongest peaks corresponding to ^{32}S and ^{34}S isotopes.

The electron impact mass spectra of some of titanium aryloxides carried out by Lappert and coworkers (290) did not show parent ion peak $[M]^+$ except in case of $[TiCl_2(OC_6H_3Me_2\text{-}2,6)_2(THF)_2]$, which displayed a highest ion peak corresponding to $[M\text{-}2THF]^+$ and a peak $[M\text{-}Cl]^+$ with loss of chloride ion. Malhotra and coworkers (291) have rationalized different mass ion peaks for titanium(IV) naphthoxides in terms of definite fragmentation pattern, wherein, weak peaks higher than the expected monomeric m/z peaks have been attributed to the dimeric structures in confirmity with physicochemical studies made on these complexes. Fragmentation patterns have been reported for the coordination compounds of cobalt(II) and nickel(II) with Schiff's bases (292,293).

The mass spectral analysis of $[Ta(OC_6H_3Me_2\text{-}2,6)_5]$ and $[TaCl_3(OC_6H_3Bu^t_2\text{-}2,6)_2]$ has been reported to show a strong parent molecular ion peak with distinctive fragmentation due to loss of chlorine (when present) or aryloxide group. However, for complex of composition $[TaCl_2(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3]$ and $[TaCl_3(OC_6H_3Pr^i_2\text{-}2,6)_2]$, the presence of $[Ta(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_4Cl^+]$ in low abundance has been reported. These observations may either be indicative of the dimeric nature of these complexes in solid state or else to be due to ligand exchange occurring within the mass spectrometer.

In the present work, the [ES] mass spectra of newly synthesized niobium(V) 2/4-isopropylphenoxide of composition $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ (M) have been recorded to examine the fragmentation pattern displayed by these complexes. Both the complexes did not display any molecular ion peak at m/z 368. The occurrence of fragment ions of magnitude higher

than molecular mass, suggested dimeric nature of complexes. The fragment ion appeared at m/z 617 in complex $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ corresponded to $[2M\text{-}(OPhPr^i\text{-}2)+CH_3+H]^+$. The base peak at m/z 417 has been assigned to $[Nb_2(OPhPr^i\text{-}2)(OC_6H_5)+4H]^+$. The fragment ions at m/z 321, 299, 187, 155 and 125 corresponded to $[Nb_2(OPhPr^i\text{-}2)]^+$, $[NbCl_2(OPhPr^i\text{-}2)+H]^+$, $[Nb_2H]^+$, $[NbO_2+2Me]^+$ and $[NbO_2]^+$ respectively. In complex of composition $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$, the fragment ions at m/z 587, 551, 519, 505, 353 and 337 corresponded to $[2M\text{-}3Cl\text{-}Pr^i\text{-}H]^+$, $[Nb_2(OPhPr^i\text{-}4)_2+(HOC_6H_5)+H]^+$, $[MH+HOPhPr^i\text{-}4+Me]^+$, $[MH+HOPhPr^i\text{-}4]^+$, $[M\text{-}Me]^+$ and $[M\text{-}2Me\text{-}H]^+$ respectively. The complex displayed a base peak at m/z 217/218 assignable to $[Nb_2O_2]^+$. The fragment ions at m/z 321, 273, 187, 169 and 123 corresponded to $[Nb_2(OPhPr^i\text{-}4)]^+$, $[Nb_2+2Pr^i+H]^+$, $[Nb_2H]^+$, $[Nb(C_6H_5)\text{-}H]^+$ and $[Nb+2Me]^+$ respectively (Table 9).

The [ES] mass spectra $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4]$ (M) displayed peaks at m/z 670 assignable to $[M+2H]^+$. The higher fragment ions than molecular mass suggested the dimeric nature of complexes. The fragment ion appeared at m/z 1207 in complex $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ corresponding to $[2M\text{-}3Pr^i]^+$ indicated primary decomposition by the removal of three isopropyl substituents. The base peak at 217/218 corresponded to $[Nb_2O_2]^+$. The fragments ions at m/z 1169, 988, 804, 670, 655, 602/603, 591, 523, 417, 273, 185, 155, 122 corresponded to $[2M\text{-}3Pr^i\text{-}Cl\text{-}2H]^+$, $[Nb_2(OPhPr^i\text{-}2)_5(OPh)Cl\text{-}H]^+$, $[NbCl(OPhPr^i\text{-}2)_4]^+$ + $[(HOPhPr^i\text{-}2)]^+$, $[M+2H]^+$, $[Nb_2Cl(OPhPr^i\text{-}2)_3+ 2Me]^+$, $[M\text{-}Cl\text{-}2Me]^+$, $[NbCl(OPhPr^i\text{-}2)_4\text{-}Cl\text{-}Pr^i+H]^+$, $[Nb_2O_2Cl(OPhPr^i)_2]^+$, $[Nb_2(OPhPr^i\text{-}2)(OPh)+3H]^+$, $[(HOPhPr^i\text{-}2)_2+H]^+$, $[Nb(OC_6H_5)\text{-}H]^+$, $[NbO_2+2Me]^+$ and $[Nb+2Me\text{-}H]^+$ respectively (Table 10).

In $[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$, the fragment ions appeared at m/z 1293 and 1173 corresponding to $[2M\text{-}Pr^i]^+$ and $[2M\text{-}3Pr^i\text{-}Cl]^+$ indicated decomposition by one isopropyl group and three isopropyl groups and chloride ion respectively (Figs. 21-23). The base peak at 551 has been attributed to $[Nb_2OCl(OPhPr^i)_2+Pr^i+H]^+$. The fragment ions at 507, 217, 155 and 122 corresponded to $[Nb_2OCl(OPhPr^i)_2]^+$, $[Nb_2O_2]^+$, $[NbO_2+2Me]^+$ and $[Nb+2Me\text{-}H]^+$ respectively.

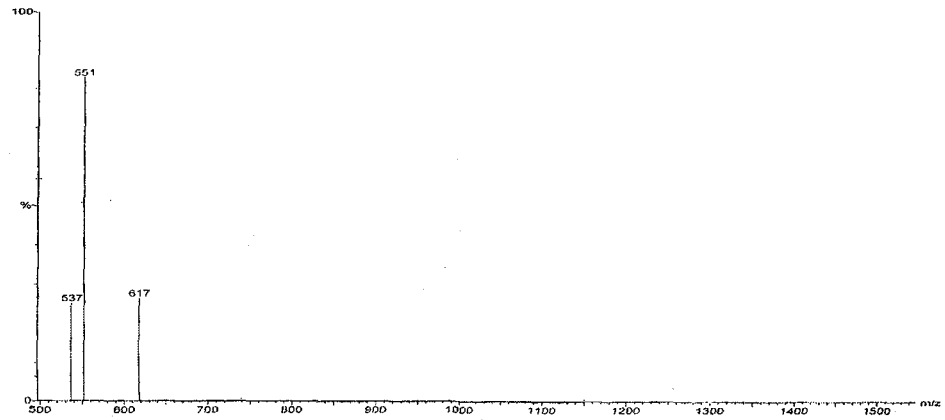
2.1.6. X-ray Diffraction Studies

X-ray diffraction is a versatile, non-destructive analytical technique for identification and quantitative determination of various crystalline forms known as phases of compounds present in the powdered and solid samples. The identification is achieved by comparing the X-ray diffraction pattern obtained for unknown sample with an internationally recognized database

Table 9. Selected positive-ion electrospray mass spectral data for *niobium*(V) 2-/4-isopropylphenoxides

$NbCl_4(OC_6H_4CH(CH_3)_2$-2) [M]	m/z	Int%	$NbCl_4(OC_6H_4CH(CH_3)_2$-4) [M]	m/z	Int%
$[2M-(OPhPr^i$-2)$+CH_3+H]^+$	617	26	$[2M-3Cl-Pr^i-H]^+$	587	3
$[Nb_2(OPhPr^i$-2)$_2+(HOC_6H_5)+H]^+$	551	83	$[Nb_2(OPhPr^i$-4)$_2+(HOC_6H_5)+H]^+$	551	4
$[Nb_2(OPhPr^i$-2)$_2Cl+3Me+H]^+$	537	26	$[M+(HOPhPr^i$-4)$+Me+H]^+$	519	11
$[Nb_2(OPhPr^i$-2)$(OC_6H_5)+4H]^+$	417 (B.P.)	100	$[M+(HOPhPr^i$-4)$+H]^+$	505	4
$[Nb_2(OPhPr^i$-2)$]^+$	321	6	$[Nb_2(OPhPr^i$-4)$_2+2Me]^+$	483	8
$[NbCl_2(OPhPr^i$-2)$+H]^+$	299	2	$[M-Me]^+$	353	4
$[Nb_2O_2]^+$	217/218	29	$[M-2Me-H]^+$	337	6
$[Nb_2H]^+$	187	6	$[Nb_2(OPhPr^i$-4)$_2]^+$	321	99
$[NbO_2+2Me]^+$	155	25	$[(HOPhPr^i$-4)$_2+H]^+$	273	74
$[Nb_2O_2+Me-H]^+$	139	7	$[NbCl_4+Na+H]^+$	257	25
$[NbO_2]^+$	125	7	$[Nb_2O_2]^+$	217/218(B.P)	100
$[C_6H_5]^+$	77	3	$[Nb_2H]^+$	185/187	14
			$[Nb(C_6H_5]-H]^+$	169	4
			[Nb+2Me]	123/100	35

where $HOPhPr^i = HOC_6H_4CH(CH_3)_2$-2/4



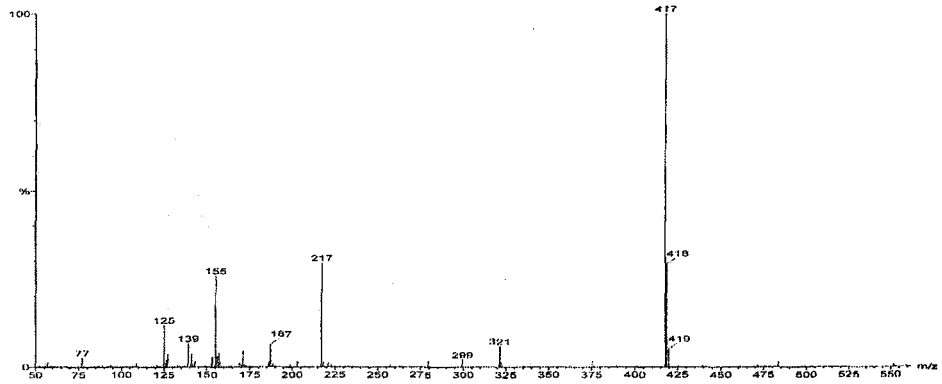
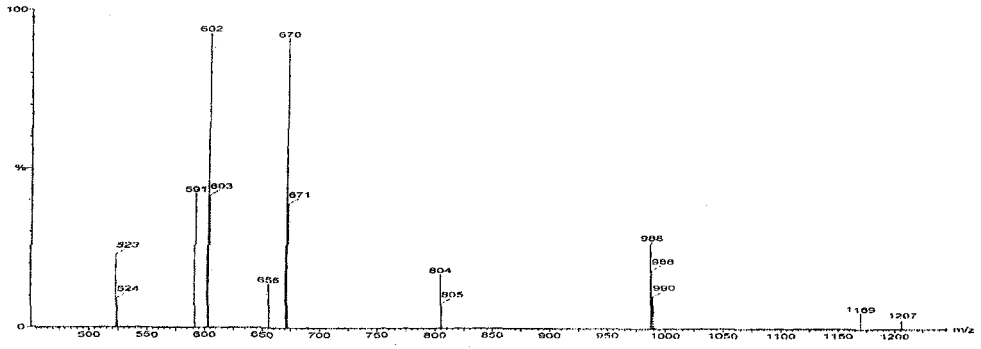


Fig 21. Mass spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$



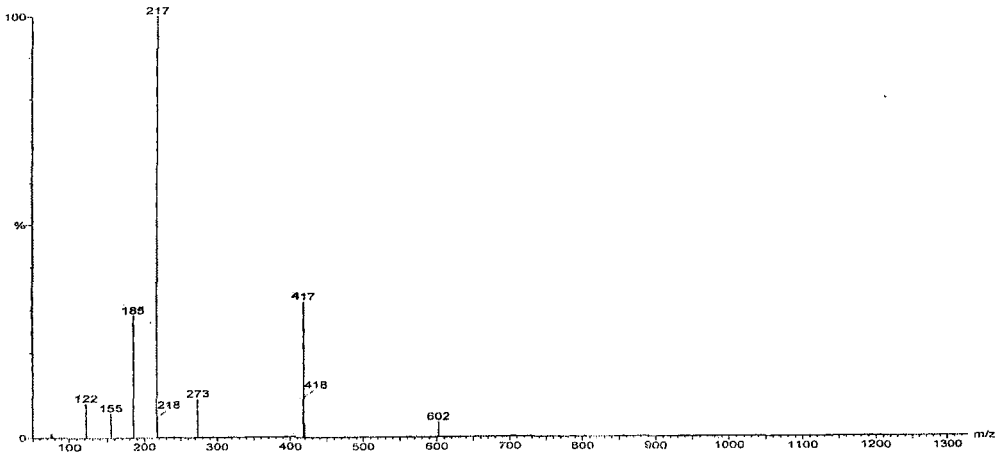
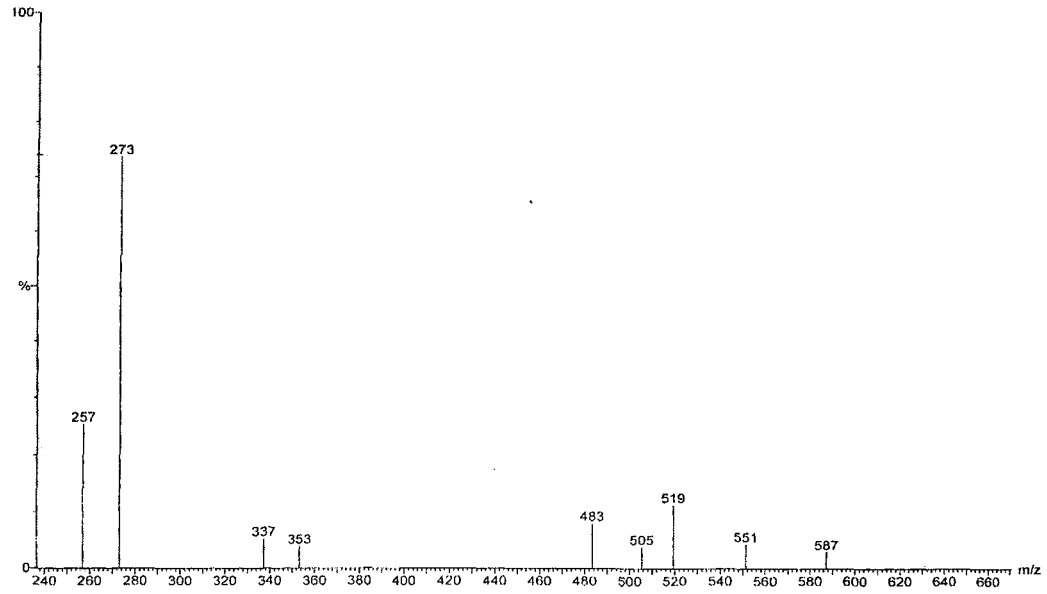


Fig 22. Mass spectrum of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$



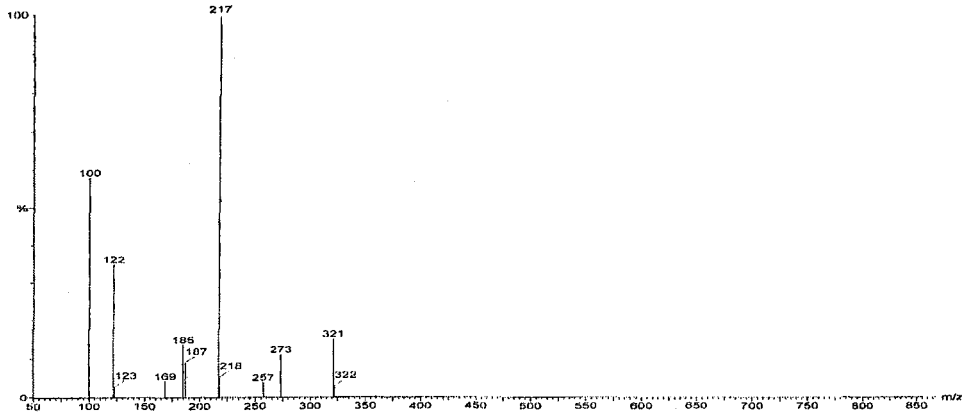


Fig 23. Mass spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$

Table 10. Selected positive-ion electrospray mass spectral data for niobium(V) 2-/4-isopropylphenoxides

$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$ [M]	m/z	Int%	$NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$ [M]	m/z	Int%
$[2M\text{-}3Pr^i]^+$	1207	3	$[2M\text{-}Pr^i]^+$	1293	16
$[2M\text{-}3Pr^i\text{-}Cl\text{-}2H]^+$	1169	5	$[2M\text{-}3Pr^i\text{-}Cl]^+$	1171	12
$[Nb_2(OPhPr^i\text{-}2)_5(OPh)Cl\text{-}H]^+$	988	28	$[Nb_2(OPhPr^i\text{-}2)_5(OPh)\text{-}H]^+$	952	36
$[NbCl(OPhPr^i\text{-}2)_4 + (HOPhPr^i\text{-}2)]^+$	804	17	$[Nb_2Cl_2(OPhPr^i\text{-}2)_4]^+$	797	28
$[M+2H]^+$	670	91	$[NbCl(OPhPr^i\text{-}2)_4 + Me+H]^+$	699	14
$[Nb_2Cl(OPhPr^i\text{-}2)_3 + 2Me]^+$	655	14	$[NbOCl(OPhPr^i\text{-}2)_4]^+$	684	56
$[M\text{-}Cl\text{-}2Me]^+$	602/603	93	$[Nb_2(OPhPr^i\text{-}2)_3Cl\text{-}H]^+$	625	87
$[NbCl(OPhPr^i\text{-}2)_4\text{-}Cl\text{-}Pr^i+H]^+$	591	42	$[Nb_2OCl(OPhPr^i)_2+Pr^i+H]^+$	551(B. P.)	100
$[Nb_2O_2Cl(OPhPr^i)_2]^+$	523	23	$[Nb_2OCl(OPhPr^i)_2]^+$	507	23
$[Nb_2(OPhPr^i\text{-}2)(OPh)+3H]^+$	417	32	$[Nb_2O_2]^+$	217/218	34
$[(HOPhPr^i\text{-}2)_2+H]^+$	273	9	$[NbO_2+2Me]^+$	155	13
$[Nb_2O_2]^+$	217/218 (B. P.)	100	$[Nb+2Me\text{-}H]^+$	122	27
$[Nb(OC_6H_5)\text{-}H]^+$	185	29			
$[NbO_2+2Me]^+$	155	6			
$[Nb+2Me\text{-}H]^+$	122	8			

where $HOPhPr^i = HOC_6H_4CH(CH_3)_2\text{-}2/4$

reference patterns (JCPDS). A crystal lattice is a regular array of atoms in space which are arranged in space to form a series of parallel planes separated from each other by distance d, which varies according to the nature of materials. For any crystal plane oriented in different direction has different d spacing. When a monochromatic X-ray beam with wavelength λ is incident on the lattice planes in the crystal at an angle, θ, diffractions occur only when the distance travelled by rays reflected from successive phases differs by a complete number 'n' of λs as Bragg's condition given below

$$n\lambda = 2d\sin\theta$$

The plotting of angle position and intensity of the resultant diffraction peaks produces a pattern which is characteristic of the sample. For a sample containing a mixture of phases, the XRD pattern is formed by addition of individual patterns.

The X-ray diffraction patterns of complexes have been examined in the present work to verify their nature (amorphous or crystalline) Phillips PW 3071 X'PERT-PRO X-ray diffractometer (XRD) was used in 5-70° 2θ range with 0.017 step size in continuous scanning mode at 25°C. Phillips X'Pert software was used to obtain precise value of parameters such as peak position, peak counts, d-spacing, full width at half maximum (FWHM) and relative intensities of the peaks.

The, particle size from each diffraction peak has been calculated using Scherrer equation:

$$\textit{Particle size} = \frac{0.9 \times \lambda}{\beta \cos\theta}$$

where $\lambda = 1.54060$ A°

β = Full Width at Half Maximun

and average particle size of 8.62 nm has been determined for the complex

The X-ray diffractograms of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ and $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ their exhibited only two reflections in each case of 2θ ranging from 25° to 50° suggesting their amorphous nature (Figs. 24 and 25). Complexes of composition $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ and $[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$ have also recorded only two reflections in each case of 2θ ranging from 25° to 50° indicative of amorphous nature (Figs. 26 and 27).

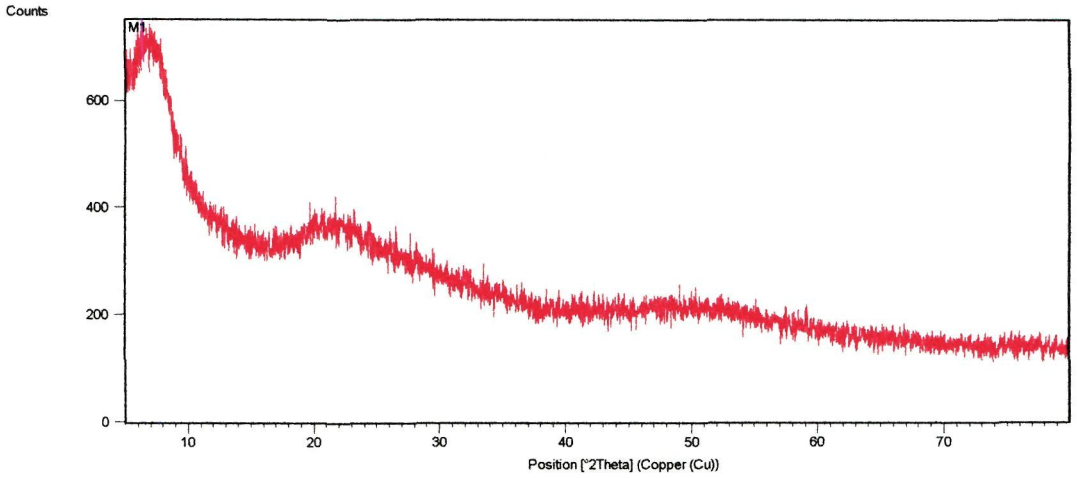


Fig 24. XRD pattern of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$

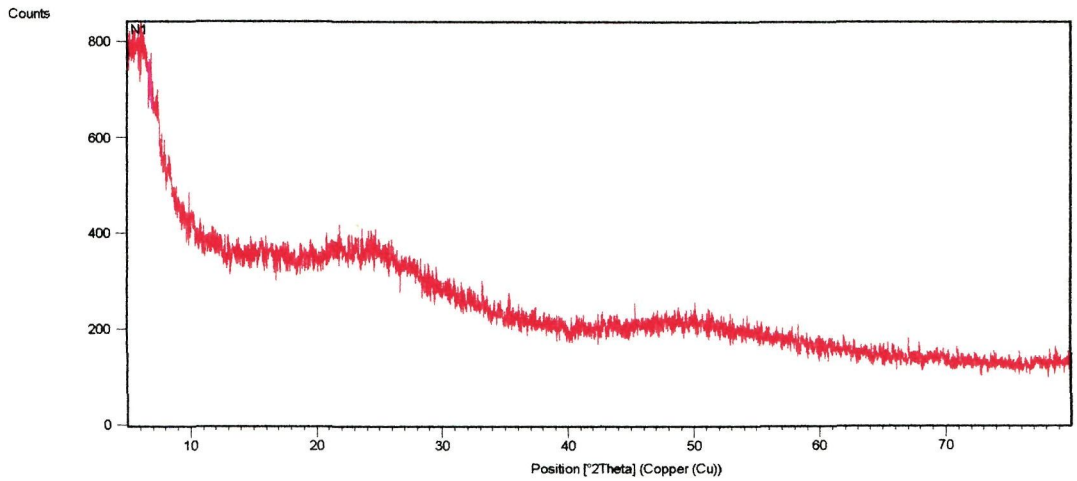


Fig 25. XRD pattern of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$

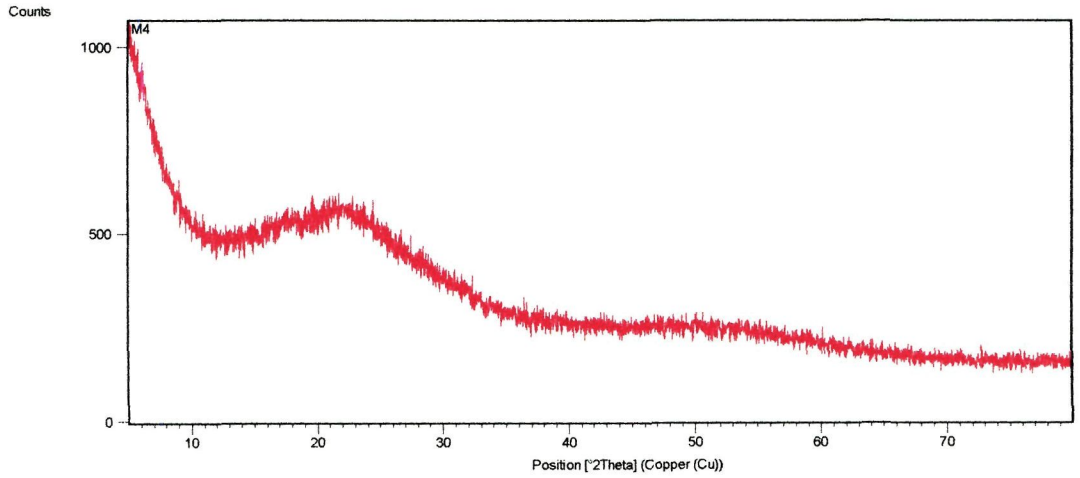


Fig 26. XRD pattern of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$

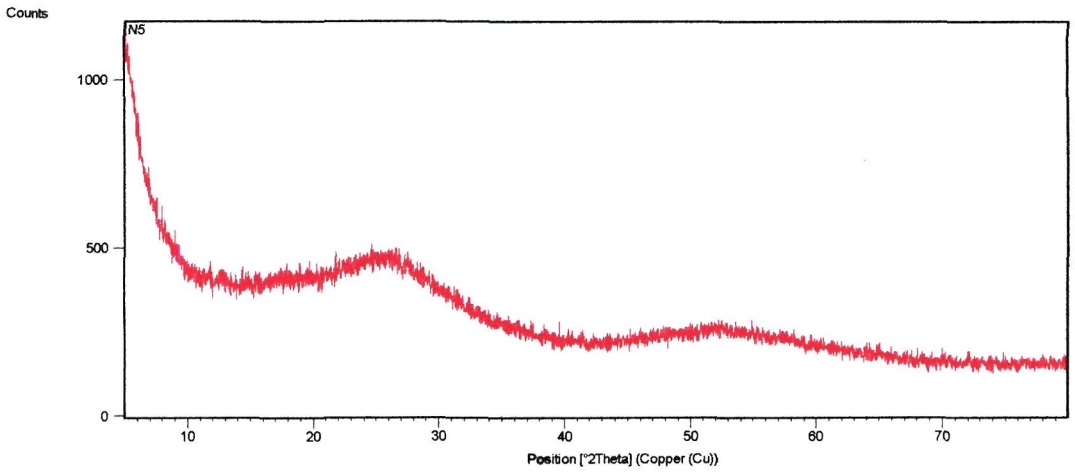


Fig 27. XRD pattern of $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

The XRD pattern of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$ however revealed both high and low intense peaks (Fig. 28). The indexing of XRD peaks was done from $\sin^2\theta$ values. The indices hkl contained in N where $N = h^2 + k^2 + l^2$ and were calculated by dividing the various $\sin^2\theta$ values by the various integer i.e. the possible N values (Table 11). To find hkl planes for the sample what we do is to find the value of $\sin^2\theta/N$ and find the common value for each peak, corresponding to the value of N, one is able to find hkl planes.

The values of N for each peak were determined upon dividing the $\sin^2\theta$ values by its common factor. The N values are then factorized by trial and error whereby the hkl values obtained represent the indices for the corresponding lines and every observed line is indexed (Table 12), indicative of its polycrystalline nature. An approximate value of the lattice parameter 'a' was calculated from common factor, N and $\lambda = 1.54$ A° using equation $a = \frac{1}{2}\lambda\sqrt{N}/\sin^2\theta$. An error function was calculated using equation $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$.

2.1.7. Molecular Modelling

Computational methods, in recent years constitute an indispensable part of the modern research of which molecular modelling exemplifies this approach. Molecular modelling is a collective term assignable to theoretical methods and computational techniques to model or mimic the behaviour of molecules. Using various molecular modelling methods, one can visualize, rotate, manipulate and optimize models on a computer display. This technique finds use in the fields of computational chemistry, computational biology and material science for studying molecular systems ranging from small chemical systems to large biological molecules and material assemblies.

Molecular mechanics is one aspect of molecular modelling which is also known as energy refinement or energy minimization procedure. It is based on the assumption that energy minimized structure is closer to the stable geometry and probably closer to the determined structure. Molecular models typically describe atoms (nucleus and electrons collectively) as point charges with an associated mass. The interactions between neighbouring atoms are described by spring like interactions (representing chemical bonds) and vander waals forces. Molecular modelling methods are now routinely used to investigate the structure, dynamics and thermodynamics of inorganic, biological (such as protein folding, enzyme catalysis, protein stability, conformational changes associated with bimolecular function and molecular recognition of proteins, DNA and membrane complexes), polymeric systems and also in drug designing.

Table 11. Calculations for hkl planes ($Nb(Cl(OC_6H_4CH(CH_3)_2\text{-}4)_4)$)

Peaks	N=1	N=2	N=3	N=4	N=5	N=6	N=7	N=8	N=9	N=10	N=11	N=12	N=13
Peak 1	**0.00257**	0.00129	0.000858	0.00064	0.000515	0.00043	0.00037	0.00032	0.00029	0.00026	0.00023	0.00021	0.000198
Peak 2	0.02058	0.01029	0.006861	0.00515	0.004116	0.00343	0.00294	**0.00257**	0.00229	0.00206	0.00187	0.00172	0.001583
Peak 3	0.00656	0.00328	**0.002186**	0.00164	0.001312	0.00109	0.00094	0.00082	0.00073	0.00066	0.00059	0.00055	0.000504
Peak 4	0.03857	0.01928	0.012856	0.00964	0.007713	0.00642	0.00550	0.00482	0.00429	0.00386	0.00351	0.00321	0.00296
Peak 5	0.00569	**0.00282**	0.001880	0.00141	0.001130	0.00094	0.00080	0.00070	0.00625	0.00057	0.00051	0.00047	0.00044
Peak 6	0.02180	0.01090	0.007260	0.00545	0.004360	0.00363	0.00311	0.00272	**0.00242**	0.00218	0.00198	0.00181	0.00168
Peak 7	0.03257	0.01628	0.010800	0.00814	0.006514	0.00542	0.00465	0.00407	0.00361	0.00326	0.00296	0.00271	**0.002505**

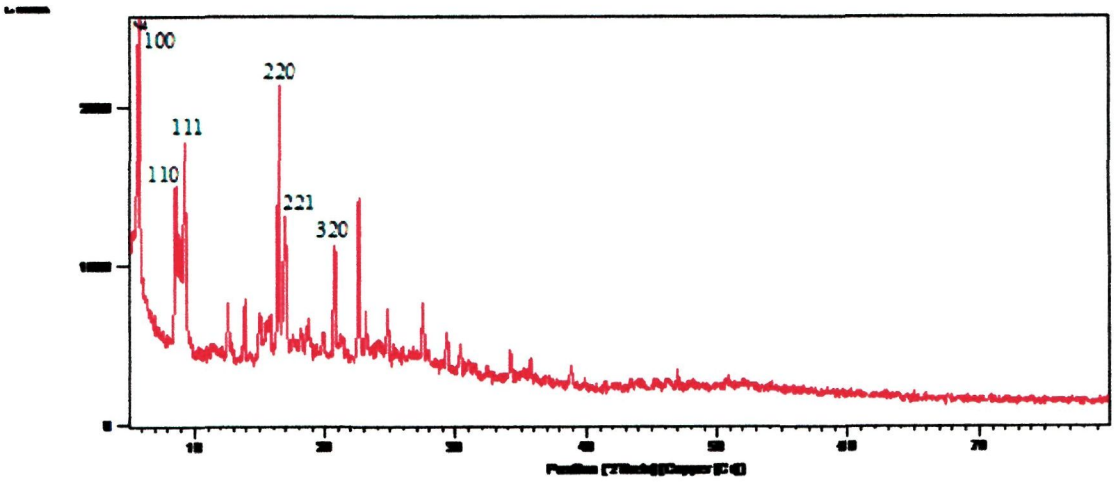


Fig 28. XRD pattern of $NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$

Table 12: Indexing of the Reflections and the Determination of the Lattice Parameter of ($Nb(Cl(OC_6H_4CH(CH_3)_2\text{-}4)_4$)

$Sin^2\theta$	$N = sin^2\theta/comm.\ fa.$	hkl	Quadratic forms of Miller Indices	$a = \frac{1}{2}\lambda\sqrt{N/sin^2\theta}$	Error function $\frac{1}{2}(cos^2\theta/sin\theta + cos^2\theta/\theta)$
0.002574	1	(100)	Sc and Hexagonal	15.18	9.99
0.020584	8	(220)	Sc, Fcc, Bcc, Diamond and Hexagonal	15.18	3.47
0.00656	3	(111)	Sc, Fcc, Diamond and Hexagonal	16.47	6.24
0.03856	15	----	Hexagonal	15.18	2.49
0.00569	2	(110)	Sc and Hexagonal	14.44	6.70
0.02180	9	(221)	Sc and Hexagonal	15.65	3.37
0.032572	13	(320)	Sc and Hexagonal	15.38	2.73

where Sc = Simple cubic, Fcc = Face centered cubic, Bcc = Body centered cubic

Molecular modelling of transition metal complexes is complicated by the partially filled d-orbitals of the metal ions that are responsible for the multifarious structures of coordination compounds with a large variety of possible coordination numbers and geometries. The coordination geometry of a metal complex is always a compromise between the size and electronic structure of the metal ion and the type, size, geometry and rigidity of the coordinated ligands. The fact that ligand-metal-ligand angles vary over a much larger range than corresponding parameters of organic molecules indicates that the competition between the ligand and the metal ion in terms of coordination geometry is generally dictated by the ligand. Thus, the structure of coordination compounds and therefore its thermodynamics, reactivity and electronics is strongly influenced by the ligand structure. Since empirical force field calculations have been shown to be a powerful tool for estimating the structure of organic molecules, molecular mechanics constitute a variable tool for modelling coordination compounds. For a molecular modelling technique to be useful and to achieve widespread application, it must readily and reliably reproduce molecular properties that closely resemble experimentally determined data.

In the present work, molecular modelling has been used to further support the proposed structures of complexes inferred from different spectroscopic studies using HyperChem 7.5 (student evaluation). The structures of complexes of composition $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$, $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$, $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$, $NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$ and $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$ were drawn in the workspace. The initial strained structure related to the most probable geometry of each metal complex was drawn. The geometry of the complex was energetically optimized through molecular mechanics applying MM^+ force field in vacuo with the Polka-Ribiere algorithm and RMS gradient 0.01 kcal/mole followed by molecular dynamics. The molecular dynamics simulation was done upto 1000K (for both relaxation time 1 ps) followed by molecular mechanics calculation again and the process was repeated five times to ensure that the true energy minimum had been reached. The strain energy was noted after each calculation and then the structures with minimum strain energy have been selected as most probable geometry of the complexes.

On the basis of analytical and IR, ^1H and ^{13}C NMR, electronic and mass spectral data combined with molecular modelling calculations, a dimeric structure bridging through iso-propylphenoxy groups exhibiting an octahedral environment around niobium has tentatively been proposed for niobium(V) complexes. The structures for perspective complexes are presented in Figs. 29-33.

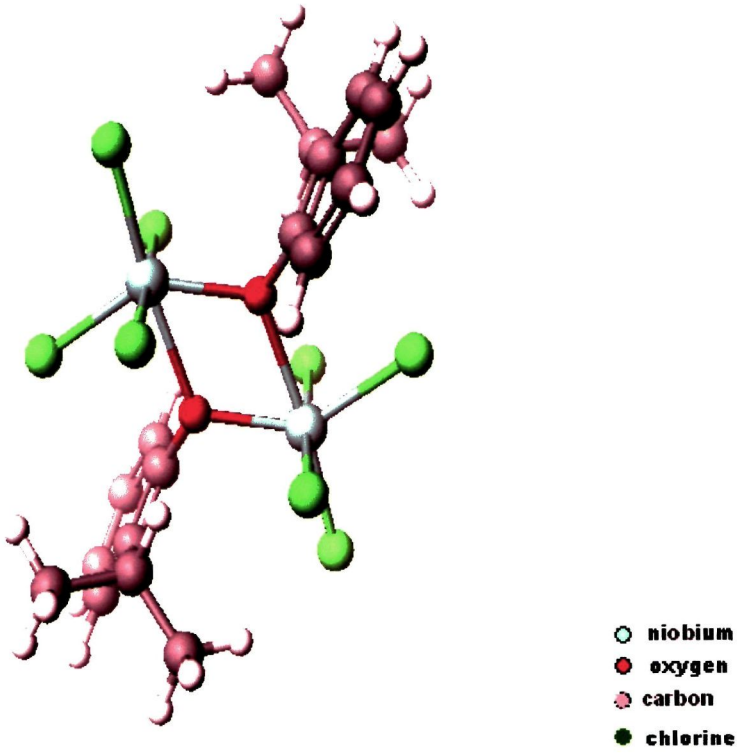


Fig. 29: Perspective dimeric structure of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$

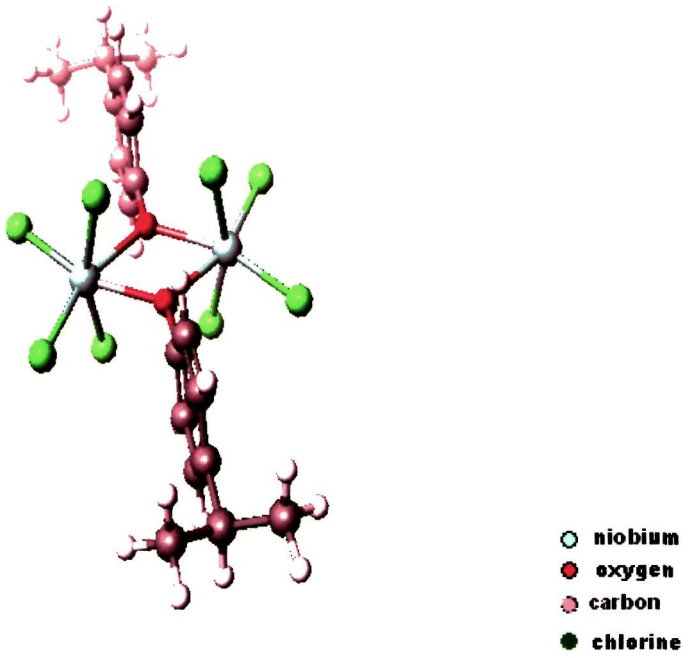


Fig. 30: Perspective dimeric structure of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$

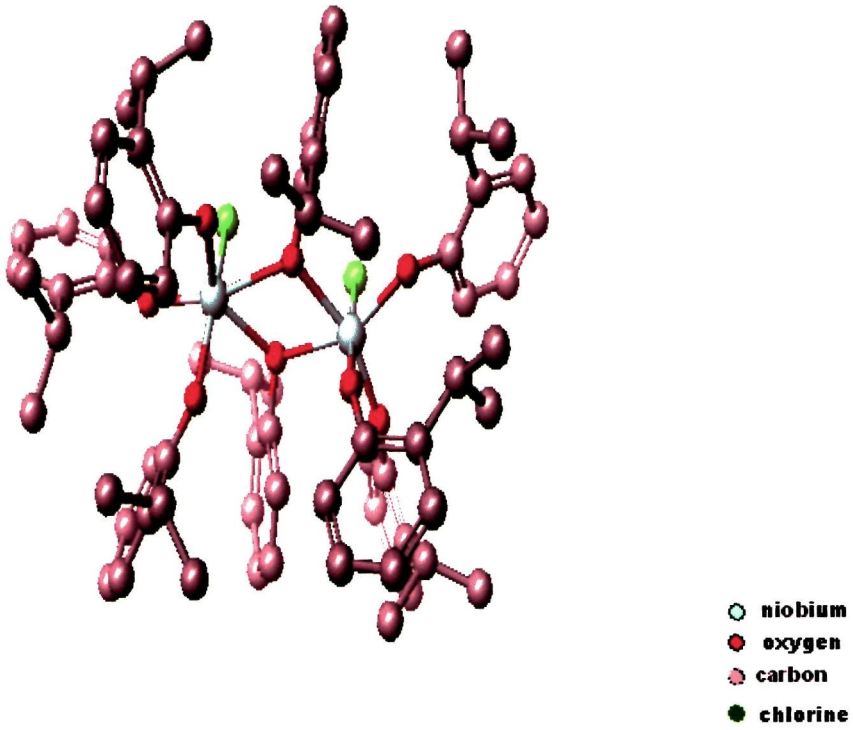


Fig. 31 Perspective dimeric structure of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$

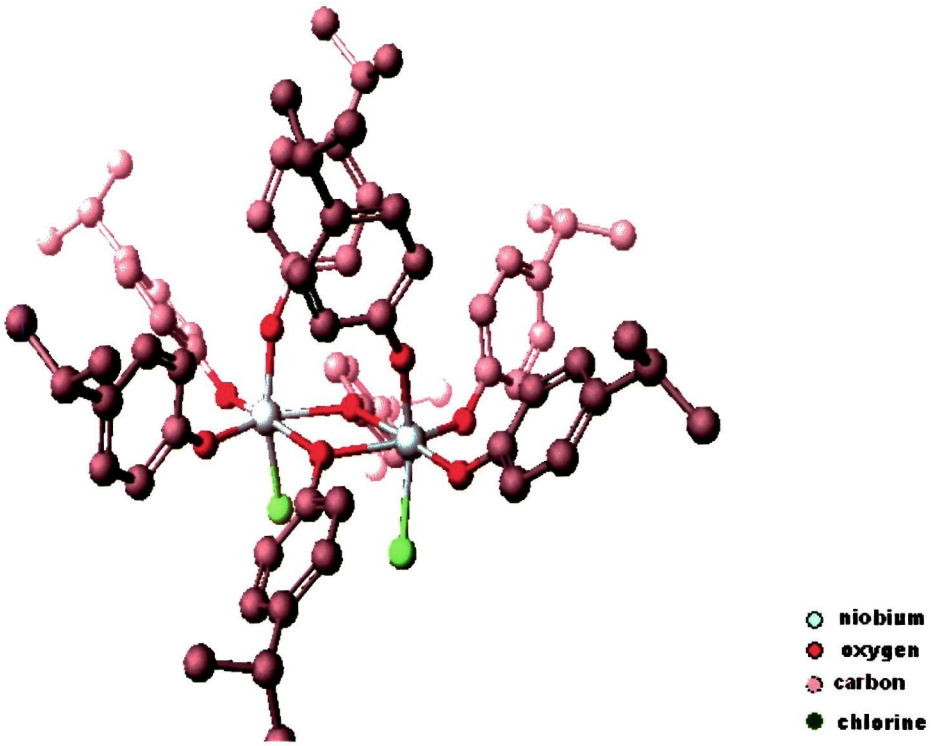


Fig.32: Perspective dimeric structure of $NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$

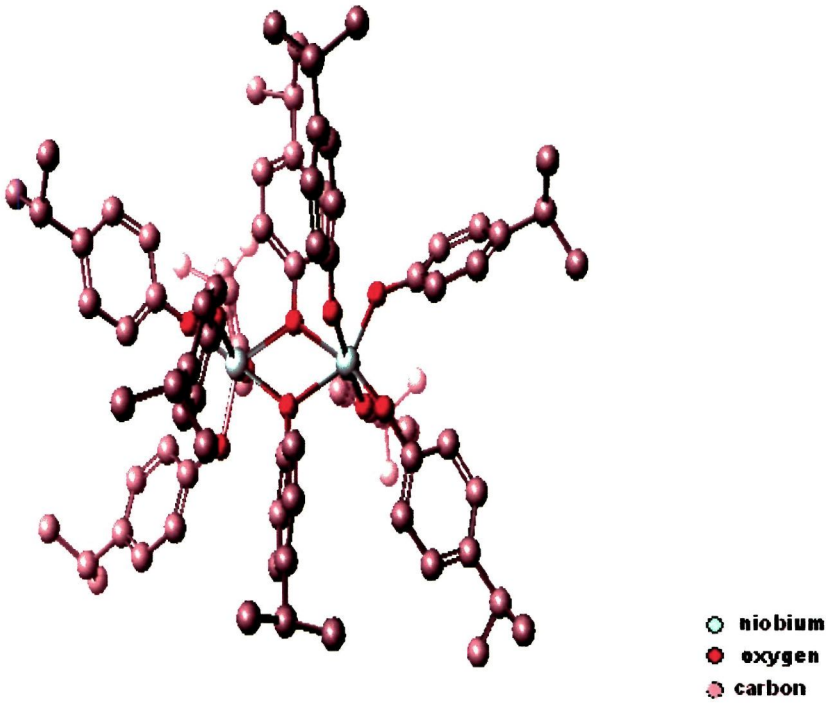


Fig. 33: Perspective dimeric structure of $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

2.1.8. Thermal studies

There have been tremendous developments of the principles and techniques of various physico-chemical methods of investigations over the years. Perhaps, one of the fastest growing areas has been those of thermal analytical techniques. These techniques have been developed systematically to such an extent that thermal analysis in recent years has acquired considerable prominence in virtually all branches of science and technology. It is no longer confined to the recording of heating curves and identification of minerals or the determination of mass loss temperature curves but has reached high degrees of sophistication due to rapid advances in electronics and computer science. The techniques viz. thermogravimetry (TG), differential thermogravimerty (DTG), differential thermal analysis (DTA), thermodilatometric analysis (TDA), thermo-optical analysis (TOA), thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) have progressed beyond recognition.

The DSC has probably seen the greatest step forward with the introduction of modulated differential scanning calorimetry (MDSC). The introduction of micro-DSC for thermo analysis in biochemistry, biology, food, pharmacy and cosmetics has gathered an ever-increasing interest. Its use in oxidative reactions and in solution chemistry, are evidences of reaching new heights. The emergence of temperature modulated DSC (TMDSC/TMC) has also offered important new possibilities by which equilibrium (reversible) and non-equilibrium (irreversible) processes can be studied.

The constant rate thermal analysis (CRTA) (294) modified further by Ortega (295) to constant acceleration thermal analysis (CATA) have gained immense applications. The relaxational techniques of dynamic mechanical thermal analysis (DMTA), dielectric thermal analysis (DETA) and emanation thermal analysis (ETA) find applications in the field of advanced materials with tailored properties e.g. the characterization of the thermal behaviour of solid precursors of advanced ceramic materials in the form of films, bulk or nano structure particles. The potential role of thermal analytical techniques in the identification of minerals, clays, metallic alloys, flame proof materials, sealants, coal, polymers, composites and many such systems that are integral part of metallurgy and material science has widen their acceptability. The importance of these techniques in understanding thermodynamics, kinetics and phase transformations etc. of many industrially important processes has also been acknowledged in recent years. The use of thermal analysis in the development of a better understanding of frozen

food stability has been studied (296). Thermal dehydration of some food products and kinetic parameters of the process have been reported. Thermal analysis and kinetic study of decomposition processes of some pesticides have also been described (297).

