

Synthesis and Characterization of Mixed-Metal Acetato-Isopropylphenoxides [M₂Nb₂(OAc)₂(OC₆H₄Prⁱ-2/4)₁₀] (M = Cd, Pb) as Precursors to Oxides

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ABSTRACT: The pentakis(2- and 4-isopropylphenoxo)niobium(V) complexes of composition Nb(OC₆H₄Prⁱ-2)₅ (1) and Nb(OC₆H₄Prⁱ-4)₅ (2) have been synthesized by the reactions of niobium pentachloride with five equivalents of 2- and 4-isopropylphenol in carbon tetrachloride and characterized by elemental analysis, molar conductance, molecular weight determination and IR, ¹H and ¹³C NMR spectral techniques. The reactions of [Nb(OC₆H₄Prⁱ-2/4)₅] with divalent metal acetates M(OAc)₂ [M = Cd, Pb] in 2:1 molar ratios in hexane yielded heterometallic complexes [M₂Nb₂(OAc)₂(OC₆H₄Prⁱ-2/4)₁₀]. The characterization of heterometallic complexes has been accomplished by physicochemical and FTIR and ¹H NMR spectral studies. The acetate group seemed to act as assembling ligand. The X-ray diffraction data of [CdNb₂(OAc)₂(OC₆H₄Prⁱ-4)₁₀] has indicated to be polycrystalline over amorphous nature of parent complex [Nb(OC₆H₄Prⁱ-4)₅] suggesting thereby the transformation of non-crystalline material to crystalline. Thermal behaviour of mixed-metal acetatoaryloxides studied by TGA-DTA techniques have yielded mixed-metal oxides.

Keywords: Niobium (V) complexes; 2-/4-isopropylphenol; metal acetates; alkali metal isopropylphenoxides; spectral studies.

INTRODUCTION: In recent years much research has been focused on the chemistry of niobium because of increasing interest in the applications of niobium compounds as catalysts and in material science [1-11]. The potential applications of niobium has primarily been centered on the synthesis of mono-, di- or tri-valent metal niobates and ferro or piezo electric resonator materials viz. lead magnesium niobate (PMN) and niobium doped lead zirconate titanate (PNZT) [12-15]. There is also a great deal of interest in niobium containing non-linear optical materials viz. LiNbO₃. The formation of such materials requires metal-organic molecules with unique characteristics as precursors. In this context, the niobium complexes derived from various alcohols and substituted phenols have been of enormous importance. The metal alkoxides, oxoalkoxides, aryloxides or chloroaryloxides constitute versatile molecular precursors of metal oxides [12,16]. The nature of substituents on alkoxy or phenoxy group is known to display quite marked effects upon stereochemistry of complexes. A large number of metal phenoxides containing t-butyl, phenyl, isopropyl, methyl, methoxy, chloro, nitron groups etc. as the substituents, especially at 2-, 4- and 6- positions of the aromatic ring have been reported to study their steric and electronic effects [17-30]. It has been well-established that the phenolic ligand containing ortho substituent may undergo chelation to metal centre and the alkyl substituents in the para position exert little steric influence within the coordination sphere but can help to control

solubility and modify the properties of metal derivatives. As part of our interest in the chemistry of niobium aryloxides [31-37], we report here the synthesis and characterization of pentakis(2-/4-isopropylphenoxo) niobium(V) complexes. The reactivity of Nb(OC₆H₄Prⁱ-2/4)₅ towards lead & cadmium acetates has also been studied.

EXPERIMENTAL:

Materials and Methods: NbCl₅ (Fluka) was used without further purification and its purity was checked by chlorine analysis. 2-Isopropylphenol (Merck b.pt. 210 °C) was purified by vacuum distillation and 4-isopropylphenol was recrystallized from benzene (m.pt. 59 °C). Anhydrous metal acetates were obtained by refluxing cadmium and lead acetate hydrates with acetic anhydride for about 20 h. Solvents were made anhydrous before use by standard methods.

