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Reactivity of Niobium(V) Complex Towards Hydroxamate Ligands

Mala Sharma[1,*], Kumari Bandna[2]

Abstract

A niobium(V) complex with the composition [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$] was synthesized by reacting niobium pentachloride with four equivalents of 2-isopropylphenol in carbon tetrachloride as a solvent, yielding the product in good quantity. The complex was characterized using elemental analysis, molar conductance measurements, IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. Spectroscopic results indicate that the complex exists in a dimeric form, with bridging occurring through isopropylphenoxo ligands. X-ray diffraction analysis suggests that the complexes are amorphous in nature. The methanolic solution of the synthesized complex, monochlorotetrakis(2-isopropylphenoxo)niobium(V), [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$], reacts with equimolar amounts of potassium benzohydroxamate and p-chlorobenzohydroxamate in benzene to form mixed-ligand phenoxo-hydroxamato niobium(V) complexes. These products were confirmed through physicochemical studies along with IR and ^{1}H NMR spectral analyses. The spectral evidence indicates that potassium benzohydroxamate and p-chlorobenzohydroxamate effectively cleave the isopropylphenoxo bridging bonds, resulting in the formation of monomeric (unimolecular) complexes.

Keyword: Niobium(v), 2-isopropylphenoxide, potassium benzohydroxamate, p-chlorobenzohydroxamate, coordination compounds, spectroscopic studies

INTRODUCTION

Niobium alkoxides and aryloxides have attracted significant research interest due to their diverse structural geometries, catalytic potential, and applications in the synthesis of oxides and mixed metal oxides in materials science [1–5]. Among various ligands capable of forming coordination complexes, hydroxamic acids – both natural and synthetic – are particularly important as biologically relevant ligands [6]. Their chemical and biological significance has led to extensive research and the synthesis of numerous hydroxamic derivatives [7, 8]. Hydroxamic acids are well known for their ability to inhibit proteolytic enzymes such as thermolysin, elastase, and aminopeptidases [9]. These enzymes belong to the metalloproteinase family, and inhibition occurs mainly through chelation of metal ions at the active site, thereby reducing catalytic activity [10]. In addition, hydroxamic acids exhibit a wide range of biological and pharmacological properties, including antibacterial, antifungal, antimicrobial, antimalarial, antitumor, anticancer, and antitubercular activities. They also show therapeutic potential in treating cardiovascular diseases and iron overload disorders [11, 12].

Structurally, hydroxamic acids are notable for their keto–enol tautomerism and E–Z conformational isomerism [13]. As derivatives of both hydroxylamine and carboxylic acids, they can exist in two forms: the N-acyl form and the O-acyl form.

***Author for Correspondence**
Mala Sharma
E-mail: sharmamala1411@gmail.com

[1]Assistant Professor, Department of Chemistry, Sidharth Govt. Utkrisht College Nadaun, Hamirpur, Himachal Pradesh, India
[2]Assistant Professor, Department of Chemistry, Govt. College Nalagarh, Solan, Himachal Pradesh, India

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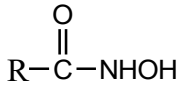

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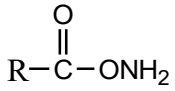
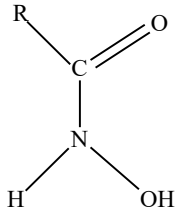


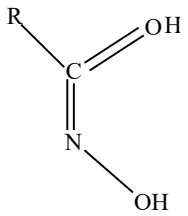
(II)

Among the two possible forms, the N-acyl form is more commonly observed. Substantial evidence supports the presence of tautomeric forms in monohydroxamic acids, which exist as keto (hydroxamic) and enol (hydroximic) forms. This keto–enol tautomerism offers multiple coordination sites, enabling effective chelation with metal ions. Furthermore, when rotation about the C-N bond is restricted, the keto form can exist in both Z and E geometrical isomers.

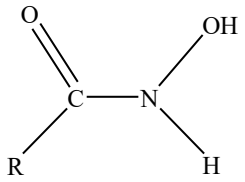
Based on these considerations, the reactivity of the complex $[NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4]$ was investigated in the presence of potassium benzohydroxamate and potassium 4-chlorobenzohydroxamate, designated as KHL_1 and KHL_2, respectively.



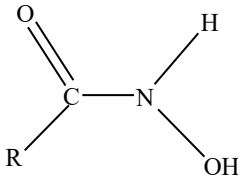
Keto form of Hydroxamic form



Enol form of Hydroximic form



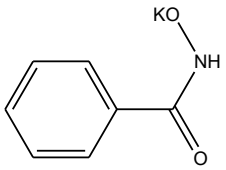
Z



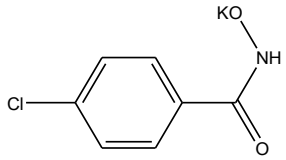
E

Hydroxamic Acids

(a) Potassium benzohydroxamate, (KHL1)



(b) Potassium 4-chlorobenzohydroxamate, (KHL2)



EXPERIMENTAL

Materials and Physical Measurements

Niobium pentachloride ($NbCl_5$, Fluka) was used without further purification, and its purity was verified through chlorine analysis. 2-Isopropylphenol (Merck, boiling point 210 °C) was purified by vacuum distillation prior to use. All solvents were dried using standard procedures to ensure anhydrous conditions.