The applications of thermal analysis to the study of inorganic materials, determination of temperature appropriate for drying or ignition for analysis, kinetic and thermogravimetric data for reactions in solid state have been described (298-303). The use of thermal methods of analysis as a technique for studying bonding and structures of coordination compounds is of enormous interest (304).

Compared to well-documented synthetic chemistry of metal alkoxides and aryloxides, only scant reports are available in literature regarding their thermal behaviour. Thermal decomposition of silicon tetraethoxide is known to yield SiO and SiO_2 (305). Thermogravimetric study of yttrium isopropoxide and dispersant burn out in aluminium nitride ceramic processing has been described (306). The preparation and characterization of meta stable zirconia solid solutions from zirconium alkoxide and ytterrium acetylacetonate has been reported (307). The pyrolytic decomposition of aluminium tri-sec-butoxide during chemical vapour deposition (CVD) of thin alumina films has been described.

Fischer and coworkers have shown that metal phenoxides decompose before red hot to give liquid products such as benzene, phenol, diphenylene oxide, diphenyl ether etc. The mixed alkoxide-phenoxides of aluminium(III) and titanium(IV) of composition $[Al(OPh)_2(OBu^t)]$, $[Al(OPh)(OBu^t)_2]$ and $[Ti(OPh)_2(OBu^t)_2]$ have been observed to decompose through the formation of the intermediates $\{Ph[OAl(OH)]_4OPh\}$ and $\{Ph[OTi(OBu^t)(OH)]_4\}$ respectively. Thermal stability and decomposition products of various metal mercaptides derived from aromatic halogen substituted thiols have been reported (308,309). Thermal explosion of nitrophenates of transition metals has also been reported (310).

A few niobium containing materials have been studied using thermal techniques. The radiance temperatures (in the wavelength region at 658 and 898 nm) of niobium at its melting point have been reported. The preparation of $LiNbO_3$ powder from the thermal decomposition of a precursor salt obtained by an evaporative method has been described (311).The preferential orientation of dielectric/pyroelectric properties of sol-gel derived $[Pb(Mg,Zn)_{1/3}Nb_{2/3}O_3]$ thin films has been reported. An influence of Ti/Sn ratio and synthetic method in iron niobate doped with tin and titanium $[Fe_{0.4}Ti_{0.2-x}Sn_xNb_{0.4}O_2]$ solid solutions has been reported to be studied

(312). The effect of microstructure on the dielectric and piezoelectric properties of lead metaniobate has been investigated (313). Thermal studies of pentaoxides of vanadium, niobium and tantalum doped zirconia ceramics have been reported (314). Thermal stability and brazing characteristics of $[Zr_{0.7-x}M_xBe_{0.3}]$ (M = Ti or Nb) ternary amorphous filler materials have been reported (315). The non-isothermal reaction kinetics of $SrNb_2O_6$ and $BaNb_2O_6$ for the formation of $[Sr_xBa_{1-x}Nb_2O_6]$ have been described (316). The crystallization behaviour of Fe (Nb, Cu) Si-B metallic glasses has been reported (317). The phase diagram and oxygen ion conductivity in Y_2O_3-Nb_2O_5 system has been reported.

Thermal decomposition of $[NbCl_2(OMe)_3]$ in an argon or oxygen atmosphere is known to give Nb_2O_5 and ethylene as the main products (318). Complexes of composition $[NbCl_3(OC_6H_4Cl)_2]$ and $[Nb(OC_6H_4Cl)_5]$ have been reported to give niobium oxytrichloride, $NbOCl_3$ and niobiumdioxymonochloride NbO_2Cl and $NbO(OPh)_3$ and $NbO_2(OPh)$ as the intermediates in respective complexes (319). The intermediates of similar composition have been reported for $[NbCl_4(ONp)]$ (ONp = anion of naphthol) and $[Nb(ONp)_5]$ (320) giving Nb_2O_5 as the ultimate residue. The by-products of these decompositions have been proposed to be dichlorobenzene, dichlorophenylether, chloronaphthalene and dinapthyl ether for the respective complexes, in agreement with earlier reports on the decomposition trends of alkali metal (321) and transition metal phenoxides (322).

In view of these studies, it is imperative to gain an insight into the thermal behaviour of newly synthesized niobium(V) 2-/4-isopropylphenoxides using TGA and DTA techniques. These investigations are expected to provide information about the thermal stability of complexes, the nature of thermolytic products formed during their decompositions and final residue.

Thermal Behaviour of Niobium(V) 2-Isopropylphenoxides

Thermogravimetric curves of niobium(V)-2-isopropylphenoxides are illustrated in Figs. 34-37 and the thermal data is presented in Table 13.

$[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n]$ (n = 1→4)

The TG curve of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ (Fig. 34) has shown it to be thermally stable upto 39.20°C after which temperature, the complex seems to decompose in a continuous manner in single step as is indicated by the non-observance of any plateau in TG curve thereby excluding

Table 13. Thermal data of niobium(V) 2-/4-isopropylphenoxides

Complex	Initial decomp. Temp. (°C)	Stages of decomp.	TGA data			DTA data	
			Decomp. Range (°C)	% wt. loss obs. (Calc.)	Decomp. products	Peak temp. (°C)	Peak nature
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$	39.20	Single	39.2-516.5	42.33	$NbOCl_3$	474.02°C 89.98°C	Exothermic Endothermic
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$	55.00	Single	55-600.03	37.31	$NbO(OC_6H_5)_3$	---	---
$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3$	56.63	Single	56.63-600.03	48.66	$NbO_2(OC_6H_5)$	---	---
$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$	53.86	Two	53.86-500.66 500.66-600.66	60.10 18.99	$NbO_2(OC_6H_5CH(CH_3)_2$ Nb_2O_5	475.00°C 550.00°C	Exothermic
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$	51.35	Single	51.35-796.86	42.37	$NbOCl_3$	354.24°C 130.08°C	Exothermic Endothermic
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$	56.01	Single	56.01-475.02	71.67	Nb_2O_5	495.00°C	Exothermic
$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3$	55.40	Single	55.4-138	76.62	Nb_2O_5	---	---
$NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$	54.92	Single	54.92-500.13	80.10	Nb_2O_5	375.00°C	Exothermic
$Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$	30.06	Single	30.06-516.99	80.53	Nb_2O_5	358.10°C 185.56°C	Exothermic Endothermic

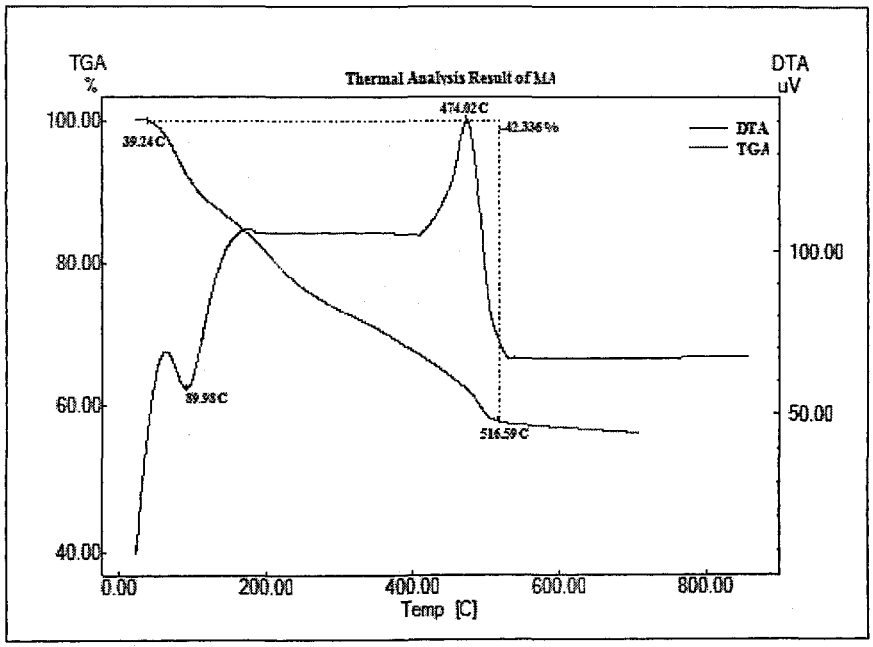


Fig 34. TG-DTA curve of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$

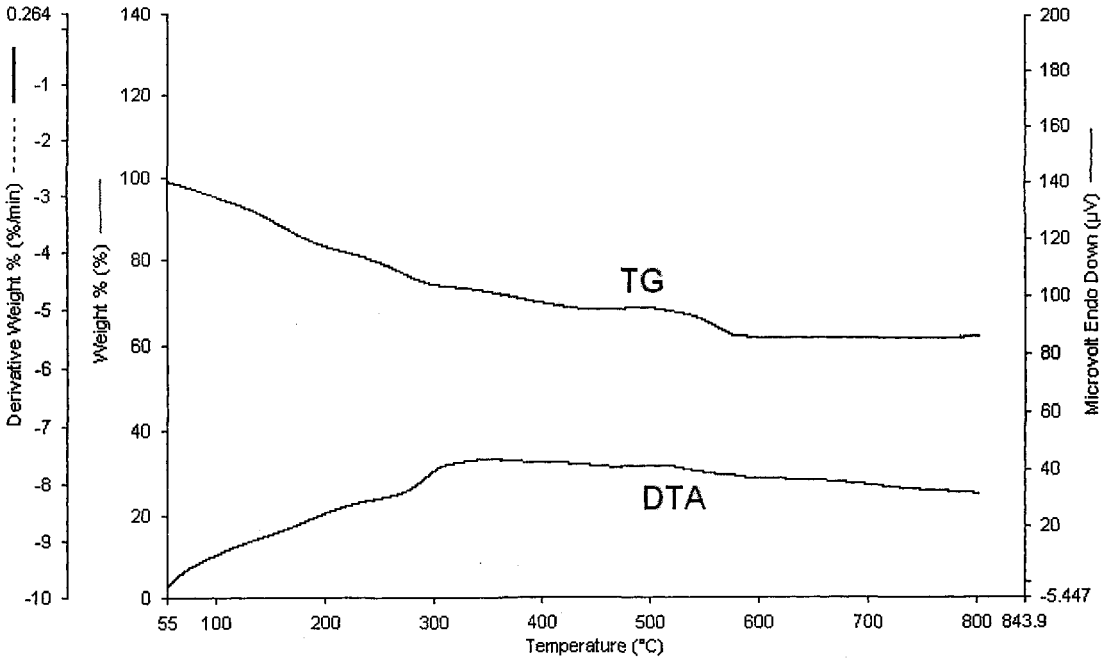


Fig 35. TG-DTA curve of $NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$

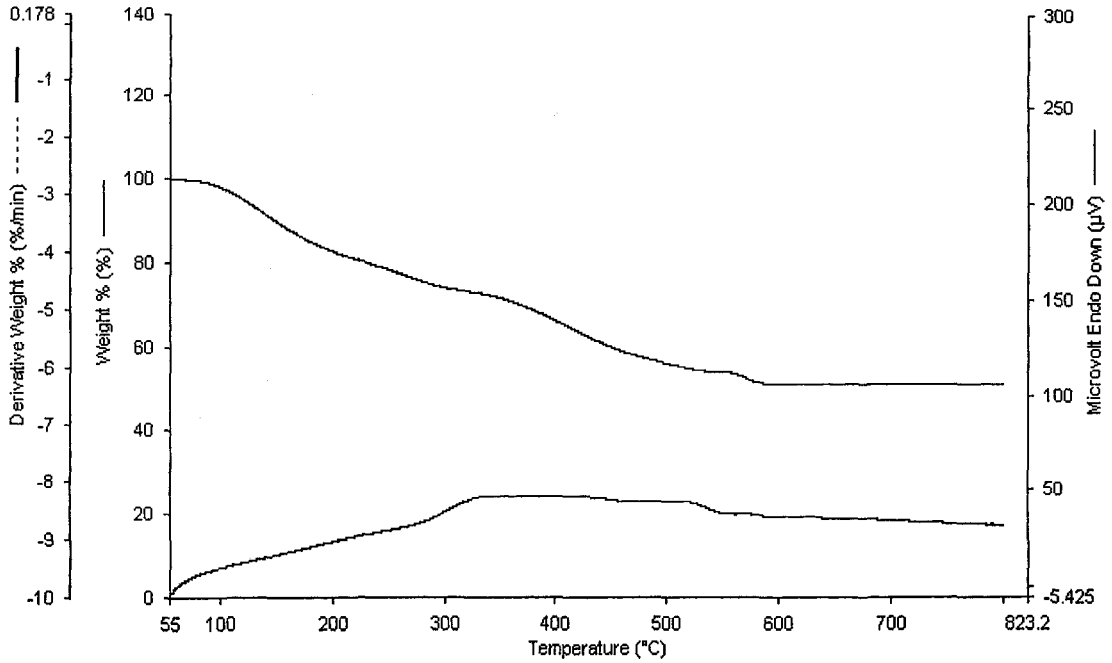


Fig 36. TG-DTA curve of $NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3$

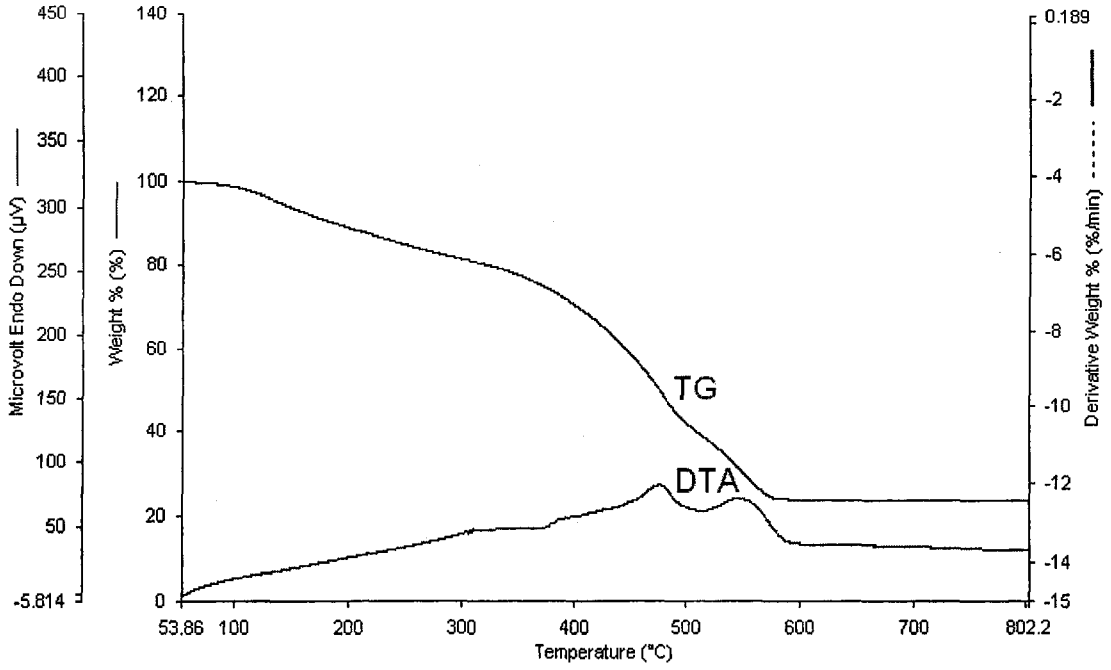


Fig 37. TG-DTA curve of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$

the possibility of formation of any intermediate. The observed total weight loss of 42.33% has accounted for the formation of $NbOCl_3$ as the ultimate product of decomposition according to the equation:

$$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2) \longrightarrow NbOCl_3 + \text{Organic matter}$$

The DTA curve of complex $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ has shown both endothermic and exothermic peaks at 89.98°C and 474.02°C respectively.

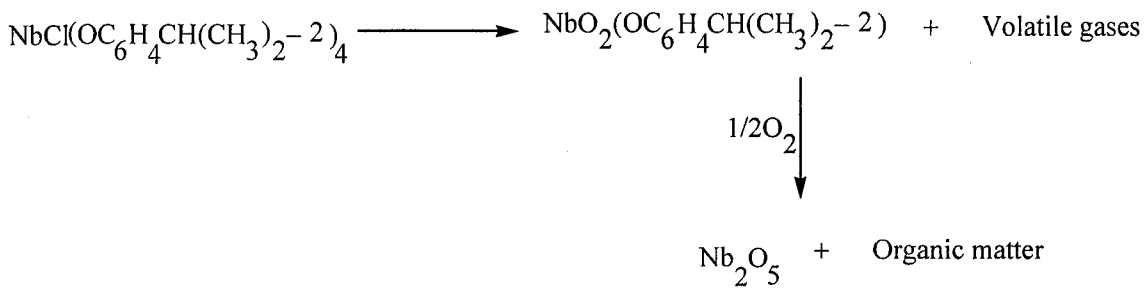
The TG curves of $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2]$ and $[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3]$ in Figs. 35 and 36 respectively have shown their initial temperature of decomposition as 55.0°C and 56.63°C respectively. The single step decomposition pattern and the weight loss of 37.31% and 48.66% in respective complexes accounted for the formation of $NbO(OC_6H_5)_3$ and $NbO_2(OC_6H_5)$ as the respective final products of decomposition. The following scheme of decomposition for these complexes may be written as:

$$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2 \longrightarrow NbO(OC_6H_5)_3 + \text{Organic matter}$$

$$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3 \longrightarrow NbO_2(OC_6H_5) + \text{Organic matter}$$

Strikingly, the DTA curve of $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2]$ and $[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3]$ did not display any physical change corresponding to thermal decomposition in TGA.

The TG curve of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ in Fig. 37 has indicated it to be thermally stable upto 53.86°C after which temperature, it has been observed to decompose in two steps. The weight loss of 61.10% in first step of decomposition corresponds to the formation of $NbO_2(OC_6H_5CH(CH_3)_2\text{-}2)$ as the probable intermediate. The weight loss of 18.99% in second step has been attributed to the oxidative decomposition of the intermediate to yield Nb_2O_5 as the final product of decomposition in accordance with the equation:

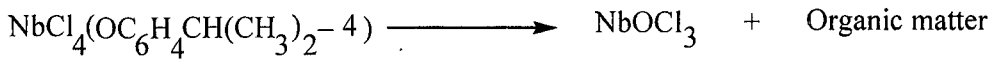


The DTA curve of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ exhibited two exothermic peaks at 475.0°C and 550.0°C.

Thermal Behaviour of Niobium(V) 4-Isopropylphenoxides $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)n]$ (n = 1→5)

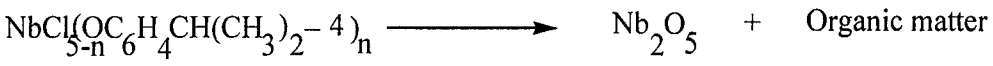
The TG-DTA curves of niobium(V)-4-isopropylphenoxides recorded in air are illustrated in Figs. 38-42 and the thermal data is presented in Table 13.

The thermogravimetric curve of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ Fig. 38 has shown it to be thermally stable upto 51.35°C after which temperature the complex has been found to decompose in single step. The observed weight loss of 42.37% in temperature 51.35-796.86°C range has been attributed to the formation of $NbOCl_3$ as the final product as follows:



The DTA curve of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ has shown both endothermic and exothermic peaks at 130.08°C and 354.24°C respectively.

The TG curves of $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2]$, $[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3]$, $[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$ and $[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$ in Figs. 39, 40, 41 and 42 respectively have depicted these to be thermally stable upto 56.01, 55.40, 54.92 and 30.06°C respectively. The weight loss of 71.04%, 76.07%, 79.41% and 80.53% in respective complexes against theoretical weight loss of 71.67%, 76.62%, 80.10% and 82.68% has accounted for the formation of Nb_2O_5 as the ultimate residue as:



(where n = 2→5)

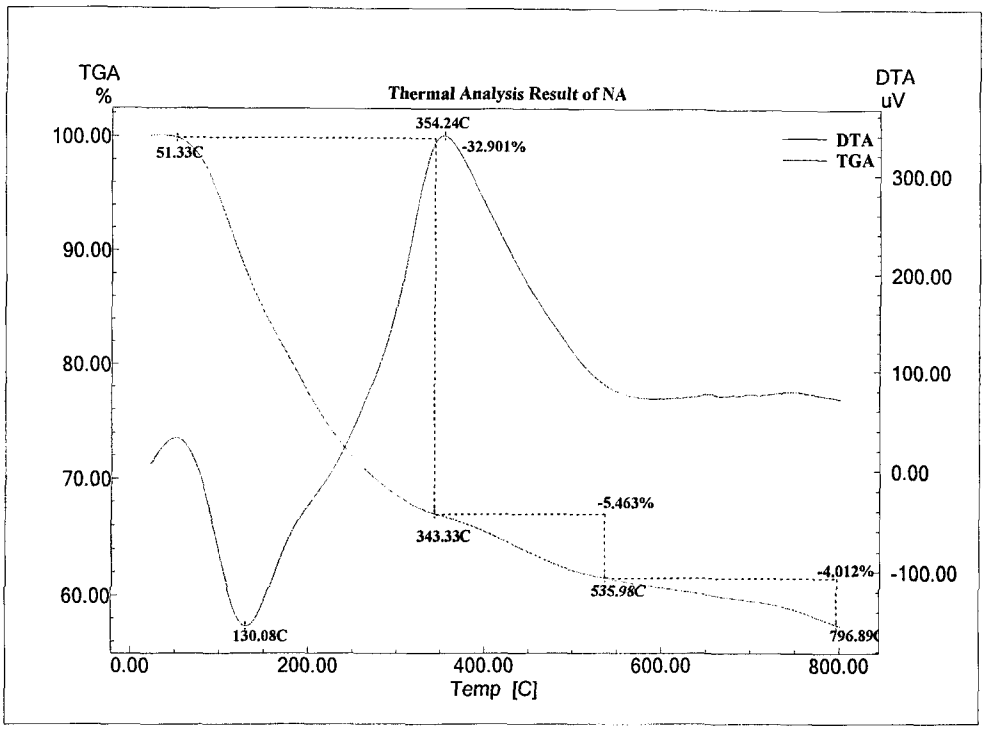


Fig 38. TG-DTA curve of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$

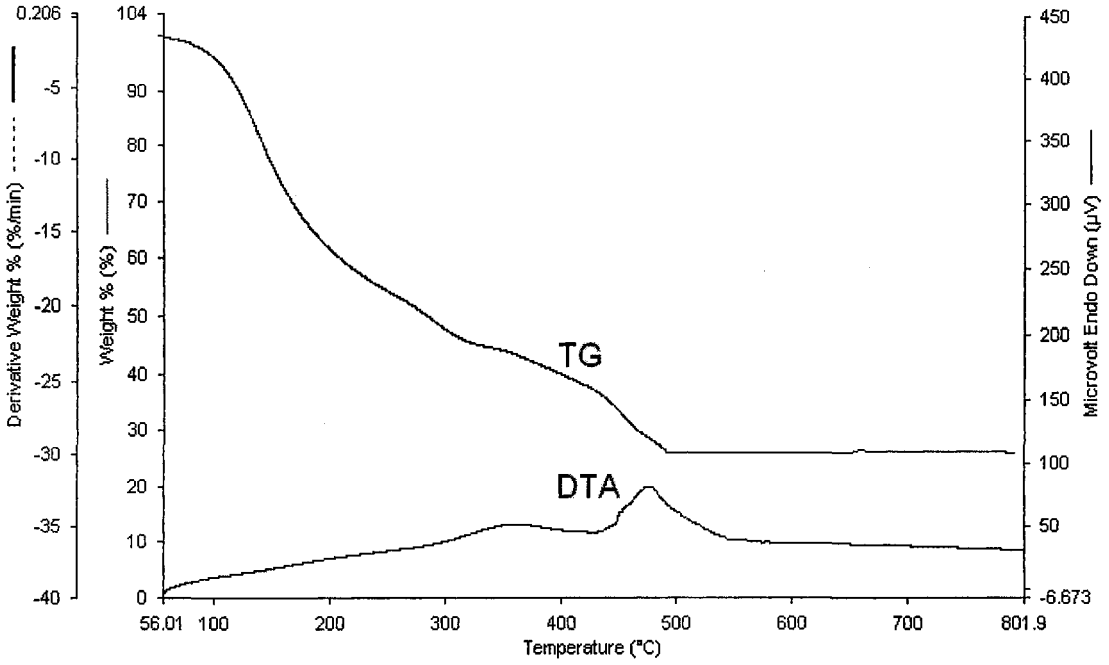


Fig 39. TG-DTA curve of $NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$

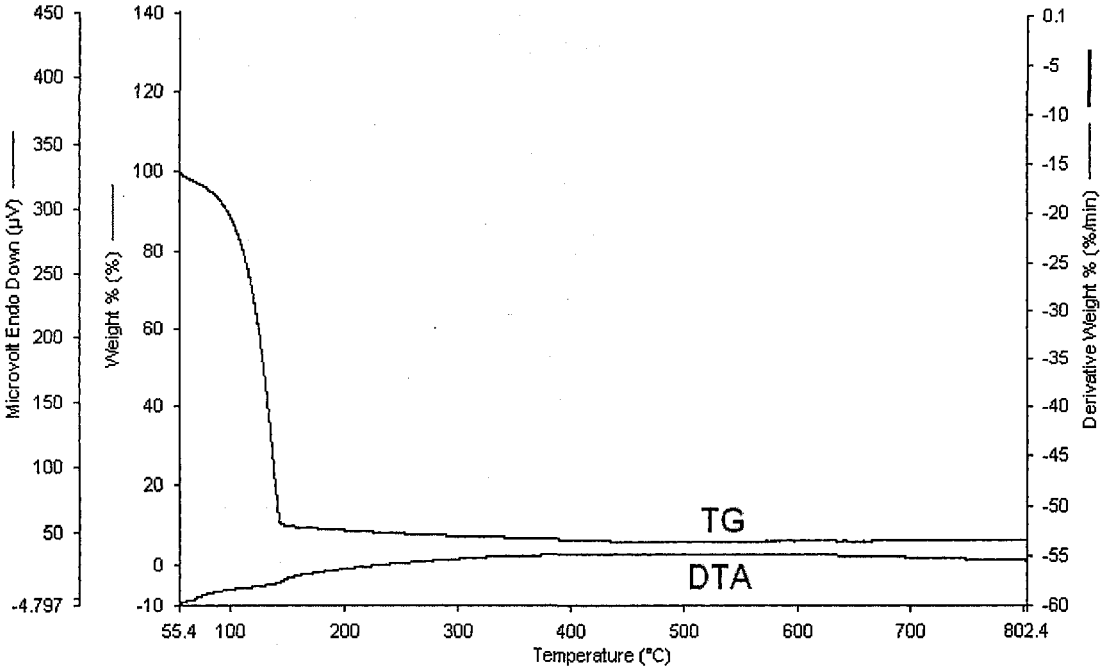


Fig 40. TG-DTA curve of $NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3$

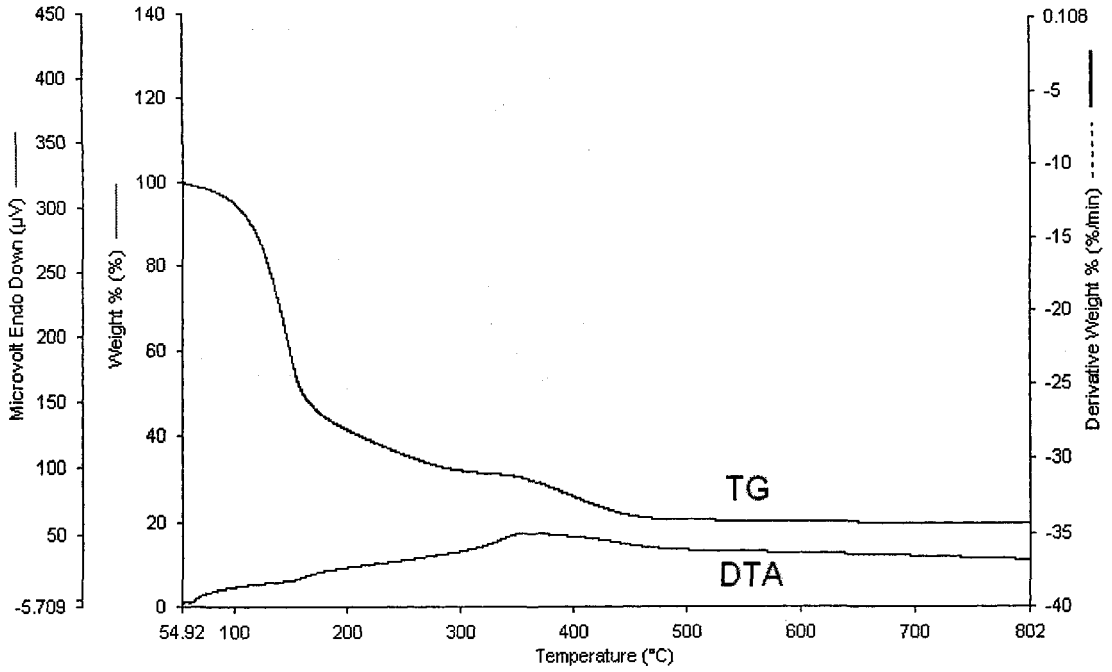


Fig 41. TG-DTA curve of $NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$

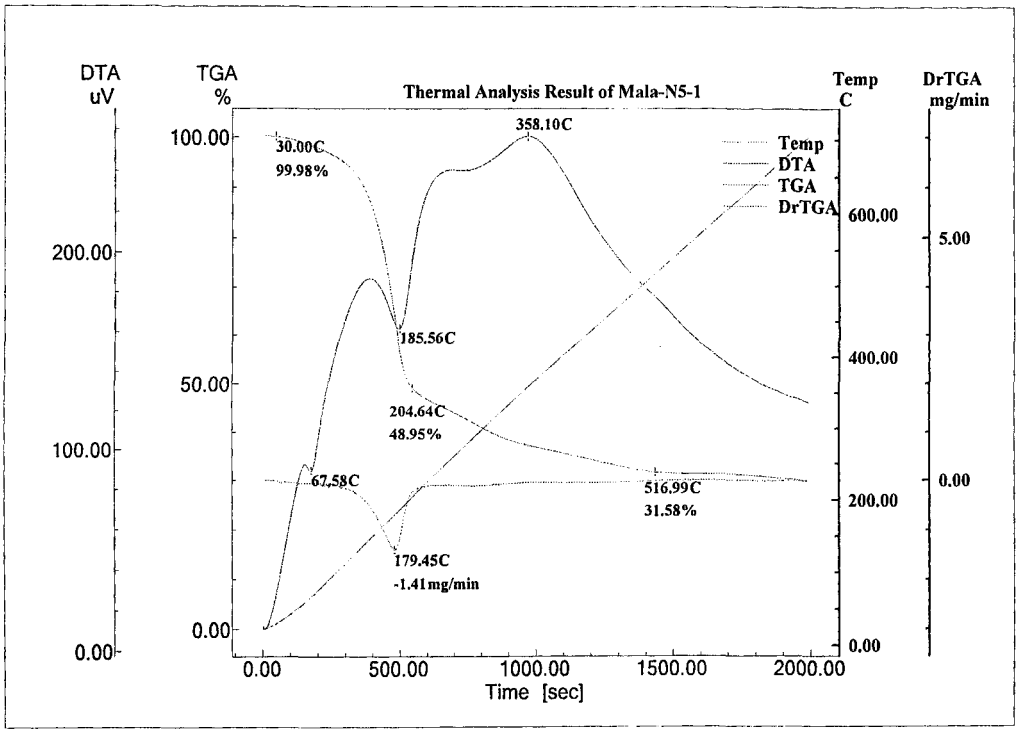


Fig 42. TG-DTA curve of $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

The DTA curves of complex as $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2]$ and $[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$ showed single exothermic peak at 495.0°C and 375.0°C respectively. The complex $[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3]$ did not show any physical change corresponding to thermal decomposition. The DTA curve of complex $[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$ has shown both endothermic and exothermic peaks at 185.56°C and 358.10°C respectively.

On the basis of above results, some useful conclusions can be drawn as:

(i) The thermogravimetric curves of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ and $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ have indicated the formation of $NbOCl_3$ as the ultimate decompositional product.

(ii) The complexes of composition $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2]$ and $[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3]$ although have similar initial temperature of decomposition (IDT) yet, yielded $NbO(OC_6H_5)_3$ and $NbO_2(OC_6H_5)$ respectively as the final products of decomposition.

(iii) Of complexes of composition $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ and $[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$, the former has been observed to decompose into two steps accounting for the formation of $NbO_2(OC_6H_5CH(CH_3)_2\text{-}2)$ as the probable intermediate and Nb_2O_5 as the final product while the latter in single step of decomposition has afforded the formation of Nb_2O_5 as the ultimate residue.

(iv) The complex of composition $[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$ has been observed to be least thermally stable.

(v) The decompositions occurring in (55-600.66°C) range for these two series of niobium(V) phenoxides have indicated their nearly identical thermal stability perhaps because of the similarity in their nature and structures.

(vi) In the absence of any unambiguous evidence of the proposed intermediates resulting from thermal decompositions, the possibility of composition of intermediate cannot be ruled out.

2.1.8.(a) Kinetic parameters from Non-Isothermal Decomposition of complexes using Thermogravimetric Data

The kinetics of thermal decompositions play a crucial role in drawing important conclusions about the molecular properties and in understanding the reaction mechanism followed during the decompositional process. Although, the determination of kinetic parameters by both non-

isothermal (linear programmed temperature) and isothermal methods (constant temperature) has been reported yet, non-isothermal methods are known to offer interesting advantages over conventional isothermal studies (323) as non-isothermal methods involve lesser number of experiments while in isothermal methods, various experiments at different constant temperatures need to be performed. Furthermore, non-isothermal methods not only require less time for each analysis but also the available literature contains quite a large number of such methods for the evaluation of data.

The growing applications of thermo-analytical techniques have led to the development of various new methods for the evaluation of kinetic parameters using TG, DTG, DTA, DSC and many other techniques. As TG technique involves the measurement of mass, the degree of accuracy by this method has been shown to be higher than in case of DTA and DSC which involve the measurement of ΔT and dH/dt respectively. The mathematical treatment given to thermogravimetric data has been classified as:

i) Integral method developed by Doyle and Coats and Redfern. Doyle's method (324) was further developed by Zsako (325).
ii) Differential method was initially suggested by Achar which was further developed by Horowitz (326).
iii) Differential method was given by Freeman and Carrol (327).
iv) Method especially applicable to initial rate.
v) Non-linear cyclic heating rate methods.

Flynn and Wall (328) reviewed these methods and suggested that differential methods have several disadvantages, of which the difficulty in the correct estimation of a continuous varying slope in TG curve and the poor reproducibility of the order of reaction are the prominent one. The oldest differential method by Freeman and Carroll, (327) though is most criticized (328) yet still generally used. Wentworth and Carroll (329,330) method gives insignificant values for the reaction order. Integral methods are therefore accepted as more reliable methods for the determination of kinetic parameters from thermoanalytical data. Coats and Redfern method (331) has been described as the less tedious method compared to other methods as it does not involve the determination of tangents and hence is the most suitable and popular.

The methods used to obtain the kinetic data, are often applied to the decomposition reaction which involves one step irreversible, unimolecular or pseudomolecular reactions

$$X_{(S)} \rightarrow Y_{(g)} + Z_{(S)}$$

The rate of disappearance of X (the starting material) may be expressed as

$$\frac{d\alpha}{dt} = k.(1-\alpha)^n \quad \text{---------- (1)}$$

where α = fraction of X decomposed at time t, n = order of reaction and k = rate constant given by the expression

$$k = A.e^{-E^*/RT} \quad \text{---------- (2)}$$

where A = frequency factor and E^* = activation energy of the reaction. A mechanism of higher complexity which is not reducible to a simple one-step process is one involving two consecutive irreversible first order reactions:

$$X \xrightarrow{K1} Y + gas$$

$$Y \xrightarrow{K2} Z + gas$$

In these expressions, X, Y and Z denote, starting material, intermediate product and the final product respectively, K_1 and K_2 represent the rate constants for the two steps. The concentrations of X, Y and Z are a function of time which can readily be estimated once the rate constants are known. For a linear heating rate of say β deg min^{-1}

$$\beta = dT/dt \quad \text{---------- (3)}$$

Combining equations (1), (2) and (3), rearranging and integrating the rate equation between the limits of α=0 at T=0 and α=α at temperature T, one gets

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_0^{T} e^{-E^*/RT}.dT \quad \text{---------- (4)}$$

Depending now on how further derivation is done and what assumptions are made, different representations are obtained for the relation between E and n. The integral of LHS of the equation is $g(\alpha)$. The $f(\alpha)$ and $g(\alpha)$ are related to each other as $f(\alpha)$ is the integral form of $1/g(\alpha)$ pertaining to the classification of the solid state mechanism. The $g(\alpha)$ is a mathematical

expression in α and represents the particular type of mechanistic model of non-isothermal decomposition used.

The RHS of the above equation cannot be integrated in a closed form but by making the substitution and using the relation given by Rainville, the equation (4) becomes

$$\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \left(\frac{ART^{2}}{\beta E^{*}}\right)\frac{1-2RT}{E^{*}}e^{-E^{*}/RT} \qquad \text{---------- (5)}$$

Different authors have used different techniques to evaluate the exponential integral by (i) approximation method, (ii) series expansion method, (iii) numerical solution method using tabulated values, in series expansion or integral method but most popular is probably Coats-Redfern method in the form

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^{2}}\right] = \log_{10}\frac{AR}{\beta E^{*}}\left[1-\frac{2RT}{E^{*}}\right] - \frac{E^{*}}{2.303\ RT} \qquad \text{----- (6)}$$

$$\log_{10}\left[\frac{-2.303\ (1-\alpha)}{T^{2}}\right] = \log_{10}\frac{AR}{\beta E^{*}}\left[1-\frac{2RT}{E^{*}}\right] - \frac{E^{*}}{2.303\ RT} \qquad \text{----- (7)}$$

$$\alpha = \frac{w_{o} - w_{t}}{w_{o} - w_{c}}$$

where W_O, W_f and W_t are the initial mass, final mass or weight of the residue at the completion of heating and mass of the sample at temperature T respectively. It may also be represented as

$$\alpha = \frac{w}{w_{c}}$$

β is the linear heating rate

'n' is the order of reaction

A plot of either

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^{2}}\right] \text{ vs } 1/T \text{ for } n \neq 1 \text{ i.e} = ½, 2/3 \text{ or } ¾$$

or

$$\log\left[\frac{-2.303\log_{10}(1-\alpha)}{T^2}\right] \text{ vs } 1/T \text{ for n = 1}$$

results into a straight line of slope $\frac{-E^*}{2.303\,R}$ for the correct value of 'n'. For most values of E and for the temperature range over which reactions generally occur the expression:

$$\log_{10}\frac{AR}{\beta E^*}\left[1-\frac{2RT}{E^*}\right]$$ is sensibly constant.

Thus the energy of activation (E*) and frequency factor 'A' are calculated from the slope and intercept of the line respectively. The equations may be applied by a simple graphical technique. Since, there is theoretical justification for orders of reaction, 0, ½, 2/3 and 1 in solid state kinetics, these values are substituted into equation (6) or equation (7) when n = 1, to obtain the appropriate plots or to use a computational approach to select a value of n which gives the best straight line through the points on the assumption that the order is constant throughout the reaction. The activation parameters like entropy (S*) (325) free energy (G*) (332) and specific reaction rate constants 'k_r' (333) are obtained from relations:

$$S^* = 2.303\,.\log_{10}\left(\frac{Ah}{kT_s}\right)$$

$$G^* = E^* - T_s S^*$$

$$k_r = A\,.\exp^{\frac{-E^*}{RT}}$$

where k is Boltzmann's constant, 'h' is Planck's constant and 'T_s' is the peak temperature from DTG. The enthalpy of activation is calculated from the relationship:

$$H^* = E^* - k_r T_s$$

From the non-isothermal TG data, the kinetics of thermal decomposition of complexes have been computed using Coats–Redfern equation and the parameters obtained namely, the activation energy E*, frequency factor 'A', reaction order 'n', entropy of activation S* etc. are given in Table 14. Theoretically higher the magnitude of activation energy, higher is the thermal stability

Table 14. Kinetic parameters of Niobium(V) 2-/4-isopropylphenoxides

Complex	Stage of decomp.	Activation Energy 'E*' ($kJmol^{-1}$)	Frequency Factor 'A' (S^{-1})	Correlation coefficient 'r'	Entropy of Activation 'S*' ($kJmol^{-1}\ K^{-1}$)	Free Energy of Activation 'G*' ($kJmol^{-1}\ K^{-1}$)	Enthalpy of Activation 'H*' ($kJmol^{-1}$)	Model
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$	1st	20.43	2.93×10^{-6}	0.962	-357.03	24.46×10^{4}	20.43	R3
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$	1st	5.93	1.31×10^{-4}	0.994	--	--	5.93	A2
$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}2)_3$	1st	6.35	1.07×10^{-4}	0.998	--	--	6.35	A3
$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1st	6.77	8.95×10^{-5}	0.998	--	--	6.77	A3
	2nd	30.99	--	0.866	-691.31	74.41×10^{4}	30.99	R3
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$	1st	22.29	1.68×10^{-6}	0.983	-361.65	24.94×10^{4}	22.29	R3
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$	1st	5.20	1.02×10^{-4}	0.997	--	--	5.20	A3
$NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3$	1st	10.69	2.63×10^{-5}	0.943	-338.79	22.34×10^{4}	10.69	R3
$NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$	1st	4.92	1.06×10^{-4}	0.989	--	--	4.92	A4
$Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$	1st	23.17	1.67×10^{-6}	0.920	-361.70	25.03×10^{4}	23.17	R3

of the complex. In general, with decrease in the values of activation energy (E*), the magnitude of frequency factor (A*) should increase. This is what has been observed for the complexes under study. The negative values of entropy of activation, however, indicate that the activated complexes have more ordered structure (334) than the reactants and that the reactions are slower than normal (335-336). The magnitude of enthalpy of activation (H*) has indicated that the E* and H* are nearly equivalent.

2.1.8.(b) Analysis of Non-Isothermal data for Mechanism and Activation Energy

For the mechanistic analysis of TG data, the mathematical expressions of the functions f(α) corresponding to some of the mechanisms of thermal decomposition found in literature (337) are collected in Table 15. The analysis of NIK (non-isothermal kinetic) data is directed towards identifying the rate equation and Arrhenius parameters as in isothermal kinetic studies and hence, called the inverse kinetic problem (IKP). The solution of IKP involves:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\cdot\frac{dt}{dT} = \frac{d\alpha}{dt}\cdot\frac{1}{\beta} \qquad \text{---- i}$$

where β = dT/dt the heating rate. On the assumption that the reactions of thermal decomposition of solids can be expressed by equation:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\cdot\frac{1}{\beta} = \left(\frac{A}{\beta}\right)e^{\frac{E^*}{RT}}\cdot f(\alpha) \qquad \text{---- ii}$$

where α is the fraction of material that has reacted at time t, E* is the activation energy, f(α) is a function which depends on the actual reaction mechanism and 'A' is the pre-exponential Arrhenius factor. By differentiating the logarithmic form of equation (ii) with respect to d in (1-α), one obtains:

$$\frac{d\ln\alpha'}{d\ln(1-\alpha)} = \frac{E^* d\left(\frac{1}{T}\right)}{Rd\ln(1-\alpha)} + \frac{d\ln f(\alpha)}{d\ln(1-\alpha)}$$

or

$$\frac{\Delta\ln\alpha'}{\Delta\ln(1-\alpha)} = \frac{E^* \Delta\left(\frac{1}{T}\right)}{R\Delta(1-\alpha)} + \frac{\Delta\ln f(\alpha)}{\Delta\ln(1-\alpha)}$$

Table 15 : Algebraic Expressions of Functions of the Most Common Reaction Mechanisms Operating in Solid State Reactions

Symbol	Mechanism	g(α)	f(α)
	Based on Diffusion Mechanisms		
D1	One Dimensional Diffusion (Parabolic)	$1/2\alpha$	α^2
D2	Two Dimensional Diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	Three Dimensional Diffusion : Jander Equation	$(3/2)(1-\alpha)^{-2/3}[1-(1-\alpha)^{-1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
D4	Three Dimensional Diffusion : Ginstling-Brounshtein Equation		$(1-2\alpha/3)-(1-\alpha)^{2/3}$
	Random Nucleation and Nuclei Growth		
A2	Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
B1	Prout Tompkins Equation	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$
E1	Exponential Law	α	$\ln\alpha$
	Based on Order of the Reaction		
F1	First Order Random Nucleation (Mample unimolecular Law)	$(1-\alpha)$	$-\ln(1-\alpha)$
F2	Second Order	$(1-\alpha)^2$	$(1-\alpha)^{-1}$
F3	Third Order	$(1/2)(1-\alpha)^3$	$(1-\alpha)^{-2}$
	Limiting surface reaction between both phases : Geometric models		
R2	Phase Boundary Reaction : Cylindrical Symmetry	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R3	Phase Boundary Reaction : Sherical Symmetry	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

$$\text{and} \quad \frac{\Delta \ln \alpha' - \Delta \ln f(\alpha)}{\Delta \ln(1-\alpha)} = \frac{E^* \Delta\left(\frac{1}{T}\right)}{R \Delta \ln(1-\alpha)}$$

Thus the plot of

$$\frac{\Delta \ln \alpha' - \Delta \ln f(\alpha)}{\Delta \ln(1-\alpha)} \; vs \; \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \ln(1-\alpha)}$$

should be a straight line with a slope of –E*/R irrespective of the f(α) values employed. One can select the f(α) value that best fits the actual mechanism of reaction studied, using the intercept value, which should nearly be zero. It is important to mention here that primarily based on minimum intercept values, the mechanisms have been suggested rather than the correlation/ coefficient values ('r') as the values of 'r' over a considerable range, thereby, limiting the contribution of 'r' to authenticate the suggested mechanism for the thermal decomposition of complexes.

In earlier reports, the values of 'r' have been employed to a large extent by various authors in conjunction with Coats and Redfern method (331) to ascertain mechanisms (and corresponding E* values). However, the utilization of 'r' to determine mechanism from TG data was indicated by various workers to be unsatisfactory (338-340). It was found very difficult to ascertain a probable mechanism based on 'r' values only since at least half of the expressions tested, afforded values of $r \geq 0.995$. The experimental values in terms of correlation, coefficient, slope, intercept have been computed from various mechanisms tested for stepwise decompositions. It has been inferred from the detailed mechanistic analysis of TG data of complexes that the rate controlling process follows R3 (phase boundary reaction spherical symmetry)/A2, A3 and A4 (Avrami-Erofeev) mechanisms.

2.2. Heterometallic niobium(V) aryloxides

An attractive feature of metal alkoxides is to form mixed-metal species called "double alkoxides" (341) or Meerwein salts or the more general term heterometallic alkoxides (342). The heterometallic alkoxides are known to act as catalysts in Zieglar-Natta polymerization (343) or olefin metathesis (344) reactions, as well as in nitrogen activation (345). The reactions between metal oxoalkoxides and metal alkoxides offer a route to form heterometallic oxoalkoxides. The heating of $Mo_2(OPr^i)_6$ with $WO(OPr^i)_4$ in hexane has been reported to yield $Mo_2WO(OPr^i)_{10}$

(346). The heterometallic oxoalkoxides have been found to be selective catalysts for the polymerization of heterocyclic compounds (347) or for oxidation reactions (348), if metal is in a low oxidation state viz. iron(II), chromium(II) and molybdenum(II). In recent years, a heterometallic oxo alkoxide anion $[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]^{2-}$, has been reported to be formed in the course of nitrogen fixation (349). The heterometallic compounds with oxygen ligands such as catecholates (350), oxalates (351), squarates (352) and carboxylates (353), find use in material science (354-356).