The niobium content in complexes was estimated as Nb₂O₅ after decomposing the complexes with a mixture of conc. H₂SO₄ and HNO₃ followed by heating at 650-700 °C. Chlorine was determined by Volhard's method. Micro-analysis for carbon and hydrogen were performed on Eager 300 NCH System Elemental Analyzer. The molar conductances (10⁻³ M solutions) of complexes in nitrobenzene were obtained at 25±0.1 °C on an Elico conductivity bridge (type CM-82T). The molecular weights were determined cryscopically in benzene (0.0015-0.0020 M) using a Beckmann thermometer. IR spectra of complexes

were recorded as (KBr pellets) on Nicolet-5700 FTIR spectrometer. ¹H and ¹³C NMR spectra were recorded on BRUKER AVANCE II 400 spectrometer using CDCl₃ as solvent. X-ray diffraction pattern of 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 sizes in continuous scanning mode at 25 °C using Cu-Kα radiation. Philips X'Pert software was used to obtain precise value of parameters. The molecular modelling calculations using Hyper-Chem 7.5 (student version) were performed to visualize the probable geometry acquired by complexes applying MM⁺ force field with Polka-Ribiere algorithm and RMS gradient 0.01 kcal/mole. The molecular dynamic simulation was done up to 1000K (relaxation time 1 ps). 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.

Synthesis of Metal Complexes:

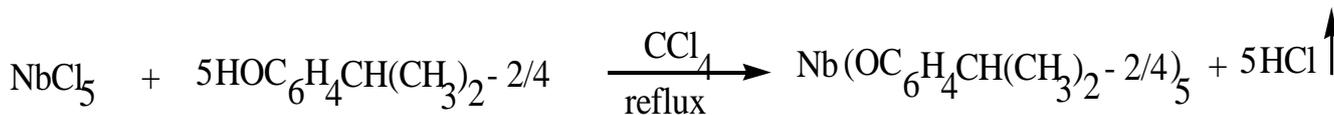
Nb(OC₆H₄Prⁱ-2)₅ (1) and Nb(OC₆H₄Prⁱ-4)₅ (2): To a suspension of niobium pentachloride (2.0 g, 0.007 mol/2.50 g, 0.009 mol) in CCl₄ (25 ml) were added five equivalents of 2-isopropylphenol (5.03 ml, 0.035 mol) and 4-isopropylphenol (6.24 g, 0.045 mol) respectively in the same solvent (25 ml). The mixing 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 till the evolution of hydrogen chloride gas ceased to ensure the completion of the reaction. No separation of any solid was observed during the course of the reaction. It was filtered and excess solvent was then removed by distillation. The concentrate was treated with petroleum ether (40-60 °C range) and was dried under vacuum

when maroon and yellow solids respectively were obtained. Anal. Calcd. for [Nb(OC₆H₄CH(CH₃)₂-2)₅] (1) (%): C, 70.31; H, 7.16; Nb, 12.11. Found: C, 70.30; H, 7.15; Nb, 12.10. Λ_m (PhNO₂): 0.37 Scm²mol⁻¹. Anal. Calcd. for [Nb(OC₆H₄CH(CH₃)₂-4)₅] (2) (%):C, 70.31; H, 7.16; Nb, 12.11. Found: C, 70.29; H, 7.17; Nb, 12.08. Λ_m (PhNO₂): 0.53 Scm²mol⁻¹. Mol wt Calcd: 768, Found: 767.5.

Synthesis of CdNb₂(OAc)₂(OC₆H₄CH(CH₃)₂-2/-4)₁₀ and PbNb₂(OAc)₂(OC₆H₄CH(CH₃)₂-2/-4)₁₀: In a typical reaction, anhydrous Cd(OAc)₂ (0.5 g, 0.002 mol) was added to a solution of Nb(OC₆H₄CH(CH₃)₂-2/4)₅ (3.3 g, 0.004 mol) in hexane (25 ml) at room temperature. The reaction mixture was stirred for 8 to 10 h at room temperature, whereupon colour change was observed. The resulting solid so obtained was repeatedly treated with petroleum ether and dried under vacuo. The purity of the compounds was checked by elemental analysis. The other mixed-metal acetatoaryloxide were obtained by the same procedure.