Meerwein and Bersin (357) reported that alcoholic solution of alkoxides of aluminium(III), iron(III), titanium(IV) and zirconium(IV) were acidic and could be titrated to a sharp end-point with an alkali metal alkoxide using thymolphthalein as indicator

$$Na(OEt) + Al(OEt)_3 \longrightarrow Na[Al(OEt)_4]$$

The products were considered as alkoxy salts derived by neutralization of the alkoxy acid by the base. In general, it was suggested that the more "basic" alkoxide (i.e. one derived from the more electropositive metal) transferred its alkoxide group to the more "acidic" alkoxide through a complex ion involving metal in its higher coordination number. These interesting features have been well recognized as playing a historic and important role in the growth of chemistry of metal alkoxides. Thereafter, stable double alkoxides of aluminium(III), titanium(IV), zirconium(IV) (357,358), tin(IV), niobium(V) and tantalum(V) have also been synthesized. Tungsten(V) ethoxide and sodium ethoxide in ethanol react to give yellow paramagnetic solid mass which has been characterized as a compound of composition $Na[W(OEt)_6]$ (359). Albers and coworkers (360) have reported a volatile uranium(IV) aluminium alkoxide of composition $[UAl_4(OPr^i)_{16}]$ whereas uranium(V) forms double alkoxides of the type $NaU(OEt)_6$, $CaU_2(OEt)_{12}$ and $U_3Al(OEt)$ (361).

Mehrotra and Aggarwal (362) have reported double alkoxides of aluminium and lanthanides of composition $MAl_3(OPr^i)_{12}$ (M = La, Pr) exhibiting a structure analogous to that of the tetrameric $Al_4(OPr^i)_{12}$. The heterometallicalkoxides containing the isopropoxoaluminate ligand include many of the possible combinations of metals (363-365) from group 3 to 13. The alcoholysis of tetraisopropoxo derivative $[M(Al(OPr^i)_4)_2]$ is known to result in the replacement of only three of the four isopropoxide groups in $[Al(OPr^i)_4]^-$ with the formation of complexes of cobalt (366), nickel (367) and copper (368) of composition $[M(Al(OPr^i)(OBu^t)_3)_2]$. The

alkoxoaluminate derivatives have been reported to show variation in their coordination number with the nature of the alkyl group. The six coordination number in $[Ni(Al(OR)_4)_2]$ tends to change to four in $[Ni\{(\mu\text{-}OPr^i)_2Al(OPr^i)_2\}_2]$ containing more sterically demanding isopropyl groups (366). The heterobimetallic alkoxides of the type $[ClM(Al(OBu^t)_4)]$ and $[M(Al(OBu^t)_4)_2]$ (M = Co^{II}, Ni^{II} and Cu^{II}) have been reported to be prepared by the interactions of MCl_2 with $[KAl(OBu^t)_4]$ in 1:1 and 1:2 molar ratios respectively. The hydrolytic studies on $[Zr(OPr^i)_2(Al(OPr^i)_4)_2]$ have been described by Mehrotra (369). The incorporation of lanthanides in alumina matrices by a sol-gel process employing heterometallic alkoxides $[M(Al(OPr^i)_4)_3]$ as precursors has recently been reported (370). Rai and Mehrotra (371,372) have reported the hydrolysis of $[Mg(Al(OR)_4)_2]$ and $[Ca(Al(OR)_4)_2]$ in the absence of chelates. The preparation of magnesium aluminate spinel from hydrolysis of $[Mg(Ag(OR)_4)_2]$ has been reported by Jones et al (373).

A number of bimetallic alkoxides $[Cr(M(OR)_6)_3]$ (M = Nb or Ta, R = Me, Et, Pr^i and Am^t) have been reported to be synthesized by alcoholysis of $[Cr(M(OPr^i)_6)_3]$ with methanol, ethanol and t-amyl alcohol (374). The bimetallic alkoxides of copper(II) of composition $[Cu(M(OPr^i)_6)_2]$ (M = Nb or Ta) are known to undergo facile alcohol interchange with primary alcohols such as methanol, ethanol, n-proponol and n-butanol forming complexes of the type $[Cu(M(OR)_6)_2]$ (R = Me, Et, Pr^n and Bu^n) while with t-butanol, $[Cu(Ta(OPr^i)_2(OBu^t)_4)_2]$ is formed. Novel termetallic isopropoxides $[(OPr^i)_4M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ have been reported to be synthesized from the reaction of $M(OPr^i)_5$ with $Pr^iOBe(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ (M = Nb(V) and Ta(V)) (375). A variety of other mixed metal and mixed alkoxo compounds of the type $\{XSn[Al(OPr^i)_4]\}$, $\{XSn[Zr_2(OPr^i)_9]\}$, $\{XSn[M(OPr^i)_6]\}$, $\{Al(OPr^i)_4\}Sn\{Zr_2(OPr^i)_9\}$and $\{Nb(OPr^i)_6\}Sn\{Ta(OPr^i)_6\}$ (X = Cl, OPr^i, OBu^t; M = Nb, Ta) have been reported by Mehrotra and coworkers (376). The reaction of $SnCl_4$ with an appropriate salt $[K(M(OPr^i)_6)]$ in the necessary molar ratios is known to yield $[Cl_{4-n}Sn(M(OPr^i)_6)_n]$ (M = Nb, Ta; n = 1→3) which yield $[(RO)_2Sn(M(OPr^i)_6)_2]$ (R = Me, Pr^i), $[(Ta(OPr^i)_6)_2]$, $[Sn(Nb(OPr^i)_6)_2]$ and $[(Al(OPr^i)_4)_4ClSn(Nb(OPr^i)_6)_2]$ by halide atom replacement with the appropriate potassium alkoxide salt.

Compared to well-documented study of heterometal alkoxides, it is surprising to note that the reports on analogous phenoxides are scarce. The bimetallic phenoxides of titanium(IV), niobium(V) and tantalum(V) have been reported (377,378). In view interesting reports it has therefore been considered worthwhile to explore the possibility of formation of double phenoxides of niobium(V) by the reaction of parent pentaphenoxides of niobium(V)

$[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ with the respective alkali metal phenoxides. The overall reaction may be rationalized as

$$Nb(OC_6H_4CH(CH_3)_2^{-}\ 2/4)_5 + M(OC_6H_4CH(CH_3)_2^{-}\ 2/4) \xrightarrow{\text{benzene}} [MNb(OC_6H_4CH(CH_3)_2^{-}\ 2/4)_6]$$

(where M = Li and Na)

The stoichiometric composition of complexes has been established by elemental analysis (Table 16). The complexes are moisture sensitive and are quite stable in dry air and are appreciably soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of complexes in nitrobenzene have indicated their appreciable electrolytic nature relative to parent pentaaryloxides.

2.2.1. IR spectra

The infrared spectra of bimetallic complexes have shown that υ(C–O) mode has been found to shift towards higher regions relative to parent pentaaryloxides. This has been attributed to the fact that the negative charge existing on metal in $[Nb(OPh)_6]^-$ decreases the drainage of electron density from the ring to the metal, thereby strengthening the C–O bond and resultant higher frequencies for the υ(C–O) mode.

2.3. Hetero-metal niobium(V) acetatoaryloxides

Mixed-metal oxides represent an important class of advanced materials due to their technological applications (379) as catalysts, structural ceramics, sensors, actuators and smart materials (380). The formation of such materials, through chemical vapour deposition (CVD), sol-gel process, metal-organic decomposition, molecular beam epitaxy etc. requires metal-organic molecules with specific physical and chemical properties as precursors. The preparation of inorganic materials from metal-organic precursors generally has the advantages over 'traditional routes' of low temperatures of formation and/or crystallization, better compositional uniformity and conformal coverage in the case of films (381). Metal alkoxides $[M(OR)_n]$ or oxoalkoxides $[MO(OR)_n]$ are versatile molecular precursors of metal oxides, owing to their solubility in a large variety of solvents and their ability to form heterometallic species, especially by mixing alkoxides of different metals (382). However, to overcome difficulty in handling alkoxides and/or in their availability, more commonly accessible derivatives such as carboxylates (often acetates), nitrates, halides, hydroxides or β-diketonates have often been used in conjunction with metal alkoxides. Metal acetates are the most common precursors associated with metal alkoxides.

Table 16. Analytical data of bimetallic niobium(V) aryloxides

Complex Molecular formula (Formula weight)	Colour	Elemental Analysis, % Found (Calcd.)			Molar Cond. in $PhNO_2$ (Scm^2 $mole^{-1}$)
		Nb	C	H	
$Li[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_6]$	Brown	10.20	71.10	7.23	11.09
$C_{54}H_{66}O_6NbLi$ (911)		(10.21)	(71.13)	(7.24)	
$Na[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_6]$	Light brown	10.02	69.96	7.10	12.58
$C_{54}H_{66}O_6NbNa$ (926)		(10.04)	(69.98)	(7.13)	
$Li[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_6]$	Yellow	10.22	71.12	7.21	13.56
$C_{54}H_{66}O_6NbLi$ (911)		(10.21)	(71.13)	(7.24)	
$Na[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_6]$	Yellow	10.03	69.97	7.15	14.01
$C_{54}H_{66}O_6NbNa$ (926)		(10.04)	(69.98)	(7.13)	

The reactions between metal alkoxides and carboxylates have generally been considered to proceed by elimination of an ester as a volatile byproduct, thus giving oxo derivatives. These reactions however can occur in very mild conditions (room temperature and non-polar solvents), giving compounds whose formulation results from a simple addition.

The reactions between anhydrous metal acetates $M(OAc)_2$ (M = Mg, Cd, Pb) and niobium ethoxide and isopropoxide have been reported owing to the attractive properties of niobates and tantalates as electrooptical ceramics [$LiNbO_3$; $(Sr,Ba)Nb_2O_6$ (SBN); $(Pb,La)(Ti, Nb)O_3$ (BLNT); $Pb(Sc,Nb)O_3$(PSN)] (383); ceramics for microwave resonators [$PbMg_{1/3}Nb_{2/3}O_3$ (PNM), $BaZn_{1/3}Ta_{2/3}O_3$ (BZT), $BaMg_{1/3}Ta_{2/3}O_3$ (BMT)] (384,385), or as dielectric ceramics [$CdNb_2O_6$] (386). The reactions between niobium isopropoxide and anhydrous cadmium, magnesium and lead acetates are known to proceed smoothly and quantitatively in toluene/hexane over 1 or 2h, with progressive dissolution of the acetate yielding mixed-metalacetatoalkoxides. The excess of metal acetates is easily removed by filtration in these reactions, while the novel compounds are crystallized out almost quantitatively from the filtrate (387). The experimental conditions, choice of solvents and temperature of reactions are important in determining the reaction products. The reactions are selective leading to the formation of smallest aggregates which allow the metals to achieve their common coordination numbers.

In view of these interesting observations, in the present work, the reactions between [$Nb(OC_6H_5CH(CH_3)_2$-2/4)$_5$] and cadmium and lead acetates have been undertaken. The interaction of niobium(V) 2-/4-isopropylphenoxides with metal acetates in 2:1 molar ratios in hexane at room temperature has resulted in the formation of compounds according to the equation:

$$2\,Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5 + M(OAc)_2 \xrightarrow{\text{hexane}} [MNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$$

(where M = Cd and Pb)

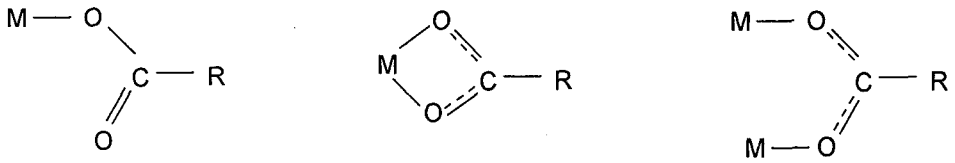
The stoichiometric composition of the isolated compounds has been established by elemental analysis (Table 17). The compounds are light yellow to light brown solids and quite stable in dry air. These are appreciably soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of these compounds in nitrobenzene are too low to be attributed to their behaviour as 1:1 electrolyte.

Table 17. Analytical data of hetero-metal acetatoaryloxides of niobium(V)

Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %			Molar Cond. in $PhNO_2$ (Scm^2 $mole^{-1}$)
		Nb	C	H	
$[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$ $C_{49}H_{61}O_9NbPb$ (1093)	Maroon	8.50 (8.51)	53.79 (53.80)	5.55 (5.58)	0.28
$[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$ $C_{49}H_{61}O_9NbCd$ (998)	Brown	9.30 (9.32)	58.91 (58.92)	6.10 (6.11)	0.25
$[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$ $C_{49}H_{61}O_9NbPb$ (1093)	Light Yellow	8.52 (8.51)	53.77 (53.80)	5.57 (5.58)	0.44
$[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$ $C_{49}H_{61}O_9NbCd$ (998)	Yellow	9.28 (9.32)	58.90 (58.92)	6.13 (6.11)	0.38

2.3.1. IR spectra

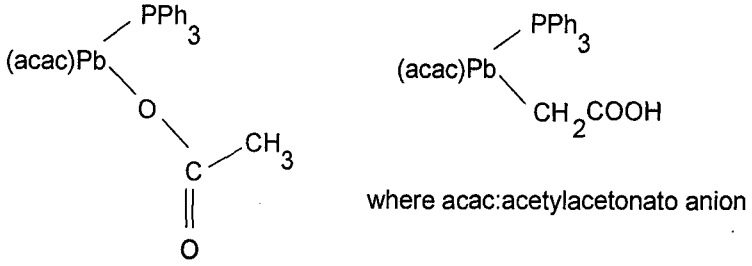
Extensive infrared studies have been reported on metal complexes of carboxylic acids. The infrared frequencies and band assignments for the formate and acetate ions have been reported by Itoh and Bernstein (388). The carboxylate ions may coordinate to a metal in one of the following modes:



I II III

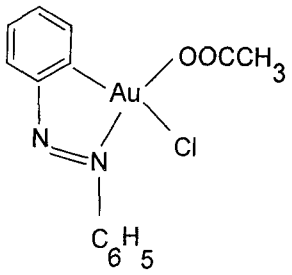
The free acetate ion (CH_3COO^-) exhibits the $\upsilon_{asym}(COO)$ and $\upsilon_{sym}(COO)$ modes at 1578 and 1414 cm^{-1} respectively. If it is covalently bonded to a metal as a unidendate ligand, the υ_{asym} and υ_{sym} are shifted to higher and lower frequencies, respectively.

The separation of υ_{asym} and υ_{sym} of magnitute 460 cm^{-1} has been described for unidentate coordination (389). The unidendate acetates exhibit three bands (COO deformation) in 920–720 cm^{-1} and a strong band [$\pi(CO_2)$] at 540 cm^{-1} which are absent in bridging complexes and are reduced in number in bidendate complexes (390). The linkage isomerism involving the acetate group has been reported by Baba and Kawaguchi (391):

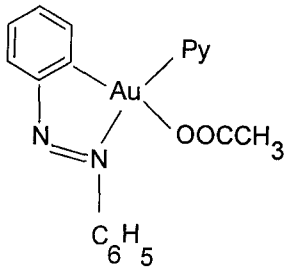


where acac:acetylacetonato anion

The O-isomer exhibits $\upsilon(C=O)$ at 1640 cm^{-1}, whereas the C-isomer shows $\upsilon(C=O)$ at 1670 and 1650 cm^{-1} and $\upsilon(OH)$ in 2700–2500 cm^{-1} region. It is also possible to distinguish two acetate groups having trans ligands by their frequencies:



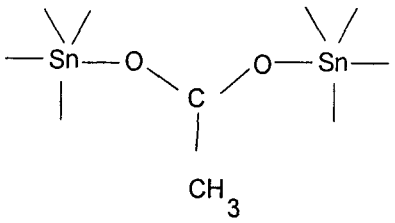
(A)



(B)

Complex (A) exhibits $\upsilon_{asm}(COO)$ and $\upsilon_{sym}(COO)$ at 1665 and 1360 cm^{-1} respectively whereas complex (B) exhibits these vibrations at 1620 and 1300 cm^{-1} respectively (392).

The tin compounds of composition $[Sn(CH_3)_3(CH_3COO)]$ and $[Sn(CH_3)_2Cl(CH_3COO)]$ exhibiting two $\upsilon(COO)$ modes near 1600 and 1420 cm^{-1} have indicated the ionic character of the tin-acetate interaction (393,394). In $[Sn(CH_3)_3(CH_3COO)_2]$, however, the two acetate groups occupy the axial positions of the trigonal-bipyramidal structure, and are covalently bonded to tin metal as unidendate ligands (395). The polymerization also occurs in $[Sn(CH_3)_3(CH_3COO)]$ (396) as :



As expected for symmetric bidendate coordination, the separation of the υ_{asym}(1600 cm^{-1}) and υ_{sym}(1363 cm^{-1}), (237 cm^{-1}) is much smaller than those observed for unidendate coordination (~ 460 cm^{-1}) (393).

On the basis of careful examinations of IR spectra of many acetates and trifluoroacetates having known X-ray crystal structures, Deacon and Phillips (397) gave the following conclusions:

1. Unidendate complexes (structure I) exhibit Δ values $[\upsilon_{asym}(CO_2^-) - \upsilon_{sym}(CO_2^-)]$ greater than the ionic complexes. Compounds of composition $[(CH_3)_3Sn(CH_3COO)]$ and $[(CH_3)_2SnCl(CH_3COO)]$ having Δ values of magnitude 180 cm^{-1} are indicative of the ionic character of tin-acetate interaction.

2. Chelating (bidentate) complexes (structure II) exhibit Δ values which are significantly less than that of the ionic values.

3. The Δ values for bridging complexes (structure III) are greater than those of chelating (bidendate) complexes, and close to the ionic values.

The acetate groups acting as assembling/bridging ligands exhibit Δ value $\upsilon_{asym}COO - \upsilon_{sym}COO < 200\ cm^{-1}$.

In view of above reports, a comparison of the IR spectra of newly synthesized heterometal acetatoaryloxides with that of respective free metal acetates and parent complexes recorded in 4000-200 cm^{-1} region has been made. The bands characteristic of $\upsilon_{asym}(CO_2)$ and $\upsilon_{sym}(CO_2)$ vibrations of the acetate ligand in the isolated complexes $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ have been observed to occur at 1544 and 1414 cm^{-1} respectively in compounds with lead acetate while these modes have appeared at ~ 1565 and 1422 cm^{-1} in compounds with cadmium acetate shifted to higher frequencies with respect to those of the free acetates. The observed shifts of these bands to higher wave numbers excludes the formation of mixed crystals of type $[M(OAc)_2.2Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ and a chelating or bridging-chelating behaviour for the OAc ligand has been suggested (397). All important bands are given in Table 18.

2.3.2. ^{1}H-NMR Spectra

A comparison of the ^{1}H NMR spectra of isolated hetero-metal acetatoaryloxides with that of parent pentakis(2-/4-isopropylphenoxo)niobium(V) of composition $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_5]$ and $[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$ gave supporting evidences for their formation. The ^{1}H NMR spectra of hetero-metal acetatoaryloxides, displayed a diagnostic signal, due to acetate ligand shifted upfield relative to that occurring at δ 2.02 ppm in $Cd(OAc)_2$ and $Pb(OAc)_2$. It is worth mentioning here that in case of $[CdNb_2(OAc)_2(OCH(CH_3)_2)_{10}]$ and $[PbNb_2(OAc)_2(OCH(CH_3)2)_{10}]$, the signal due to acetate ligand has been reported to occur at δ 1.95 and δ 1.97 ppm respectively. The ^{1}H NMR spectra of complexes of composition $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$ and $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$ exhibited the signal due to acetate ligand at δ 1.88 ppm while in case of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$ and $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$, it appeared at δ 1.86 and δ 1.95 ppm respectively. The signals due to aromatic protons were found to undergo slight upfield shift by δ 0.06–0.29 ppm in hetero-metal acetatoaryloxides derived from pentakis(2-isopropylphenoxo) niobium(V) and by δ 0.10-0.12 ppm in hetero-metal acetatoaryloxides of pentakis(4-isopropylphenoxo) niobium(V) (Figs. 43-46). The signal due to methyl protons of isopropyl substituent has been found to shift slightly upfield and appeared in δ 1.15–1.21 ppm range in hetero-metal acetatoaryloxides relative to that occurring in δ 1.20–1.30 ppm range in parent complexes. The

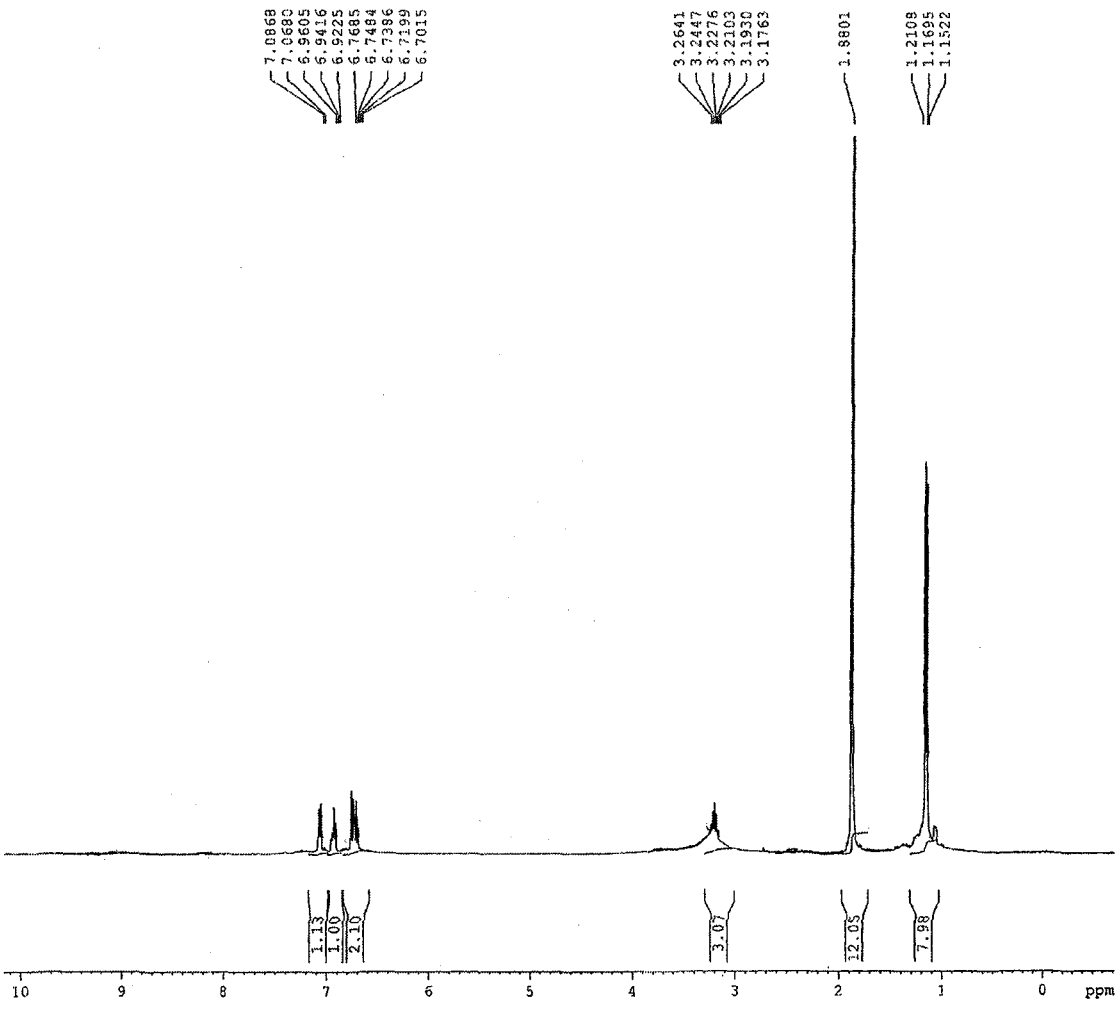


Fig. 43 ^{1}H NMR spectrum of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$

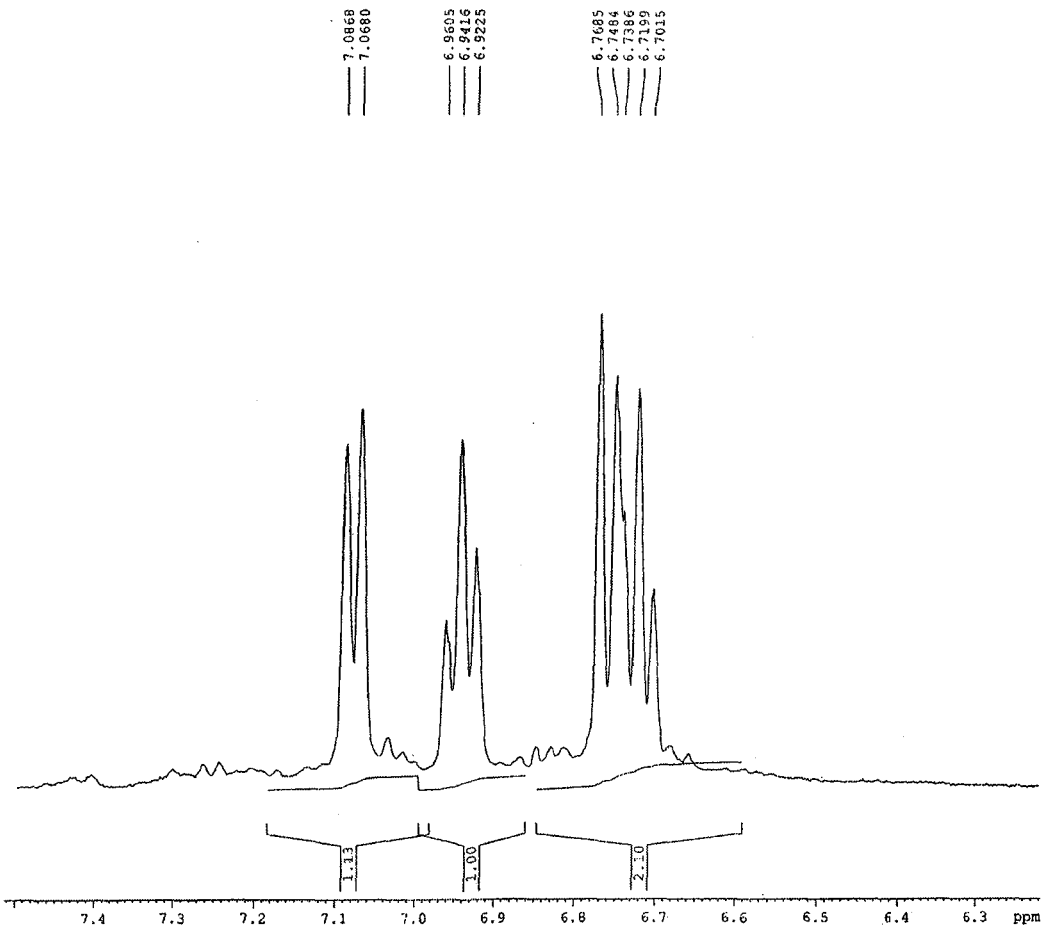


Fig. 43 ^{1}H NMR spectrum of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$

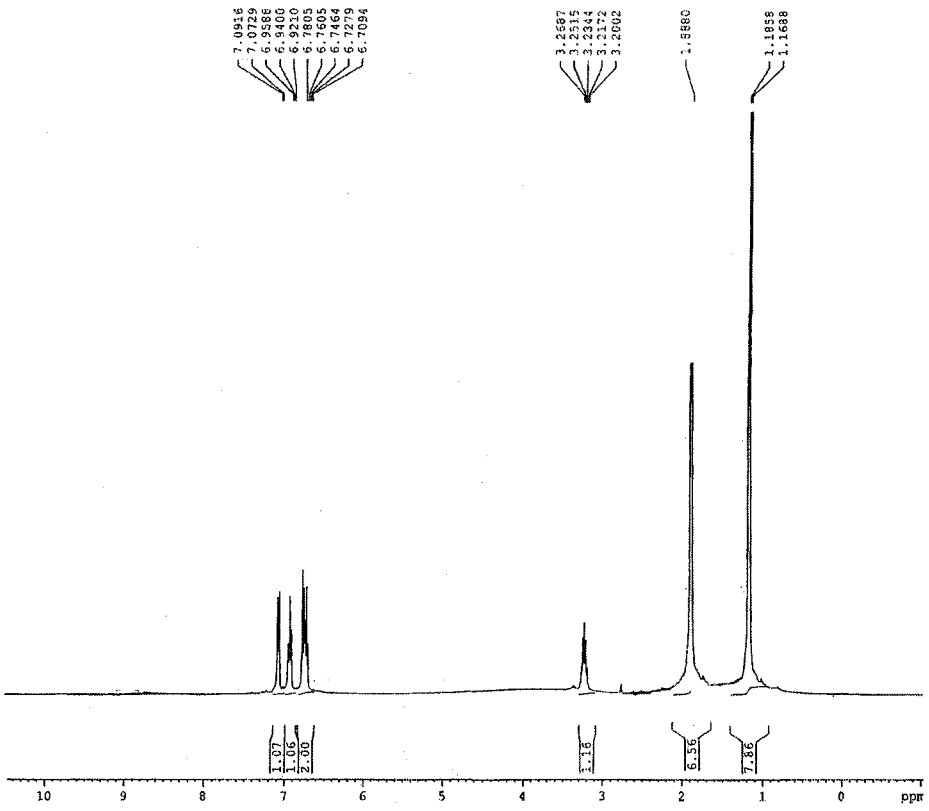


Fig. 44 ^{1}H NMR spectrum of $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$

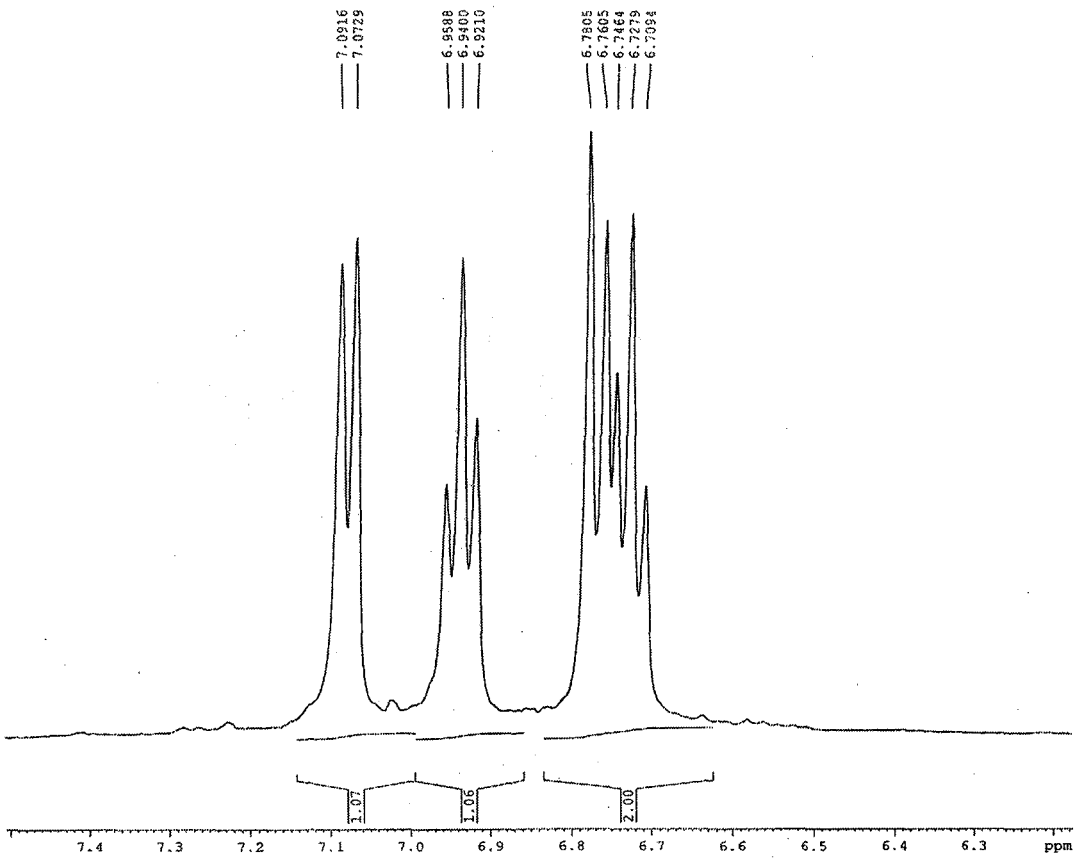


Fig. 44 ^{1}H NMR spectrum of $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$

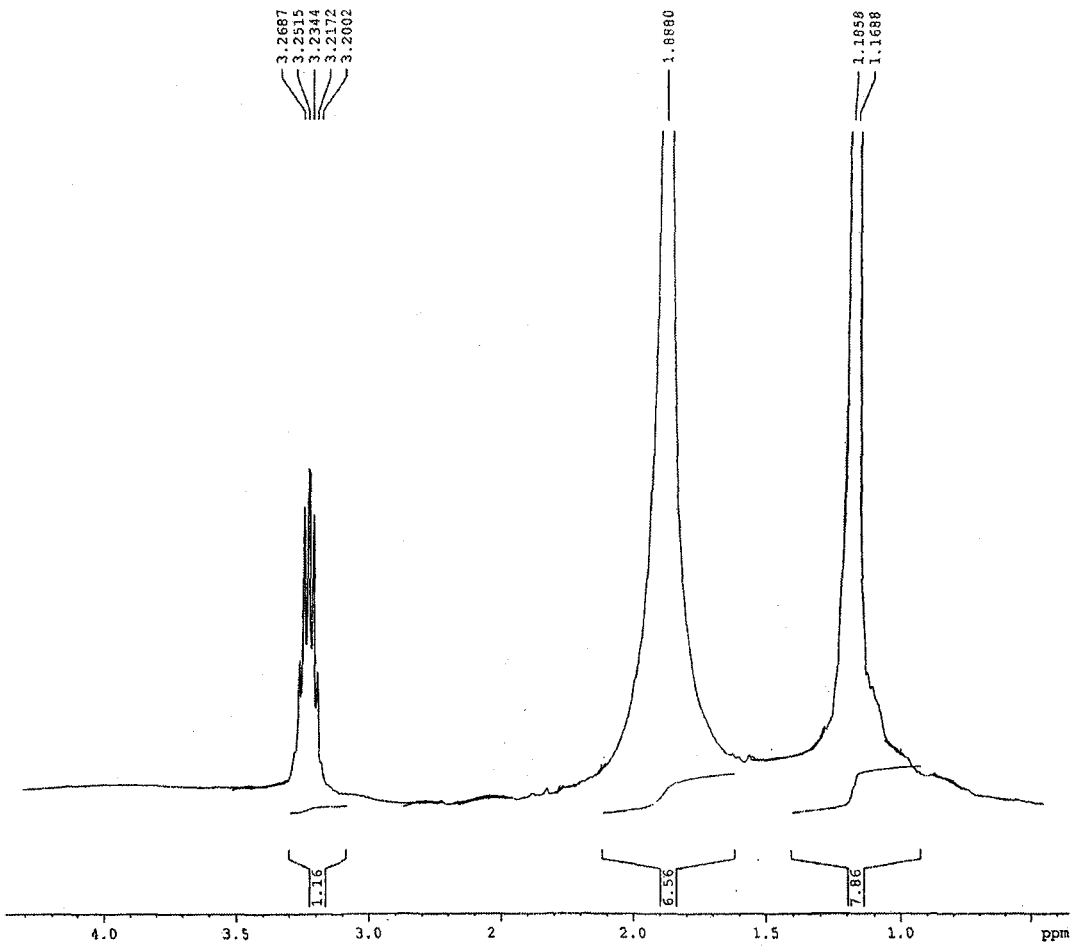


Fig. 44 ^{1}H NMR spectrum of $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$

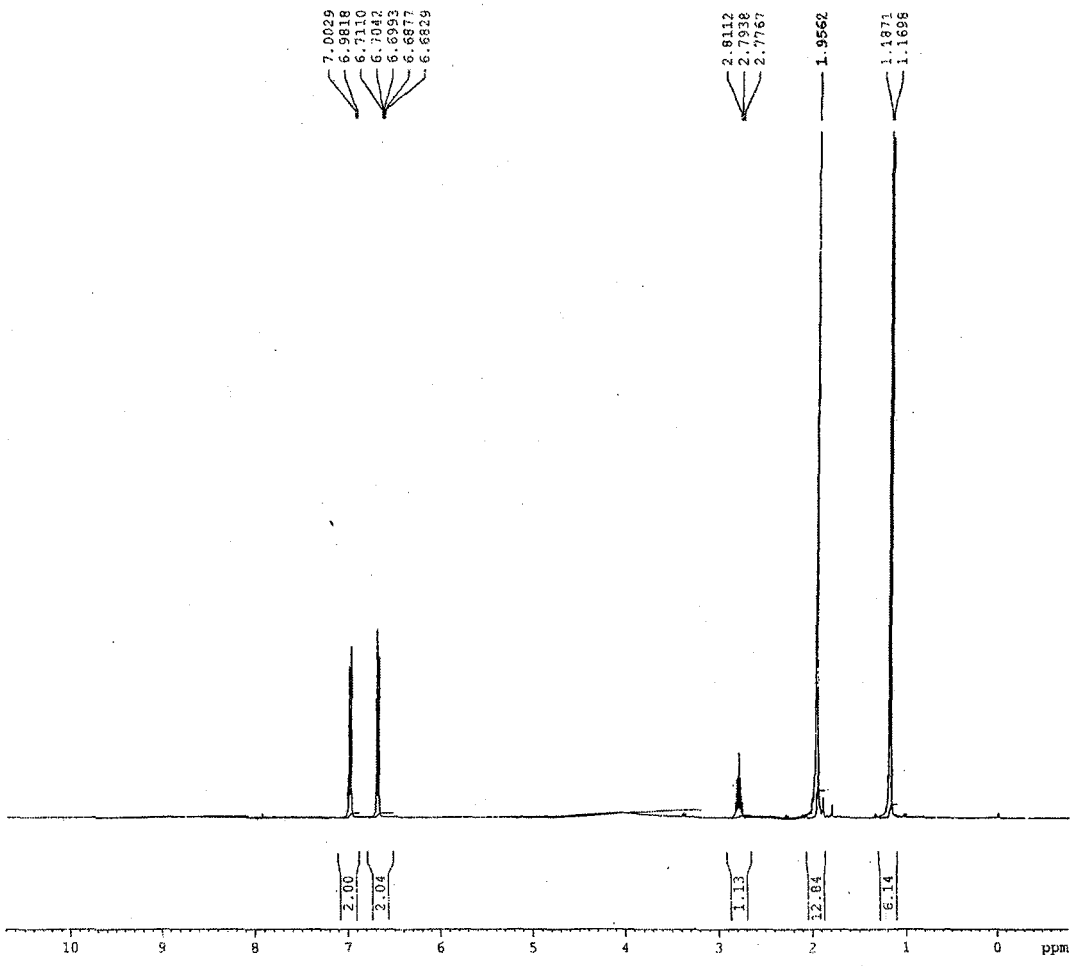


Fig. 45 ^{1}H NMR spectrum of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

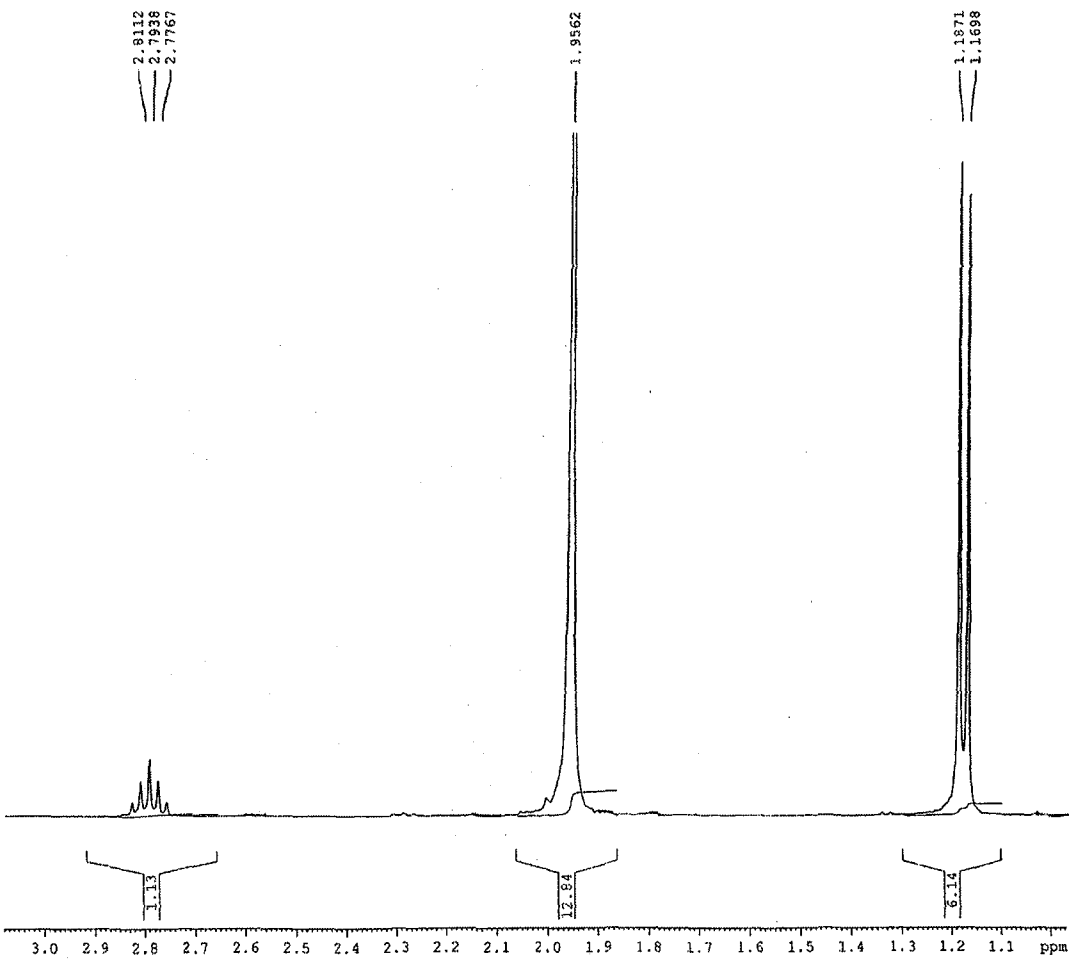


Fig. 45 ^{1}H NMR spectrum of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

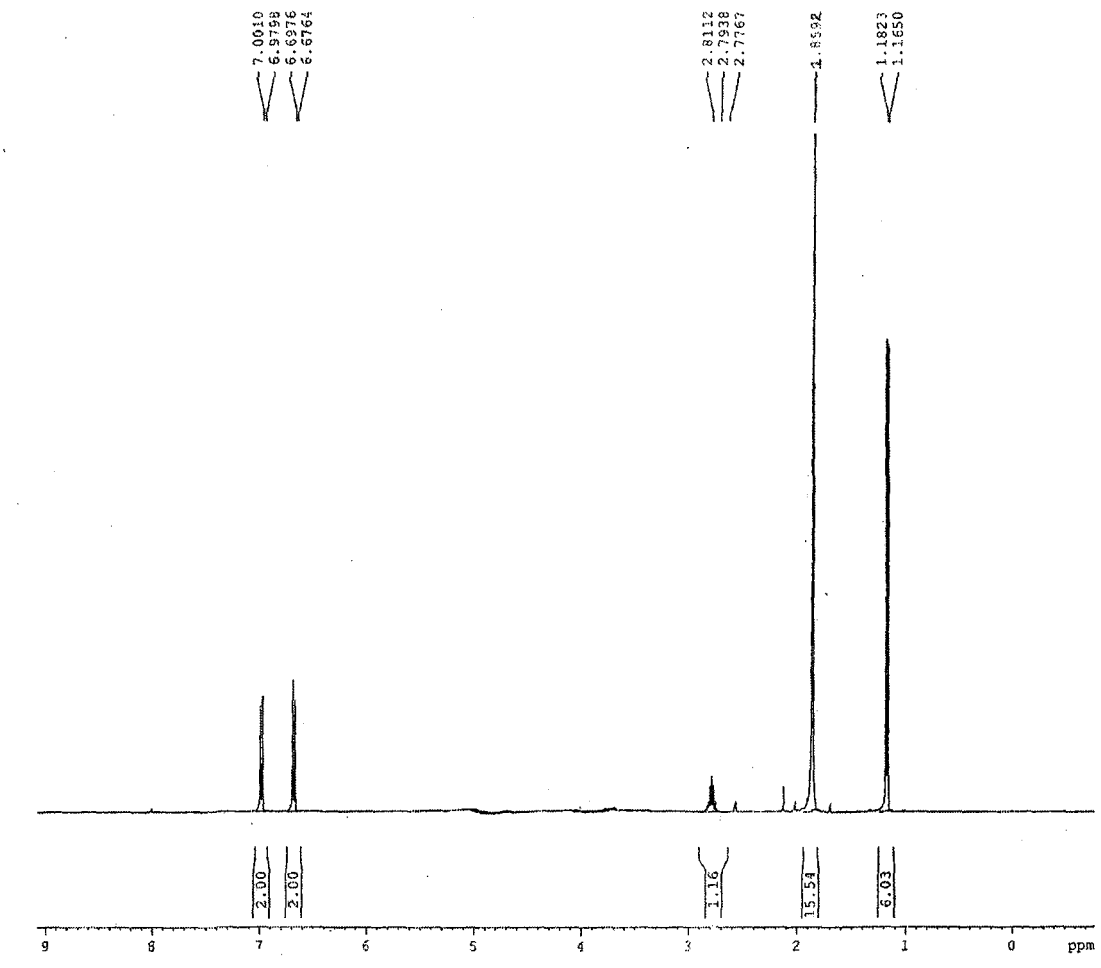


Fig. 46 ^{1}H NMR spectrum of $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

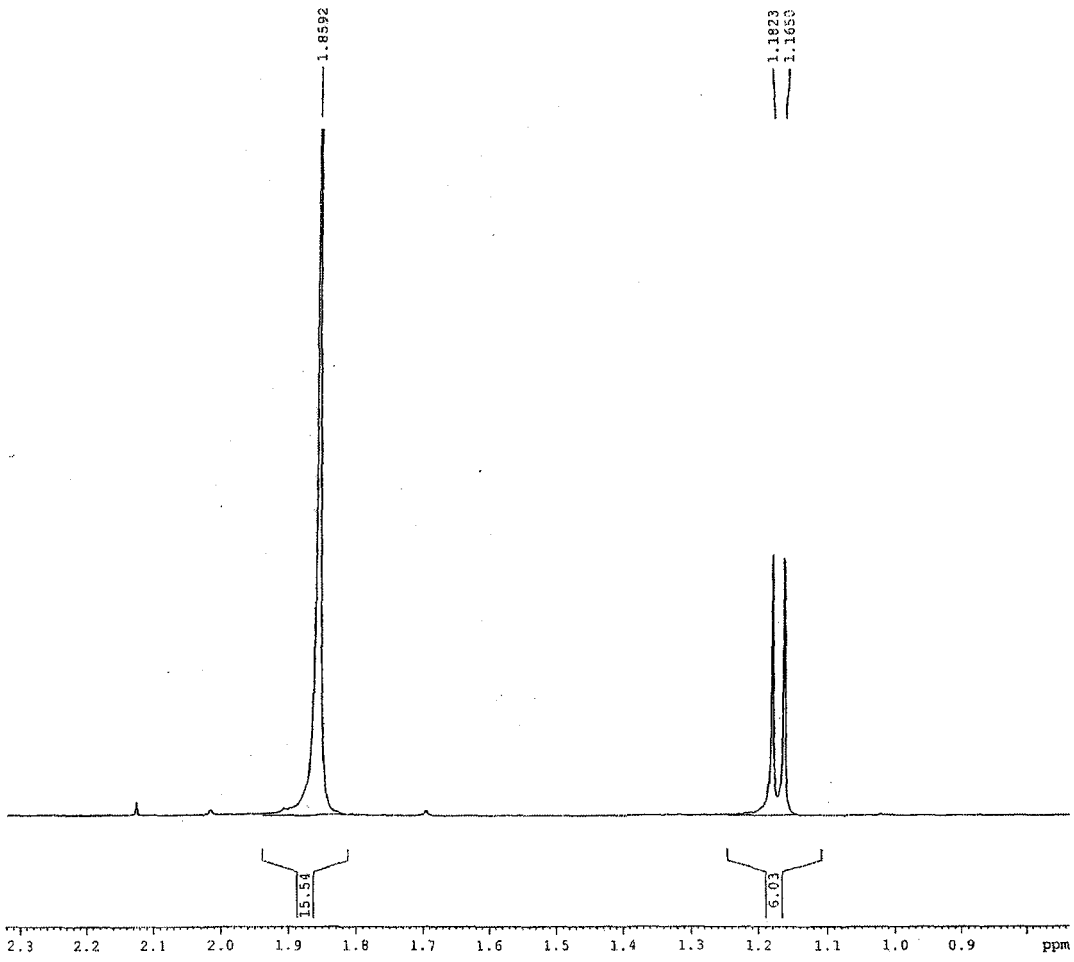


Fig. 46 ^{1}H NMR spectrum of $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

Table 18. IR spectral data (cm^{-1}) of hetero-metal acetatoaryloxides of niobium(V)

Compound	Bands (cm^{-1})
$[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$	3754, 3430, 3231, 2953, 2925, 2849, 1750, 1629, 1567s, 1422s, 1339s, 1253b, 1189s, 1085s, 1022s, 952s, 923, 894, 790, 755, 673s, 616, 580, 530s, 483, 455.
$[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$	3394, 3231, 3063, 2962vs, 2930, 2866s, 1544s, 1542s, 1416s, 1415s, 1339s, 1285s, 1246s, 1189s, 1147s, 1113s, 1083s, 1024s, 969, 935, 865, 826s, 796s, 752, 715, 665, 616s, 570, 518, 420.
$[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$	2959, 2930, 2855, 2076, 1565s, 1421s, 1345s, 1263s, 1166s, 1114, 1020s, 935, 830, 738, 676s, 623s, 582s, 536, 443.
$[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$	2958, 2924, 2861, 1544vs, 1542vs, 1414vs, 1409vs, 1340s, 1262s, 1160s, 1114, 1019vs, 935s, 834s, 778, 663vs, 665, 618s, 576s, 466.

signal due to –CH proton remained unaltered in hetero-metal acetatoaryloxides derived from pentakis(2-isopropylphenoxo) niobium(V) while it moderately shifted upfield by δ 0.69–0.76 ppm in case of mixed-metal acetatoaryloxide complexes derived from pentakis(4-isopropylphenoxo) niobium(V) (Table 19). It is anticipated that these compounds may find potential as single source precursors for Nb–Pb and Nb–Cd oxide materials.