Anal. Calcd. for [PbNb₂(OAc)₂(OC₆H₄CH(CH₃)₂-2)₁₀] (%): C, 53.80; H, 5.58; Nb, 8.51. Found: C, 53.79; H, 5.55; Nb, 8.50. Λ_m (PhNO₂): 0.28 Scm²mol⁻¹. Anal. Calcd. for [CdNb₂(OAc)₂(OC₆H₄CH(CH₃)₂-2)₁₀] (%):C, 58.92; H, 6.11; Nb, 9.32. Found: C, 58.91; H, 6.10; Nb, 9.30. Λ_m (PhNO₂): 0.25 Scm²mol⁻¹. Anal. Calcd. for [PbNb₂(OAc)₂(OC₆H₄CH(CH₃)₂-4)₁₀] (%): C, 53.80; H, 5.58; Nb, 8.51. Found: C, 53.77; H, 5.57; Nb, 8.52. Λ_m (PhNO₂): 0.44 Scm²mol⁻¹. Anal. Calcd. for [CdNb₂(OAc)₂(OC₆H₄CH(CH₃)₂-4)₁₀] (%):C, 58.92; H, 6.11; Nb, 9.32. Found: C, 58.90; H, 6.13; Nb, 9.28. Λ_m (PhNO₂): 0.38 Scm²mol⁻¹.

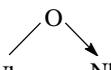
RESULTS AND DISCUSSION: The NbCl₅ reacts with five equivalents of 2-/4-isopropylphenols in carbon tetrachloride under reflux to afford the formation of pentakis(2-/4-isopropylphenoxo)niobium(V) complexes according to the equation:



The micro analytical data of the complexes are consistent with their stoichiometric formulations. The complexes are moisture sensitive, brown to orange solids and are sparingly soluble in CHCl₃, C₆H₆ and C₆H₅NO₂. The molar conductance values of 1 and 2 in nitrobenzene indicated these to be non-electrolytes [38]. The cryoscopic molecular weight determination of the complexes in benzene suggested these to be dimers in this solvent.

Infrared spectra: A comparison of IR spectra of complexes with that of respective free 2- and 4-isopropylphenols substantiated their formation. The broad band occurring at 3431 cm⁻¹ in 2-isopropylphenol and at 3313 cm⁻¹ in 4-isopropylphenol due to intermolecular hydrogen bonded -OH group was absent in complexes suggesting thereby deprotonation of the phenolic proton upon complexation. The bands appeared in 1364-1236 cm⁻¹ and 1362-1221 cm⁻¹ regions [39,40] ascribed to ν(C-O) mode in free 2- and 4-

isopropylphenol respectively appeared in 1380-1253 cm⁻¹ and 1383-1258 cm⁻¹ regions in 1 and 2 respectively, diagnostic of ν(C–O–Nb) mode are suggestive of Nb←OAr π bonding in these complexes. The appearance of bands in 590-580 cm⁻¹ and 550-520 cm⁻¹



regions assigned to ν(Nb–O) and Nb–O–Nb mode respectively indicated their dimeric nature in agreement with previous reports on niobium alkoxides and phenoxides [41].

¹H NMR spectra: A comparison of ¹H NMR spectra of complexes with that of respective free 2- and 4-isopropylphenol showed that the complexes did not display signal due to phenolic –OH proton occurring at δ 5.42 ppm and at δ 4.91 ppm in respective phenols suggesting thereby the deprotonation on complexation. The uncoordinated 2-isopropylphenol exhibited two doublets centered at δ 6.85 and δ 7.37 ppm due to H – 6 and H – 3 respectively and two triplets appeared at δ 7.08 and δ 7.20 ppm ascribed to H – 5 and H – 4 respectively. The resonances due to methine and methyl substituents appeared as heptet and doublet at δ 3.39 and δ 1.42 ppm respectively. The 4-isopropylphenol is reported to display respective signals due to aromatic ring protons and aliphatic methine and methyl protons at δ 6.75, δ 7.23 and at δ 3.20 and δ 1.24 respectively.

Complex of composition Nb(OC₆H₄CH(CH₃)₂-2)₅ showed two distinct doublets centered at δ 7.24 ppm and δ 6.76 ppm due to aromatic protons at position 3 and 6 respectively and two triplets at δ 7.09 and δ 6.94 ppm due to aromatic protons at position 5 and 4 respectively. The Nb(OC₆H₄CH(CH₃)₂-4)₅ exhibited signals due to ortho (H - 2 and H - 6) and meta (H - 3 and H - 5) aromatic protons in δ 6.86- 7.36 ppm range. The downfield shifts 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 the metal atom as (ArO --- Nb) [41,42]. The proton resonances due to methine and methyl groups remained almost unaltered upon complexation (Table 1). The integration of protons supported the formation of complexes (Fig. 2 and Fig. 3).