2.3.3. X-ray Diffraction Studies

The XRD pattern of complex of composition $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$ revealed both high and low intense peaks (Fig. 47). The indexing of XRD peaks was done from $\sin^2\theta$ values. The indices hkl contained in N where $N = h^2 + k^2 + l^2$ and were calculated by dividing the various $\sin^2\theta$ values by the various integer i.e. the possible N values (Table 20). To find hkl planes for the sample what we do is to find the value of $\sin^2\theta/N$ and find the common value for each peak, corresponding to the value of N, one is able to find hkl planes.

The values of N were determined upon dividing the $\sin^2\theta$ values by the average common factor. The N values are then factorized by trial and error whereby the hkl values obtained represent the indices for the corresponding lines and every observed line is indexed (Table 21) which indicated its polycrystalline nature. An approximate value of the lattice parameter 'a' was calculated from common factor, N and $\lambda = 1.54$ A° using equation $a = ½\lambda\sqrt{N}/\sin^2\theta$. An error function was calculated using equation $½(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$.

2.3.4. Crystallite Size

The crystalline size of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$ has been calculated using Scherrer equation:

$$\text{Crystalline size} = \frac{k\lambda}{\beta\cos\theta}$$

where k is the constant of proportionality (Scherrer constant) and depends on how the width line is determined. The value of k is generally taken as 0.9, λ represents the wavelength of the X rays and has a value of 1.54 A°, θ is the half of the angle (2θ) of diffraction and β is the value of broadening of line at Full Width Half Maximum (FWHM) in radians. The average crystalline size has been found to be 12.07 nm.

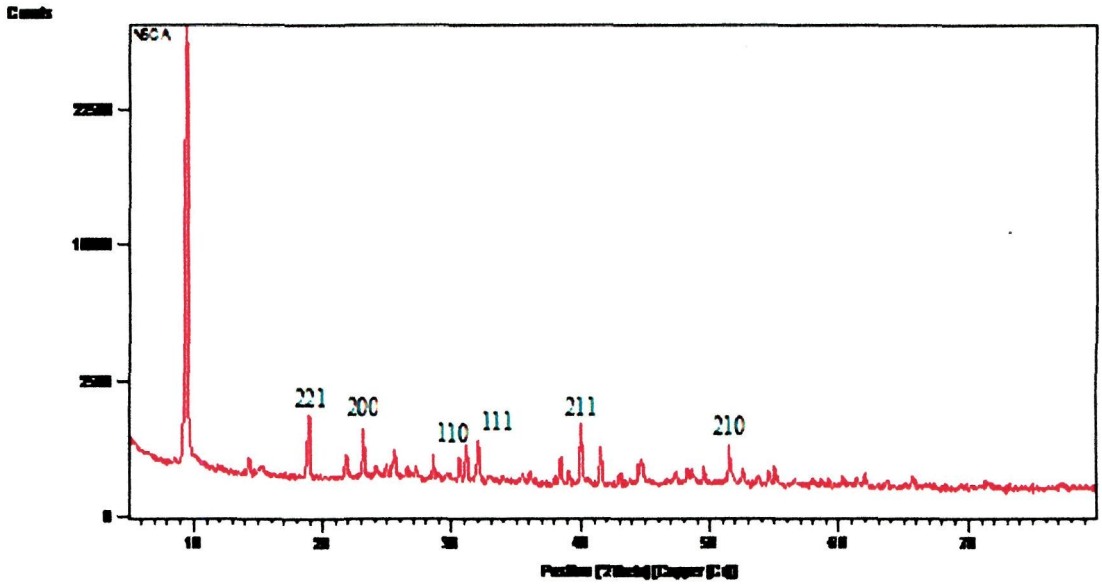


Fig. 47. XRD pattern of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

Table 19. ^{1}H-NMR data of hetero-metal acetatoaryloxides of niobium(V)

Compound	Substituent (Isopropyl protons)		CH_3(Ac)	Aromatic phenolic ring protons
	$-(CH_3)_2$	-CH		
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_5$	1.23-1.30	3.25-3.29	----	6.76-7.29
$[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$	1.17-1.19	3.20-3.27	1.88	6.70-7.00
$[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$	1.15-1.21	3.17-3.26	1.88	6.70-7.08
$Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$	1.20-1.30	3.51	----	6.79-7.10
$[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$	1.16-1.18	2.77-2.81	1.86	6.67-7.00
$[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$	1.16-1.18	2.77-2.81	1.95	6.68-7.00

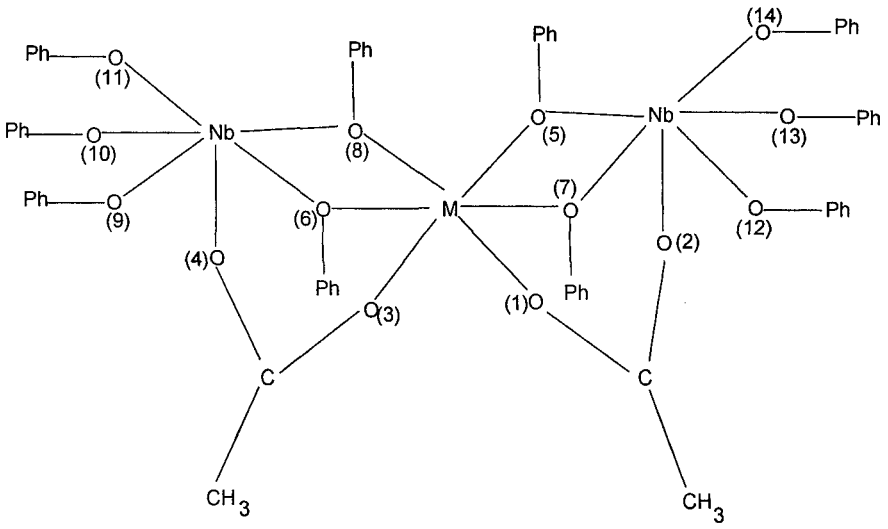
Table 20. Calculations for hkl planes of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

Peaks	N=1	N=2	N=3	N=4	N=5	N=6	N=7	N=8	N=9
Peak 1	0.1885	0.0942	0.0628	0.0471	0.0377	0.0314	0.0269	0.0235	**0.0209**
Peak 2	0.1257	0.0628	0.0419	0.0314	0.0251	**0.0209**	0.0179	0.0157	0.0139
Peak 3	0.1444	0.0722	0.4816	0.0361	0.0288	0.0240	**0.0206**	0.0180	0.0160
Peak 4	0.1169	0.0584	0.0389	0.0292	**0.0233**	0.0194	0.0167	0.0146	0.0129
Peak 5	0.1082	0.0541	0.0360	**0.0270**	0.0216	0.0180	0.0154	0.0135	0.0120
Peak 6	0.0696	0.0348	**0.0232**	0.0174	0.0139	0.0116	0.0099	0.0087	0.0077
Peak 7	0.0489	**0.0244**	0.0163	0.0122	0.0097	0.0081	0.0069	0.0061	0.0054

Table 21. Indexing of the Reflections and the Determination of the Lattice Parameter of $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$

$Sin^2\theta$	$N = sin^2\theta/comm.$ fa.	hkl	Quardic forms of Miller Indices	$a = \frac{1}{2}\lambda\sqrt{N}/sin^2\theta$	Error function $\frac{1}{2}(cos^2\theta/sin\theta + cos^2\theta/\theta)$
0.1885	9	(221)	Sc and Hexagonal	5.32	0.95
0.1257	6	(211)	Sc, Bcc and Hexagonal	5.32	1.25
0.1448	7	---	Hexagonal	5.35	1.14
0.1169	5	(210)	Sc and Hexagonal	5.03	1.31
0.1082	4	(200)	Sc, Fcc, Bcc and Hexagonal	4.68	1.38
0.0696	3	(111)	Sc, Fcc, Diamond and Hexagonal	5.05	1.79
0.0489	2	(110)	Sc, Bcc and Hexagonal	4.92	2.19

Thus, based upon IR and ^{1}H NMR spectral data in hand for $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ and $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ and the reported molecular structures of $[CdNb_2(OAc)_2(\mu\text{-}OCH(CH_3)_2)_4(OCH(CH_3)_2)_6]$ and $[PbNb_2(OAc)_2(\mu\text{-}OCH(CH_3)_2)_4(OCH(CH_3)_2)_6]$ (387), the following structure may tentatively be proposed for the newly synthesized hetero-metal acetatoaryloxides:



(where OPh = $OC_6H_4CH(CH_3)_2$-2/4 and M = Cd, Pb)

These trinuclear species display a bent, open-shell structure (Nb–M–Nb) with alternating Nb and M atoms, all metal atoms being six-coordinate, but displaying a distorted surrounding, wherein the distortion may be more for the central metals cadmium and lead.

CHAPTER – II

Lewis acid Character of Niobium(V) 2-/4-isopropylphenoxides Towards Nitrogen, Phosphorus, Arsenic and Oxygen Donor Ligands.

3.1. Introduction

The most frequent coordination number displayed by niobium and tantalum is six, however stable compounds with coordination number of seven (especially in lower oxidation states), eight, nine and even ten are known. In contrast, coordination numbers below five are rare. The relatively large atomic radii (1.47Å) have been ascribed to account for the less tight coordination sphere, and hence for the stereodynamic character often encountered in their complexes. The characteristic feature of Lewis acid behaviour of MX_5 (M = Nb or Ta) are their reactions with donor molecules. The niobium pentachloride, is however known to behave both as a softer and weaker Lewis acid than tantalum pentachloride towards ethers and sulphides (398).

Fowles and coworkers (399,400) have made a detailed study on the reactions of metal pentahalides with primary, secondary and tertiary amines, wherein the derivatives formed are diamagnetic and do not show any tendency to undergo reduction. The pentafluorides of niobium and tantalum are known to form simple 1:1adducts with mono-, di- and tri-alkylamines while pentachlorides and bromides undergo replacement reactions. The formation of 1:2 compounds of composition $[NbCl_5.2N(CH_3)_3]$, $[TaCl_5.2N(CH_3)_3]$ and $[NbBr_5.2N(CH_3)_3]$ with trimethylamine has been described. The reaction of niobium(V) pentachloride with N-allylphenylamine has been reported to yield bis[phenyl(2propenyl)ammonium]pentachloro(phenylamido)niobium(IV), $[NC_9H_{12}][NbCl_5(NC_6H_5)]$, wherein, the co-ordinated secondary amine loses its allyl group in forming an imino-metal bond while the unreacted N-allylphenylamine behaves as a proton donor and counter ion (401).

Niobium(V) bromide is known to react with Me_3SiNPh_2 to give the trigonal-bipyramidal complex, $[Nb(NPh_2)_3Br_2]$ (402). The reactions of niobium and tantalum pentachlorides, MX_5, with dialkylureas (tetramethyl- and tetraethylurea, TMU and TEU), amides (N,N-dimethylformamide, N,N-diethylformamide, N-phenylacetamide) and phosphoryl compounds (triphenylphosphane oxide, TPPO and trimethyl phosphate, TMP) (L) have been described to depend on the reactant to metal molar ratio, and yield hexacoordinate complexes of composition $[MX_5(L)]$ (403). The reactions of 1,2,5-triphenylphosphole (TPP) and 1,2,5-triphenylphosphole oxide (TPPO), sulphide (TPPS) and selenide (TPPSe) with some transition metal halides have been studied in dry oxygen-free organic solvents. The reactivity of these ligands is clearly a function of the oxidation state of the metal, with the order being M(II) < M(III) < M(IV) < M(V). The ligands do not react with metal and the metal halides (Mn, Fe, Ni), while rapid reactions

occur with niobium(V) and tantalum(V) (404). The chelating trisphenol ligands viz. tris(2-hydroxyphenyl) amine(Cp1) and tris(2-hydroxy-4,6-dimethylbenzyl)amine(Cp2) have been found to be excellent precursors for the chelating phenoxides and the latter finds use to prepare a series of cyclopentadienyl metal derivatives of early transition metals. For niobium and tantalum, reactions of [$CpMCl_4$] with these ligands afford [CpMCl(1)] and [CpMCl(2)] (where M = Nb and Ta) (405).

Unlike the reactions of niobium and tantalum pentahalides with aliphatic amines, the reactions of these metal pentahalides with pyridine and related ligands such bipyridyl or phenanthroline have been reported to depend upon critical conditions. The reactions of pyridine with niobium pentabromide proceed by oxidation-reduction to yield niobium(IV) derivative [$NbBr_4(C_5H_5N)_2$] and the oxidation products 1-(4-pyridyl) pyridinium bromide and pyridinium bromide. The reduction of niobium pentachloride by pyridine has been reported. The tantalum pentaiodide has been reported to dissociate in pyridine to give the adducts [$TaI_5(C_5H_5N)_2$] and the pyridine adduct of elemental iodine (406).

The nitrogenous bases 2,2′-bipyridyl and 1,10-phenanthroline are also known to reduce niobium and tantalum pentahalides in acetonitrile to oxidation state + 4 and yield monoadducts of type [MX_4(bipy)] at room temperature while at 0°C the reactions yield [$NbCl_5$(bipy)(MeCN)] and [$TaCl_5$(bipy)(MeCN)] (X = Cl or Br). A nitrogen adduct of zerovalent niobium, tris-2,2′-bipyridylniobium(0), [$Nb(bipy)_3$], has been reported to be formed by Herzog and Schuster by the reaction of niobium(V) chloride with dilithium bipyridyl in tetrahydrofuran. Compounds of composition [$MX_5(bipy)_2$] formulated as the eight coordinate [$(MX_4(bipy)_2)X$] (407) have been reported to be formed by the reaction of niobium pentabromide and tantalum pentaiodide with 2,2′-bipyridine. It has, however been established that the reduction of metal can be prevented, even at room temperature when the reaction is conducted in dry benzene and a series of isomorphous hepta-coordinate compounds of type [MX_5(bipy)] have been described (408). The poorly soluble and moisture sensitive compounds of composition [MBr_5(terpy)], [$NbCl_5$(terpy)] and [Ta_2Cl_{10}(terpy)] have been reported to be formed by the reactions of MX_5 (X = Cl, Br) with 2,2′,2′′-terpyridyl (409). The formation of complexes of the type [NbX_4L_2] and [TaX_5(2,2′-bipyridine)] (X = NCS^- or $NCSe^-$, L = 2,2′-bipyridine or , 4,4′-dimethyl-2,2′-bipyridine) has been reported by the reaction of metal hexaisothiocyanate or hexaisoselenocyanate complexes with organic ligands. The formation of complexes of composition [$Nb(NCS)_4(C_{10}H_8N_2)_2$] and [$Nb(NCSe)_4(C_{10}H_8N_2)_2$] has been reported by the reduction of niobium(V) hexaisothiocyanate or

hexaisoselenocyanate complexes. The pyridine complexes of composition $[Nb(NCS)_4(py)_2]$ and $[Ta(NCS)_4(py)]$, has also been similarly prepared (410). The neutral tris-2,2′-bipyridine(bipy) and 1,10-phenanthroline(phen) (L) compounds $Mbipy_3$ and $Mphen_3$ have been reported to be formed conveniently in high yield by sodium amalgam reduction of the chlorides of Ti, Zr, Hf, V, Nb, Ta, Cr, $MoCl_4L$, WCl_4L and $ReCl_4(THF)$ in tetrahydrofuran.

The complexes of niobium(V) and tantalum(V) halides with various oxygen donors ligands have been reported (411,412). The formation of 1:1 adducts of niobium and tantalum pentahalides with dimethyl (413), diethyl (412) and di-n-propyl (413) ethers and 1,4-dioxane (414) have been reported. The abstraction of oxygen from the ethers is reported to occur at around 100°C to produce oxytrihalides and alkyl halides (407). The ability of crown ethers to coordinate and reduce MCl_5 has been described in complexes of the type $[(MCl_5)_2L]$ and $[MCl_5L]$ (L = dibenzo-18-crown-16, 18-crown-16 and 15-crown-5) which tend to disproportionate (415). Niobium and tantalum pentachlorides react with oxygen donor ligands in anhydrous alcohol to yield halo-alkoxide complexes of the type $[M(OR)_2Cl_3.L]$ (where M = Nb, Ta; R = CH_3, C_2H_5; X = Cl, Br; L = $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$, $(C_6H_5)_3SO$). The formation of $[((CH_3)_2N)_3PO.NbOCl_3.\ 2((CH_3)_2N)_3PO)]$ has been reported by the reaction of niobium pentachloride with excess of hexamethylphosphoramide in methanol (416). The formation of niobium oxychloride cluster compounds of composition $[A_5Ti_8Nb_{18}Cl_{53}O_{12}]$ (A = K, In), has been reported from a mixture containing $NbCl_5$, Nb_2O_5, Nb, Ti and KCl or In by solid-state reactions at 750°C (417).

The organo derivatives of the heavier elements of groups V and VI, i.e. phosphorus, arsenic, antimony, sulphur, selenium and tellurium serve frequently as ligands in addition compounds with transition elements in low valence states. A few complexes of these elements have been reported in which the central atom is a transition element in its highest valence state. The ability of tertiary phosphines to stabilize low oxidation state transition-metal halide complexes which contain metal-metal multiple bonds has permitted the exploration of the redox chemistry of these species. The reactions of monodentate tertiary phosphines with hydrated niobium and tantalum chloride clusters $[M_6Cl_{14}.8H_2O]$ and $[M_6Cl_{15}.7H_2O]$ have been reported to yield complexes of stoichiometry $[(M_6Cl_{14})Cl_2.(PR_3)_4]$ (418). The formation of half-sandwich high-valent niobium(V) phosphinomethylidyne complex $[CpNb\{CPPh_3\}Cl_2]$ has been reported by the transylidation reaction of $CpNbCl_4$ with $Ph_3P{=}CH_2$ (419). Complexes of composition $[MCl_5(SPh_2)]$, $[2MCl_5(dithiane)]$, $[2MCl_5(bte)]$ and $[2MCl_5(pte)]$ (where dithiane

= thioacetal, bte = 1,2-di-t-butylthioethane, pte= 1,2-diphenylthioethane and M = Nb, Ta) containing six-coordinate metal have been reported. The 1:1 complexes of niobium and tantalum pentachloride with 1,2-bisdiphenylphosphinoethane and of tantalum pentachloride with N,N,N′,N′-tetramethyl-o-phenylenediamine have been reported (420). The reactions of niobium and tantalum pentachlorides and pentabromides and tungsten hexachloride with fluorinated ditertiary arsines, 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene, 1,2-bis(dimethylarsino)-3,3,4,4,5,5-hexafluorocyclobutene and 1,2-bis(dimethylarsino)-4-fluorobenzene have been reported to form MX_5(diarsine) which are the first metal complexes containing fluoro ligands coordinated to metal atoms in high oxidation states (421).

Compared to the pronounced acceptors properties of the metal halides, the acceptor properties of both metal alkoxides and phenoxides are less studied. The replacement of halogen atoms by alkoxy or phenoxy group decreases the acceptor ability of the central metal atom due to the polymeric nature of these complexes, in which the central metal atom has already achieved its preferred coordination number e.g. haloisopropoxides of aluminium are known to be strong acceptors than aluminium triisopropoxide (422,423). The incorporation of electron withdrawing group in alkoxide ion is known to reduce the degree of polymerization and thereby enhances its acceptor properties (424). The reactions of metal alkoxides with stronger bases have been reported to result in the breakdown of alkoxy bridging, followed by coordination of the ligand to metal (425). The detailed NMR study of the coordination compounds of niobium and tantalum with a variety of potential monodentate and bidentate ligands (426) has confirmed that ligands having high charge density on donor atom dissociate the dimer alkoxides followed by coordination.

The factors controlling the coordination chemistry of niobium and tantalum pentamethoxides have been described by Riess and coworkers (425). The adducts of niobium pentamethoxide of composition [$Nb(OMe)_5$.L] (L = pyridine, γ-picoline, morpholine, hydrazine, trimethylamine oxide and hexamethylphosphoramide) and that of tantalum pentamethoxide with hydrazine have been reported (425). The adducts of tantalum isopropoxide with ethylene-diamine of composition [$Ta_2(OPr^i)_{10}$.en] (en = ethylenediamine) has been reported (427). The niobium(V) and tantalum(V) halide alkoxides behave as Lewis acids and are known to react with O, S, N and P donor ligands to afford a number of adducts (428-431).

Literature also contains a few scattered reports on the acceptor properties of metal

phenoxides compared to metal alkoxides. The adducts of titanium tetraphenoxides with ammonia, methylamine, dimethylamine, trimethylamine, pyridine, dioxane, aniline, α-naphthylamine and acetone (432,433) have been extensively reviewed by Masthoff and coworkers (434). Lewis acid character of niobium(V) phenoxides of composition $[Nb(OC_6H_5)_5]$ and $[NbCl_4(OC_6H_5)]$ has been reported to be established by isolating compounds of composition $[Nb(OC_6H_5)_5.Base]$ (Base = py, pyNO and Ph_3AsO) and $[NbCl_4(OC_6H_5).Base]$ (Base = py and α-pic) (435). Compounds of composition $[Ta(OC_6H_5)_5.py]$, $[TaCl_4(OC_6H_5).py]$ and $[TaCl_4(OC_6H_5).\alpha\text{-pic}]$ have also been reported (435). The coordination compounds of composition $[MCl_{5-n}(OC_6H_5)_n.L]$ (M = Nb or Ta); n = 1 or 2 and L = pyridine N-oxide, α, β and γ-picoline N-oxide, $POCl_3$, TPPO (triphenylphosphine oxide) HMPA (hexamethylphosphoramide) have also been reported (436). The mixed chloro-aryloxide complexes $[\{M(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3\}_2]$ (M = Nb,Ta) react with pyridine(py) and PMe_2Ph to produce a series of adducts cis-mer-$[MCl_3(OC_6H_3Pr^i_2\text{-}2,6)_2(L)]$ and trans-mer-$[MCl_2(OC_6H_3Pr^i_2\text{-}2,6)_3(L)]$ (437). The reactions between niobium(V), tantalum(V) and protactinium(V) chlorides and bromides with sodium N,N′-diethyldithiocarbamate (Nadtc) have been examined in non-aqueous, non-oxygenated organic solvents (438). Arimondo *et al.* (439) have reported the dialkylcarbamato complexes $[M(O_2CNR_2)_n]$ (M = Nb or Ta, R = Et, n = 5; M = Nb, R = Et, Pr^i, n = 4).

In view of above observations, it has been considered worthwhile to study the nature of newly synthesized niobium(V)isopropylphenoxides of composition$[NbCl_3(OC_6H_4\text{-}C(CH_3)_3\text{-}2/4)_2]$, and $NbCl_4(OC_6H_4\text{-}C(CH_3)_3\text{-}2/4)$ with nitrogenous, phosphorus, arsenic and oxygenous donors. The various bases used are:

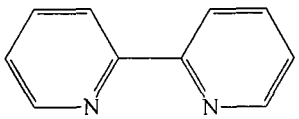
(A) Nitrogenous bases – 2,2′-Bipyridyl and 1,10-Phenanthroline.

(B) Oxygenous bases – Triphenylphosphine oxide and triphenylarsine oxide.

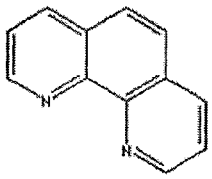
(C) Phosphorus and arsenic containing ligands – Triphenylphosphine, triphenylarsine and arsenic trithiophenoxide

3.2. Reactions of trichlorobis(2-/4-isopropylphenoxo)niobium(V) $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ with 2,2′-bipyridyl and 1,10-phenanthroline

The ligands, 2,2′-bipyridyl and 1,10-phenanthroline find extensive use in both analytical and coordination chemistry and complexes with unusual stereochemistries, coordination numbers and magnetic properties have been reported to be formed from these ligands



2,2′-Bipyridyl



1,10-Phenanthroline

The literature contains many examples of iron, ruthenium and osmium complexes ligated by 2,2′-bipyridine. In complexes of the type $[(M(L)_3)^{2+}]$ (where L = a substituted 2,2′-bipyridine), reduction of the complex is known to result by the addition of the electrons primarily localized on the bipyridine ligands to π-orbitals of metal (440,441). Futhermore, unsubstituted 2,2′-bipyridine bound to these metals, has been found easier to reduce than the 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy) (442,443). The vinyl containing pyridine and bipyridine complexes polymerize much more rapidly and efficiently when the respective complex is reduced by two electrons rather than one. The chloroalkoxides show similar behaviour to metal pentahalides in forming adducts readily with bipyridyl (408). The thiocyanatoalkoxobipyridyl complexes of composition $[M(NCS)_2(OR)_3(bipy)]$ (M = Nb or Ta, R = Me or Et) have been reported and eight-coordinate structure around metal atom has been proposed (444). The oxygen-18 labelled niobium oxychloride is known to form complexes of composition $NbOCl_3$.bipy and $NbOCl_2(OR)$.bipy (R = C_2H_5, n-C_3H_7) with bipyridyl (445).

The reduction of niobium pentahalides in the presence of pyridine (446) or bidendate nitrogen and arsenic ligands has been reported (447). The red coloured (2,2′-bipyridine) lithium, Li(bipy) and green dilithium complex Li_2(bipy) have been reported as reducing agents by Herzog (448), Li(bipy) is a very powerful reducing agent and reduction of niobium is known to proceed to as far as zero or even -1 oxidation state (449). Djordjevic and coworkers (450) have described the preparation and properties of crystalline mixed-ligand niobium(V) complexes of formula $[NbCl_3(OR).bipy]$ (R = Me, Et, Pr^n or Bu^n) by controlled reduction of $[NbCl_2(OR)_3]$ complexes using Li(bipy) in tetrahydrofuran. Futhermore, Coffindafer and co-workers (451) have investigated the reduction of a series of niobium(V) aryloxides in the presence of chelating phosphine (dmpe) (Me_2p-$CH_2CH_2PMe_2$) whereby a new class of aryloxide derivatives of niobium in lower oxidation state are formed.

A polymeric nature of $[MX_5(bipy)]$ has been suggested by chemical and spectral properties (452) as bridging halides may raise the coordination above seven. The structural information

available in literature on the stereochemistry of niobium(V) and tantalum(V) complexes has indicated that eight-coordination occurs only in compounds where most of the participating ligands are fairly electronegative and do not allow a large charge transfer to the central metal ion. In mixed-ligand spheres, the charge transfer, or orbital overlap has been described to be modified easily by bond angles and bond distances. For bipyridyl, by accommodating the bond length and accordingly the orbital overlap, the existence of six-coordinated $[NbOCl_2(OEt)(bipy)]$, eight-coordinated $[M(O_2)_3(bipy)]$ and $[M(NCS)_2(OR)_3(bipy)_2]$ complexes has been described.

The octahedral arrangements around niobium have been reported in dimeric pentaalkoxides (453), dimeric pentachlorides (454), polymeric oxotrichloroniobium(V) (454) and oxodichloroethoxobipyridyl niobium(V) (455) complexes. Seven coordination has been reported for spheres involving electro-negative fluoride and oxygen ligands such as $[NbF_7^{2-}]$, $[NbOF_5^{2-}]$ (454), $[NbO(C_2O_4)_3]^{3-}$ (456,457), $[H_2NbO(OH)(C_2O_4)_2(H_2O)]$ (458,459) and for $[MX_5(diarsine)]$ (460). The highest coordination in a niobyl derivative, containing the Nb=O group in the ligand sphere, observed so far is thus seven. Complexes with ligand spheres invoving four chelated peroxo groups, are eight coordinated. The same is the case for substituted peroxo-derivatives, involving three or two peroxides, and one or two, respectively, bidentate nitrogen (bipy, o-phen) or oxygen ($C_2O_4^{2-}$) ligands (461,462).

In view of the interesting nature of 2,2′-bipyridyl and 1,10-phenanthroline, it has been of interest to undertake the reactions of $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ with these nitrogenous bases. The interaction of niobium(V) 2-/4-isopropylphenoxides of composition $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ with 2,2′-bipyridyl(bipy) and 1,10-phenanthroline(phen) (B) in equimolar amounts in dry benzene led to the formation of coordination compounds according to the equation:

$$NbCl_3(OC_6H_4CH(CH_3)_2^{-}\ 2/4) + B \longrightarrow NbCl_3(OC_6H_4CH(CH_3)_2^{-}\ 2/4)\cdot B$$

The 1:1 stoichiometric composition of the coordination compounds has been established by elemental analysis (Table 22). The adducts are moisture sensitive yellowish solids but are quite stable in dry air. The compounds are appreciably soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of compounds in nitrobenzene suggested these to be non-electrolytic in nature.

Tables 22. Analytical data of coordination compounds of niobium(V) isopropylphenoxides with nitrogenous bases

Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %					Molar Cond. in $PhNO_2$ (Scm^2 $mole^{-1}$)
		Nb	Cl	C	H	N	
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$.bipy	Yellow	14.84	17.01	53.70	4.79	4.49	0.45
$C_{28}H_{30}Cl_3O_2N_2Nb$ (625.50)		(14.87)	(17.03)	(53.72)	(4.80)	(4.48)	
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$.bipy	Orange	14.85	17.02	53.75	4.78	4.47	0.70
$C_{28}H_{30}Cl_3O_2N_2Nb$ (625.50)		(14.87)	(17.03)	(53.72)	(4.80)	(4.48)	
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$.phen	Off white	14.30	16.39	55.41	4.60	4.30	0.43
$C_{30}H_{30}Cl_3O_2N_2Nb$ (649.50)		(14.32)	(16.40)	(55.43)	(4.62)	(4.31)	
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$. phen	Yellow	14.31	16.41	55.40	4.63	4.29	0.67
$C_{30}H_{30}Cl_3O_2N_2Nb$ (649.50)		(14.32)	(16.40)	(55.43)	(4.62)	(4.31)	

where bipy = 2,2′-bipyridyl and phen = 1,10-phenanthroline

3.2.1. IR spectra

A comparison of IR spectra of niobium(V) compounds with that of free bases and parent complexes provided evidence for their formation (Table 23). The absorption bands due to C=C and C=N ring stretching modes of free bipyridyl (452,463) known to occur in 1580-1475 cm^{-1} region have been observed to shift to high wave numbers by about 20–30 cm^{-1} upon complexation. The C–H out of plane deformation mode occurring at 750 cm^{-1} has been observed to split up into two bands and appeared at 766 and 730 cm^{-1} in compounds (464) which is suggestive of the bidentate nature of 2,2′-bipyridyl (465). The absorption bands of free base at 626 cm^{-1} (inplane ring deformation) and 416 cm^{-1} (out of plane ring deformation) have been found to shift towards higher frequencies in coordination compounds (466). The C–H stretching bands of the free ligand observed ~ 3075, 3050 and 3000 cm^{-1} have been observed to shift slightly towards higher frequencies in adducts. The non-observance of a strong band between 1000 cm^{-1} and 900 cm^{-1} which could be attributed to ring deformation modes is indicative of the presence of a neutral 2,2′-bipyridine ligand (467). An important feature of the spectra of coordination compounds of bipyridine is, the absence of absorption bands near 2400 cm^{-1} for the bipyridinium cation (452).The trends of shifts suggest the coordination from both the nitrogen atoms of 2,2′-bipyridyl to niobium metal and are in agreement with earlier reports in literature (464). The Nb–O modes have been observed at ~ 560 cm^{-1} in coordination compounds.

The IR spectra of uncoordinated 1,10-phenanthroline is known to exhibit bands in two frequency regions 1600-1400 cm^{-1} and 900-700 cm^{-1}. The absorption bands at 1578, 1562, 1504 and 1449 cm^{-1} assigned to symmetric ring stretching and inplane antisymmetric ring vibrations of free 1,10-phenanthroline have been observed to undergo an appreciable shift towards higher wave numbers by 20–35 cm^{-1} upon coordination with metal. An explanation to these observations may be reasoned as that the primary effect of coordination is on nitrogen atom and the centre ring has no nitrogen atom to provide any donor site. The multiple weak bands occurring in 870–735 cm^{-1} region in IR spectra of uncoordinated 1,10-phenanthroline due to out of plane hydrogen motion on the heterocyclic rings, and to the hydrogen on the centre ring respectively appeared in 890–727 cm^{-1} region in compounds. Likewise, a medium intensity band occurring at 990 cm^{-1} due to totally symmetric inplane ring breathing frequency moved to 1031–1004 cm^{-1} region. The absorption bands of free ligand occurring in 1250–1125 cm^{-1} region due to inplane hydrogen deformation motion or possible ring vibrations also shifted towards higher wave numbers in coordination compounds. Usually, 1,10-phenanthroline acts as a bidentate

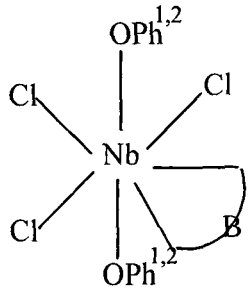
Table 23. IR spectral data (cm^{-1}) of coordination compounds of niobium(V) isopropylphenoxides with nitrogenous bases

Complex	Bands (cm^{-1})
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$. bipy	3329, 2964, 2921, 2857, 1665, 1606s, 1568, 1525, 1509, 1475, 1443s, 1380, 1320s, 1283, 1246, 1161s, 1106, 1063, 1020, 834, 766s, 730, 656s, 542, 494, 435, 414, 365, 316.
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$. bipy	3755s, 3404, 3213, 3115, 3076, 3028, 2959s, 2924, 2866, 2600, 1976, 1901, 1602vs, 1559, 1514vs, 1474s, 1443vs, 1380s, 1357s, 1318, 1257b, 1171b, 1101s, 1067s, 1026s, 987s, 877, 834, 825s, 768s, 734, 703, 654s, 583, 553, 478, 417, 362, 339, 302, 236.
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2)_2$. phen	3367, 3056, 2916, 2841, 1627, 1573, 1519, 1455, 1427, 1342, 1224, 1147, 1108, 1106, 1031, 929, 849, 773, 727s, 655, 607, 494, 427, 306, 279.
$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2$. phen	3431, 3225, 3062s, 3011, 2958s, 2926s, 2867s, 1750, 1605, 1568, 1543, 1514s, 1501s, 1463s, 1428s, 1386, 1363, 1339, 1311s, 1244vs, 1172s, 1144, 1105s, 1054, 1004, 930vs, 890vs, 844vs, 767, 727vs, 686, 651s, 611, 585s, 552s, 507, 485s, 460, 429, 336s, 246, 233

where bipy = 2,2′-bipyridyl and phen = 1,10-phenanthroline

ligand however in case of vanadium(III) (468), adducts of bis(acetylacetonato) and bis(trifluoroacetylacetonato)oxovanadium(IV) and vanadium(V) (469) complexes with 1,10-phenanthroline and related nitrogen bases, unidendate nature of the ligand has been suggested. The trends of the shifts of various bands of 1,10-phenanthroline upon coordination are suggestive of bonding through both of its nitrogen atoms. The appearance of entirely new bands in ~ 495–485 cm^{-1} region attributed to υ(Nb←N) mode have further substantiated bonding through nitrogen.

Based upon the limited data available, a seven coordinate environment around niobium may tentatively be proposed for coordination compounds of niobium(V) isopropylphenoxides with 2,2′-bipyridyl and 1,10-phenanthroline.



$[NbCl_3(OPh^{1,2})_2.B]$

(where $OPh^{1,2}$ = $OC_6H_4CH(CH_3)_2$-2/4 and B = 2,2′-bipyridyl(bipy) and 1,10-phenanthroline(phen))

3.3. Reactions of $[NbCl_4(OC_6H_4CH(CH_3)_2$-2/4] with Ph_3P, Ph_3As, $As(SPh)_3$, Ph_3PO and Ph_3AsO

Literature contains numerous reports on the donor characteristics of tertiary phosphine and arsine ligands towards various metals in different oxidation states (470). The tertiary phosphine and arsine oxides also constitute an interesting class of oxygenous donors. The metal pentachlorides and trichlorides are known to form addition compounds with Ph_3PO and Ph_3AsO (471,472). The potential of arsenic trithiophenoxide, $As(SPh)_3$ complex has also been examined (473). The interaction of methanolic solutions of $[NbCl_4(OC_6H_4CH(CH_3)_2$-2/4)] with equimolar amounts of Ph_3P, Ph_3As, $As(SPh)_3$, Ph_3PO and Ph_3AsO (L) in benzene, afforded the formation of

1:1 addition compounds in confirmity with elemental analyses (Table 24) according to the equation.

$$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4) + L \longrightarrow NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)\cdot L$$

(where L = donors ligands)

The adducts are moisture sensitive, light brown solids but are quite stable in dry air. The additions compounds are soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of the adducts in nitrobenzene indicated their non-electrolytic nature.

3.3.1. IR spectra

A comparison of infrared spectra of coordination compounds with that of parent complexes and uncoordinated donor ligands gave supporting evidences for their formation. The characteristic vibrations of Ph_3P and Ph_3As which deserve attention are due to υ(C–C), υ(C–H) and bending (P–C) and (As–C) modes coupled with aromatic ring vibrations. The occurrence of diagnostic bands at 1484, 1437, 1021, 726, 541, 501 and 420 cm^{-1} in $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3P]$ and at 1560, 1444, 1121, 1091, 726, 622 and 495 cm^{-1} in $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).Ph_3P]$ established their formation. The spectra of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3As]$ showed bands at 1513, 1481, 1435, 1021, 738, 693, 669 and 466 cm^{-1} suggesting its formation.

The IR spectra of arsenic trithiophenoxide $As(SPh)_3$ is known to exhibit bands at 492 s, 400w and 372 vs cm^{-1} due to υ(As–S) mode and at 744 vs and 684 vs cm^{-1} due to υ(As–S–C) mode. A moderate to appreciable shift to lower wave numbers in υ(As–S) mode has been observed upon coordination. The bands appeared at 460, 376, 740 and 680 cm^{-1} and at 483, 372, 744 and 685 cm^{-1} due to υ(As–S) and υ(As–S–C) modes in $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).As(SPh)_3]$ and $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).As(SPh)_3]$ respectively suggested their formation.

The characteristic vibrations of Ph_3PO and Ph_3AsO which can be informative to support the formation of adducts are due to υ(P=O), υ(As=O), υ(P–C), and υ(As–C) modes. The bands known to occur at 455 and 479 cm^{-1} in Ph_3PO and Ph_3AsO, respectively, ascribed to υ(P–C) and υ(As–C) mode, shifted to higher spectral regions and appeared at 540 and 588 cm^{-1} in respective complexes in agreement with earlier reports (474,475). The absorbtion bands due to υ(P=O) and υ(As=O) modes known to occur at 1192 and 879 cm^{-1} in triphenylphosphine oxide and

Table 24. Analytical data of adducts of niobium(V) isopropylphenoxides with phosphorus, arsenic and oxygen donors

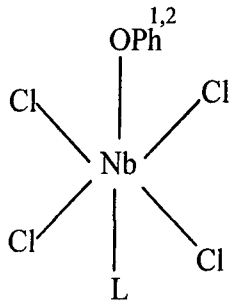
Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %				Molar Cond. in $PhNO_2$ (Scm^2 $mole^{-1}$)
		Nb	C	H	Cl	
$NbCl_4(OC_6H_4CH(CH_3)_2$-2).Ph_3P	Maroon	14.70	51.25	4.09	22.43	0.60
$C_{27}H_{26}OCl_4PNb$ (632)		(14.72)	(51.27)	(4.11)	(22.47)	
$NbCl_4(OC_6H_4CH(CH_3)_2$-2).Ph_3As	Brown	13.72	47.91	3.83	21.00	0.57
$C_{27}H_{26}OCl_4AsNb$ (676)		(13.76)	(47.93)	(3.85)	(21.01)	
$NbCl_4(OC_6H_4CH(CH_3)_2$-2).$As(SPh)_3$	Brown	12.01	43.00	3.35	18.40	0.51
$C_{27}H_{26}OS_3Cl_4AsNb$ (772)		(12.05)	(43.01)	(3.37)	(18.39)	
$NbCl_4(OC_6H_4CH(CH_3)_2$-2).Ph_3PO	Maroon	14.33	49.97	4.03	21.92	0.54
$C_{27}H_{26}O_2Cl_4PNb$ (648)		(14.35)	(50.00)	(4.01)	(21.91)	
$NbCl_4(OC_6H_4CH(CH_3)_2$-2).Ph_3AsO	Brown	13.41	46.80	3.71	20.53	0.53
$C_{27}H_{26}O_2Cl_4AsNb$ (692)		(13.44)	(46.82)	(3.76)	(20.52)	
$NbCl_4(OC_6H_4CH(CH_3)_2$-4).Ph_3P	Yellow	14.71	52.23	4.10	22.45	0.75
$C_{27}H_{26}OCl_4PNb$ (632)		(14.72)	(51.270	(4.11)	(22.47)	
$NbCl_4(OC_6H_4CH(CH_3)_2$-4).$As(SPh)_3$	Yellow	12.03	43.04	3.35	18.35	0.70
$C_{27}H_{26}OS_3Cl_4AsNb$ (772)		(12.05)	(43.01)	(3.37)	(18.39)	

triphenylarsine oxide (474,476) respectively appeared at 1166 and 796 cm^{-1} in respective adducts (Table 25). The shift of the absorption bands due to υ(P=O) and υ(As=O) modes to lower wave number is ascribed to overall decrease in the bond order of P=O and As=O due to decrease in pπ–dπ bonding. It has also been reported in literature that υ(P=O) mode is shifted to lower frequency upon coordination to metal, while υ(As=O) mode may move to higher or lower wave numbers than the free ligand. The occurrence of absorption bands at 540 cm^{-1} only due to υ(Nb–O) mode suggested the rupture of bridging isopropylphenoxy groups in parent complexes upon coordination.

3.3.2. ^{1}H-NMR spectra

The ^{1}H NMR spectra of coordination compounds with oxygen, phosphorus and arsenic donors further substantiated their formation. Apparently, ^{1}H NMR spectra of adducts exhibited signals in four distinct ranges. The higher field signals in δ 1.12–1.32 & δ 3.05–3.64 ppm range ascribed to protons due to methine and methyl groups of isopropyl substituent and lowfield signals in δ 6.21–7.35 ppm and further δ 7.43–7.86 ppm ranges are due to aromatic protons of phenolic ring and aryl protons of the donor ligands viz Ph_3P, Ph_3As, $As(SPh)_3$, Ph_3PO and Ph_3AsO [L] respectively. A perusal of ^{1}H NMR spectral data (Table 26) of adducts showed that the signals due to methine and methyl protons of the substituent undergo insignificant to moderate downfield shifts relative to parent complex (Fig. 48 and 49). The coordination of $As(SPh)_3$ to niobium has been inferred from the occurrence of thiophenyl proton resonances at δ 7.43–7.50 ppm relative to δ 7.25–7.46 ppm in $As(SPh)_3$.

Based upon IR and ^{1}H NMR spectral data, a distorted octahedral structure around niobium for coordination compounds may tentatively be suggested as:



$[NbCl_4(OPh^{1,2}).L$

(where $OPh^{1,2}$ = $OC_6H_4CH(CH_3)_2$-2/4 and L = Ph_3P, Ph_3As, $As(SPh)_3$, Ph_3PO and Ph_3AsO)

Table 25. IR spectral data (cm^{-1}) of adducts of niobium(V) isopropylphenoxides with phosphorus, arsenic and oxygen donors

Complex	Bands (cm^{-1})
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3P$	3427, 3225, 3057, 2959s, 2926s, 2855s, 2363s, 1750, 1631s, 1577s, 1484s, 1437s, 1386, 1322, 1270s, 1122s, 1079s, 1021s, 992s, 940, 830, 726vs, 693vs, 541vs, 501s, 420b.
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3As$	3182b, 2961s, 2924, 2872, 2097s, 1750, 1640, 1579s, 1513vs, 1481s, 1435s, 1363, 1339s, 1274s, 1183, 1149s, 1115s,1081s, 1021, 917s, 877, 836s, 738vs, 693s, 669s, 620, 576, 466, 414, 379, 354, 319s, 275, 235.
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).As(SPh)_3$	3238s, 3046s, 2961s, 2918, 2861s, 2362, 1941, 1872,1629, 1577vs, 1502s, 1475vs, 1436s, 1362s, 1272vs, 1183, 1172s, 1149vs, 1114s, 1072s, 1022s, 836, 807, 740s, 688s, 584, 460, 376, 287, 232.
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3PO$	3734b, 3051, 2962s, 2918s, 2849s, 2361s, 1640, 1581s, 1484s, 1437vs, 1322, 1261s, 1166, 1117s, 1085s, 1016s, 929s, 871, 802vs, 750vs, 692vs, 586, 540vs, 449, 397b, 310s.
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3AsO$	3393, 3221, 3054, 2959s, 2918s, 2861s, 1640, 1571s, 1519s, 1490s, 1438s, 1363s, 1277s, 1270s, 1183s, 1149s, 1085s, 796s, 743s, 688s, 588s, 466s, 356s.
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).Ph_3P$	3863, 3754, 3674, 3654, 3363, 2959, 2924, 2849, 1739, 1646, 1620, 1560, 1508, 1444, 1386, 1311, 1262, 1121, 1091, 1021, 888, 726, 691, 669, 622, 576, 547, 495, 402, 379, 281.
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).As(SPh)_3$	3754, 3416, 3196, 2958, 2913, 2843, 2363, 1620, 1553, 1506, 1438, 1403, 1259, 1183, 1120, 813, 685, 585, 483, 372.