¹³C NMR spectra: The ¹³C NMR spectra of Nb(OC₆H₄CH(CH₃)₂-2)₅ (1) and Nb(OC₆H₄CH(CH₃)₂-4)₅ (2) showed signals at δ 154.57 ppm and δ 155.61 ppm respectively shifted

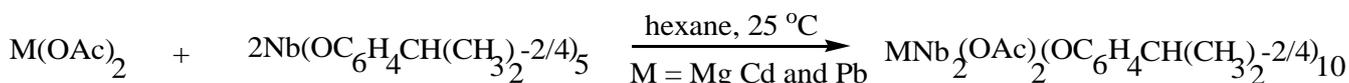
downfield by δ 1.43 ppm and δ 1.11 ppm in respective complexes relative to this signal occurring at δ 153.14 and δ 154.50 ppm in 2- and 4-isopropylphenol respectively. The observed downfield shifts are indicative of stronger bonding of 4-isopropylphenoxy group than 2-isopropylphenoxy group. The other carbon resonances showed a moderate shift upon complexation viz C-2, C-3, C-5 and C-6 in (1) shifted upfield by δ 0.52, δ 0.88, δ 0.99 and δ .801 ppm (Fig. 4 and Fig. 5) relative to free phenols. The carbon resonances due to C - 4 showed downfield shifts by δ 2.38. The carbon resonances due to methine and methyl groups showed slight shifts (Table 2).

X-ray Diffraction Studies: The X-ray diffraction pattern of Nb(OC₆H₄CH(CH₃)₂-4)₅ (2) has recorded only two reflections of 2θ ranging at 25° and 50° suggesting its amorphous nature (Figure 6).

Molecular modeling: The structures of complexes inferred from spectroscopic studies have further been substantiated from molecular modelling studies. The initial strained structure related to the most probable geometry of each metal complex was drawn and 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 physicochemical and IR, ¹H and ¹³C-NMR spectral studies, an octahedral geometry around niobium has tentatively been proposed (Fig. 7).

Reactions of [Nb(OC₆H₄CH(CH₃)₂-2)₅] (1) and [Nb(OC₆H₄CH(CH₃)₂-4)₅] (2) with divalent metal acetates M(OAc)₂ [M = Cd, Pb]: The reactions between [Nb(OC₆H₄CH(CH₃)₂-2/4)₅] and anhydrous metal acetates M(OAc)₂ (M = Cd, Pb) in hexane at room temperature afforded the formation of heterometallic acetatoaryloxides in terms of the following equation:

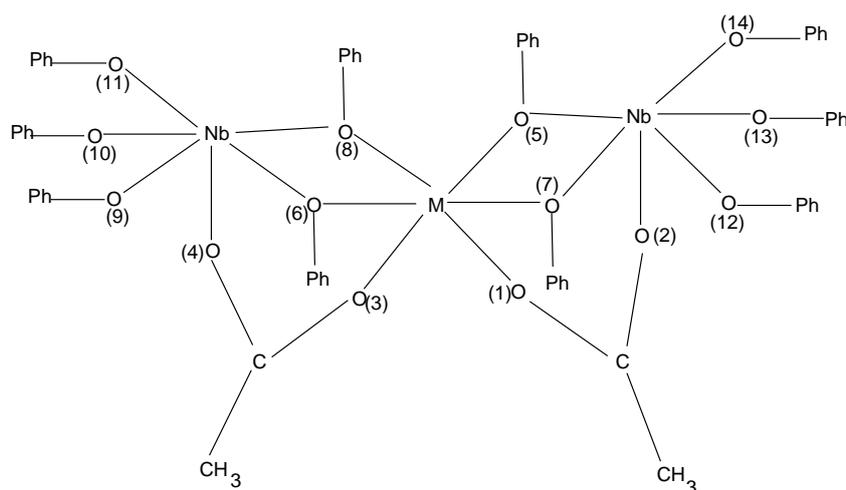


The stoichiometric composition of the isolated compounds has been established by elemental analysis. The compounds are moisture sensitive solids but are quite stable in dry air. The compounds are appreciably soluble in benzene, nitrobenzene and chloroform. The molar conductance values of the millimolar solutions of compounds in nitrobenzene are too low to be attributed to their behaviour as 1:1 electrolyte.