Table 26. ^{1}H-NMR data of adducts of niobium(V) isopropylphenoxides with phosphorus, arsenic and oxygen, donors (ppm)

Complex	Substituent (Isopropyl protons)		Aromatic phenolic ring protons	Aromatic protons (donor ligands)
	$-(CH_3)_2$	-CH		
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)$	1.27-1.30	3.20-3.29	6.75-7.29	------
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3P$	1.13-1.26	3.05-3.64	6.78-7.35	7.48-7.71
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3As$	1.15-1.32	3.26-3.33	6.90-7.35	7.70-7.85
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).As(SPh)_3$	1.12-1.26	3.33-3.48	6.21-7.35	7.43-7.50
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3PO$	1.13-1.26	3.30-3.40	6.77-7.35	7.46-7.69
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3AsO$	1.13-1.26	3.24-3.35	6.72-7.30	7.72-7.86
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$	1.25	2.88	6.79-7.12	------
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).Ph_3P$	1.17-1.19	2.71-2.81	6.70-7.01	7.33-7.50
$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).As(SPh)_3$	1.16-1.18	2.75-2.82	6.67-7.00	7.25-7.50

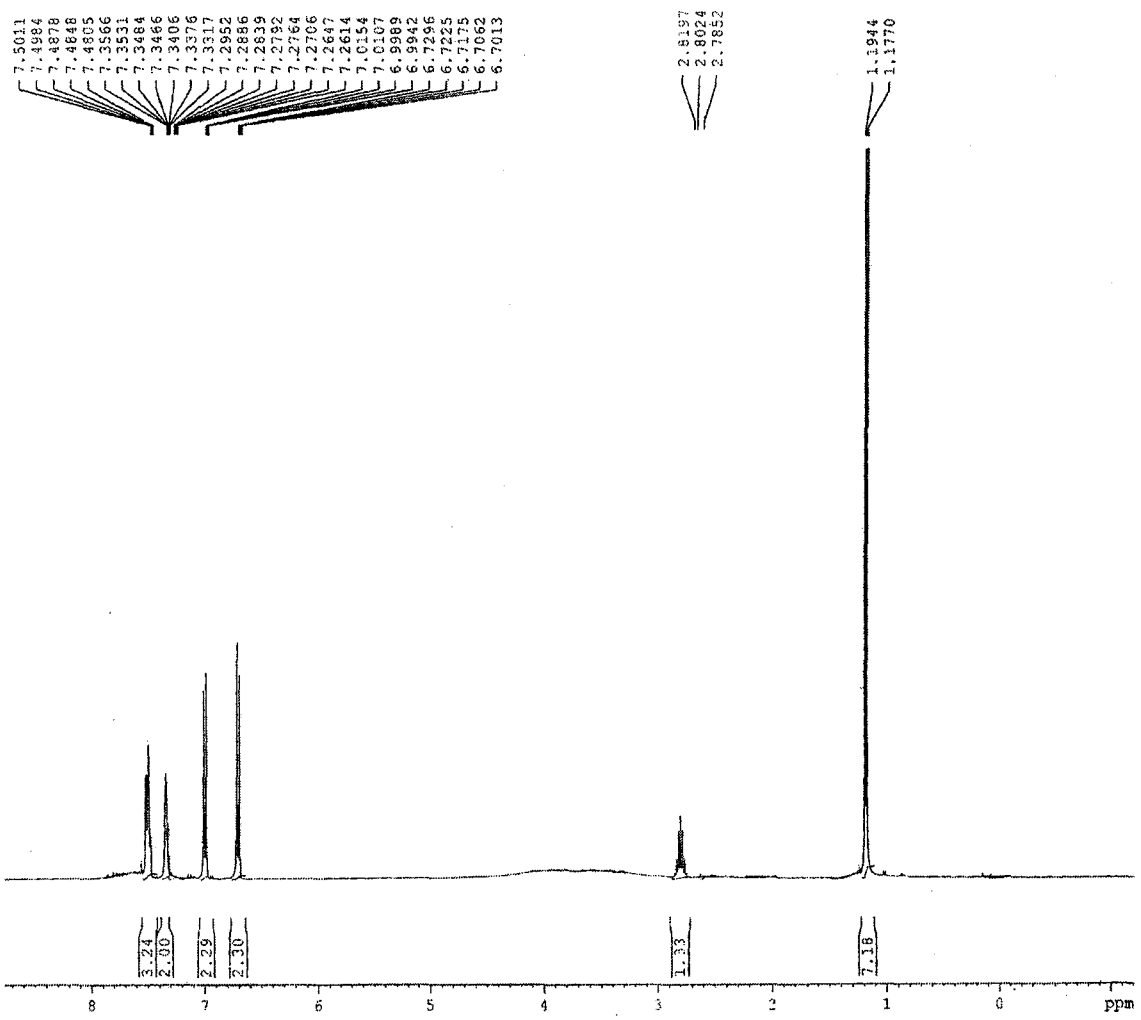


Fig. 48 ^{1}H NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).PPh_3$

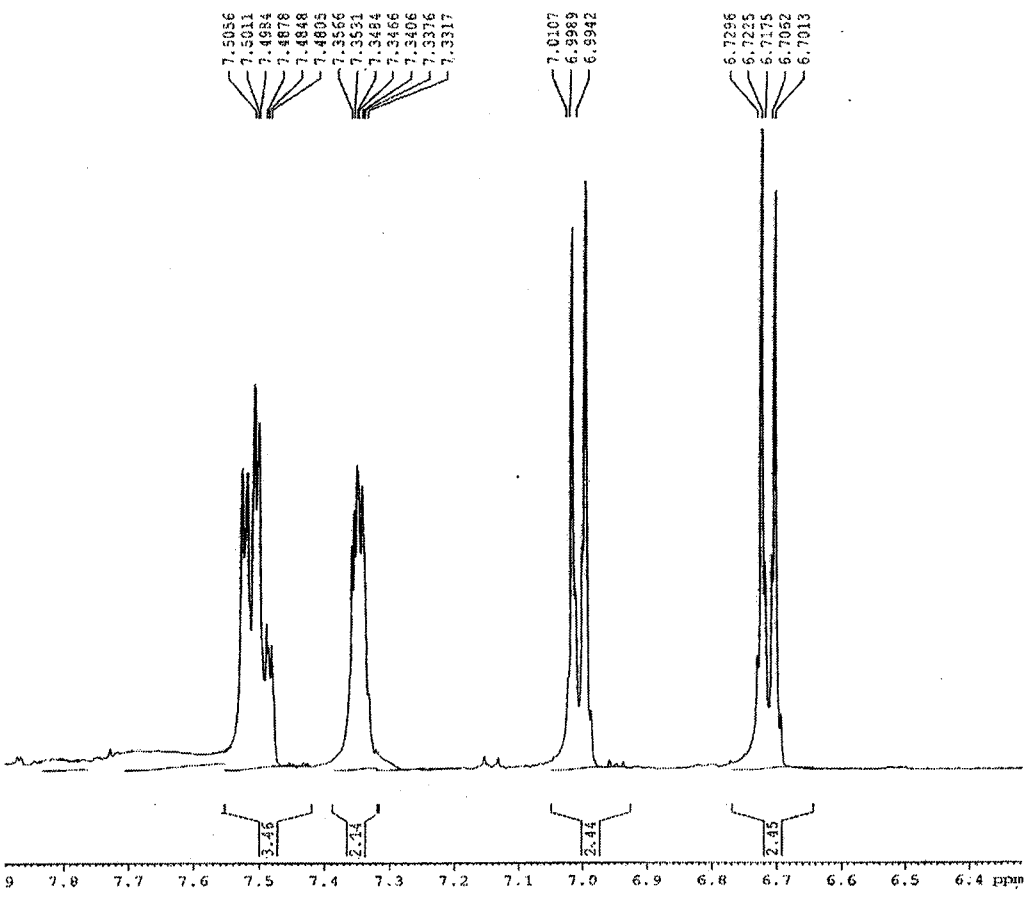


Fig. 48 ^{1}H NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).PPh_3$

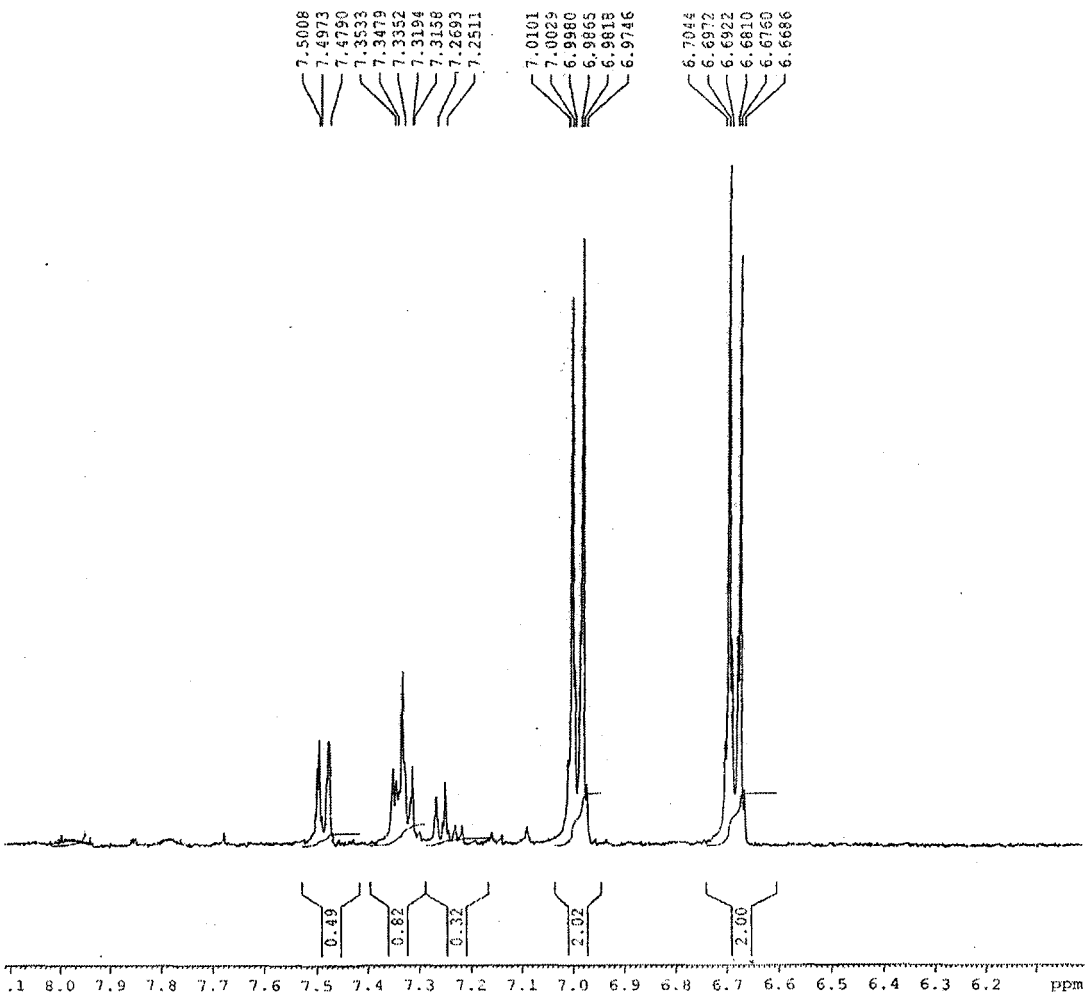


Fig. 49 ^{1}H NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).As(SPh)_3$

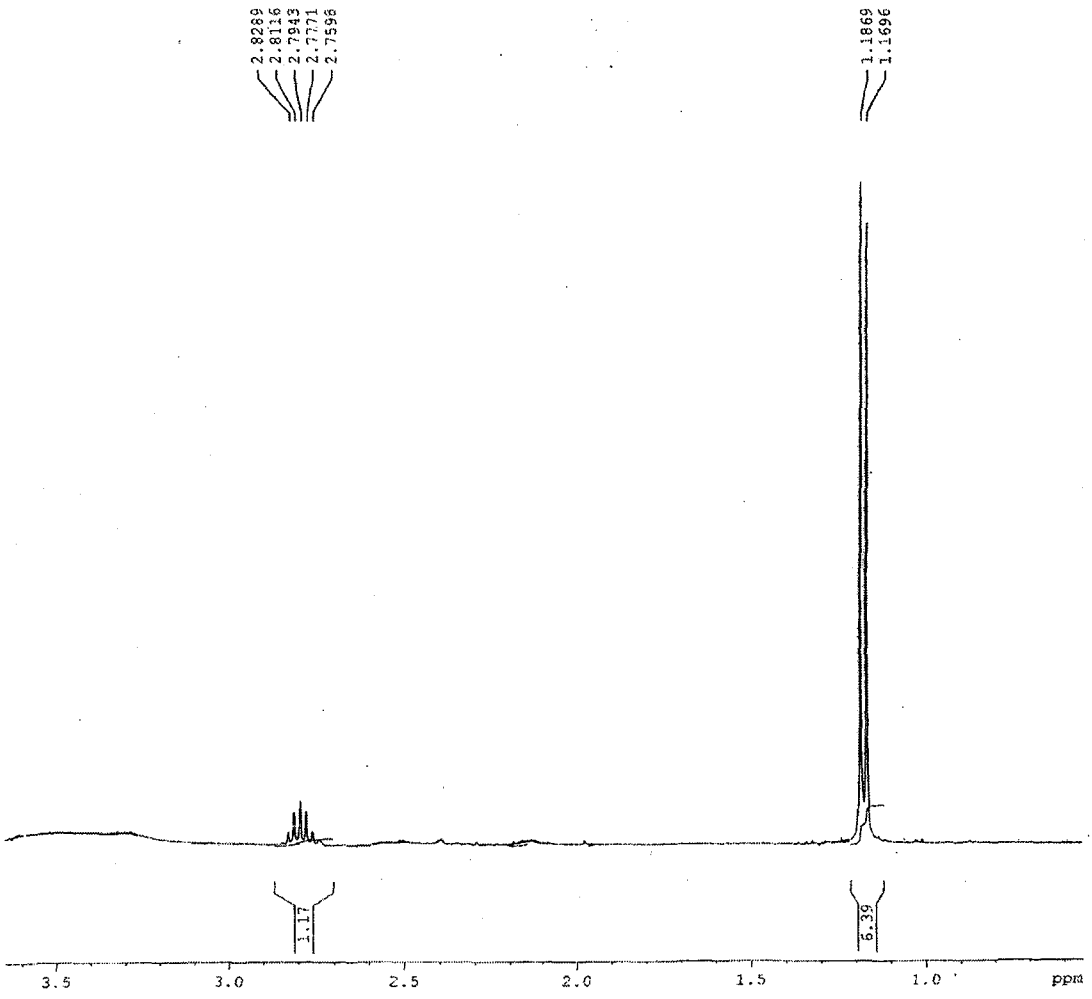


Fig. 49 ^{1}H NMR spectrum of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).As(SPh)_3$

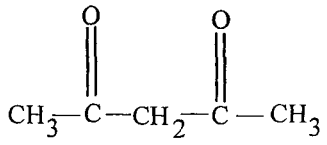
CHAPTER - III

Reactivity of Niobium(V) Isopropylphenoxides Towards Chelating Ligands and Sodium Alkoxides.

4.1. Introduction

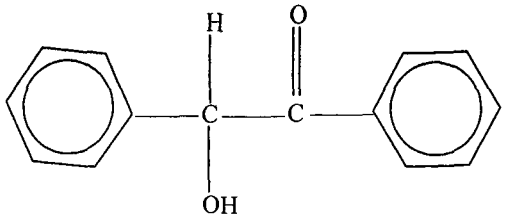
This chapter describes the reactions of monochlorotetrakis2-isopropylphenoxoniobium(V), $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with following chelating ligands:

(1) (a) β-Diketone



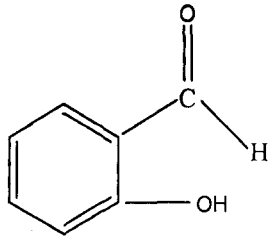
Acetylacetone (acacH)

(b) α-Hydroxyketone



Benzoin (benzH)

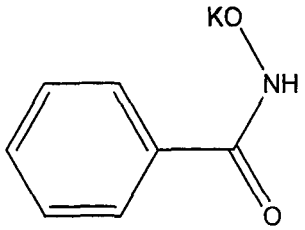
(c) α-Hydroxyaldehyde



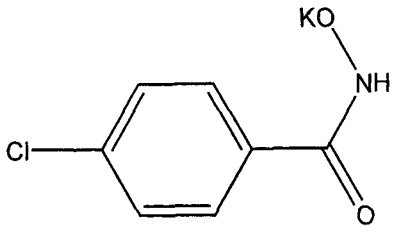
Salicylaldehyde (salH)

(2) Hydroxamic Acids

(a) Potassium benzohydroxamate, (KHL^1)



(b) Potassium 4-chlorobenzohydroxamate, (KHL^2)



The basis of exploring these reactions is associated with an ever-increasing knowledge about the ability of metal ions to influence many of the complex reactions upon which vital processes of living organism depend. The participation of complex compounds in nearly every phase of biological activity is known to involve bond formation and cleavage, exchange of functional groups, blocking of functional groups, influence upon stereochemical configuration, oxidation-reduction reactions, storage transfer and transmission of energy. The property of the chelating ligands to react with metal aryloxides to yield mixed-ligand derivatives and in some cases fully substituted pure metal chelates, depending upon the stoichiometric amounts of the ligands are of much interest.

The alkoxides readily react with the protons of a large number of organic hydroxyl compounds such as alcohols, glycols, carboxylic acids, β-diketones, alkanolamines etc. containing reactive hydroxyl groups with the replacement of the alkoxo group by the new organic ligand. These reactions are quite versatile and appear to be subjected to either kinetic factors e.g. the reactions with highly ramified alcohols are generally slower and may even be sterically hindered in some cases (477) or the reactions of alkoxides with molecules containing reactive protons such as those having –NH and –SH groups are controlled mainly by thermodynamic factors and are known to be governed by comparative stability of M–O, M–N and M–S bonds. The N–H group of alkanolamines and higher amines are reactive towards tin(IV) and alkyltin(IV) alkoxides (478-481) but not with zirconium analogues.

The synthesis of chelating bis(aryloxide) ligand 2,2′-ethylenebis(6-isopropylphenol) (H_2BIPP) and its transition metal complexes from the alkylation of [(BIPP)$TiCl_2$] viz. formation of [(BIPP)$TiMe_2$] and [(BIPP)$(CH_2Ph)_2$] and alkylation of [(BIPP)$TiCl_3$] to form [(BIPP)$TaMe_3$] and [(BIPP)$Ta(CH_2Ph)_2$] has been reported (482). The photosensitive inorganic-organic hybrid gels are fabricated using a silica-PEO(poly-(ethylene oxide) polymeric network and several chelated metal alkoxides viz. [$Ti(OEt)_4$], [$Al(OBu^{sec})_4$] and [$Zr(OPr^n)_4$]. The chemical modification of metal alkoxides with organic additives such as β-diketones and β-

ketoesters is known to be very effective method to control the reactivity of metal alkoxides and the final properties of the gels (483). The metal alkoxides stabilized by β-ketoester or β-diketones and γ-glycocidoxypropyltrimethoxysilane (GPTS) find use as precursors (484) to metal oxides.

4.2. Reactions of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with acetylacetone, benzoin and salicylaldehyde

The chemistry of metal β-diketonates broadly follows the pattern of development of inorganic chemistry, since their first synthesis in 1887 and yielding three types of metal β-diketonate complexes: (i) oxygen bonded (ii) carbon bonded (iii) both oxygen and carbon bonded synthesized by a variety of routes. The β-diketones as well as β-ketoesters are well known to show tautomerism, the enol form of which has a hydroxyl group available for reaction. These reagents, therefore depict a facile reactivity towards metal alkoxides in which the alkoxy group is replaced by the enolate form of the β-diketonate or β-ketoester, thereby liberating alcohols which can be distilled out as azeotropes with suitable solvents like benzene (485). The use of compounds of β-diketones in laser technology, NMR shift reagents (486), gas chromatography, solvent extraction, spectral studies etc., is well known. The increasing applications of sophisticated structural determination techniques (487) and studies on trimeric nickel acetylacetonates opened a new chapter in this direction. The bonding through 3–C atom has been reported in $\{K[Pt(acac)_2Cl]\}$ (488). The electronic state and optical absorption spectra of metal alkoxides stabilized with β-diketones having a variety of substituents have been calculated using first-principle molecular orbital methods (489).

A large number of bis-(β-diketonates) have been reported (490-492). The reactions of tin(II) (493), tin(IV) (494), antimony(III), aluminium(III) (495), titanium(IV) and organoantimony(V) (496-498) with β-diketones have been reported. The reactions of $[Ti(OPr^i)_4]$ or $[Zr(OPr^i)_4]$ with 3-alkyl-substituted acetylacetone derivatives viz. 3-acetyl-6-trimethoxysilylhexane-2-one or 3-acetylpentane-2-one have been reported to give not only the corresponding β-diketonate complexes but also result in about 15% hydrodeacylation of β-diketone. In case of stronger Lewis acid, $[Al(OBu^s)_3]$, hydrodeacylation has been described. Nevertheless, hydrodeacylation is suppressed when metal alkoxide and β-diketone are reacted in 1:5 molar ratio (499). The preparation and characterization of some titanium dichloro complexes of ethyl esters of some β-diketo acids have been reported (500). The synthesis of fluoro-β-diketonate derivatives of titanium of composition $[(OR)_{4-n}Ti(OC(CF_3)=CHOR')_n]$ (R = Et and

Pr^i; R′ = CF_3.Ph and C_4H_3S and n = 1 or 2), has been reported by the reactions of titanium alkoxides with fluoro-β-diketones (501).

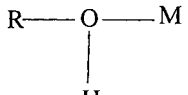
The reactions between $Cu(acac)_2$ and metal alkoxides viz. $[(Y(OC_2H_4OR)_3)_m]$ (R = Me, Pr^i) and $[(Al(OSiMe_3)_3)_2]$ affording $[Cu_4(\mu_3,\eta^1\text{-}OC_2H_4OPr^i)_4(acac)_4]$ and $[Cu(acac)(\mu\text{-}OSiMe_3)_2Al(OSiMe_3)_2]$ respectively have been reported (502). The synthesis of new tin(IV) modified alkoxides $[Sn(OEt)_2(\eta^2\text{-}acac)_2]$ and $[Sn_4(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)(OEt)_6(\eta^2\text{-}acac)_2]$ has been reported (503). The catalytic activity of complexes derived from β-dicarbonyl compounds, $RCOCH_2COR'$, where R = alkyl, and R′ = alkyl or o-alkyl) has been reported to increase as the electron-donating properties of R and R′ groups increase (504). A series of lanthanide clusters of composition $[Ln_5(DBM)_{10}(OH)_5.n(solvent)]$ (where = DBM = dibenzoylmethanido; Ln = Nd, Gd, Er and Yb; solvent = CH_3CN or toluene) have been reported (505). The reaction of $YCl_3.6H_2O$ with ortho-hydroxydibenzomethane (HO-DBMH), has been reported to yield pale yellow block-like crystals (506). The formation of tetranuclear lanthanide clusters of composition $[Ln_4(\mu_3\text{-}OH)_2(Ph_2acac)_{10}]$ (Ln = Pr, Nd and Sm) (Ph_2acac = dibenzoylmethanide) has been reported from the reactions of $[LnCl_3.(nH_2O)]$ (n = 6,7) with dibenoylmethane (507).

A series of niobium(V) acetylacetonate complexes $[Nb(OCH_3)_4.acac]$, $[NbCl_2(OCH_3)_2.acac]$ (508,509) and $[NbBr_2(OCH_3)_2.acac]$ have been reported. The synthesis of complexes of composition $[M(OC_2H_5)_4.L]$, $[M(OC_2H_5)_2.L_3]$ (where M = Nb or Ta and L = benzoylacetone (510), ethylbenzoylacetate (511), methylacetoacetate and ethylacetoacetate (512) has been reported from metal pentaethoxide and the corresponding ligands. The reactions of niobium and tantalum pentachlorides in methanol with salicylaldehyde, acetoacetanilide, benzoylacetanilide, 2-hydroxyacetophenone, o-hydroxybenzophenone and benzoylacetone(L) have been reported to yield crystalline compounds of stoichiometry $MCl_2(OCH_3)L$ (513). Complexes of the type $[MX_2acac(OR)_2]$, (where M = Nb(V), Ta(V); X = Cl, Br; acac = acetylacetonate ion; R = CH_3, C_2H_5) have been reported to be synthesized from the reactions of metal pentahalides with acetylacetone in parent alcoholic solutions resulting from (514) metal-controlled assembly.

Unlike metal alkoxides, the reactivity of metal phenoxides towards such ligands is less studied and only scattered references are available in literature. The reactions of $[Al(OC_6H_4Cl\text{-}o)_3]$ with acetylacetone, benzoylacetone, ethylacetoacetate and dibenzoylmethane have been reported to yield mixed phenoxo β-diketonates and pure β-diketonate derivatives (515). The reactions of titanium(IV), niobium(V) and tantalum(V) phenoxides with α-hydroxyaldehydes, ketones and β-diketones have been reported (516-518). The reactions of $Ta(OC_6H_4Bu^t\text{-}4)_5$ with α-hydroxyaldehydes and ketones (L) have been reported to yield six- and seven coordinate

$[Ta(OC_6H_4Bu^t\text{-}4)_3.L_2]$ complexes (519-520).

Like enolic form of β-diketones, α-hydroxyketones contain both carbonyl as well as hydroxyl group. The hydroxyl proton on β-diketones is quite labile due to conjugation and stabilization of the anion through resonance, while in α-hydroxyketones it is, not so labile probably due to the absence of any conjugation. Thus two modes of coordination (one in which



proton is retained, i.e. and second, where proton is substituted by metal i.e. [R–O–M] are possible in α-hydroxyketones. A large number of donor-acceptor complexes of α-hydroxyketones with Lewis acids are known (521). An important α-hydroxyketone, benzoin in which intramolecular hydrogen bonding is suggestive of its cis-form is known to form chelate complexes. The polymeric complexes of chromium(III) and iron(III) with benzoin have been reported (522). Complexes of group (IV) halides with benzoin and substituted benzoin have also been reported (523). The halides of zinc(II), cadmium(II), mercury(II), cobalt(II) and nickel(II) are known to form complexes with benzoin having unusual structural features (524). The complexes of pentachlorides of niobium, tantalum and molybdenum with benzoin have been reported (525).

α-Hydroxyaldehyde viz. salicylaldehyde and its derivatives, like other chelating ligands containing labile proton, have been studied extensively (526-531). Gopinathan and his co-workers (532) have reported the synthesis of salicylaldehydo-oxotitanium monoalkoxides. Mehrotra and coworkers (533) have also demonstrated the reactivity of metal alkoxides with salicylaldehyde. In view of above observations, it is therefore of interest to investigate the reactions of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with chelating ligands.

The reactions of methanolic solution of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with equimolar amounts of acetylacetone(acacH), benzoin(benzH) and salicylaldehyde(salH) (LH) in benzene yield complexes of composition $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.L]$. The reactions may be represented as:

$$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4 + LH \xrightarrow{\text{benzene/methanol}} Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4L + HCl$$

where LH = acacH, benzH and salH and L = anions of acac, sal and benz.

The elemental analysis of the isolated complexes agreed well with their stoichiometric composition (Table 27). The complexes are fine coloured powders and are fairly soluble in common organic solvents. The molar conductance values of the millimolar solutions of complexes in nitrobenzene have indicated their non-electrolytic nature.

4.2.1. IR spectra

The infrared spectra scanned in 4000–200 cm^{-1} region for the complexes has provided further information on their formation. The absence of absorption band at ~ 3333 cm^{-1} due to simple hydrogen bonded –OH group (534) of the enolic form of acetylacetone, in complex suggested the loss of hydrogen of the –OH group as HCl gas. The sharp bands observed in 1600–1580 cm^{-1} and 1370–1350 cm^{-1} regions ascribed to υ_{asym}(C=O) and υ_{sym}(C=O) modes in the enolic form of acetylacetone have been observed to move to lower wave numbers by 20–25 cm^{-1} upon complexation. These trends are suggestive of bonding through oxygen atoms to the niobium metal in agreement with the earlier reports on metal acetylacetonates (535-539). The sharp bands observed in 1535–1520 cm^{-1} region have been assigned to υ(C = C) mode.

The IR spectra of niobium(V) complexes derived from benzoin have shown the absence of absorption band due to υ(OH) mode known to occur at ~ 3360 cm^{-1} in pure benzoin, confirming the hydrogen chloride gas evolution during the reactions of monochloroniobium(V)2-/4-isopropylphenoxides with the ligand. The bands due to υ(C–O) mode known to occur in 1110–1090 cm^{-1} region in free benzoin appeared at lower wave numbers in complex. These observations are indicative of the fact that hydroxyl oxygen is bonded to niobium. All important bands are given in Table 28.

The υ(C=O) mode of free benzoin known to occur at ~ 1690 cm^{-1} has been observed to move to lower wave numbers confirming the bonding through carbonyl oxygen to the metal. It has thus been inferred from these observations that a simultaneous coordination from carbonyl as well as hydroxyl oxygen has resulted into the formation of niobium(V) chelate complex, is in agreement with the earlier reports on spectra of similar complexes (522,524,526,527,528).

The absence of band due to υ(OH) mode known to occur in infrared spectra of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4.sal]$ at 3180 cm^{-1} in pure salicylaldehyde suggested the formation of compounds through deprotonation of –OH group. The υ(C=O) mode of free salicylaldehyde

Table 27. Analytical data of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$ with chelating ligands

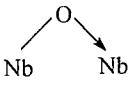
Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %					Molar Cond. in $PhNO_2$ ($Scm^2\ mole^{-1}$)
		Nb	Cl	C	H	N	
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.acac$	Brown	12.65	---	67.10	7.05	---	0.37
$C_{41}H_{52}O_6Nb$ (733)		(12.69)	---	(67.12)	(7.09)		
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.benz$	Dark Brown	11.01	---	71.01	6.60	---	---
$C_{50}H_{56}O_6Nb$ (845)		(11.00)	---	(71.00)	(6.63)		
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.sal$	Brown	12.30	---	68.30	6.61	---	0.30
$C_{43}H_{50}O_6Nb$ (755)		(12.32)	---	(68.34)	(6.62)		
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1$	Dark Brown	12.05	---	67.11	6.49	1.80	---
$C_{43}H_{50}O_6NNb$ (769)		(12.09)	---	(67.10)	(6.50)	(1.82)	
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^2$	Brown	11.55	4.40	64.20	6.11	1.75	0.28
$C_{43}H_{49}O_6ClNNb$ (803.50)		(11.57)	(4.42)	(64.22)	(6.10)	(1.74)	

where acac = ion of acetylacetone, benz = ion of benzoin, sal = ion of salicylaldehyde, HL^1 = ion of potassium benzohydroxamate and HL^2 = ion of potassium 4-chlorobenzohydroxamate

Table 28. IR spectral data (cm^{-1}) of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$ with chelating ligands

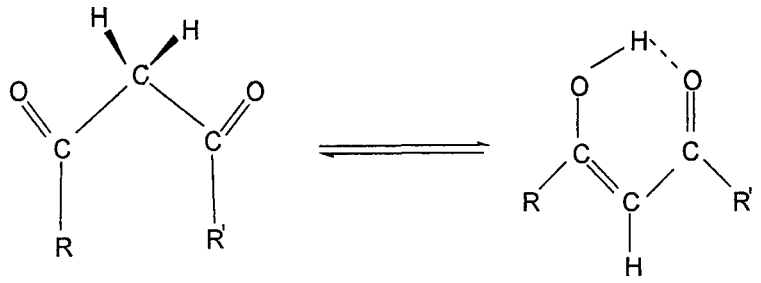
Complex	Bands (cm^{-1})
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.acac	3864s, 3754s, 3654s, 3421, 2962, 2924, 2872, 2962s, 2924s, 2872s, 2062, 1634, 1587, 1525s, 1484s, 1457s, 1420, 1368s, 1328s, 1261s, 1195s, 1149s, 1108s, 1079, 1027, 917, 888, 859, 836, 796, 744, 709, 663, 616, 582, 564, 530, 472, 426.
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.benz	3414, 2961, 2918, 2866, 1664s, 1629s, 1594s, 1513s, 1484s, 1448s, 1420, 1330s, 1282s, 1250s, 1206, 1166s, 1149s, 1113, 1079s, 940, 871s, 830, 796, 752, 719, 674, 642, 582, 426, 356.
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.sal	3391, 2961, 2930, 2866, 1663, 1629, 1546s, 1490s, 1461, 1397, 1279s, 1218, 1150s, 1117, 1073, 1027, 883, 836, 760, 709, 663, 612, 489, 449, 350.
$C_6H_5C(O)NHOK$ (KHL^1)	3249(s), 1686(s), 1609(w), 1570(s), 1522(w), 1483(m), 1445(w), 1384(s), 1378(s), 1272(w), 1182(m), 1158(m), 1076(w), 1044(w), 1022(w), 923(s), 837(m), 695(w), 678(w), 642(m), 614(m), 506(w), 385(w)
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1$	3430, 3213, 3063, 2961s, 2927s, 2861s, 1744, 1658, 1601s, 1526s, 1483s, 1442s, 1379s, 1282, 1260, 1154, 1114, 1079s, 1023, 969, 918, 819, 784, 749, 691, 573, 472, 431, 356, 292.
$4\text{-}ClC_6H_4C(O)NHOK$ (KHL^2)	3192(s), 1680(s), 1602(w), 1579(s), 1475(m), 1442(w), 1382(s), 1378(s), 1270(w), 1175(w), 1073(s),1040(w), 923(s), 901(w), 868(w), 765(m), 740(w), 696(w), 660(m), 558(s), 422(m), 385(w).
$Nb(OC_6H_4CH(CH_3)_2\text{-}2).HL^2$	3863s, 3754, 3674, 3654, 3399, 3217, 3104, 3057, 2962s, 2930s, 2871s, 2704, 2363, 2074, 1912, 1744, 1597vs, 1517s, 1481, 1403, 1363, 1339, 1281, 1254, 1189, 1152, 1093, 1014, 969, 916, 877s, 838s, 751, 721s, 673, 577, 426, 368, 327, 286, 237.

where acac = ion of acetylacetone, benz = ion of benzoin, sal = ion of salicylaldehyde, HL^1 = ion of potassium benzohydroxamate and HL^2 = ion of potassium 4-chlorobenzohydroxamate

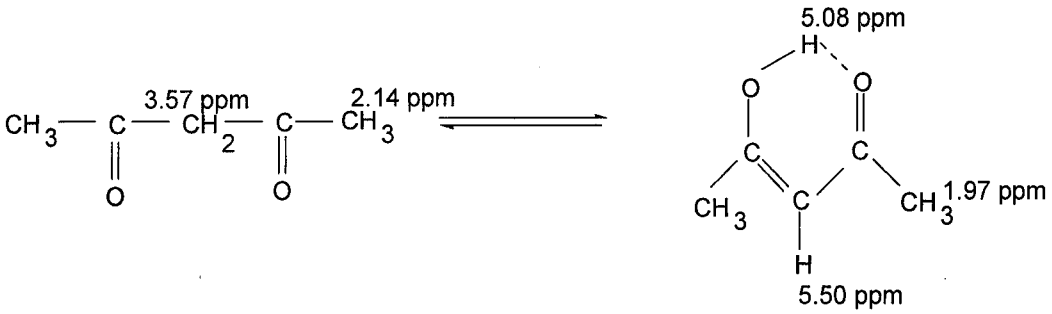
occurring at 1660 cm^{-1} has been found to shift to lower regions by ~ 25–30 cm^{-1} on complexation, which may be attributed to the coordination of carbonyl oxygen to niobium. This is supplemented by a shift in the band at 1200 cm^{-1} in salicylaldehyde assignable to υ(C–C) mode to higher regions on complexation. These shifts are in agreement with the earlier reports on the spectra of similar complexes of metal halides. The sharp bands observed in 580–570 cm^{-1} region have been assigned to terminal υ(Nb–O) mode (319,540). No band that could be assigned to bridging  mode expected around 520 cm^{-1} were observed in IR spectra of complexes suggesting the absence of phenoxy bridging, characteristic of parent niobium(V) complex.

4.2.2. ^{1}H NMR spectra

Further evidence on the formation of mixed ligand niobium(V) complexes derived from acetylacetone, benzoin and salicylaldehyde (LH) has been obtained from a comparison of their room temperature ^{1}H NMR spectra with that of free ligands and parent complex $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$. The ^{1}H NMR spectra of free acetylacetone is known to display signals at δ 2.14 and δ 3.57 ppm due to methyl and methylene protons respectively while the enolic form of acetylacetone exhibits signals at δ 5.08, δ 1.97 and δ 5.50 ppm due to OH, methyl and methine protons respectively. The most stable tautomeric form of 1,3-diketones is the enol form; the carbon-carbon double bond of the enol form is in conjugation with the second carbonyl group.



The hydroxylic absorption of enols occurs at very low field δ 4.0 to δ 5.0 ppm and is usually unaffected by dilution or solvent interaction. In spectra of acetic acid solutions of enols, both hydroxyl and carboxyl absorptions may be observed, which indicate negligible chemical exchange even in this solvent. The resonance due to hydroxyl group of the enol form of acetylacetone is reported to occur at δ 5.08 ppm.



The ^{1}H NMR spectra of enols show signals of both keto and and enols forms. Thus, interchange between these two forms on the NMR time scale is very slow. Integration of the spectrum of acetylacetone indicates the presence of 84% of the enol form and 16% of the keto form in the pure liquid at 40°. The acetylacetone is present in the enol form to the extent of about 15% in aqueous solutions and about 92% in hexane. The greater enolization in hexane results from stabilization of the enol form by internal hydrogen bonding. In aqueous solutions the carbonyl groups are hydrated, or hydrogen bonded to water molecules, and there is less to gain by enolization. Therefore, polar solvents which stabilize the keto carbonyls will decrease the percent of enolization depending on the degree of their stabilization. An increase in the concentration of a polar solvent in a solution will increase the degree of interaction with acetylacetone (Table 29). Experiments have established that the intramolecular hydrogen bond of acetylacetone stabilizes the enol tautomer by 5 to 10 kcal and the conjugated system further stabilizes this tautomer by another 2 to 3 kcal.

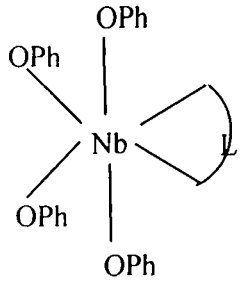
The ^{1}H NMR spectra of [Nb($OC_6H_4CH(CH_3)_2$-2)$_4$.acac] displayed signals at δ 2.01 and δ 3.44 ppm due to methyl and methylene protons respectively. The aromatic protons of the phenolic ring were found to undergo slight upfield shifts by δ 0.05–0.08 ppm and appeared at δ 6.69–7.09 ppm in mixed-ligand complexes relative to that in the parent complex occurring at δ 6.77–7.14 ppm. The ^{1}H NMR spectra of free benzoin is known to exhibit signals at δ 2.0, δ 6.01 and in 7.19–7.86 ppm range due to OH, CH and aromatic protons respectively. The free salicylaldehyde exhibits signals due to OH, CH and aromatic protons at δ 5.0, δ 10.24 and δ 6.92–7.64 ppm range respectively. The aromatic protons due to chelating ligands benzoin and salicylaldehyde appeared in δ 7.58–7.95 ppm and δ 7.46–7.68 ppm range respectively in their complexes (Fig. 50-52).

Thus, based upon IR and ^{1}H NMR spectral data coupled with physicochemical studies, a distorted octahedral structure for complexes [Nb($OC_6H_4CH(CH_3)_2$-2)$_4$.L] isolated from the reactions of parent monochloro 2-isopropylniobium(V) phenoxide with chelating ligands may tentatively be proposed as:

Table 29. ^{1}H-NMR data of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$ with chelating ligands (ppm)

Complex	Substituent (Isopropyl protons)		Aromatic phenolic ring protons	(Ligands)			
	$-(CH_3)_2$	-CH		$-CH_2$	$-CH_3$	-CH	$-C_6H_5$
$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1.20	3.26-3.37	6.77-7.14	---	---	---	---
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.acac	1.15-1.17	3.20-3.25	6.69-7.08	3.44	2.01	---	---
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.benz	1.15-1.19	3.20-3.25	6.69-7.08	---	---	---	7.58-7.96
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.sal	1.18-1.25	3.34-3.52	6.72-7.09	---	---	10.15	7.46-7.68

where acac = ion of acetylacetone, benz = ion of benzoin and sal = ion of salicylaldehyde

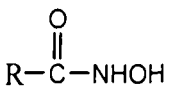


(where OPh = $OC_6H_4CH(CH_3)_2$-2 and L = anions of Acetylacetone (acacH), Benzoin (benzH) and Salicylaldehyde (salH))

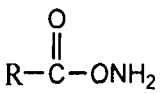
4.3. Reactions with Hydroxamic Acids

Of numerous classes of ligands known to form complexes, hydroxamic acids, whether naturally occurring or synthetic, are an important family of organic bioligands (541). In biomolecules, usually oxygen (oxide, hydroxide, water, alcoholate, phenolate, carboxylate, hydroxamate and catecholate); nitrogen (amide and amine) and sulphur, (sulphide and thiolate) are present as coordinating atoms. The naturally occurring hydroxamic acids (siderophores) are involved in the microbial transport of iron (542). The oxalohydroxamic acid was first isolated by Lossen (543) from the reaction of ethyl oxalate and hydroxylamine. The reaction of hydroxylamine with benzoyl chloride afforded a mixture of mono-, di- and tribenzoyl derivatives but the structural investigations could not be made due to polymorphism, stereoisomerism and tautomerism (544). The formation, structure and reactions of hydroxamic acids were thereafter reviewed by Yale (545). The chemistry of hydroxamic acids with regard to their structural investigation, isomerization occurring in various alkylated derivatives and synthesis of cyclic N-hydroximides has also been reviewed by Exner and Bauer (546).

Hydroxamic acids regarded as derivatives of both hydroxylamine and carboxylic acids are known to exist in two forms: the N-acyl derivative (I) or the O-acyl derivative (II).



(I)



(II)

Of the two, the N-acyl form is the most common. A considerable amount of evidence has substantiated the existence of tautomeric forms of the monohydroxamic acids as:

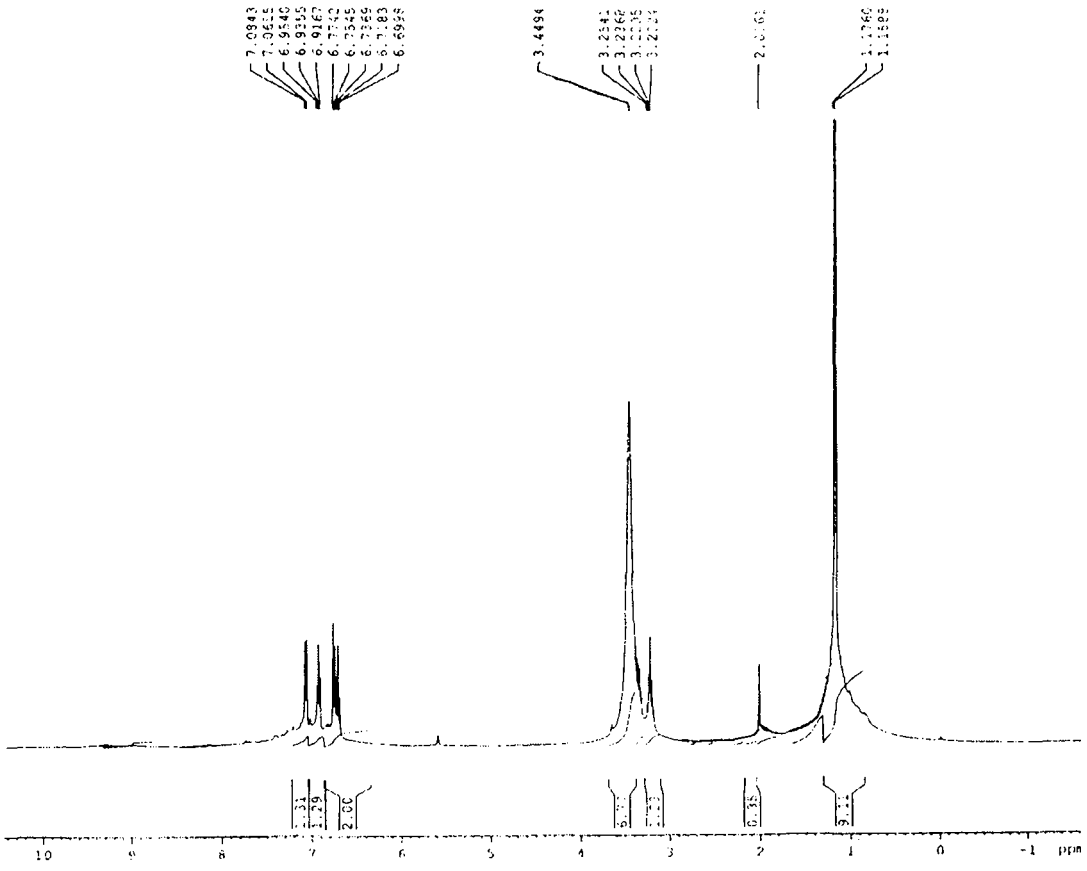


Fig. 50 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.acac

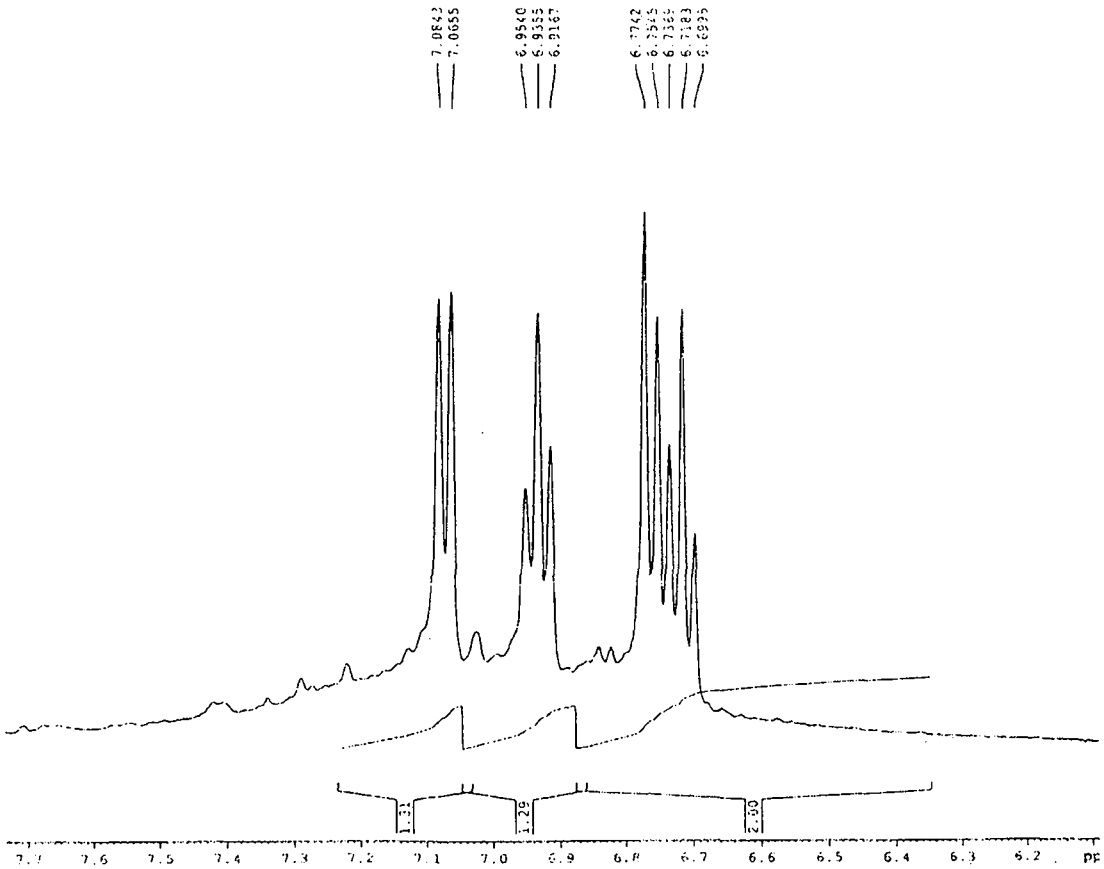


Fig. 50 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.acac

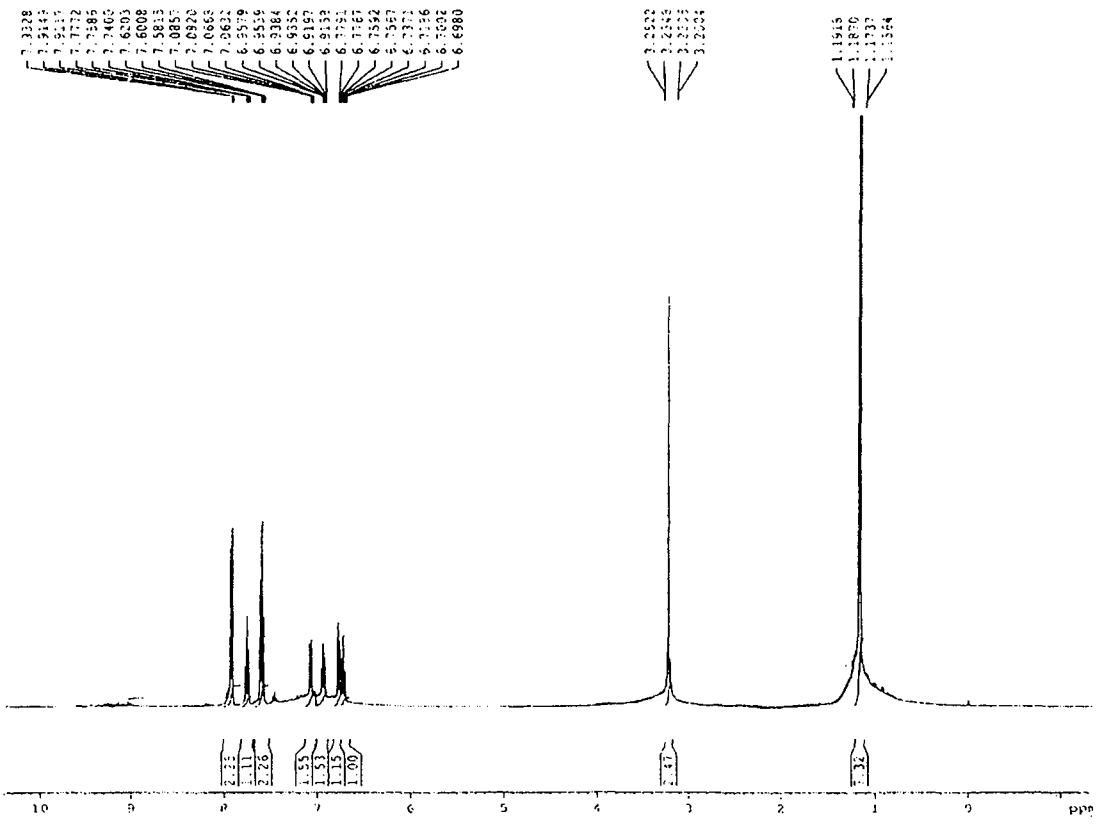


Fig. 51 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.benz

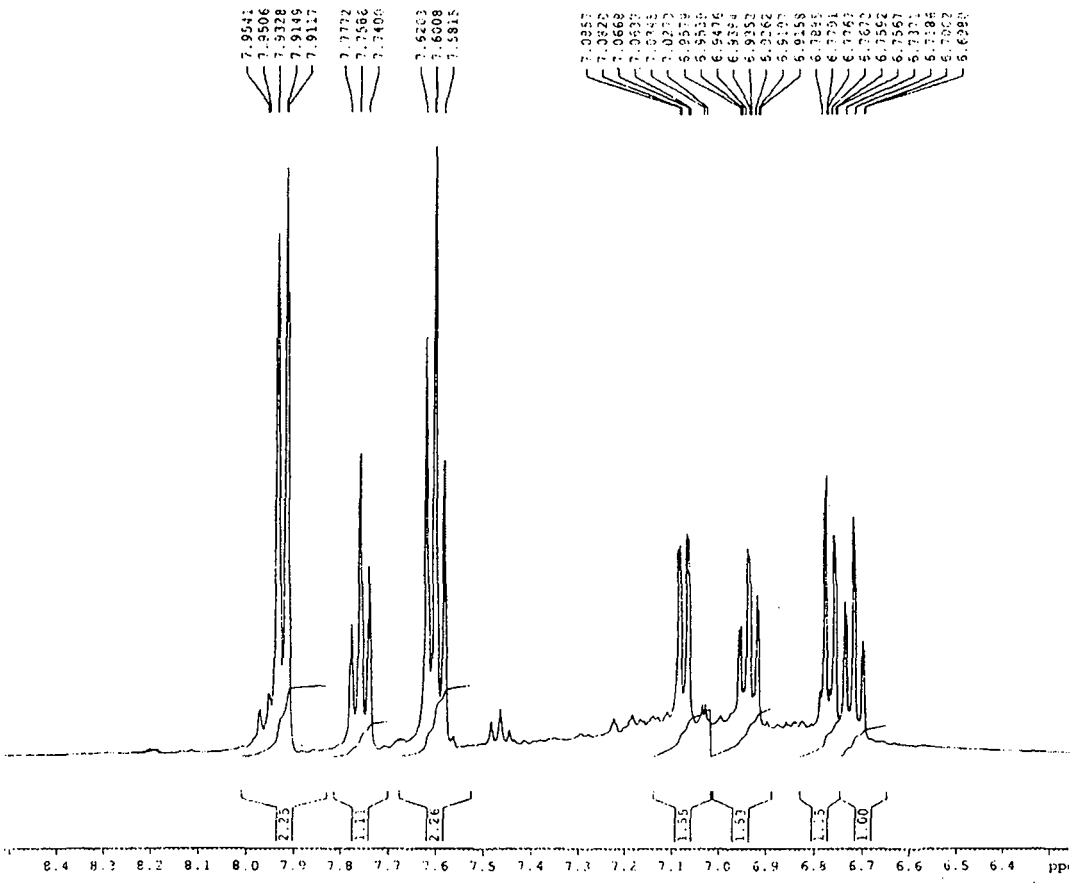


Fig. 51 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.benz

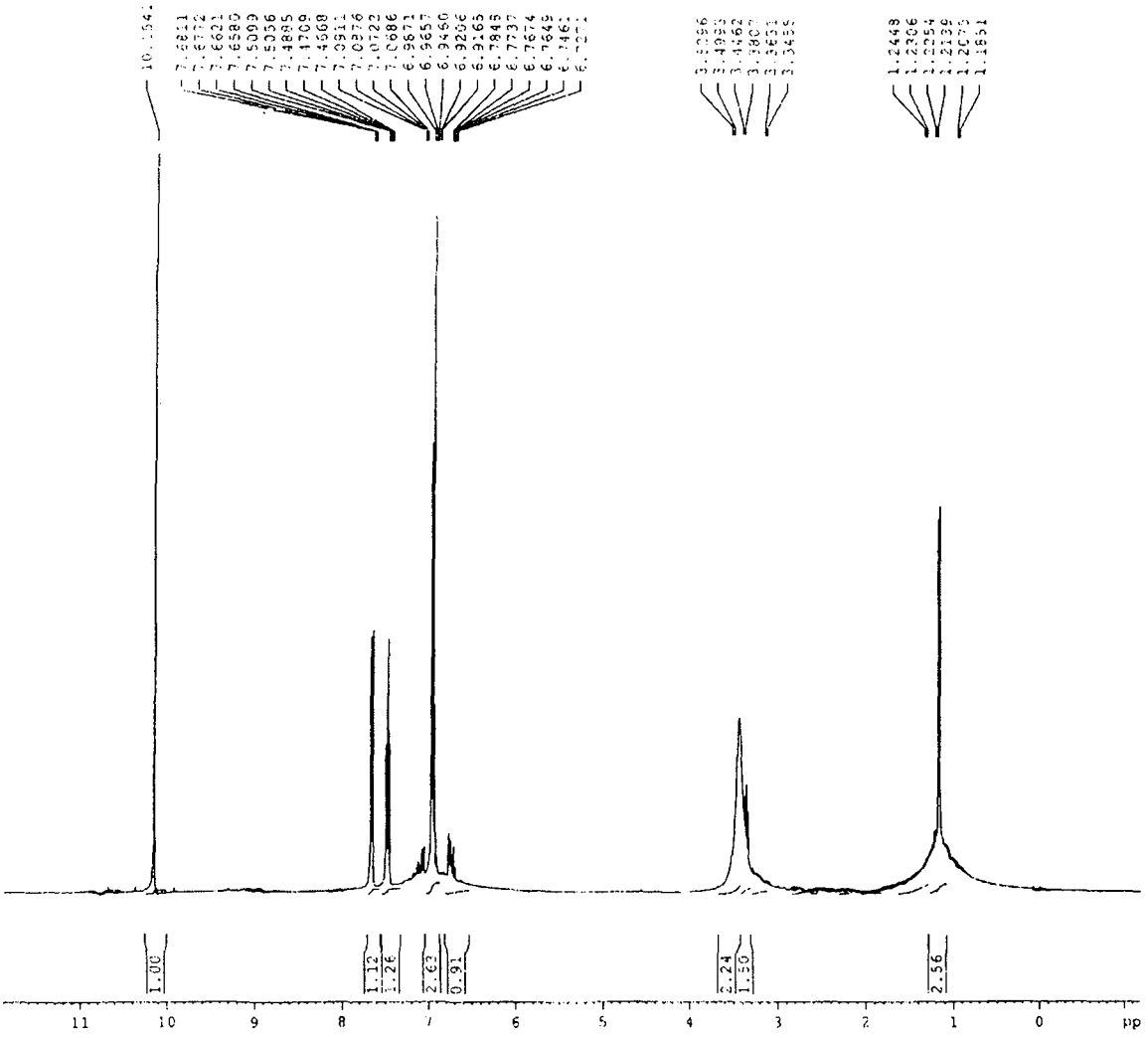


Fig. 52 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.sal

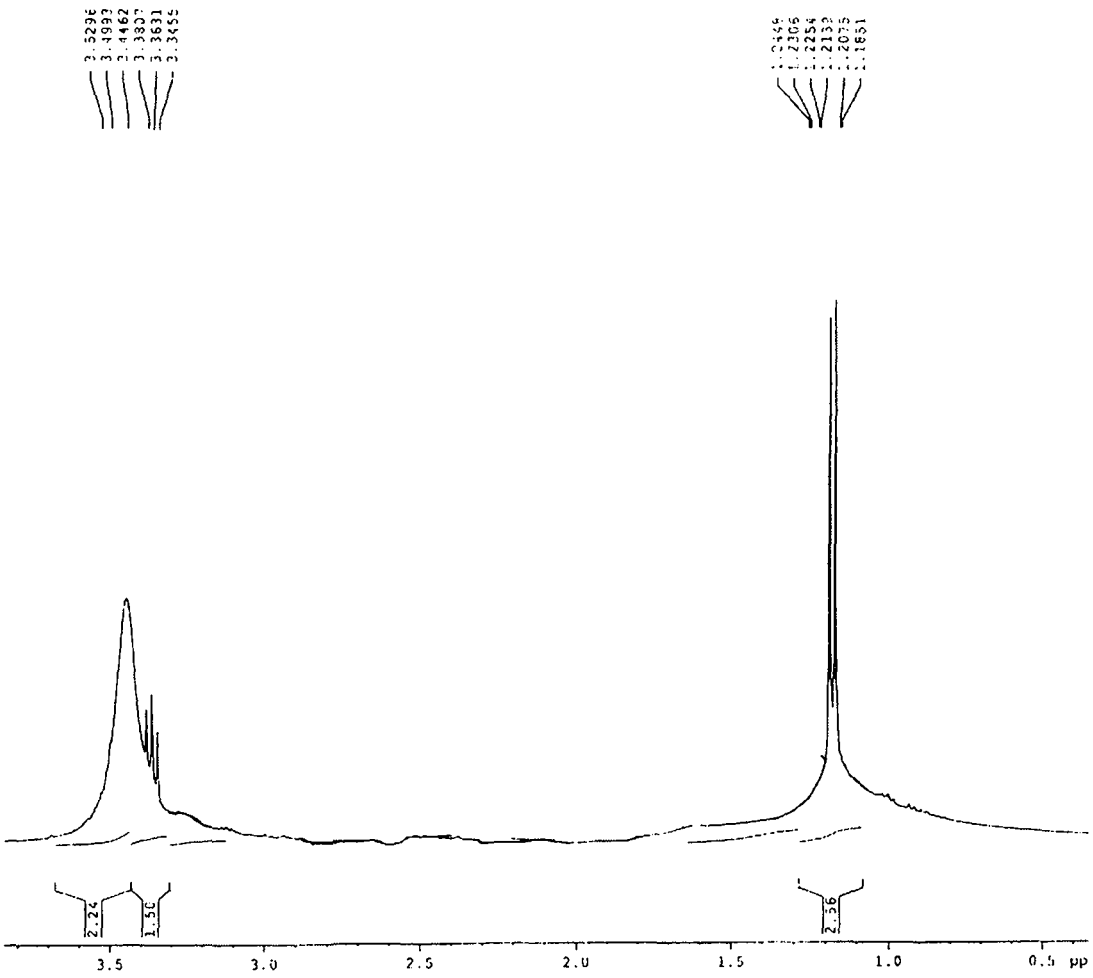


Fig. 52 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$.sal

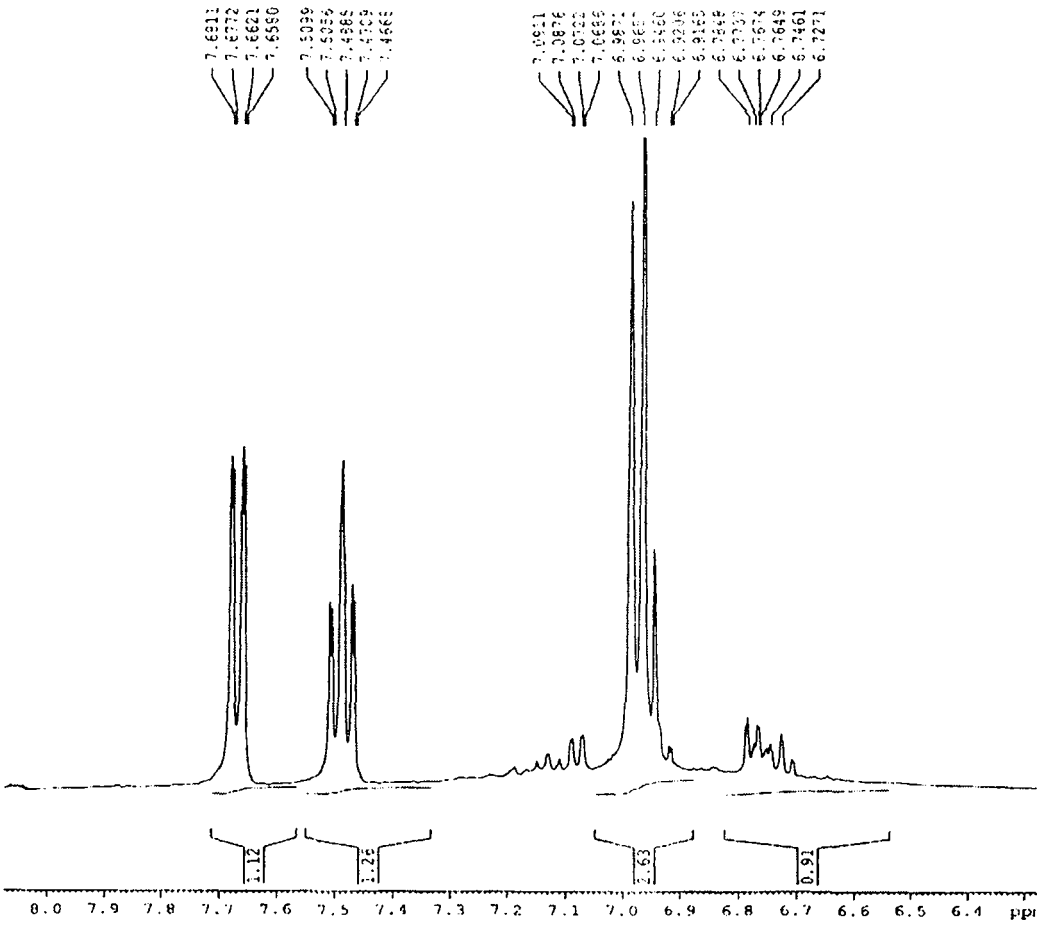
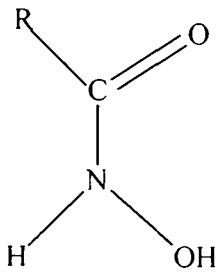
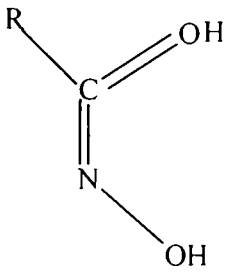


Fig. 52 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.sal$

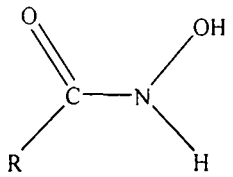


Keto form of Hydroxamic form

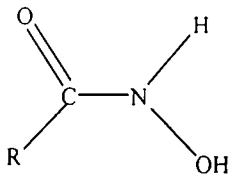


Enol form of Hydroximic form

Such keto-enol tautomerism provides a number of coordination sites for chelation. The keto form having one replaceable hydrogen atom is known to behave as monobasic acid while enol form, has two replaceable hydrogens. The former structure predominates in acidic medium while the latter in alkaline medium (547). The preference of hydroxamic acids to form metal complexes through the hydroxamide form and not through the hydroxime form has been confirmed by IR (548) & NMR (546) spectral studies. If there is restricted rotation about the C–N bond, then both the Z and E isomers of the keto form exist (549).



Z



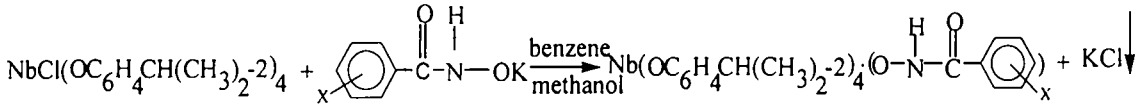
E

NMR spectra has confirmed that both Z and E forms exist in solution, as do the enol forms (the Z–E isomer ratio is solvent dependent) (550).

Hydroxamic acid derivatives have widely been investigated as inhibitors of protolytic enzymes, thermolysin (551), elastase (552) and aminopeptidases (553). The enzymes are metalloproteinases and the mechanism of inhibition appears to involve chelation of metals at their active sites. It is also known that hydroxamic acids reveal a number of pharmacological actions including antineoplastic, antimicrobial, fungicidal, antituberculous and antileucemic activities (554,555). Benzohydroxamic acids (hydroxyl and amino-substituted) have been found to inhibit mammalian ribonucleotide reductase and exhibit antineoplastic activity in leukemic mice. The p-butoxyphenylacetohydroxamic acid (bufexamic) is known to possess antiflammatory and analgesic effects (556).

The hydroxamic acids have been widely used as colorimetric and gravimetric reagents (557-560). The precipitation of niobium in the presence of tantalum has been reported to occur with N-(o-tolyl)benzohydroxamic acid (561). The separation of titanium and zirconium from niobium is made by N-phenylacetohydroxamic acid (562). Niobium and tantalum have been reported to be estimated by quinaldohydroxamic acid and benzohydroxamic acid (563). A few niobium(V) and tantalum(V) complexes of benzo, phenylaceto, salicyl and cinnamylhydroxamic acid of composition $[MO(RH)_3]$ (where M = Nb or Ta); RH_2 = a molecule of hydroxamic acid) have been described (563). The cinnamyl-hydroxamic acid is known to precipitate niobium(V) completely from 5% H_2SO_4 solution at pH ~ 6.5 to yield oxobis(cinnamylhydroxamato) niobium(V) which is stable upto 225°C and may be used for gravimetric estimation.

In view of above observations and reports by Pal and Kapoor (564) on the reactions of isopropoxides of aluminium(III), titanium(IV) and zirconium(IV) with benzo and phenylacetohydroxamic acids to yield products of the type $[Al(OPr^i)_{3-n}.L_n]$ and $[M(OPr^i)_{3-n}.L_n]$ (where M = Ti or Zr and L is the respective hydroxamate ion), the reactivity of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ has been studied in the presence of potassium benzohydroxamate and 4-chlorobenzohydroxamates formulated as KHL^1 and KHL^2. The interaction of methanolic solution of the parent complex with potassium benzohydroxamate and p-chlorobenzohydroxamate in benzene led to the formation of solids whose elemental analysis suggested their formulation according to the equation:



(where X = H and 4-Cl,)

The mixed-ligand phenoxohydroxamato niobium(V) complexes are dark brown solids, quite moisture sensitive but are stable at room temperature under moist free conditions. The complexes are soluble in polar solvents and the molar conductance values of the millimolar solutions of the complexes in nitrobenzene indicated their non-electrolytic nature (Table 27).

4.3.1. IR spectra

A comparison of IR spectra of the mixed-ligand complexes with those of the parent niobium(V) complexes and uncoordinated hydroxamate ions suggested their formation. The presence of three specific donor sites viz. hydroxylamine oxygen, the carbonyl oxygen and

nitrogen as well as the delocalization of double bond within hydroxamic group makes its binding ability unique and strong metal coordination. The characteristic bands of hydroxamic group which may undergo a significant change on complexation due to υ(C=O), υ(C–N), υ(N–O) and υ(N–H) modes. The absorption bands occurring in 1610–1585 cm^{-1} region due to υ(C=O) mode in free hydroxamate ligands have been reported to shift to lower wave numbers by 40–60 cm^{-1} upon coordination by ketonic oxygen to metal (565,566), which is accompanied by the small shift in υ(C–N) mode occurring in 1370–1310 cm^{-1} region. The bonding through hydroxylamine oxygen is reported to result in shift of υ(N–O) mode occurring in 945–910 cm^{-1} region in free hydroxamate ions to higher wave number in complexes. The bands due to υ(N–H) and NH deformations are known to occur at ~ 3200 cm^{-1}, 3080–3060 and 1440–1400 cm^{-1} regions in uncoordinated hydroxamate ligands (567).

The free potassium benzohydroxamate and potassium 4-chlorobenzohydroxamate exhibited absorption bands in 1686–1570 cm^{-1} region due to υ(C=O) mode. The observance of sharp absorption bands due to υ(C=O) mode in 1658–1597 cm^{-1} region in complexes derived from benzohydroxamate derivatives (KHL^1 and (KHL^2) suggested bonding through carbonyl oxygen to niobium. The absorption band due to υ(C–N) mode occurring in 1378–1370 cm^{-1} region in free ligands appeared in 1379–1363 cm^{-1} region in newly synthesized complexes. The absorption bands occurring in 3249–3192 cm^{-1} region due to υ(N–H) mode in complexes suggested that –NH group is retained and coordination through nitrogen atom is excluded. The υ(N–O) mode in $KHL^1$and KHL^2 observed at ~ 923 cm^{-1} is found to appear at ~ 969 cm^{-1} in complexes indicating thereby bonding through oxygen atom of –NHO group (568).

Apart from these significant changes, the bands due to υ(C–O) phenolic and υ(Nb–O) modes in parent complex have been observed to undergo only slight changes in their positions upon complexation. The absence of sharp bands ~ 340 cm^{-1} due to υ(Nb–Cl) mode further substantiated the formation of complexes. The important IR bands are given in Table 28.

4.3.2. ^{1}H NMR spectra

A comparison of ^{1}H NMR spectra of mixed-ligand complexes with that of uncoordinated benzohydroxamate ligands further supported their formation. The ^{1}H NMR spectra of potassiumbenzohydroxamate(KHL^1) exhibited one triplet and two doublets in δ 7.45–7.84, δ 7.41–7.43 and δ 7.82–7.84 ppm range respectively while potassium 4-chlorobenzohydroxamate(KHL^2) exhibited two doublets in δ 7.31–7.33 and δ 7.78–7.80 ppm range due to aromatic protons and a singlet at δ 8.18 ppm due to –NH group. The complexes of

composition [$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1$] and [$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^2$] showed distinct proton resonances due to aromatic protons of 2-isopropylphenoxy ligand and benzohydroxamate/4-Cl-benzohydroxamate ligands. The signals due to former aromatic protons appeared in δ 6.70–7.10 ppm range in both the complexes. The resonances due to aromatic protons of ligands occurred in δ 7.42–7.86 ppm and δ 7.37–7.82 ppm range in respective complexes. The signal due to –NH was observed to shift significantly downfield and appeared at δ 8.83 and δ 9.02 ppm in respective complexes (Fig. 53,54). These observations suggested the bonding through hydroxylamine oxygen and that –NH is retained in complexes (Table 30).

4.4. Reactions of $NbCl(OC_6H_4\text{-}C(CH_3)_3\text{-}2/4)_4$ with Sodium alkoxides NaOR(OR = OMe, OEt and OBu^t)

Literature contains numerous reports on the preparation of mixed alkoxo and alkoxo-phenoxo metal complexes by the phenol interchange method. Metal alkoxides are known to react with a variety of primary, secondary and tertiary alcohols as well as with phenols in accordance with the equation:

$$M(OR)_n + xR'OH \longrightarrow [M(OR)_{n-x}(OR')_x] + xROH$$

whereby the displaced alcohols can be removed by fractional distillation or as an azeotrope by adding a suitable solvent (569). These transesterification reactions have been extensively used for the preparation of alkoxides. The mixed alkoxides $[M(OR)_{5-x}(OR')_x]$ have been reported to be formed from alcoholysis reactions. The exchange reactions between $Nb(OEt)_5$ or $Nb(OPr^i)_5$ and organic acetates have been reported to yield higher alkoxides. The trialkylsiloxo derivatives have been reported to be prepared by the reaction of metal pentaethoxides with trialkylsilanols or trialkylsilylacetates, or of dialkylamides with triethylsilanol. The formation of mixed alkoxo-siloxo derivatives has been reported from the reactions of $M(OEt)_5$ with Me_3SiOAc.

The reaction of zirconium tetramethoxide, $Zr(OMe)_4$ with t-amylalcohol is known to yield $[Zr(OMe)(OAm^t)_3]$ (570). The reactions of zirconium tetra-t-butoxide with methanol and ethanol afford the formation of complexes of composition $[Zr(OMe)(OBu^t)_3]$ and $[Zr(OEt)_2(OBu^t)_2]$. The preparation of mixed alkoxides of titanium in the presence of a base (triethylamine or pyridine) has been described (571).

Contrary to this, the reports on the reactions of metal phenoxides with alcohols are rather limited. By passing ammonia through a solution containing titanium tetraphenoxide, $Ti(OPh)_4$ and isopropanol in benzene, the replacement of only one phenoxy group by an isopropoxide ion to yield $[Ti(OPh)_3(OPr^i)]$ has been reported (572). Compound of similar composition is reported

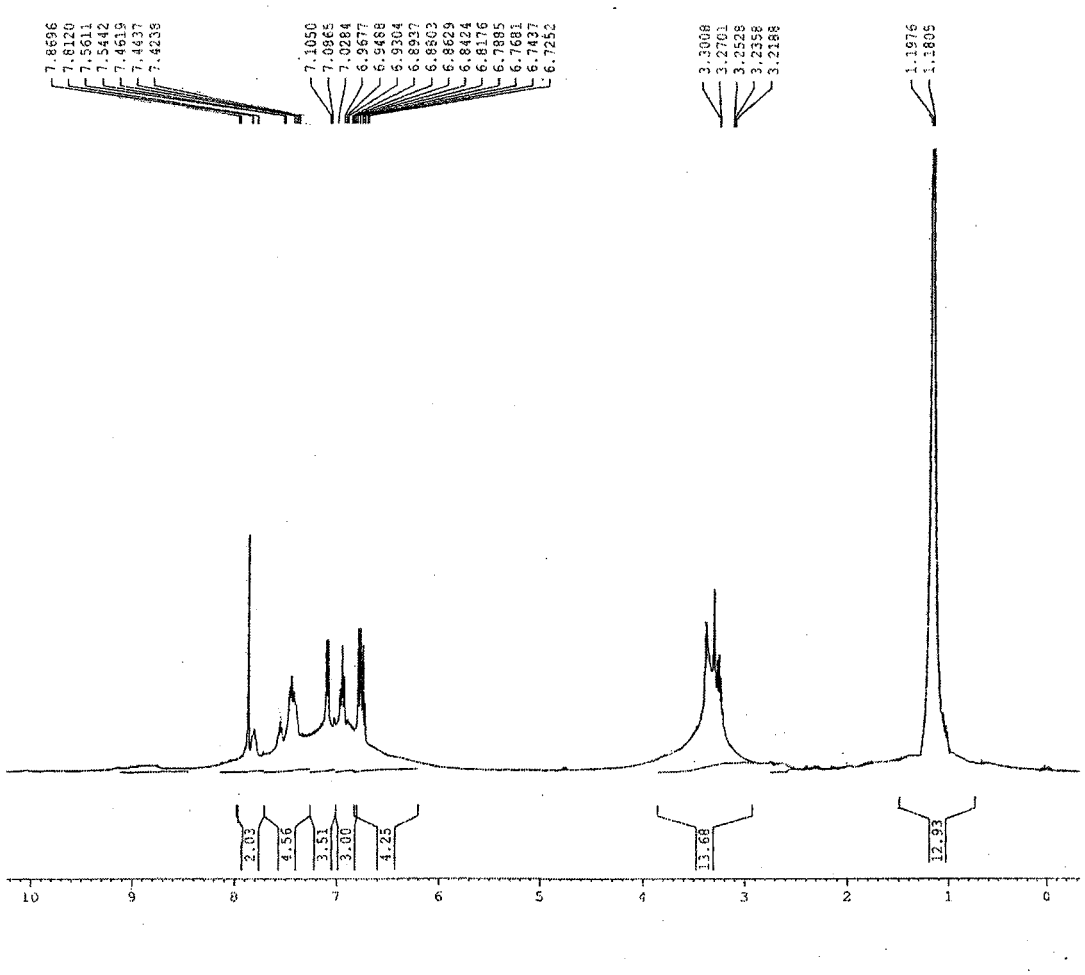


Fig. 53 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1$

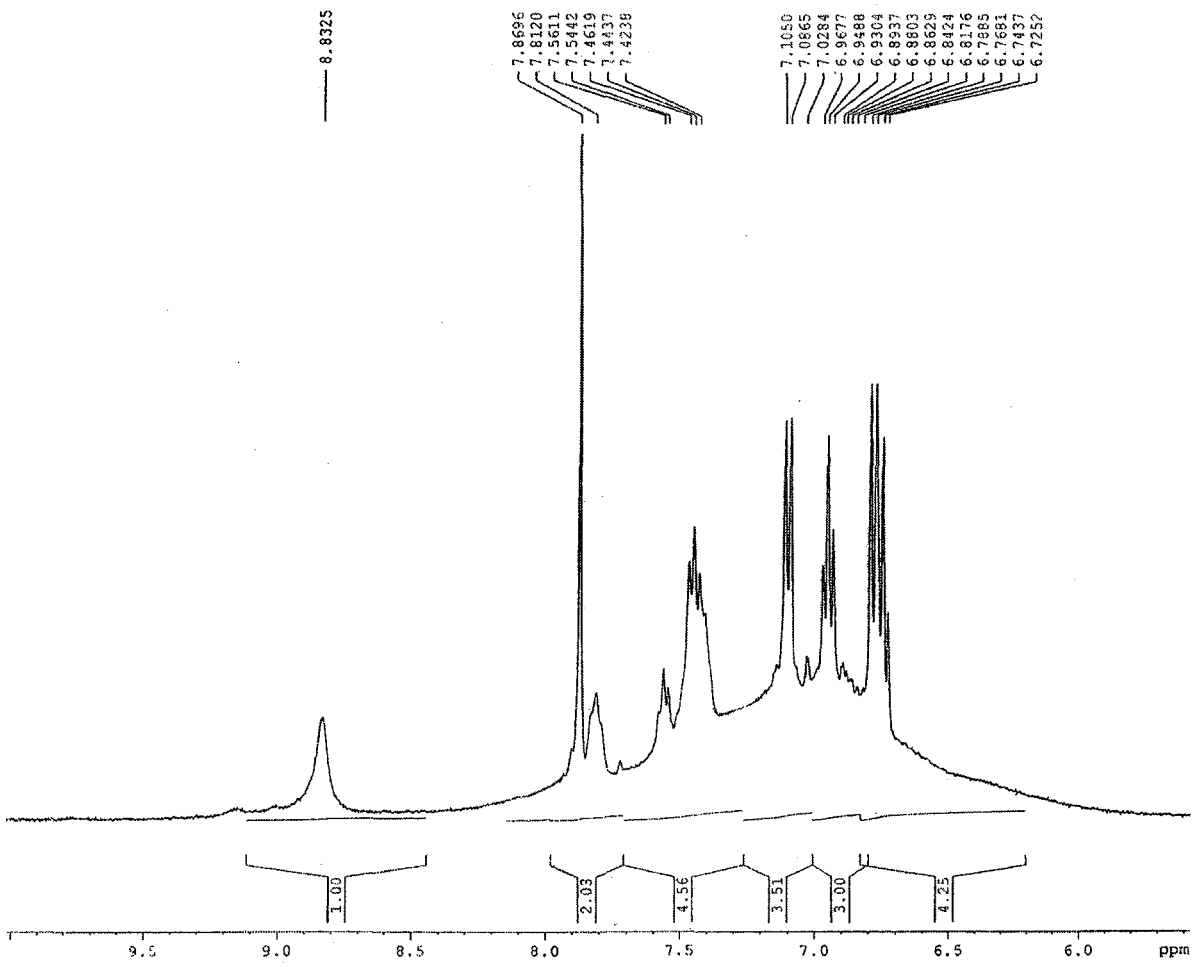


Fig. 53 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1$

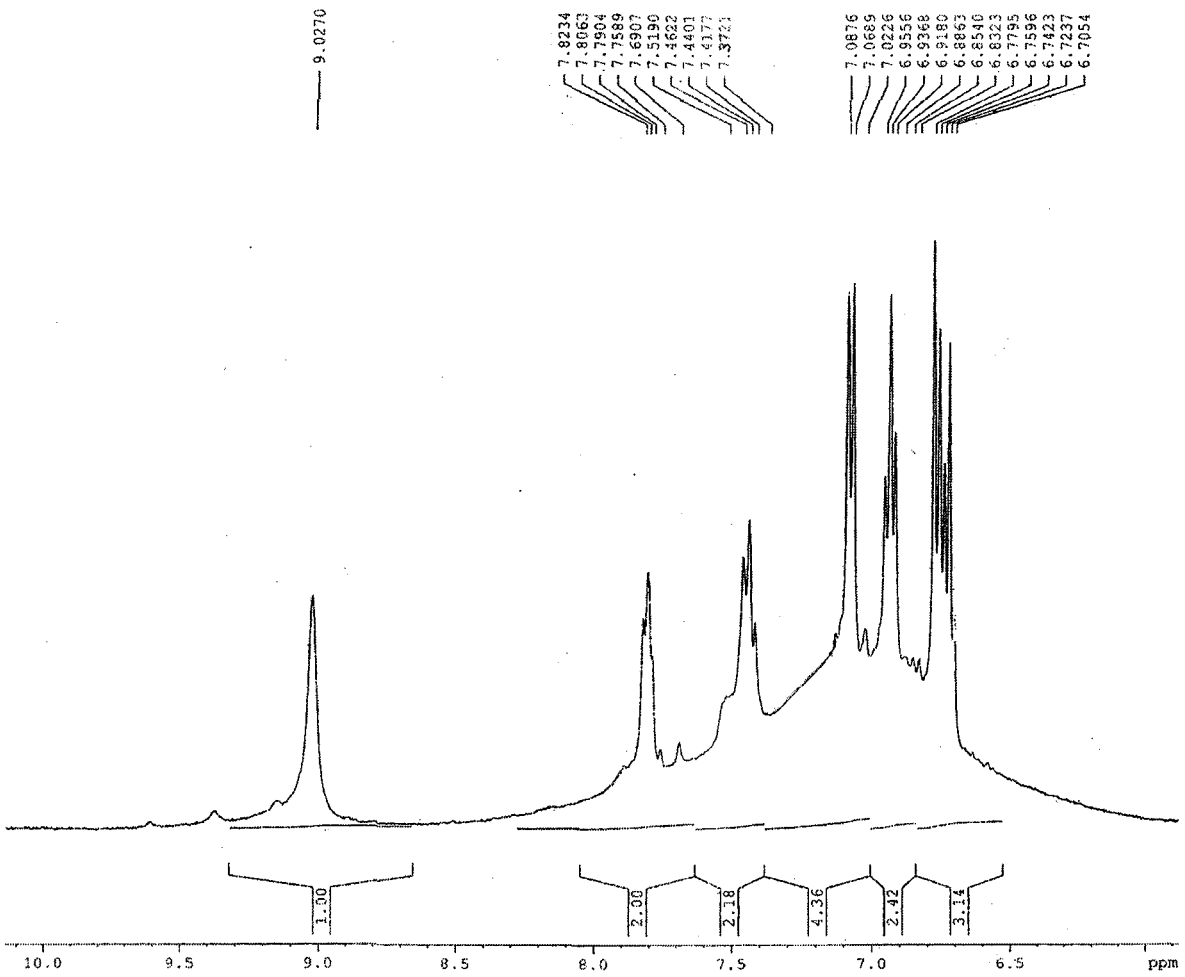


Fig. 54 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^2$

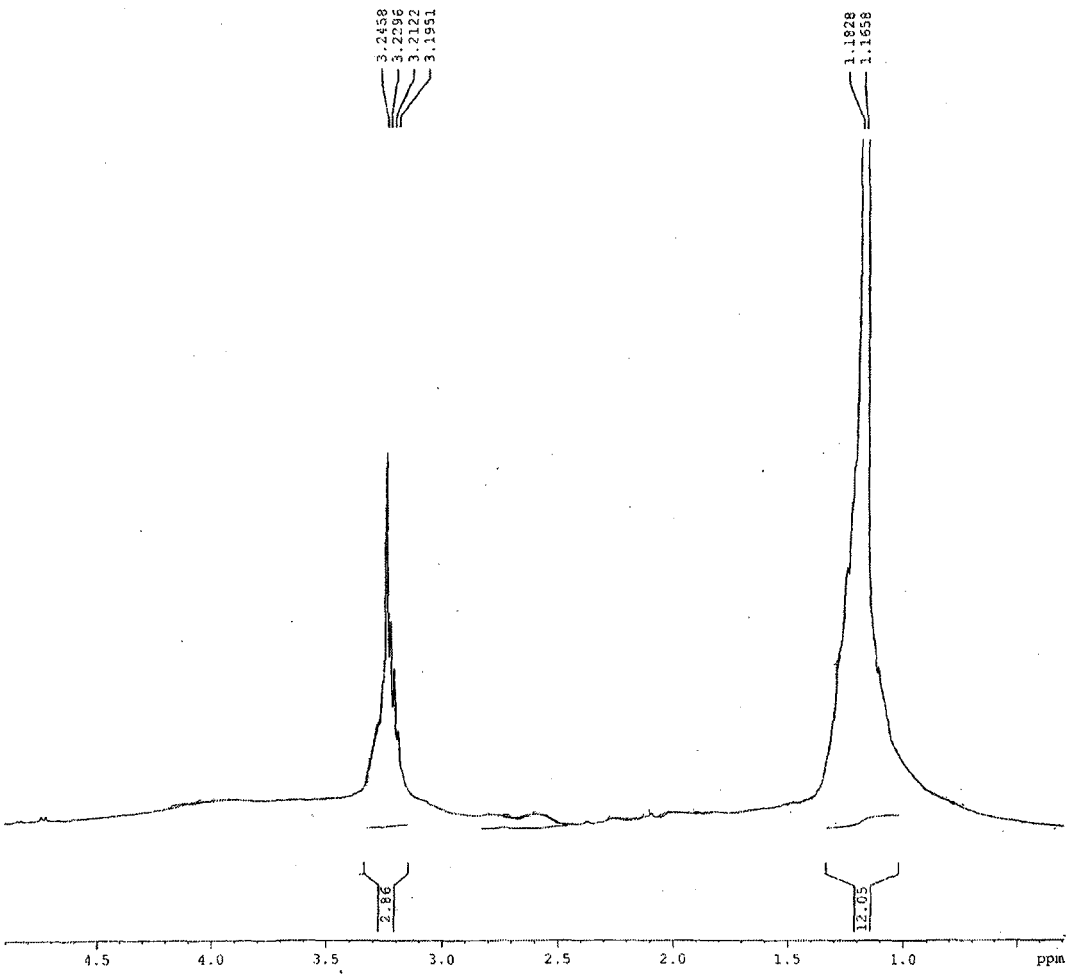


Fig. 54 ^{1}H NMR spectrum of $Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^2$

Table 30. ^{1}H-NMR data of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$ with hydroxamate ligands (ppm)

Complex	Substituent (Isopropyl protons)		Aromatic phenolic ring protons	(Ligands)	
	$-(CH_3)_2$	-CH		$-C_6H_5$	-NH
$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1.20	3.26-3.37	6.77-7.14	---	---
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1$	1.18-1.19	3.21-3.30	6.72-7.10	7.42-7.86	8.83
$Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^2$	1.16-1.18	3.19-3.24	6.70-7.08	7.37-7.82	9.02

where HL^1 = ion of potassium benzohydroxamate and HL^2 = ion of potassium 4-chlorobenzohydroxamate

to be formed if $Ti(OPh)_4$ is refluxed with ethanol or isopropanol in 1:4 molar ratio in benzene. Mortimer and coworkers (573) have reported that $W(OPh)_6$ upon refluxing for eight hours with butanol does not undergo any change, however, the reaction of tungsten hexaphenoxide with m- and p-nitrophenols leads to the formation of a variety of tungsten m- and p-nitrophenoxides.

In view of these interesting observations, the reactions of complexes of composition $[NbCl(OC_6H_4\text{-}C(CH_3)_3\text{-}2/4)_4]$ towards different sodium alkoxides have been undertaken to explore the possibility of formation of mixed alkoxo-phenoxo complexes. The reactions of $[NbCl(OC_6H_4\text{-}C(CH_3)_3\text{-}2/4)_4]$ with equimolar solution of sodium alkoxides in respective alcohols afforded the formation of $[Nb(OR)(OC_6H_4\text{-}C(CH_3)_3\text{-}2/4)_4]$ according to the the equation:

$$NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4 + NaOR \longrightarrow Nb(OR)(OC_6H_4CH(CH_3)_2\text{-}2/4)_4 + NaCl$$

(where OR = OMe, OEt and OBu^t)

The elemental analyses of the isolated complexes agreed fairly well with their stoichiometric formulations (Table 31). The mixed alkoxo-phenoxo niobium(V) complexes are fairly soluble in methanol. The molar conductivities of the millimolar solutions of the complexes in methanol at 25±0.1°C have suggested their non-electrolytic nature.

4.4.1. IR spectra

The formation of complexes has been ascertained from their infrared spectra scanned in 4000–200cm^{-1} region. A particular interest was focussed to look for the absorption bands assignable to the presence of alkoxo groups. In metal alkoxides, the characteristic υ(C–O) vibrational modes of the coordinated alkoxo groups are known to occur in 1150–1000cm^{-1} region (574,575). Also the number and band positions are related to the terminal and bridged alkoxo groups (576) in parent alcohols. The υ(CO) mode is reported to usually shift to higher frequencies upon complexation and a splitting of band in the presence of bridged and terminal alkoxo groups may occur.

A careful and close examination of the IR spectra of complexes have shown absorption bands in 1189–1010 cm^{-1} region attributed to υ(CO) mode of terminal alkoxo groups. It is noteworthy that, quite a large number of absorption bands have been observed in C–O stretching region for complexes containing an ethoxide ion over methoxide ion in line with previous reports

Table 31. Analytical data of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4$ with sodium alkoxides

Complex Molecular formula (Formula weight)	Colour	Elemental Analysis Found (Calc.) %				Molar Cond. in $PhNO_2$ ($Scm^2\ mole^{-1}$)
		Nb	Cl	C	H	
$Nb(CH_3O)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	Brown	14.01	----	66.85	7.05	0.36
$C_{37}H_{47}O_5Nb$ (664)		(14.00)		(66.87)	(7.08)	
$Nb(CH_3CH_2O)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	Pink	13.73	----	67.27	7.20	---
$C_{38}H_{49}O_5Nb$ (678)		(13.72)		(67.26)	(7.23)	
$Nb(Bu^tO)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	Brown	13.15	----	67.97	7.50	0.28
$C_{40}H_{53}O_5Nb$ (706)		(13.17)		(67.99)	(7.51)	
$Nb(CH_3CH_2O)(OC_6H_4CH(CH_3)_2\text{-}4)_4$	Light Yellow	13.70	----	67.25	7.21	---
$C_{38}H_{49}O_5Nb$ (678)		(13.72)		(67.26)	(7.23)	

(577). The absorption bands characteristic of alkoxy groups due to υ(CH) and υ(C-H) modes occurring at ~ 2900cm^{-1} and ~ 1450cm^{-1} also appeared in complexes. The absorption bands due to phenoxo group were found to undergo slight change in band positions and intensity. The absence of bands at 369 and 362 cm^{-1} in parent complexes due to υ(Nb–Cl) mode confirmed the substitution of chloride ion by alkoxide ions. The occurrence of absorption bands at 540 cm^{-1} due to υ(Nb–O) mode only in mixed alkoxo-phenoxo complexes suggested the rupture of bridging isopropylphenoxy groups in parent complexes (Table 32).

It is worth pointing out here that complexes containing an ethoxide ion display a large number of absorptions bands in C–O region than methoxide ion in line with previous reports (577,578). The absorption bands characteristic of alkoxy groups at ~ 2900 cm^{-1} and ~ 1450 cm^{-1} due to υ(CH) and υ(C–H) modes also apppeared in complexes. The absorption bands due to phenoxo group were found to undergo slight change in band positions and intensity. The absence of bands at 369 and 362 cm^{-1} in parent complexes due to υ(Nb–Cl) mode confirmed the substitution of chloride ion by alkoxide ions.