Infrared spectra: A comparison of the IR spectra of heterometal acetatoaryloxides with that of respective free metal acetates and parent complexes substantiated their formation. The bands characteristic of $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ vibrations of the acetate ligand have been observed to occur at 1544 and 1414 cm^{-1} respectively in $\text{PbNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2/4})_{10}$ while these modes appeared at ~ 1565 and 1422 cm^{-1} in $\text{CdNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2/4})_{10}$, shifted to higher wave numbers relative to free acetates. The occurrence of these bands has excluded the possibility of formation of mixed compounds of type $\text{M}(\text{OAc})_2.2\text{Nb}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2/4})_5$ and a chelating or bridging-chelating behaviour for the OAc ligand [43] has been indicated.

$^1\text{H-NMR}$ Spectra: The ^1H NMR spectra of mixed-metal acetatoaryloxides, displayed a diagnostic peak due to acetate ligand at $\delta 1.88$ ppm relative to that occurring at $\delta 2.02$ ppm in $\text{Cd}(\text{OAc})_2$ and $\text{Pb}(\text{OAc})_2$. The signal due to methyl protons of isopropyl substituent has been found to shift slightly upfield and appeared in $\delta 1.15$ – 1.21 ppm range in mixed-metal acetatoaryloxides relative to that occurring in $\delta 1.20$ – 1.30 ppm range in parent complexes (Table 1). The signal due to $-\text{CH}$ group appeared at almost same positions in mixed-metal complexes as in parent complexes (Figures 8-11).

Thus, based upon IR and ^1H NMR spectral data for $[\text{CdNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2})_{10}]$ (I), $[\text{PbNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2})_{10}]$ (II), $[\text{CdNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-4})_{10}]$ (III) and $[\text{PbNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-4})_{10}]$ (IV) and reported molecular structures of $[\text{CdNb}_2(\text{OAc})_2(\mu\text{-OCH}(\text{CH}_3)_2)_4(\text{OCH}(\text{CH}_3)_2)_6]$ and $[\text{PbNb}_2(\text{OAc})_2(\mu\text{-OCH}(\text{CH}_3)_2)_4(\text{OCH}(\text{CH}_3)_2)_6]$ the following structure may tentatively be proposed.



(where OPh = $\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2/4}$ and $\text{M} = \text{Cd}, \text{Pb}$)

These trinuclear species display a bent, open-shell structure (Nb–M–Nb) with alternating Nb and M atoms, all being six-coordinate.

Thermal Studies: The TG curve of $\text{Nb}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-4})_5$ has depicted it to be thermally stable upto 30.06°C . The weight loss of 80.53% in complex against theoretical 82.68% has accounted for the formation of Nb_2O_5 as the ultimate residue. The DTA curve has shown an endothermic peak and an exothermic peak at 185.56°C and 358.10°C respectively. The TG curves of $[\text{CdNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-4})_{10}]$ and

$[\text{PbNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2})_{10}]$ have shown these to be thermally stable upto 72.25°C and 65.53°C respectively. The weight loss of 78.53% and 74.82% in respective complexes have been found to correspond to the formation of CdNb_2O_6 and PbNb_2O_6 respectively.

X-ray Diffraction Studies: The XRD pattern of complex $[\text{CdNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_{2-2})_{10}]$ however, revealed both high and low intense peaks (Fig. 12). The indexing of XRD peaks suggested polycrystalline nature of the complex (Table 3).

CONCLUSIONS: The spectroscopic studies of newly synthesized niobium(V) complexes of composition $[\text{Nb}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2\text{-}2/4)_5]$ suggested dimeric structure involving bridging through 2-/4-isopropylphenoxy groups. X-ray diffraction studies showed amorphous and polycrystalline nature of $[\text{Nb}(\text{OC}_6\text{H}_4\text{CH}(\text{CH}_3)_2\text{-}2/4)_5]$ and $[\text{CdNb}_2(\text{OAc})_2(\text{OC}_6\text{H}_4\text{Pr}^i\text{-}4)_{10}]$ respectively. The newly synthesized heterometallic aryloxides from the reactions of $\text{Nb}(\text{OC}_6\text{H}_4\text{Pr}^i\text{-}2/4)_5$ with divalent metal acetates $\text{M}(\text{OAc})_2$ [$\text{M} = \text{Cd}, \text{Pb}$] can be employed as suitable molecular precursors to obtain CdNb_2O_6 and PbNb_2O_6 powders as revealed from their TG and DTA studies. The formation of these heterometallic oxides has also been supported from the complimentary IR spectral technique.

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