4.4.2. ^{1}H-NMR Spectra

The incorporation of alkoxo (OR = OMe, OEt, OBu^t) groups in new mixed-ligand alkoxo-2-/4-isopropylphenoxoniobium(V) complexes is further ascertained by ^{1}H-NMR spectra. The ^{1}H-NMR pattern was although complex because of the probable overlapping of signals due to protons of isopropyl substituent at aromatic ring and those of methoxy, ethoxy and t-butoxy groups, yet, the observance of distinct diagnostic signals confirmed the formation of mixed alkoxo-isopropylphenoxo complexes. Complex of composition [Nb(OMe)($OC_6H_4CH(CH_3)_2$-2)$_4$] showed a characteristic signal at δ 3.3 ppm assignable to Nb(OMe) group (579). In case of [Nb(OC_2H_5)($OC_6H_4CH(CH_3)_2$-2/4)$_4$] the signals due to methyl and methine groups appeared as triplet and quartet in δ 3.42–3.46 ppm and δ 1.20–1.22 ppm regions respectively. In [Nb(OBu^t)($OC_6H_4CH(CH_3)_2$-2)$_4$], a distinct signal due to t-butoxy group appeared at δ 1.25 ppm (Table 33). In addition to above signals, resonances corresponding to isopropyl substituent and phenolic protons also appeared in the expected region, though slightly shifted relative to parent complexes (Fig. 55-58).

Table 32. IR spectral data (cm^{-1}) of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4$ with sodium alkoxides

Complex	Bands (cm^{-1})
$Nb(CH_3O)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	3427s, 3231s, 2962s, 2924, 2866, 2143, 1646, 1601s, 1449s, 1357s, 1316, 1282, 1247, 1143, 1085, 1027, 877, 842, 790, 750, 715s, 677, 634s, 602s, 576s, 547s, 524s, 495, 468, 417, 391, 362, 339, 310.
$Nb(CH_3CH_2O)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	3394, 2965, 2364, 1647, 1588, 1445vs, 1316, 1285, 1074, 866, 761, 687.
$Nb(Bu^tO)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	3376, 3063, 3023, 2962s, 2942, 2867s, 2364, 1895, 1632, 1581s, 1481s, 1448s, 1374, 1339s, 1285s, 1247s, 1189s, 1148s, 1113, 1083s, 1033s, 826s, 753, 636s, 570, 428, 374, 356, 333.
$Nb(CH_3CH_2O)(OC_6H_4CH(CH_3)_2\text{-}4)_4$	3584s, 3398, 3179, 2959s, 2924, 2872, 2362, 2080, 1889, 1687s, 1602, 1502s, 1446s, 1271s, 1175s, 1114, 1062, 1010s, 880s, 837s, 796, 709, 667, 616, 553.

Table 33. ^{1}H-NMR data of reaction products of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4$ with sodium alkoxides (ppm).

Complex	Substituent (Isopropyl protons)		Aromatic phenolic ring protons				Aliphatic protons (donor ligands)	
	$-(CH_3)_2$	-CH	H-3	H-4	H-5	H-6	$-OCH_2-$	$-CH_2-$
$NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1.20-1.22	3.25-3.37	6.76-6.78(d)	6.80-6.83(t)	6.96-6.99(t)	7.12-7.14(d)	----	-----
$Nb(CH_3O)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1.15-1.17	3.36-3.55	6.72-6.74(d,d)	6.75-6.80(d,t)	6.92-6.96(d,t)	7.08-7.10(d,d)	3.30	-----
$Nb(CH_3CH_2O)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1.06-1.09	3.47-3.51	6.70-6.72(d,d)	6.74-6.78(d,t)	6.91-6.94(d,t)	7.08-7.10(d,d)	3.44 -3.46	1.22
$Nb(Bu^tO)(OC_6H_4CH(CH_3)_2\text{-}2)_4$	1.10-1.18	3.19-3.28	6.70-6.72(d,d)	6.74-6.78(d,t)	6.91-6.95(d,t)	7.06-7.08(d,d)	-----	1.25
$NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4$	1.23-1.27	2.83-2.92	7.11-7.13(d)	7.27-7.28(d)	6.77-6.78(d)	6.78-6.80(d)	-----	----
$Nb(CH_3CH_2O)(OC_6H_4CH(CH_3)_2\text{-}4)_4$	1.11-1.13	2.52-2.73	7.12-7.14(d)	7.22-7.24(d)	6.63-6.65(d)	6.92-6.94(d)	2.75-2.77	1.19-1.20

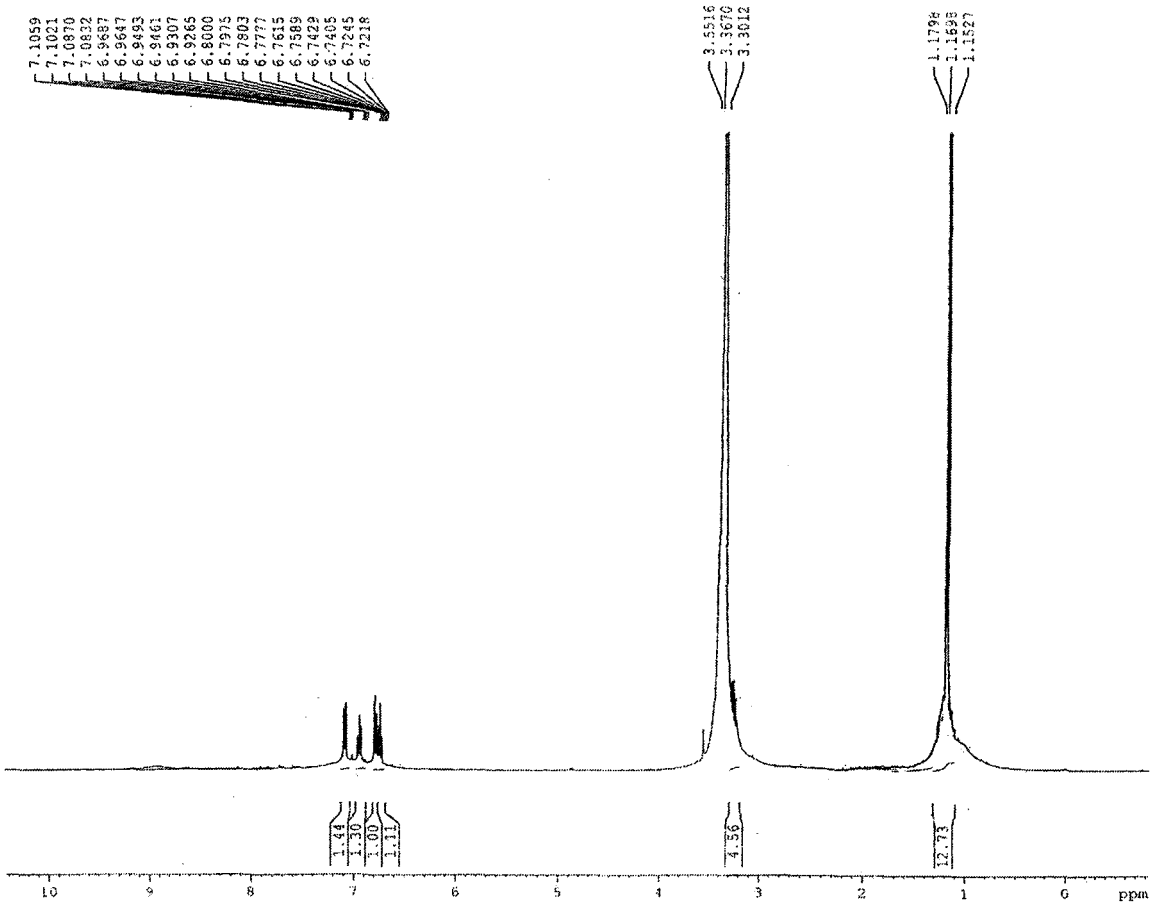


Fig. 55 ^{1}H NMR spectrum of $Nb(OCH_3)(OC_6H_4CH(CH_3)_2\text{-}2)_4$

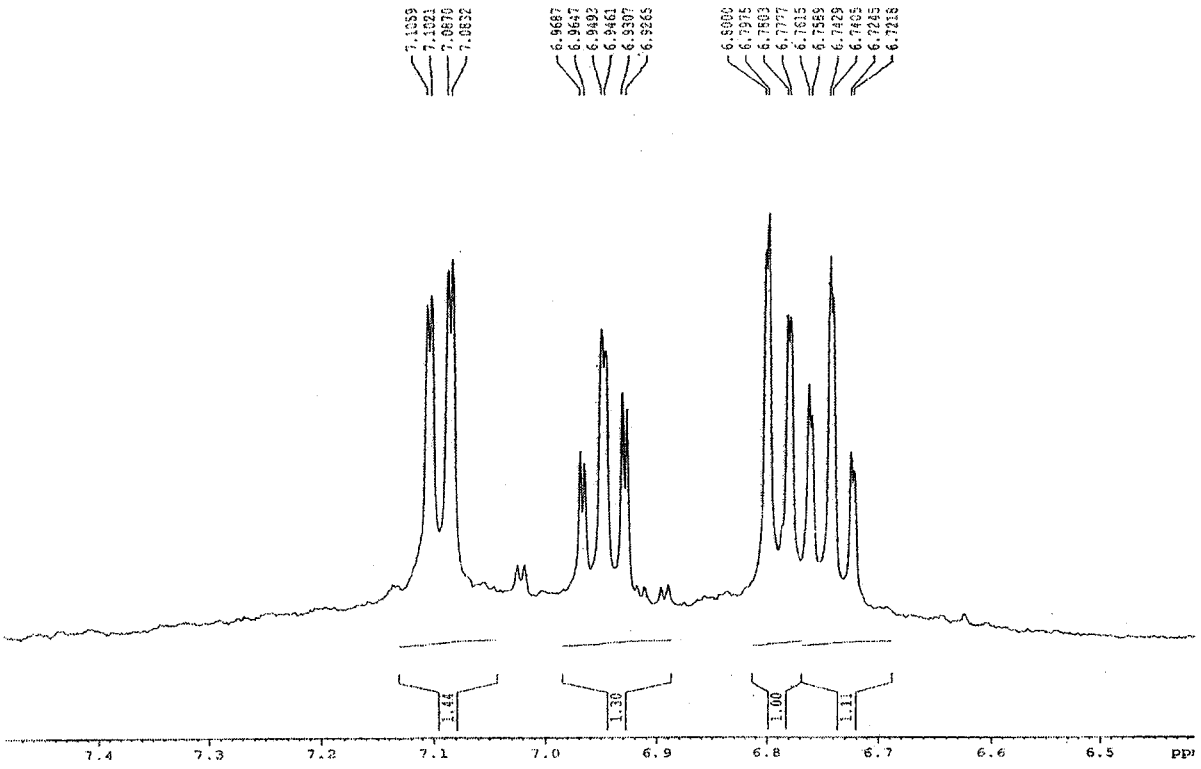


Fig. 55 ^{1}H NMR spectrum of $Nb(OCH_3)(OC_6H_4CH(CH_3)_2\text{-}2)_4$

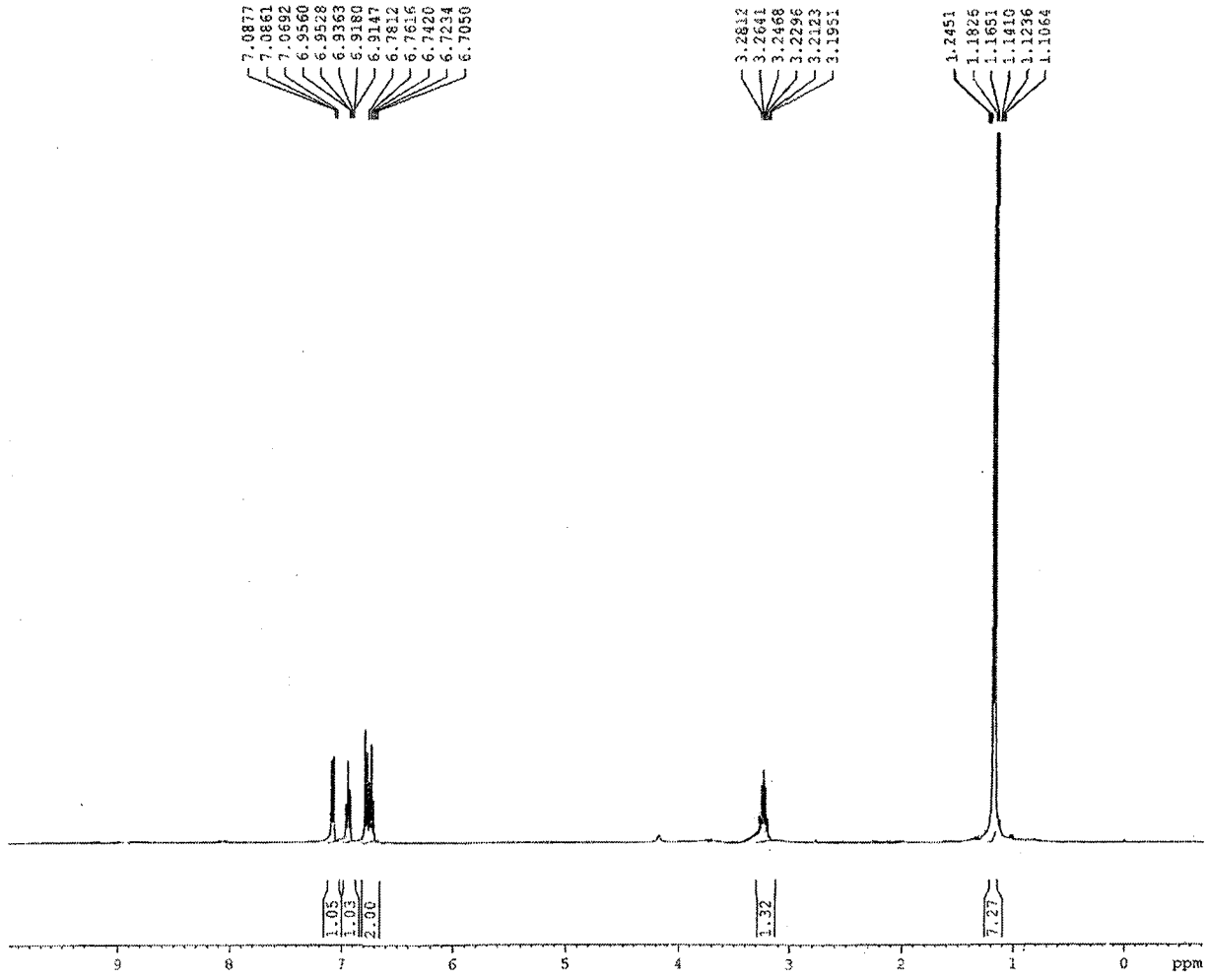


Fig. 56 ^{1}H NMR spectrum of $Nb(OBu^{t})(OC_6H_4CH(CH_3)_2\text{-}2)_4$

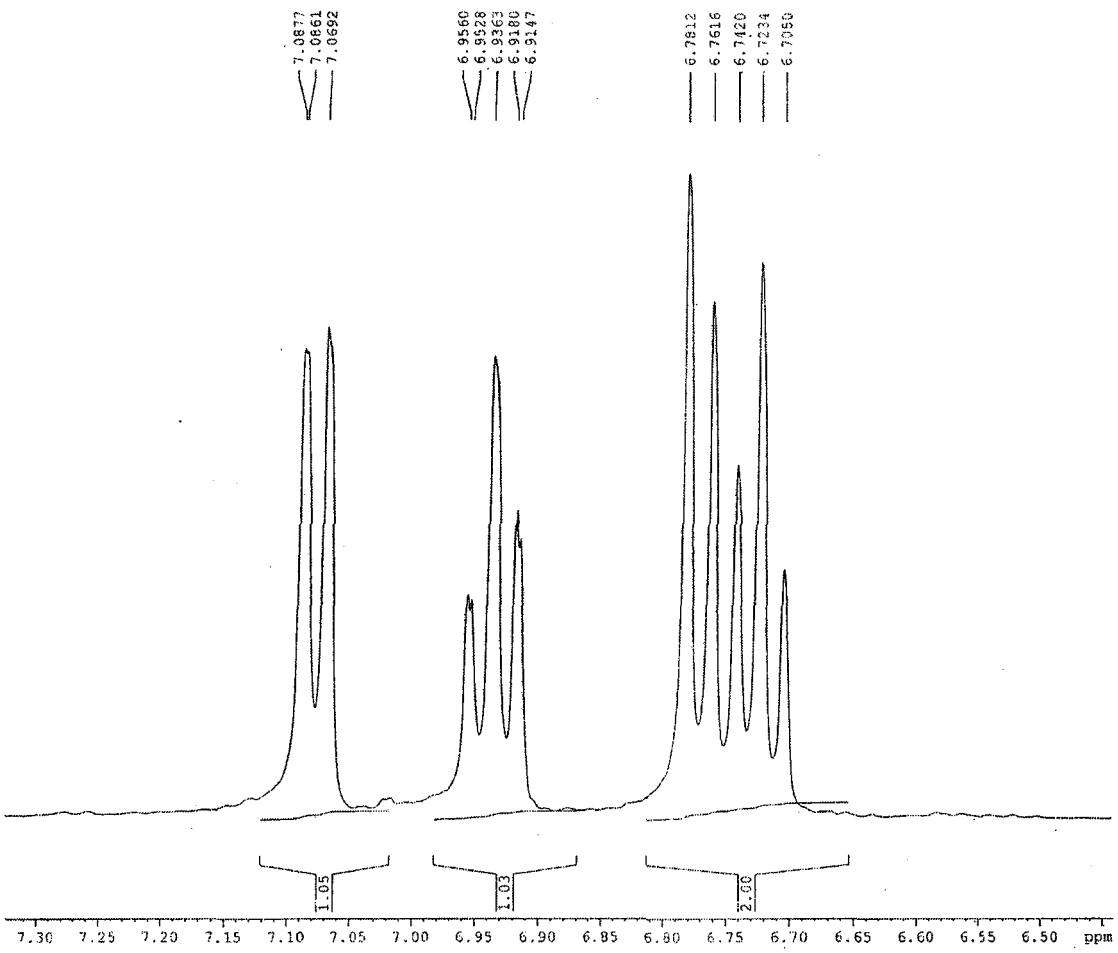


Fig. 56 ^{1}H NMR spectrum of $Nb(OBu^{t})(OC_6H_4CH(CH_3)_2\text{-}2)_4$

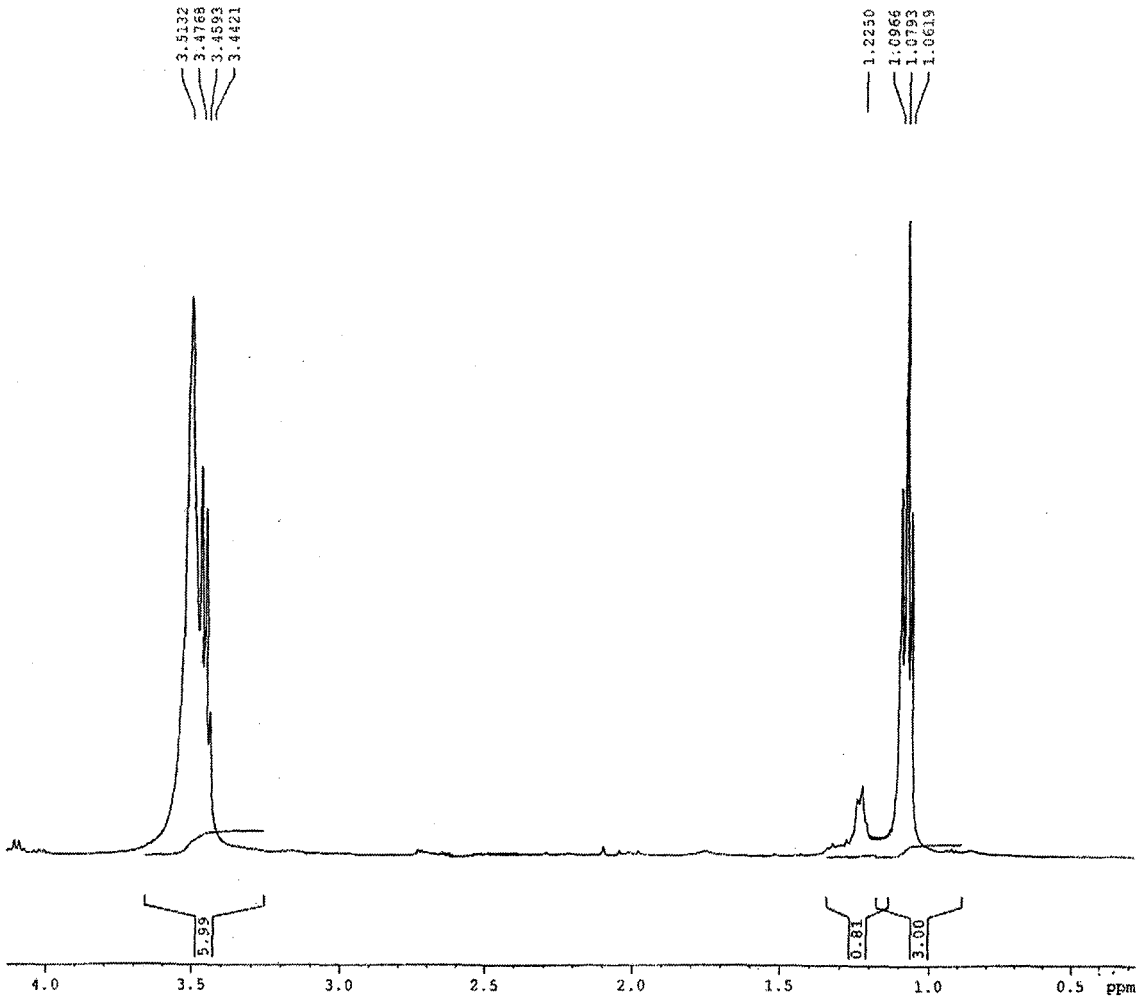


Fig.57 ^{1}H NMR spectrum of $Nb(OCH_2CH_3)(OC_6H_4CH(CH_3)_2\text{-}2)_4$

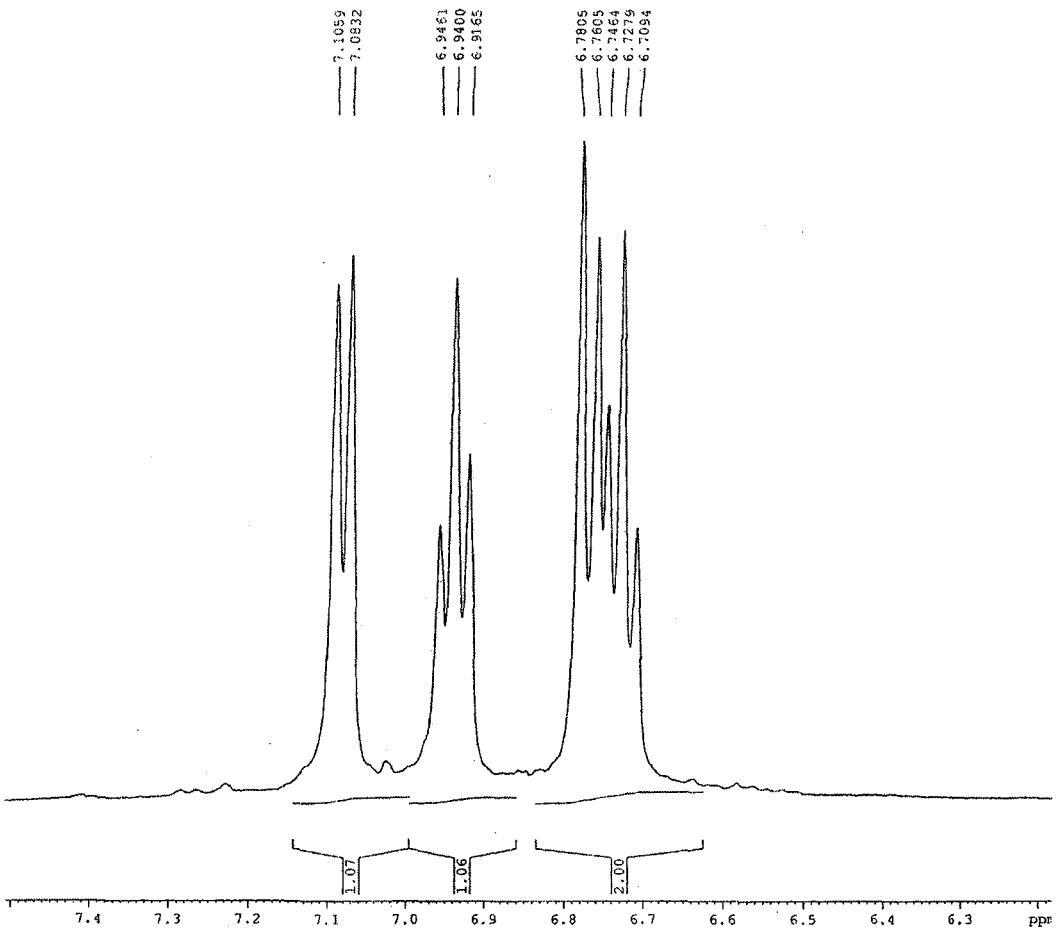


Fig.57 ^{1}H NMR spectrum of $Nb(OCH_2CH_3)(OC_6H_4CH(CH_3)_2\text{-}2)_4$

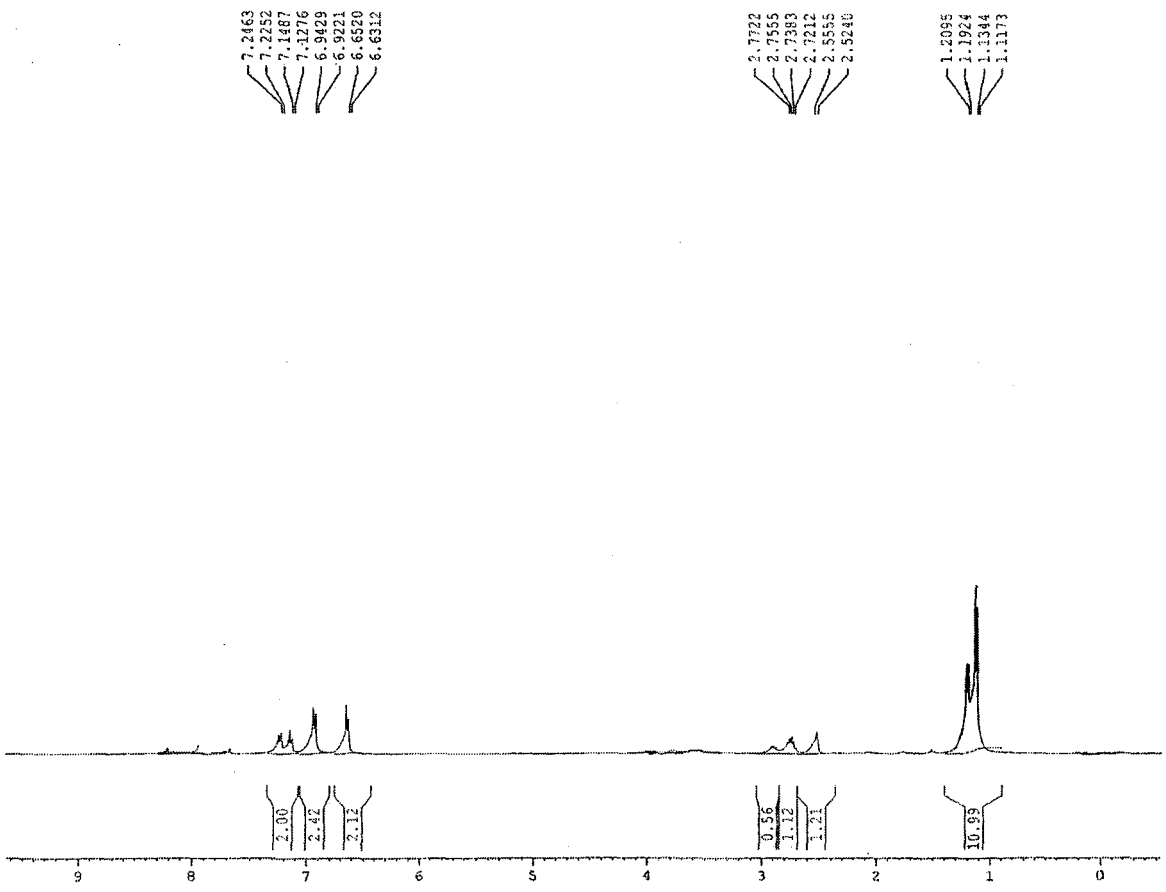


Fig.58 ^{1}H NMR spectrum of $Nb(OCH_2CH_3)(OC_6H_4CH(CH_3)_2\text{-}4)_4$

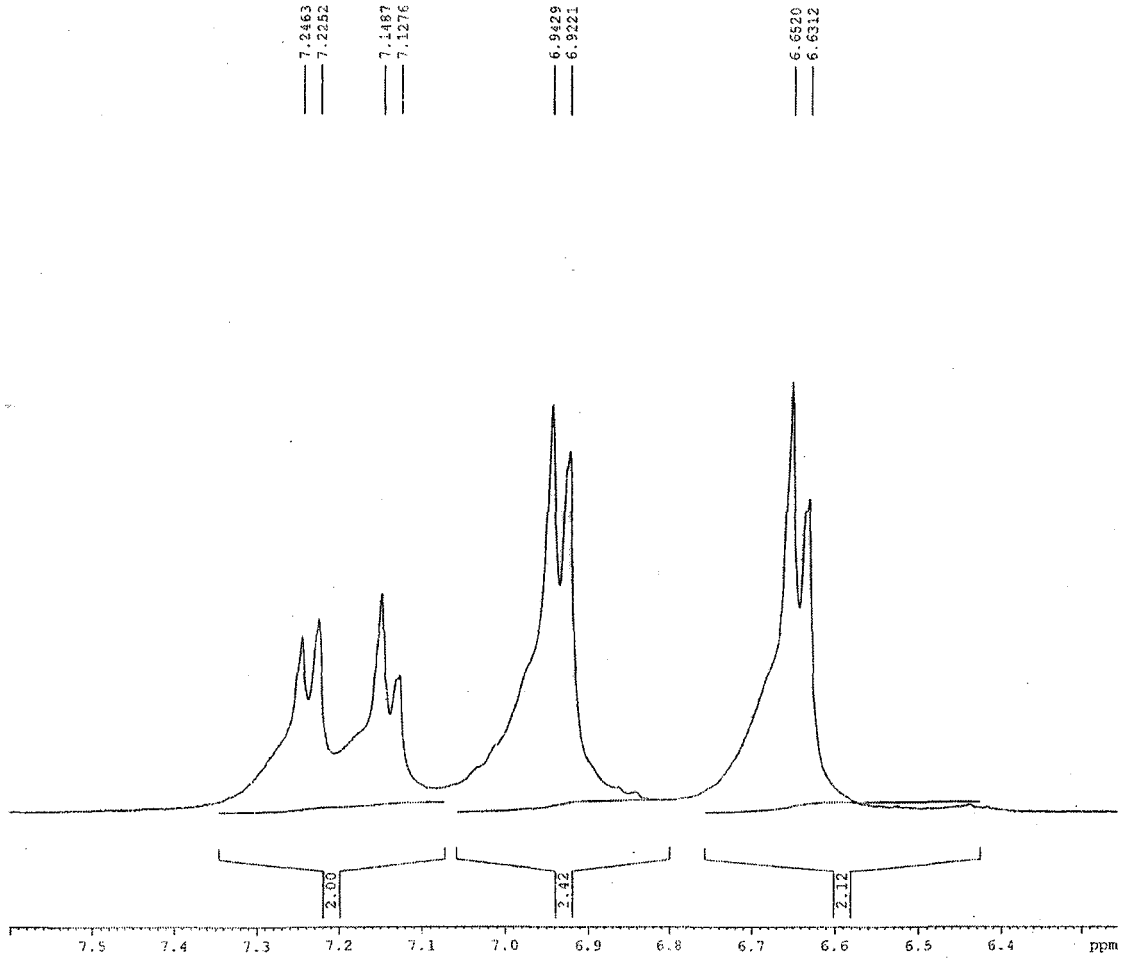


Fig. 58 ^{1}H NMR spectrum of $Nb(OCH_2CH_3)(OC_6H_4CH(CH_3)_2\text{-}4)_4$

EXPERIMENTAL

STARTING MATERIALS AND EXPERIMENTAL TECHNIQUES

5.1. Purifications

5.1.1. Solvents

Carbon tetrachloride

Carbon tetrachloride (S. D. Fine) was refluxed over phosphorus pentoxide for 4 h and was then distilled. The fraction distilling at 70°C (lit. b.pt. 76.8°C) was collected and was kept over molecular sieves (4 Å) for 48 h before use.

Benzene

Benzene (Ranbaxy) was kept over phosphorus pentoxide for 24 h and distilled. It was then kept over freshly drawn sodium wire for 24 h and was distilled again. The fraction distilling at 68 °C was collected and was kept over activated molecular sieves (4 Å) for 48 h in a properly stoppered bottle before use.

Hexane

n-Hexane (Merck) was kept over P_2O_5 for 24 h and then distilled. The distillate so obtained was kept over sodium wire for 24 hrs and then redistilled. The fraction distilling at 69°C was collected and stored in bottle containing activated molecular sieves (4 Å).

Methanol

Methanol (Ranbaxy) was refluxed over iodine and magnesium turnings for 4-5 h and was then distilled. The distillate was kept over calcium oxide and was allowed to stand overnight and redistilled. The fraction distilling at 63°C (lit. b.pt. 64.7°C) was collected and kept over activated molecular sieves (4 Å) before use.

Absolute Alcohol

Absolute alcohol (AnalaR) (99.7-100°C) was used as received.

t-Butyl alcohol (t-butanol)

t-Butyl alcohol (Ranbaxy) was used without further purification, however, its purity was checked by its melting point (25°C).

Petroleum ether

Petroleum ether (Ranbaxy) was successively distilled over sodium wire and phosphorus pentoxide. The fraction distilling at 71°C (lit. b.pt. 60-80°C) was collected and stored over activated molecular sieves (4 Å) in properly stoppered bottles before use.

Acetonitrile

Acetonitrile was kept over anhydrous $CaCl_2$ for overnight and then distilled. The fractions distilling at 78°C were collected and stored over activated molecular sieves (4 Å) before use.

Nitrobenzene

Nitrobenzene (S. D. Fine) was kept over anhydrous calcium chloride overnight and was then distilled. The distillate was kept over molecular sieves (4 Å) for 24 h and was then distilled again. The fraction distilling at 195°C (lit. b.pt. 210.9°C) was collected and stored over activated molecular sieves (4 Å) for 48 h before use.

5.1.2. Materials

Niobium(V) chloride

Niobium pentachloride (Fluka) was used without further purification, however, its purity was checked by chlorine analysis.

2-Isopropylphenol

2-Isopropylphenol (Merck) was used without further purification. The purity was checked by its boiling point (210°C).

4-Isopropylphenol

4-Isopropylphenol (Aldrich) was recrystallized from benzene and its purity was checked by its sharp melting point (59°C).

5.1.3. Nitrogenous Bases

2,2′-Bipyridyl

2,2′-Bipyridyl (Sisco) was recrystallized from absolute alcohol and was then sublimed in vacuo. The sample with melting point 69°C was used (lit. m.pt 70-73°C).

1,10-Phenanthroline

The hydrated 1,10-phenanthroline (S. D. Fine) was made anhydrous by keeping it in an oven at low temperature and was then dried over phosphorus pentoxide in a vacuum desiccator for 48 h before use.

5.1.4. Phosphorus and arsenic donors ligands

Triphenylphosphine and Triphenylarsine

Triphenylphosphine and triphenylarsine (Merck) were used as such without further purification. The purity of the samples was checked by their melting points (80°C and 60°C respectively) (lit. m.pt. 80-81°C and 58-61°C respectively).

Arsenic trithiophenoxide

To a known amount of arsenious oxide (4.72 g) was allowed to react with thiophenol (20 ml) under reflux for 1 h. The solution so obtained was filtered and the filtrate treated with petroleum ether and allowed to stand overnight when a pale yellow solid mass appeared. The solid was separated by filtration, washed repeatedly with petroleum ether and dried in vacuo. The compound was further recrystallised from solvent ether when fairly large colourless crystals were obtained. m.pt. 95°C, yield 82%. The melting point coincided exactly with the reported melting point of arsenic trithiophenoxide (580,581).

5.1.5. Oxygen Ligands

Triphenylphosphine oxide and Triphenylarsine oxide

Triphenylphosphine oxide and triphenylarsine oxide (Aldrich) were used as such without further purification. The purity of the samples was checked by their melting points (158°C and 193°C respectively) (lit. m.pt. 154-158°C and 194-196.5°C respectively).

Acetylacetone

Acetylacetone (Sisco, A.R.) was first boiled under reflux over P_2O_5 for about 2 h and was then distilled under reduced pressure. The fractions distilling at about 132°C were collected and were stored over molecular sieves for further use (lit. b.pt. is 140°C).

Benzoin

Benzoin (E. Merck) was recrystallised twice from hot benzene. The purity of the compound was checked by its sharp melting point (137°C) (lit. m.pt. 136-138°C).

Salicylaldehyde

Salicylaldehyde (AR grade) was distilled before use. The fraction distilling at 191°C was collected (lit. b.pt. is 196-197°C).

5.1.6. Metal acetates

$Cd(OAc)_2.2H_2O$ and $Pb(OAc)_2.3H_2O$ were made anhydrous by refluxing metal acetate hydrates with acetic anhydride over 15 h. These were then washed with carbon tetrachloride and were dried under vacuum.

5.2. Synthesis

5.2.1. Preparation of potassium benzohydroxamate and 4-chlorobenzohydroxamate

Potassium salts of hydroxamic acids were prepared in two steps:

(i) The first step involves the preparation of ethyl ester of carboxylic acids.

(ii) In the second step, the ester is treated with hydroxylamine hydrochloride and potassium hydroxide to obtain the desired salts.

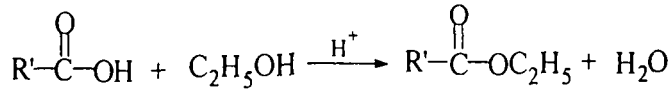
STEP 1:

Preparation of ethyl ester of carboxylic acids:

The reported method for the preparation of esters has been employed (582).

To 1 mole of the respective acid viz. benzoic acid and 4-chlorobenzoic acid was added an excess of (upto 10 moles) of ethyl alcohol and 3-4 mL of conc. H_2SO_4 very cautiously in separate reaction flasks. The reactants were then refluxed on heating mantle using water condenser for 3-6 h till whole of the acid was dissolved in ethanol. A few boiling chips were added during reflux. The solution was then cooled and transferred to 250 mL of water in a separating funnel. The lower layer of ester was removed and was washed with 100 mL of saturated $NaHCO_3$ until the effervescence ceased, indicating the complete removal of the acid. It was washed with water and was dried over 5-6 g of anhydrous sodium or magnesium sulphate.

The formation of esters involves the reaction as:



(where R′ = $-C_6H_5$ and $-C_6H_4Cl$-4)

Ethyl benzoate (b.pt = 212°C)

Ethyl 4-chlorobenzoate (b.pt = 237°C)

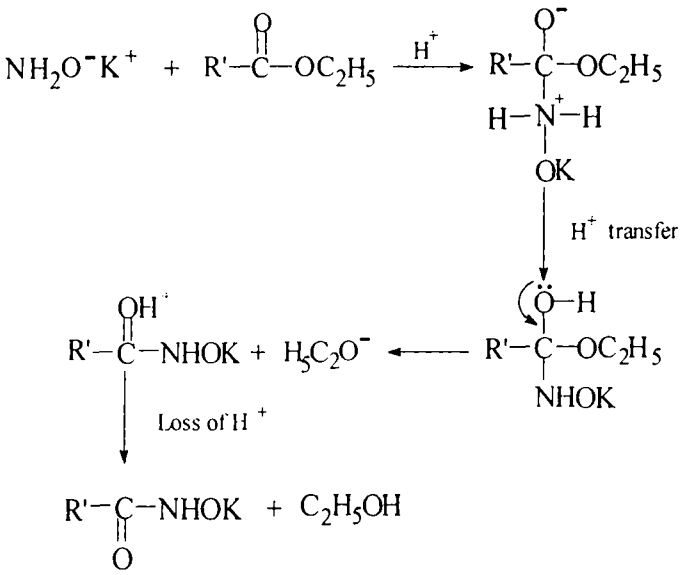
STEP 2:

Preparation of potassium hydroxamates:

The potassium hydroxamates were prepared by Houser and Renfrow (583) method. Separate solutions of hydroxylamine hydrochloride (46.7 g, 0.67 mol) in 240 mL of methanol and potassium hydroxide (56.1 g, 1 mol) in 140 mL of methanol were prepared by heating the contents on water bath. Both the solutions were cooled to 30-40 °C and the one containing alkali

was added with shaking to hydroxylamine hydrochloride solution. Any rise in temperature during the addition was however prevented by occasional cooling of the solution in an ice-bath. After the addition of alkali, whole of the mixture was allowed to cool in an ice bath for 24 h to ensure complete precipitation of potassium chloride. It was then filtered off and to the filtrate was added ethyl ester of the respective acids (50 ml, 0.33 mol) with thorough shaking. It was then filtered and the filtrate was placed in an air tight flask and was allowed to stand at room temperature. After 2-3 days the fine crystals began to appear. These were filtered off, washed with a little absolute ethyl acetate and dried in air. The yields of the products were 80-85%. The reactions involved are:

$$NH_2OH \cdot HCl + 2\,KOH \xrightarrow{MeOH} NH_2O^-K^+ + 2H_2O + KCl\downarrow$$



Where R = $-C_6H_5$ and $-C_6H_4Cl$-4

Potassium salts of Hydroxamic acids	Decomp. Temp (°C)
1. Potassium benzohydroxamate, (KHL^1)	200°C
2. Potassium 4-chlorobenzohydroxamate, (KHL^2)	210°C

5.2.2. Synthesis of Niobium(V) 2-isopropylphenoxides[$NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n$] (n = 1→5)

The direct reaction of niobium pentachloride with 2-isopropylphenol in appropriate molar ratios in dry carbon tetrachloride under reflux was employed for the preparation of niobium(V) complexes.

(i) In a typical reaction, for the preparation of complex of composition $[NbCl_4(OC_6H_4CH(CH_3)_2$-2)], to a suspension of niobium pentachloride (2.0 g, 0.007 mol) in CCl_4, an equimolar amount of 2-isopropylphenol (1.0 ml, 0.007 mol) in the same solvent was added at room temperature. The mixing of the reactants resulted in an immediate colour change from yellow to dark orange with the evolution of HCl gas. The reaction mixture was initially stirred for 3-4 h and was then refluxed over water bath till the evolution of hydrogen chloride gas ceased which ensured the completion of the reaction. No separation of any solid was observed during the course of the reaction in the mixture solution. It was filtered and the excess solvent was removed by distillation and the resultant concentrated solution was then evaporated under vacuum. It was repeatedly treated with petroleum ether and was dried under vacuum, when brownish rust coloured fine powdered complex was obtained. The stoichiometric composition of the complex was established by elemental analysis (Table 1). $[NbCl_4(OC_6H_4CH(CH_3)_2$-2)] (Yield = 1.85 g, 92.5 %).

The other niobium(V) complexes were prepared by employing the similar procedure as follows.

(ii) $[NbCl_3(OC_6H_4CH(CH_3)_2$-$2)_2]$ was prepared by reacting $NbCl_5$ (1.84 g, 0.0068 mol) with two equivalents of 2-isopropylphenol (1.85 ml, 0.0136 mol) (Yield = 1.50 g, 81.78 %).

(iii) $[NbCl_2(OC_6H_4CH(CH_3)_2$-$2)_3]$ was obtained by reacting $NbCl_5$ (2.40 g, 0.0088 mol) with three equivalents of 2-isopropylphenol (3.64 ml, 0.0264 mol) (Yield = 2.25 g, 93.75 %).

(iv) $[NbCl(OC_6H_4CH(CH_3)_2$-$2)_4]$ was isolated upon reacting $NbCl_5$ (2.50 g, 0.009 mol) with four equivalents of 2-isopropylphenol l (5.04 ml, 0.036 mol) (Yield = 2.10 g, 84 %).

(v) For the preparation of $[Nb(OC_6H_4CH(CH_3)_2$-$2)_5]$, $NbCl_5$ (2.0 g, 0.007 mol) was reacted with 2-isopropylphenol (5.03 ml, 0.035 mol) in 1:5 molar ratio (Yield = 1.30 g, 65 %).

5.2.3. Synthesisof Niobium(V) 4-isopropylphenoxides $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2$-$4)_n]$ ($n = 1 \rightarrow 5$)

The complexes were synthesized by an analogous procedure as employed for the preparation of niobium(V) 2-isopropylphenoxides i.e. the direct reaction of niobium(V) chloride with predetermined molar ratios of 4-isopropylphenol in carbon tetrachloride.

A suspension of niobium pentachloride (2.0 g, 0.007 mol) in CCl_4 was treated with a solution of one, two, three, four and five equivalents of 4-isopropylphenol (1.0 g, 0.007 mol; 1.90 g, 0.014 mol; 2.86 g, 0.021 mol; 3.81 g, 0.028 mol and 4.76 g, 0.035 mol) in the same solvent in separate experiments. The addition of phenolic solution to the solution of $NbCl_5$ resulted in an immediate colour change from yellow to dark orange with the evolution of HCl

gas. The reaction mixture was initially stirred for 3-4 h and was then refluxed over water bath till the evolution of hydrogen chloride gas ceased which ensured the completion of the reaction. No separation of any solid was observed during the course of the reaction in the mixture solution. It was filtered and the filtrate was then concentrated by distilling off the solvent. The resultant concentrated solution was treated with petroleum ether. It was dried under vacuum. The stoichiometric composition of all complexes was established by elemental analysis (Table 2).

$[NbCl_4OC_6H_4CH(CH_3)_2\text{-}4)]$	Yield 1.50g, 75%
$[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}4)_2]$	Yield 1.75g, 70%
$[NbCl_2(OC_6H_4CH(CH_3)_2\text{-}4)_3]$	Yield 1.90g, 95%
$[NbCl(OC_6H_4CH(CH_3)_2\text{-}4)_4]$	Yield 2.50g, 80%
$[Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5]$	Yield 1.40g, 70%

5.2.4. Synthesis of Alkali Metal aryloxides $[M(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ (M = Li and Na)

The alkali metal 2-isopropyl and 4-isopropylphenoxides were prepared by the reaction of a known amount of the respective phenols dissolved in benzene with an equimolar amount of the alkali metals cut in fine pieces at room temperature. The contents were continuously stirred on a magnetic stirrer for 5-6 h during which the separation of white solid was observed. It was filtered under anhydrous conditions, washed 2-3 times with dry benzene and was finally dried under vacuum.

5.2.5. Synthesis of heterometallic aryloxides $M^I[Nb^V(OC_6H_4CH(CH_3)_2\text{-}2/4)_6]$ (M = Li and Na)

In a typical reaction, to a suspension of sodium 2-isopropylphenoxide (0.35 g, 0.002 mol) in dry benzene was added a stirred suspension of niobium penta 2-isopropylphenoxide (1.70 g, 0.002 mol) in the same solvent. The reaction mixture was initially stirred and was then refluxed for 6-7 h to ensure the completion of the reaction. The resulting solid so obtained was repeatedly treated with petroleum ether and was dried in vacuo.

A similar procedure was employed for the synthesis of other heterometallic aryloxides.

5.2.6. Reactions of $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ with $Cd(OAc)_2$ and $Pb(OAc)_2$

To a suspension of $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ (3.3 g, 0.004 mol) in hexane (25 ml) anhydrous $Cd(OAc)_2$ (0.5 g, 0.002 mol) was added. The reactants were stirred for 1 to 2 h, when the colour of reaction mixture changed from dark orange to light yellow and separation of solid was

observed. The solid thus obtained was repeatedly treated with petroleum ether and dried in vacuo. The stoichiometric formulation of compounds was established by elemental analysis.
A similar procedure was employed for the synthesis of other mixed-metal acetatoaryloxides.

5.2.7. Reactions of $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ with 2,2′-bipyridyl and 1,10-phenanthroline

To a suspension of $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ in dry benzene was added benzene solution of an equimolar amount of 2,2′-bipyridyl and 1,10-phenanthroline, in separate experiments. The mixing of the reactants resulted in a change in coloration from brown to dull brown. The reactants were initially stirred for 3-4 h and were then refluxed whereupon the separation of dark brown coloured solid was observed. The compounds thus obtained were collected by decanting off the solvent. These were treated with petroleum ether and were dried in vacuum. The elemental analyses of the isolated compounds established their stoichiometric formulations.

5.2.8. Reactions of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ with Triphenylphosphine oxide and Triphenylarsine oxide

In a typical reaction, to the suspension of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ and $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ in benzene were added equimolar amounts of Ph_3PO and Ph_3AsO in methanol in separate experiments. The contents were initially stirred for 4-5 h and then refluxed for another 5-6 h, when a significant colour change from the initial brown colour was observed and the formation of solid resulted. It was treated with petroleum ether and was dried under vacuum. The analytical data of the isolated compounds established their stoichiometric formulations.

5.2.9. Reactions of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ with Triphenylphosphine, Triphenylarsine and Arsenic trithiophenoxide

In a typical reaction, to the suspension of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2)]$ and $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)]$ in benzene were added equimolar amounts of Ph_3P, Ph_3As, and $As(SPh)_3$ in methanol in separates experiments. The reactants were initially stirred for 4-5 h and then refluxed for another 5-6 h, when a significant colour change from the initial brown colour was observed and the formation of solid resulted. These were filtered, treated with petroleum ether and were dried under vacuum. The elemental analysis of the compounds established their stoichiometric formulations.

5.2.10. Reactions of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with β-Diketone, α-hydroxyaldehydes and α-hydroxyketone viz. Acetylacetone, Benzoin and Salicylaldehyde (LH)

To benzene solution of parent complex, were added methanolic solution of equimolar amount of the ligands viz. acetylacetone, benzoin and salicylaldehyde (LH) in separate experiments. These were stirred at room temperature for 3-4 h. The reaction mixture was then refluxed when a significant colour change accompanied by an evolution of HCl gas was observed. Upon completion of the reaction, when no more gas evolved, it was concentrated to $¾^{th}$ of its original volume, when the solids separated out. These were filtered, washed with petroleum ether and hexane and were dried under vacuum.

In the case of reaction of complex with salicylaldehyde, acetonitrile was added to obtain complex as solid.

5.2.11. Reactions of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with Potassium benzohydroxamate and 4-chlorobenzohydroxamate

In a typical reaction, to a suspension of monochlorotetrakis(2-isopropylphenoxo)niobium(V) in benzene, a methanolic solution containing equimolar amounts of potassium benzohydroxamate and potassium 4-chlorobenzohydroxamate, was added in separate experiments. The reaction mixture was stirred for about 1 h and was then refluxed for 18-20 h. The white solid formed during the course of reaction was removed by filtration and was identified as KCl. The excess of solvent was removed by distilling off the filtrate. The concentrate was then dried under vacuum by repeatedly treating with petroleum ether, whereupon brown solids were obtained.

5.2.12. Preparation of Sodium Alkoxides (NaOMe, NaOEt and $NaOBu^t$)

In a three necked 500 ml flask with mechanical stirrer, dropping funnel and reflux condenser was placed, sodium (13.8gm, 0.6 mol) freshly cut into small pieces. To this was added slowly 140 ml of anhydrous methanol at such a rate as to maintain the vigorous reflux. As some of the sodium was not dissolved during the addition of methanol, the mixture was heated on steam bath. An additional methanol (upto 25 ml) may be added for the effective formation of solution. It was stirred on magnetic stirrer. The preparation of the desired compound required about 30 minutes. The formation of white fluffy precipitates was observed in solution. It was kept as such. Other sodium alkoxides were prepared by an analogous procedure.

5.2.13. Reactions of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4]$ with Sodium alkoxides NaOR (OR = OMe, OEt and OBu^t)

In a typical reaction, to methanolic solution of parent complex, methanolic solution of sodium methoxide (a slight excess than 1:1 molar ratio), was added. The mixing of reactants did not

result in any change of colour of the solution. The reaction mixture was then refluxed for 6-7 h in order to ensure the completion of the reaction during which a marked colour change from maroon/yellow to brown/light yellow and formation of solid was observed. It was filtered to remove the solid formed (sodium chloride), during the course of the reaction. The filterate was concentrated under vacuum. The solid thus obtained was treated with petroleum ether and was dried under vacuum.

Similar procedure was employed in carry out reaction with sodium ethoxide and sodium t-butoxide. In the reaction of parent complex with sodium ethoxide, acetonitrile was added to obtain solid.

5.3. Analytical Estimations

C, H and N estimation

Carbon, Hydrogen and nitrogen analysis were obtained on Eager 300 N C H System Elemental Analyser from SAIF, Punjab University Chandigarh.

Estimation of Niobium as Nb_2O_5

A known weight of the complex was taken in a weighed silica crucible. The complex was treated with a mixture of conc. sulphuric acid (2 volume) and conc. nitric acid (3 volume). The crucible was heated gently to dryness in a fuming cupboard till fuming ceased. This operation was performed 2-3 times. The crucible was placed in an oven and was heated to 700°C. The residue in the crucible was weighed as Nb_2O_5. The % of niobium was then calculated as follows:

$$\% \text{ of Niobium} = \frac{\text{mol. wt. of Nb}}{\text{mol. wt. of } Nb_2O_5} \times \text{wt. of } Nb_2O_5$$

Estimation of Chlorine by Back titration (Volhard's Method)

Due to the insoluble nature of the complexes in water, chloride ions were brought into aqueous solution as follows:

A known weight of the complex was transferred in the nickel crucible containing anhydrous sodium carbonate and potassium nitrate. The complex was again covered with some more of the sodium carbonate, potassium nitrate and 5-6 pellets of sodium hydroxide. The fusion mixture along with the complex was initially heated to melt. The fused mixture was then heated very strongly till it became red hot. The nickel crucible was then immersed in distilled water in a beaker in order to dissolve the contents in distilled water. The nickel crucible was then removed

after thorough washings with distilled water. The solution was acidified with conc. nitric acid (AR) and the contents were heated to 60-70°C. To this solution, was then added a measured volume of silver nitrate solution (N/10) to ensure the complete precipitation of chloride ions as silver chloride. The precipitates were digested by heating over hot plate for some time and were then filtered through Whatman filter paper No.41. The filtrate was titrated against a standard solution of ammonium thiocyanate (N/10) using ferric alum $(NH_4)_2SO_4.Fe_2(SO_4)_3.12H_2O$ as an internal indicator. From the volume of silver nitrate used for precipitation, the % of chloride ion was determined as follows:

Let volume of silver nitrate used = a ml

Wt. of chlorine contained in-'a' ml of $AgNO_3$ = 35.5 X a X N/ 10 = b

$$\% \text{ of Chlorine} = \frac{b}{\text{wt. of complex taken}} \times 100$$

5.4. Molar Conductivity Measurements

For the molar conductivity measurements, a known weight of the complex was dissolved in dry nitrobenzene and the volume was made 25 ml in a measuring flask. The solution was then transferred in a dry cell jacket. The electrodes of the conductivity cell were dipped in the solution. The conductance of the solution was then measured at 25±0.1°C using Elico-Conductivity Bridge type CM-82T. Specific conductance was calculated by multiplying the observed conductance with cell constant and the molar conductance of the complex was calculated using the relation:

$$\text{Molar conductance} = \frac{\text{Specific cond.}}{\text{Conc. in g mole/litre}} \times 1000$$

For all measurements, millimolar solution (10^{-3} M) of the complexes in nitrobenzene was used.

5.5. Molecular weight determinations

The molecular weight of the complexes was determined by finding the depression in freezing point. Beckmann thermometer was first set for freezing point of benzene and the freezing point was noted on it. A known weight of the compound was dissolved in measured volume of pure solvent and the depression in freezing point was noted. Some more complex was weighed out and added in the same solution and further depression in freezing point was noted. Three to four

observations were made in the same manner. The molecular weight of the compound was determined by using the relation:

$$\text{Mol. Wt.} = \frac{K_f \times w \times 1000}{W \times dT_f}$$

Where:

w = weight of the complex

W = weight of the solvent

K_f = Molar freezing constant of the solvent

dT_f = difference in freezing point

5.6. Spectral studies

IR Spectra

Infrared spectra of complexes were recorded as potassium bromide pellets using Nicolet-5700 FTIR Spectrometer in Deptt. of Chemistry, H.P.U. Shimla. The pellets were prepared in a dry box to avoid the action of moisture. The following expressions have been used to denote the intensities of various absorption bands

s = sharp, vs = very sharp, m = medium, w = weak.

^{1}H NMR Spectra

^{1}H NMR spectra of niobium(V) complexes were recorded on BRUKERAVANCE II 400 Spectrometer from SAIF, Punjab University, Chandigarh using TMS as an internal standard and $CDCl_3$/DMSO as solvent.

^{13}C NMR Spectra

^{13}C NMR spectra of complexes were recorded on BRUKERAVANCE II 400 Spectrometer operating at 400.13 MHz. The data were obtained from Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The solutions were prepared in $CDCl_3$ using tetramethylsilane as an internal reference.

Electronic Spectra

Electronic spectra of complexes were recorded on Varian Cary-100 Bio UV-VIS spectrophotometer using acetonitrile/methanol as solvent.

Mass Spectra

The mass spectra of complexes were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The samples dissolved in chloroform were introduced into the ESI source through a syringe pump at the rate of 5 μl per min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The spectra were collected in 6 scans and print outs were averaged spectra of 6-8 scans.

5.7. X-ray diffraction

X-ray diffraction pattern complexes in powdered form were recorded on Philips PW 3071 X'PERT-PRO X-ray diffractometer (XRD) in 5-70° 2θ range and 0.017 step size in continuous scanning mode at 25 °C using Cu-Kα radiation from SAIF, Punjab University, Chandigarh. Phillips X'Pert software was used to obtain precise value of parameters.

5.8. Molecular model calculations

The molecular modelling calculations using Hyper-Chem 7.5 (student version) have been performed to visualize the probable geometry acquired by the complexes by applying MM^+ force field with Polka-Ribiere algorithm and RMS gradient 0.01 kcal/mole. The molecular dynamic simulation was done upto 1000K (relaxations time 1 ps).

5.9. Thermal studies

Thermograms of complexes were recorded on simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer in air at a heating rate of 20°C min^{-1} using platinum crucible. Thermocouple used was Pt/Pt-Rh (10%). The temperature range of the instrument was from room temperature to 1300 °C.

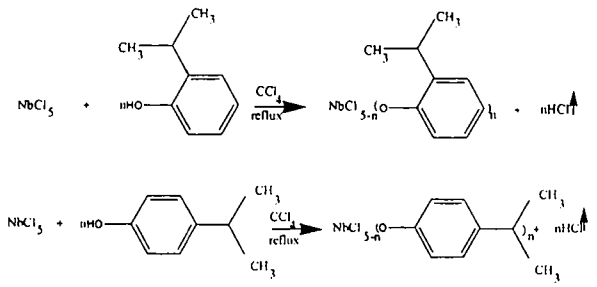
SUMMARY

The chemistry of phenol and substituted phenols as ligands continues to be the fascinating area of study owing to their ability to form metal complexes with rich structural diversity. The phenoxide ion is an important ligand because it provides a flexible organic moiety having an advantage over analogous alkoxide ligands in that electronic properties can easily be varied by changing the substituents in the phenyl ring and steric effects in close proximity to metal can be modified by varying the bulk of the substituents at ortho- and para- positions of the ring. The phenols containing tert-butyl and phenyl substituents at 2- and 6-positions have drawn a special attention because of their interesting features such as intermolecular and intramolecular C–H activation via metallation of tert-butyl group at the phenolic ring, isolation of hydrocarbon soluble mono-nuclear complexes, η^5-phenolate bonding and chelation to metal through π bonding interactions via hydrogenation of aryl rings. Literature abounds with examples of metal aryloxides of main group elements, transition metals, lanthanides and actinides. Of transition metals, the coordination and organometallic chemistry of niobium aryloxides continues to be a subject of immense research interest because of their rich structural chemistry and excellent catalytic properties. The potential applications of niobium(V) alkoxides and aryloxides as precursors for the synthesis of mono-, di- or trivalent metal niobates, ferro- or piezo- electric resonator materials viz. lead magnesium niobate (PMN) and niobium doped lead zirconate titanate (PNZT) are well-documented. A particular research interest in the synthesis of lithium niobium alkoxides, aryloxides, oxoaryloxides or chloroaryloxides has been owing to their potential utility as precursors for the preparation of $LiNbO_3$ as electro-optic material. Of numerous substituted phenols utilized as π-donors towards niobium, 2- and 4-isopropylphenols compared to analogous well-explored iso-propylalcohol and 2,6-isopropylphenol have not so far been studied as ligands. In view of these observations, niobium(V) complexes derived from 2- and 4-isopropylphenols using niobium pentachloride($NbCl_5$) as the starting material, have been synthesized with an aim to have an insight into structural assessment of the variation of niobium-aryloxide i.e. oxygen pπ to metal dπ bonding. A thorough review of literature on metal alkoxides and aryloxides and their applications in general, and analogous niobium complexes and their applications, in particular, has been incorporated in Introductory part of the thesis. After having surveyed the relevant literature, the whole work has been presented in three chapters.

CHAPTER – 1

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF NIOBIUM(V) COMPLEXES OF 2- AND 4-ISOPROPYLPHENOLS

The niobium(V) complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2/4)_n]$ (where n = 1→5) have been synthesized in quantitative yields by the reaction of niobium pentachloride with the respective substituted phenols in appropriate molar ratios in carbon tetrachloride under reflux as:



(where n = 1→5)

The elemental analyses (niobium, chlorine, carbon and hydrogen) of the isolated complexes agreed well with their stoichiometric formulations. The complexes are moisture sensitive brown/yellow coloured solids & change their colour upon exposure to atmosphere. The complexes show poor solubility in CCl_4 and CH_2Cl_2 but are fairly soluble in C_6H_6, $CHCl_3$, CH_3OH and $C_6H_5NO_2$. The molar conductance values of the millimolar solutions of the complexes in nitrobenzene are quite low to be attributed to 1:1 electrolyte. The cyroscopic molecular weight determinations of complexes in nitrobenzene are suggestive of their dimeric nature.

A comparison of IR spectra of the newly synthesized complexes with that of the respective substituted phenols scanned in 4000–200 cm^{-1} region established their formation. The absence of absorption band due to υ(OH) mode known to occur at 3431 cm^{-1} and 3313 cm^{-1} in 2-isopropylphenol and 4-isopropylphenol respectively suggested the deprotonation of phenolic proton. The free 2- and 4-isopropylphenol exhibit bands due to υ(C–O) mode in 1364–1236 cm^{-1} and 1362–1221 cm^{-1} regions respectively. The occurrence of characteristic υ(C–O)Nb bands in 1260–1218 cm^{-1} and 1172–1097 cm^{-1} regions in two series of niobium(V) complexes are suggestive of bonding through phenolic oxygen to niobium metal. Bonding through oxygen to niobium was further indicated by the occurrence of absorption bands in 580–570 cm^{-1} region assigned to infrared active υ(Nb—O) mode. The absorption bands observed in 550–530 cm^{-1}

region assigned to bridging Nb–O–Nb mode are indicative of dimeric nature of complexes. The chloride phenoxides of niobium(V) displayed sharp bands ~ 370 cm^{-1} ascribed to υ(Nb–Cl) mode.

The formation of niobium(V) complexes has further been ascertained from their ^{1}H and ^{13}C NMR spectra. The free 2-isopropylphenol displays a signal at δ 5.42 ppm due to –OH; two doublets centered at δ 6.85 and δ 7.37 ppm due to aromatic H–6 and H–3 respectively; two triplets at δ 7.08 and δ 7.20 ppm due to H–4 and H–5 respectively; a heptet and a doublet at δ 3.39 and δ 1.42 ppm due to methine and methyl protons respectively of isopropyl substituent. The signal due to –OH group was absent in complexes $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n]$. The signals due to aromatic protons of the 2-isopropylphenolic ligand are displaced slightly upfield by (-0.08)–(-0.10) ppm in complexes. This peculiarity can be explained by considering the shielding effect exerted on aromatic protons by the electron releasing isopropyl substituent at ortho position to phenolic group. The proton resonances due to methine and methyl groups also shifted slightly upfield upon complexation.

The free 4-isopropylphenol exhibits a signal at δ 4.91 ppm due to –OH; a doublet at δ 6.75 due to ortho (H–2 and H–6); a doublet at δ 7.23 due to meta (H–3 and H–5) aromatic protons; heptet and a doublet at δ 3.20 and δ 1.24 due to aliphatic methine and methyl protons respectively of isopropyl group. None of the complexes of composition $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)_n]$ (n = 1→5) displayed signal due to phenolic –OH group. The aromatic ring proton resonances shifted downfield which may be ascribed to the deshielding of these protons due to transfer of electron density from aromatic nucleus to the niobium metal as (PhO ⟹ Nb). The proton resonances due to methine and methyl groups insignificantly shifted upfield upon complexation. The integration of protons supported the formulation of complexes.

The ^{13}C NMR spectra of 2-isopropylphenol exhibited six signals in δ 115.94–153.14 ppm range due to aromatic ring carbons and two signals at δ 23.12 and δ 27.45 ppm due to methyl and methine carbons of isopropyl substituent respectively. In $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2)_n]$ (n= 1→5), C–1 resonance shifted downfield by δ 0.77–1.59 ppm while the other aromatic ring carbons and aliphatic isopropyl carbons showed moderate upfield shifts. The ^{13}C NMR spectra of 4-isopropylphenol displayed four signals in δ 115.40–154.50 ppm range due to aromatic ring carbons C–1; C–2,6; C–3,5 and C–4 and two signals at δ 24.40 and δ 31.70 ppm due to aromatic methyl and methine carbons respectively. In $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}4)_n]$ (n= 1→5), the ipso carbon resonance showed appreciable downfield shift by δ 0.99-1.13 ppm while other carbon

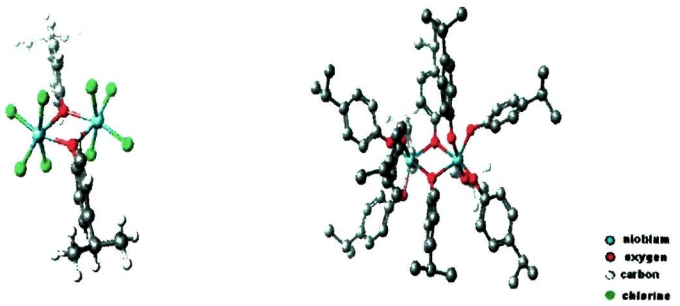
resonances showed slight upfield shifts upon complexation. Strikingly, C–4 showed significant upfield shift by δ 2.23–2.36 ppm. The methine carbon resonance shifted downfield appreciably while methyl carbon showed slight downfield shift.

The UV-visible spectra of $[NbCl_{5-n}(OC_6H_4CH(CH_3)_2\text{-}2/4)_n]$ (n= 1→5)in CH_3OH/CH_3CN displayed low to medium intensity absorption bands assignable to ligand to metal charge transfer (LMCT) transition from phenolate oxygen to empty d-orbitals of niobium metal and the $\pi \rightarrow \pi^*$ intra-ligand transitions characteristic of d^0 species.

The mass spectra of niobium(V) complexes of composition $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ and $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4]$ displayed peaks higher than molecular mass which indicated dimeric nature of complexes. The complexes exhibited different base peaks at m/z 217/218, 417 and 551. Although, most of the significant peaks have been rationalized in terms of fragment ions of a specific composition, yet, the possibility of proposition of other compositions for these fragments cannot be ruled out.

The X-ray diffraction pattern of some of the complexes have indicated amorphous or polycrystalline nature. The molecular mechanical adjustments for energy optimization from strained structures to the likely geometry of complexes were attempted. The molecular mechanics were repeated five to six times to ensure that the structure with minimized energy has been attained. The structure with minimized energy is assumed to be closer to the stable geometry in consonance with physicochemical and spectral data.

Based upon physico-chemical and IR, ^1H and ^{13}C NMR, electronic and mass spectral studies coupled with molecular modelling, a dimeric structure bridging through iso-propylphenoxy groups exhibiting an octahedral environment around niobium has tentatively been proposed for niobium(V) complexes.



Perspective dimeric structures of $NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4)$ and $Nb(OC_6H_4CH(CH_3)_2\text{-}4)_5$

Insight into the thermal behaviour of niobium(V) isopropylphenoxides using TGA-DTA techniques has provided useful information regarding their thermal stability, the probable intermediate formed and ultimate product of decomposition. All the complexes have shown single step decomposition pattern except for $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ which decomposed in two steps yielding $NbO_2(OC_6H_4CH(CH_3)_2\text{-}2)$ as the probable intermediate and Nb_2O_5 as the ultimate residue. The formation of variant final decompositional products viz. $NbOCl_3$, $NbO(OC_6H_5)_3$, $NbO_2(OC_6H_5)$ and Nb_2O_5 has been depicted by complexes. The various kinetic and thermodynamic parameters namely the energy of activation (E*), frequency factor (A), entropy of activation (S*), enthalpy of activation (H*), free energy (G*) and specific reaction rate constant (k_r) have been evaluated from TG data by Coats-Redfern equation.

After having synthesized and characterized the two series of niobium(V) isopropylphenoxides, the reactions of $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ have been carried out with the respective alkali metal isopropylphenoxides and divalent metal acetates. The bimetallic phenoxides of composition $[MNb(OC_6H_4CH(CH_3)_2\text{-}2/4)_6]$ have been synthesized by the reactions of $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_5]$ with the respective alkali metal isopropylphenoxides in 1:1 molar ratios in benzene according to the equation:

$$Nb(OC_6H_4CH(CH_3)_2^{-2/4})_5 + M(OC_6H_4CH(CH_3)_2^{-2/4}) \xrightarrow{\text{benzene}} [MNb(OC_6H_4CH(CH_3)_2^{-2/4})_6]$$

(where M = Li and Na)

The elemental analyses of complexes have established their stoichiometric composition. The molar conductance values of the millimolar solutions of complexes in nitrobenzene have indicated their appreciable electrolytic nature. The infrared spectra of bimetallic phenoxides have shown that υ(C–O) mode shifted towards higher regions relative to parent pentaaryloxides. This has been attributed to the fact that the negative charge existing on metal in $[Nb(OC_6H_4CH(CH_3)_2\text{-}2/4)_6]^-$ decreases the drainage of electron density from the ring to metal, thereby strengthening the C–O bond and resultant higher frequencies for υ(C–O) mode.

The interactions between $[Nb(OC_6H_5CH(CH_3)_2\text{-}2/4)_5]$ and cadmium and lead acetates in 2:1 molar ratios in hexane at room temperature afforded the formation of heterometal acetatoaryloxides in accordance with the equation:

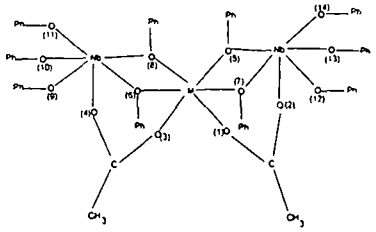
$$2Nb(OC_6H_4CH(CH_3)_2^{-2/4})_5 + M(OAc)_2 \xrightarrow{\text{hexane}} [MNb_2(OAc)_2(OC_6H_4CH(CH_3)_2^{-2/4})_{10}]$$

(where M = Pb and Cd)

A comparison of the IR spectra of heterometal acetatoaryloxides with that of respective free metal acetates and parent complexes substantiated their formation. The υ(COO) mode of acetate ion in the resulting complexes $[MNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ has been observed to shift to higher frequencies relative to free metal acetates which is suggestive of a chelating or bridging-chelating behaviour for the OAc ligands rather than the formation of mixed crystals.

The ^1H NMR spectra of hetero-metal acetatoaryloxides displayed a diagnostic signal due to acetate ligand at δ 1.88 ppm being shifted upfield relative to that at δ 2.02 ppm in $Cd(OAc)_2$ and $Pb(OAc)_2$. The signals due to aromatic ring protons of 2-/4-isopropylphenoxo group were found to be shifted upfield by δ 0.06–0.29 ppm and by δ 0.10–0.12 ppm in $[MNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2)_{10}]$ and $[MNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}4)_{10}]$ respectively. These compounds are anticipated to be potential single source precursors for Nb–Pb and Nb–Cd oxide materials.

Thus, based upon IR and ^1H NMR spectral data for $[CdNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ and $[PbNb_2(OAc)_2(OC_6H_4CH(CH_3)_2\text{-}2/4)_{10}]$ and the reported molecular structures of $[CdNb_2(OAc)_2(\mu\text{-}OCH(CH_3)_2)_4(OCH(CH_3)_2)_6]$ and $[PbNb_2(OAc)_2(\mu\text{-}OCH(CH_3)_2)_4(OCH(CH_3)_2)_6]$, the following structure may tentatively be proposed for the newly synthesized hetero-metal acetatoaryloxides:



(where OPh = $OC_6H_4CH(CH_3)_2$-2/4 and M = Cd, Pb)

CHAPTER-2
LEWIS ACID CHARACTER OF NIOBIUM(V) 2-/4-ISOPROPYLPHENOXIDES TOWARDS NITROGEN, PHOSPHORUS, ARSENIC AND OXYGEN DONOR LIGANDS

The interaction of niobium(V) isopropylphenoxides of composition $[NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)_2]$ with nitrogenous bases viz. 2,2′-bipyridyl(bipy) and 1,10-phenanthroline(phen) (B) in equimolar amounts in dry benzene led to the formation of 1:1 addition compounds in confirmity with elemental analyses in terms of the equation:

$$NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4) + B \longrightarrow NbCl_3(OC_6H_4CH(CH_3)_2\text{-}2/4)\cdot B$$

(where B = 2,2′-bipyridyl(bipy) and 1,10-phenanthroline(phen))

The coordination compounds are soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of the compounds in nitrobenzene suggested their non-electrolyte nature. The formation of coordination compounds and bonding through both the nitrogen atoms of nitrogenous bases has been indicated from the shifts of υ(C=C) and υ(C=N) ring stretching bands, C–H out of plane deformation vibrational modes of ligands to higher wave numbers. The observance of sharp and distinct bands in 500-480 cm^{-1} region assigned to υ(Nb←N) mode has further substantiated their formation. The absence of  bridging mode, a characteristic of the parent complexes are suggestive of a possible breakdown of the dimeric structure on adduct formation. The bands observed at ~ 560 cm^{-1} have been assigned to terminal υ(Nb–O) mode.

The reactions of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)]$ with equimolar amounts of phosphorus, arsenic and oxygen donors viz. Ph_3P, Ph_3As, $As(SPh)_3$, Ph_3PO and Ph_3AsO (L) in benzene+methanol afforded 1:1 coordination compounds in agreement with their analytical data as:

$$NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4) + L \xrightarrow[\text{methanol}]{\text{benzene+}} NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2/4)\cdot L$$

(where L = donors ligands)

The adducts are light brown to yellow solids and are soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of compounds in nitrobenzene suggested their non-electrolytic nature.

A comparison of the infrared spectra of coordination compounds with that of parent complexes and uncoordinated donor ligands gave evidences for their formation. The characteristic vibrations of Ph_3P and Ph_3As are due to υ(C–C), υ(C–H), stretching and bending (P–C) and (As–C) modes coupled with aromatic ring vibrations. The occurrence of diagnostic bands at 1484, 1437, 1021, 726, 541, 501 and 420 cm^{-1} in $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3P]$ and at 1560, 1444, 1121, 1091, 726, 622 and 495 cm^{-1} in $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).Ph_3P]$

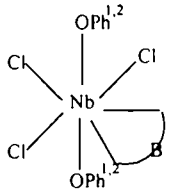
supported their formation. The spectra of $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).Ph_3As]$ exhibited bands at 1513, 1481, 1435, 1021, 738, 693, 669 and 466 cm^{-1}.

The IR spectra of arsenic trithiophenoxide $As(SPh)_3$ is known to exhibit bands at 492 s, 400w and 372 vs cm^{-1} due to υ(As–S) mode and at 744 vs and 684 vs cm^{-1} due to υ (As–S–C) mode. The bands displayed at 460, 376, 740 and 680 cm^{-1} and at 483, 372, 744, 685 cm^{-1} respectively by $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}2).As(SPh)_3]$ and $[NbCl_4(OC_6H_4CH(CH_3)_2\text{-}4).As(SPh)_3]$ ascribed to υ(As–S) and υ(As–S–C) modes suggested their formation.

The characteristic vibrations of Ph_3PO and Ph_3AsO due to υ(P=O), υ(As=O), υ(P–C), and υ(As–C) modes occurring at 1192, 879, 455 and 479 cm^{-1} respectively appeared at 1166, 796, 546 and 588 cm^{-1} in respective coordination compounds. The shift of υ(P=O) and υ(As=O) modes to lower wave number is ascribed to overall decrease in the bond order of P=O and As=O due to decrease in pπ–dπ bonding. The bands due to υ(P–C) and υ(As–C) modes moved to higher wave numbers upon complexation. The non-occurrence of absorption bands in 550–540 cm^{-1} region in coordination compounds due to υ(Nb–O–Nb) mode occurring in parent complexes, suggested that oxygen, phosphorus and arsenic donors are effective in isopropylphenoxo bridging bond-scission and yielded unimolecular compounds.

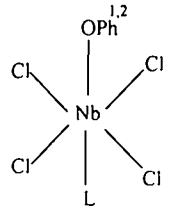
The ^1H NMR spectra of coordination compounds with phosphorus, arsenic and oxygen donors exhibited distinct signals due to aryl protons of donors, phenolic ligand and the substituents. The upfield signals in δ 1.12–1.32, δ 3.05–3.64 ppm range occurred due to methine and methyl protons of isopropyl substituent. The signals due to aryl protons of the donor ligands viz. Ph_3P, Ph_3As, Ph_3PO and Ph_3AsO (L) and aromatic protons of phenolic ring appeared in δ 7.43–7.86 and δ 6.21–7.35 ppm range respectively. Evidence for coordination of $As(SPh)_3$ to niobium has been inferred from the occurrence of thiophenyl proton resonances at δ 7.43–7.50 ppm downfield shifted relative to δ 7.25–7.46 ppm in $As(SPh)_3$.

Based upon the data, in hand, a seven-coordinate and six-coordinate environment around niobium in coordination compounds with nitrogen bases and phosphorus, arsenic and oxygenous donors may tentatively be proposed as:



$[NbCl_3(OPh^{1,2})_2.B]$

(where $OPh^{1,2}$ = $OC_6H_4CH(CH_3)_2$-2/4 and B = 2,2′-bipyridyl(bipy) and 1,10-phenanthroline(phen))



$[NbCl_4(OPh^{1,2}).L]$

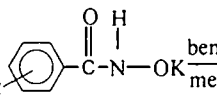
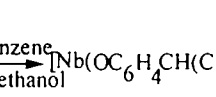
(where $OPh^{1,2}$ = $OC_6H_4CH(CH_3)_2$-2/4 and L = Ph_3P, Ph_3As, $As(SPh)_3$, Ph_3PO and Ph_3AsO)

CHAPTER-3
REACIVITY OF NIOBIUM(V) ISOPROPYLPHENOXIDES TOWARDS CHELATING LIGANDS AND SODIUM ALKOXIDES

The reactions of $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ with β-diketone viz. acetylacetone; α-hydroxyketone viz. benzoin and α-hydroxyaldehyde viz. salicylaldehyde, collectively abbreviated as (LH); with potassiumbenzohydroxamate(KHL^1) and potassium-4-chlorobenzohydroxamate(KHL^2) afforded complexes according to the equations:

A. $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4] + LH \xrightarrow[\text{methanol}]{\text{benzene+}} [Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4L] + HCl\uparrow$

(where LH = acacH, benzH and salH and L = anions of acac, sal and benz)

B. $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]_x$  $\xrightarrow[\text{methanol}]{\text{benzene}} [Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4$  $+KCl\downarrow$

(where X = H and 4-Cl)

The reactions of $[NbCl(OC_6H_4C(CH_3)_3\text{-}2/4)_4]$ with equimolar solution of sodium

alkoxides in respective alcohols under reflux afforded the formation of mixed alkoxo-isopropylphenoxo complexes according to the equation:

C. $NbCl(OC_6H_4CH(CH_3)_2\text{-}2/4)_4 + NaOR \longrightarrow Nb(OR)(OC_6H_4CH(CH_3)_2\text{-}2/4)_4 + NaCl\downarrow$

(where OR = OMe, OEt and OBu^t)

The analytical data of isolated compounds agreed well with their stoichiometric formulations. The complexes are dark-brown, light yellow and pink solids and are fairly soluble in common organic solvents. The molar conductance values of the millimolar solutions of the complexes in nitrobenzene indicated their non-electrolytic nature.

A. The IR and ^1H NMR spectra of complexes further gave supporting evidences for their formation. The IR spectra of complexes derived from acetylacetone, benzoin and salicylaldehyde have shown a lowering in υ(C=O) mode by 20–30 cm^{-1} from that occurring in 1600–1580 cm^{-1} and 1370–1350 cm^{-1} regions ascribed to υ_{asym}(C=O) and υ_{sym}(C=O) mode respectively in the enolic form of acetylacetone; at 1690 cm^{-1} due to υ(C=O) mode in free benzoin and at 1660 cm^{-1} in free salicylaldehyde. The absorption band due to υ(OH) mode occurring at 3333 cm^{-1} in enolic form of acetylacetone, 3360 cm^{-1} in free benzoin and at 3180 cm^{-1} in free salicylaldehyde was missing in complexes. The simultaneous bonding both through carbonyl and enolic or hydroxyl oxygens has suggested the chelating behaviour of these ligands.

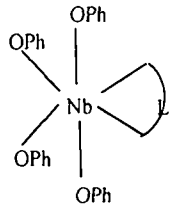
The ^1H NMR spectra of $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4acac]$ displayed signals at δ 2.01 and δ 3.44 ppm due to methyl and methylene protons of acetylacetone respectively. The signals due to phenolic ring protons were observed to shift upfield by δ 0.05–0.08 ppm and appeared at δ 6.69–7.09 ppm in mixed-ligand complex relative to that occurred at δ 6.77–7.14 ppm in parent complex. The aromatic protons due to benzoin and salicylaldehyde appeared in δ 7.58–7.95 ppm and δ 7.46–7.68 ppm range respectively in complexes.

B. The absorption bands due to υ(C=O) mode occurring in 1658–1597 cm^{-1} region in free hydroxamate ligands moved to lower wave numbers in mixed-ligand hydroxamatoisopropylphenoxoniobium(V) complexes. The υ(N–O) mode occurring at ~ 923 cm^{-1} in free KHL^1 and KHL^2 ligands appeared at ~ 969 cm^{-1} in complexes. The absorption bands due to υ(C–N) mode appeared in 1378–1370 cm^{-1} region in complexes. The bands due to υ(N–H) mode appeared in 3249–3192 cm^{-1} region in complexes. These observations are suggestive of

bonding through both carbonyl oxygen and oxygen atom of –NHO group in complexes suggesting thereby bidentate nature of ligands.

The complexes of composition $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^1]$ and $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4.HL^2]$ showed distinct proton resonances due to aromatic protons of isopropylphenolic ligand and benzohydroxamate/4-Cl-benzohydroxamate ligands. The signals due to former protons appeared in δ 6.70–7.10 ppm range in both the complexes while the resonances due to latter protons appeared in δ 7.42–7.86 ppm and δ 7.37–7.82 ppm range in respective complexes. The signal due to –NH appeared at δ 8.83 and δ 9.02 ppm in respective complexes suggesting that –NH is retained in complexes.

Based upon IR and ^1H NMR spectral data coupled with physicochemical analysis, a distorted octahedral geometry around niobium in complexes derived from acetylacetone, benzoin, salicylaldehyde and hydroxamate ligands may tentatively be proposed.



(where OPh = $OC_6H_4CH(CH_3)_2$-2 and L = anions of acetylacetone (acacH), benzoin (benzH) and salicylaldehyde (salH))

C. The occurrence of absorptions bands in 1189-1010 cm^{-1} region diagnostic of coordinated alkoxo groups attributed to υ(CO) mode suggested the formation of mixed alkoxo-isopropylphenoxo complexes. The absence of bands at 369 and 362 cm^{-1} in parent complexes due to υ(Nb–Cl) mode confirmed the substitution of chloride ion by alkoxide ions. The occurrence of absorption bands at 540 cm^{-1} only due to υ(Nb–O) mode suggested the rupture of bridging isopropylphenoxy groups in parent complexes.

The ^1H NMR spectra of $[Nb(OMe)(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ showed a distinct signal at δ 3.3 ppm assigned to [Nb(OMe)] group. In $[Nb(OC_2H_5)(OC_6H_4CH(CH_3)_2\text{-}2/4)_4]$, the signals due to methyl and methylene protons of ethoxy group appeared as triplet and quartet in δ 3.42–3.46 ppm and δ 1.20–1.22 ppm range respectively. In $[Nb(OBu^t)(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ a distinct signal due to t-butoxy group appeared at δ 1.25 ppm. The resonances due to isopropyl substituent and phenolic ring protons slightly shifted downfield relative to parent complexes.

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Symbols and abbreviations

OAc	: free acetate ion (CH_3COO^-)
bipy	: 2,2′-bipyridyl
phen	: 1,10-phenanthroline
acac	: acetylacetonate
benz	: benzoin
sal	: salicylaldehyde
KHL^1	: potassiumbenzohydroxamate
KHL^2	: potassuum4-chlorobenzohydroxamate
X	: 4-chloro-

LIST OF PUBLICATIONS

1. Thermal Investigations on Lithium-niobium Heterometallic Aryloxides as Precursors for Lithium Niobate
   Thermans, 165 (2010)

2. Synthesis, spectroscopic studies and reactivity of monochlorotetrakis(2-/4-isopropylphenoxo)niobium(V) complexes
   Turk. J Chem. (in press).

3. Synthesis and Characterization of mixed-metal acetato-isopropylphenoxides $[MNb_2(OAc)_2(OC_6H_4Pr^i\text{-}2/4)_{10}]$ (M = Cd, Pb) as precursors to oxides
   J. Coord. Chem. (in press).

4. Thermoanalytical investigations of niobium(V) complexes of 4-isopropylphenol
   J. Therm. Anal. Calorimetry (Communicated).

5. Synthesis, spectroscopic characterization and coordination behaviour of niobium(V) 2- and 4-isopropylphenoxides.
   J. Iranian Chem. Soc. (Communicated).

Thermal Investigations on Lithium-niobium Heterometallic Arlyloxides as Precursors for Lithium Niobate

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Abstract

The lithium-niobium heterometallic aryloxides of composition $Li[Nb(OAr^{1-4})_6]$ (where $OAr^1 = OC_6H_4Pr^i$-2; $OAr^2 = OC_6H_4Pr^i$-4; $OAr^3 = OC_6H_4Ph$-2 and $OAr^4 = OC_6H_4Ph$-4) have been synthesized by the reaction of niobiumpenta-aryloxides $[Nb(OAr^{1-4})_5$ with the respective lithiumaryloxide as starting materials in 1:1 molar ratio in benzene. The thermal studies of newly synthesized aryloxides by thermogravimetry (TG) and differential thermal analysis (DTA) techniques showed the formation of $LiNbO_3$, colourless solid as the ultimate product of decomposition. The characterization of $LiNbO_3$ powder has been authenticated by Fourier transform infrared spectra (FTIR).

Introduction

There has been an increasing research interest in niobium compounds not only as catalysts and catalyst components [1-3] as promoters and supporters but also owing to their significant applications in material sciences [4]. The organo-niobate ionic liquids have been reported as alternative acid catalysts in Pechmann reactions [5]. The utility of ultrafine Nb_2O_5 and mixed oxides [6] for the electronic parts has also drawn considerable attention in the preparation of metal-organic precursors affording these oxides. In this context, niobium alkoxides, chloroalkoxides, heterometallic alkoxides and aryloxides constitute an important group of complexes as potential precursors [7]. A particular interest in $Li[Nb(OEt)_6]$ [8] has been large as a precursor material for the preparation of $LiNbO_3$ (LN) which exhibits excellent piezoelectric, pyroelectric, electro-optical, photorefractive properties, an important material for optical waveguides, mobile phones, optical modulators [9] and various linear and non-linear optical applications [10]. An efficient approach for the direct synthesis of lithium niobate powders has been reported by the solid state reactions between Nb_2O_5 and Li_2CO_3 at > 1200°C using urea as a fuel [11]. The preparation of nano LN crystal using $NbCl_5$ and dihydrate lithium acetate by low-temperature sol-gel method has been described [9]. Both aqueous and non-aqueous soft-chemical routes utilising the single-source polyoxoniobate salt $Li_8[M_6O_{19}].xH_2O$ in a hydrothermal reaction and simple chemical precursors utilising butanediol respectively have been employed [12]. A method of growing thin ferroelectric films of lithium niobate has been described. With this background, that much $LiNbO_3$ research is taking place in recent years because of its having a number of characteristics exploitable for optical and electronic devices, we took up the present work on the synthesis of lithium-niobium heterometallic aryloxides with an objective to study their thermal behaviour and explore their potential as probable precursors for $LiNbO_3$.

Experimental

Materials and Methods

$NbCl_5$ (Fluka) was used without further purification and its purity was checked by chlorine analysis. 2- and 4-isopropylphenols and 2- and 4-phenylphenols were used as received. Solvents were made anhydrous before use by standard methods. The niobium content in complexes was estimated as Nb_2O_5 after decomposing the complexes with a mixture of conc. H_2SO_4 and HNO_3 followed by heating at 650-700 °C. IR spectra of complexes were recorded as (KBr pellets) on Nicolet-5700 FTIR spectrometer. Thermogravimetric and differential thermal analysis were performed on DT-TG SHIMADZUDT-60 thermal analyzer. Thermocouple used was Pt/Pt-Rh (10%). The temperature range of the instrument was from room temperature to 1300°C. The heating rate of 20°C/min was employed.

Synthesis of $Nb(OAr^{1-4})_5$

To niobium pentachloride (1.0g, 3.7 mmol) was added five equivalents of 2 and 4-isopropylphenol (2.53 g, 18.5 mmol) and 2 and 4-biphenylphenol (3.15 g, 18.5 mmol) in dry carbon tetrachloride in separate experiments. The mixing of the two solutions resulted in an immediate colour change from yellow to dark orange with the evolution of HCl gas. The reaction mixture was initially stirred for 3-4 h and was then refluxed over water bath till the evolution of HCl gas ceased which ensured the completion of the reaction. It was filtered and the excess solvent from the filtrate was then removed by distillation. The resulting concentrate was then evaporated under vacuum. It was treated with petroleum ether whereupon orange to brown solids were obtained.

Synthesis of $Li(OAr^{1-4})$

Lithium salt of 2- and 4-isopropylphenol and 2- and 4-biphenylphenol were prepared by the reaction of lithium metal cut in fine pieces with equimolar amount of respective phenols dissolved in THF at room temperature in separate experiments. The contents were stirred on a magnetic stirrer for 5-6 h. The separation of a white solid resulted during the course of the reaction. It was dried under vacuum.

Table 1: Thermoanalytical data of Heterometallic aryloxides

Complex	Initial decomp. temp. (°C)	Stages of decomp.	TGA			DTA	
			Decomp. temp. range (°C)	% Wt. loss		Peak temp. (°C)	Peak nature
				Theor.	Obs.		
[LiNb(OArPr^i-2)$_6$]	58.20	Single	58.20-700.0	83.73	82.48	182.32	Endo
[LiNb(OArPr^i-4)$_6$]	60.32	Single	60.32-700.0	83.73	81.52	185.56	Endo
[LiNb(OArPh-2)$_6$]	62.45	Single	62.45-700.0	87.39	85.18	123.49 446.96	Endo
[LiNb(OArPh-4)$_6$]	67.58	Single	67.58-700.0	87.39	86.02	131.28 450.46	Endo

Synthesis of [LiNb(OArPr^i-2and 4)$_6$] and [LiNb(OArPh-2 and 4)$_6$]

To a stirred suspension of niobium pentaaryloxides in benzene was added eqimolar amount of respective lithiumaryloxides in benzene in separate experiments. The reaction mixture was initially stirred and then refluxed for 6-7 hr to ensure the completion of the reaction. The resulting solids so obtained were repeatedly treated with petroleum ether and dried in vacuum.

Results and Discussion

The reactions between [Nb(OAr$^{i\text{-}4}$)$_5$] and [Li(OAr$^{i\text{-}4}$)] in equimolar amounts in benzene proceed smoothly and quantitatively to afford the formation of heterometallic aryloxides authenticated by elemental analysis. The formulation of complexes results from a simple addition according to the equation:

$$Nb(OAr^{i\text{-}4})_5 + Li(OAr^{i\text{-}4}) \xrightarrow[\text{reflux}]{\text{Benzene}} Li[NB(OAr^{i\text{-}4})_6]$$

This was motivated by the attractive properties of niobates as electrooptical ceramics, ceramics for microwave resonators or as dielectric ceramics. The TG-DTA curves of complexes have been recorded in air and the data are presented in Table 1. The thermogram of representative complex [Li(NbOArPr^i-4)$_6$] is given in Fig. 1. The complexes have shown their initial thermal stability to lie in 55-70°C temperature range, after which temperature the complexes undergo single step decomposition with a continuous weight-loss. The % weight-loss displayed by complexes has accounted for the formation of $LiNbO_3$, the white solid as the ultimate decompositional product as:

$Li[NB(OAr^{i\text{-}4})_6] \rightarrow LiNbO_3$ + Organic Matter

The decomposition in TG curves is substantiated by endothermic peaks only in DTA curves of complexes.

IR Spectra

In a preliminary study, the formation of $LiNbO_3$ has further been established by recording IR spectra. The FT-IR

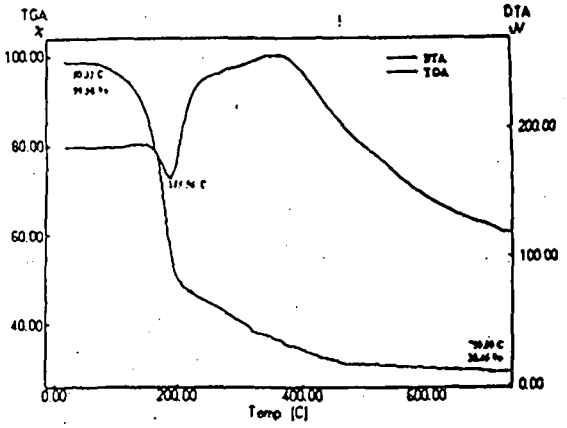

Fig. 1 Thermogram of [LiNb(OArPr^i-4)$_6$]

spectra of samples showed characteristic absorption bands ~ 622 cm^{-1} ascribed to ν(Li-O) mode. The occurrence of bands ~ 850 cm^{-1}, 685 cm^{-1} and 560 cm^{-1} may be attributed to ν(Nb-O-Nb) and ν(Nb-O) modes. It is pertinent to mention here that $LiNbO_3$ is known to consist of NbO_8 and NbO_7 groups and exhibits Raman bands in 700-500 cm^{-1} region. The confirmation of the results can, however, be made further through the XRD pattern and TEM studies.

Conclusions

The newly synthesized lithium-niobium heterometallic aryloxides from the reactions of lithiumaryloxides and niobiumpentaaryloxides derived from 2- and 4-isopropyl and phenylphenol as lithium and niobium sources respectively can be employed as suitable molecular precursors to obtain $LiNbO_3$ (LN) powders as revealed from their TG and DTA studies. The formation of $LiNbO_3$ has also been supported on the basis of complimentary IR spectral technique.

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