The niobium content in the complexes was determined as Nb_2O_5 after decomposition with a mixture of concentrated H_2SO_4 and HNO_3, followed by heating at 650–700 °C. Chlorine content was estimated using Volhard's method. Carbon and hydrogen analyses were carried out using an Eager 300 NCH elemental analyzer.

Molar conductance measurements (10^{-3} M solutions) in nitrobenzene were recorded at 25 ± 0.1 °C using an Elico conductivity bridge (model CM-82T). Molecular weights were determined cryoscopically in benzene (0.0015–0.0020 M) with the help of a Beckmann thermometer.

Infrared (IR) spectra were recorded as KBr pellets on a Nicolet-5700 FTIR spectrophotometer. Proton (^{1}H) NMR spectra were obtained using a BRUKER AVANCE II 400 MHz spectrometer with $CDCl_3$ as the solvent.

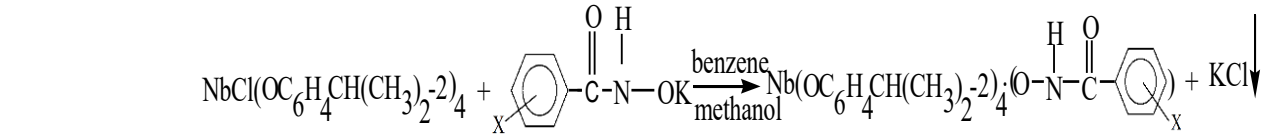
Synthesis of [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$]

A solution of $NbCl_5$ in dry carbon tetrachloride was stirred, and a stoichiometric amount of 2-isopropylphenol was added dropwise under reflux conditions. The reaction mixture was refluxed for an appropriate time until completion. The solvent was then removed under reduced pressure to concentrate the solution, leading to the isolation of the product as a solid. The complex [NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$] was obtained in quantitative yield. The product was washed with a dry solvent and subsequently dried under vacuum [14].

RESULTS AND DISCUSSION

Reactions with Hydroxamic Acids

Potassium benzohydroxamate and p-chlorobenzohydroxamate in benzene interacted with the methanolic solution of the parent complex to generate solids whose elemental analysis suggested its formulation using the following equation:



(where X = H and 4-Cl)

The dark brown, moisture-sensitive mixed-ligand phenoxohydroxamato niobium(V) complexes are stable at room temperature in the absence of moisture. The complexes are soluble in polar solvents, and their non-electrolytic nature was demonstrated by the molar conductance values of their millimolar solutions in nitrobenzene.

IR Spectra

The creation of the mixed-ligand complexes was indicated by comparing their infrared spectra with those of the parent niobium(V) complexes and uncoordinated hydroxamate ions. Its distinctive and powerful metal coordination is due to the presence of three distinct donor sites: hydroxylamine oxygen, carbonyl oxygen, and nitrogen, as well as the delocalization of a double bond inside the hydroxamic group. The characteristic bands of the hydroxamic group, which may undergo a significant change on complexation, are due to υ(C=O), υ(C–N), υ(N–O), and υ(N–H) modes. The absorption bands occurring in the 1610–1585 cm^{-1} region due to υ(C=O) mode in free hydroxamate ligands have been reported to shift to lower wavenumbers by 40–60 cm^{-1} upon coordination by ketonic oxygen to metal, which is accompanied by a small shift in the υ(C–N) mode occurring in the 1370–1310 cm^{-1} region. The bonding through hydroxylamine oxygen is reported to result in a shift of the υ(N–O) mode occurring in the 945–910 cm^{-1} region in free hydroxamate ions to higher wavenumber in complexes. The bands due to υ(N–H) and NH deformations are known to occur at ~3200 cm^{-1}, 3080–3060 cm^{-1}, and 1440–1400 cm^{-1} regions in uncoordinated hydroxamate ligands.

The free potassium benzohydroxamate and potassium 4-chlorobenzohydroxamate exhibited absorption bands in the 1686–1570 cm^{-1} region due to υ(C=O) mode. The observance of sharp absorption bands due to υ(C=O) mode in the 1658–1597 cm^{-1} region in complexes derived from benzohydroxamate derivatives (KHL1 and KHL2) suggested bonding through carbonyl oxygen to niobium.

The absorption band due to υ(C–N) mode occurring in the 1378–1370 cm^{-1} region in free ligands appeared in the 1379–1363 cm^{-1} region in newly synthesized complexes. The absorption bands occurring in the 3249–3192 cm^{-1} region due to υ(N–H) mode in complexes suggested that the –NH group is retained and coordination through nitrogen atom is excluded. The υ(N–O) mode in KHL1 and KHL2 observed at ~ 923 cm^{-1} is found to appear at ~ 969 cm^{-1} in complexes, indicating bonding through the oxygen atom of the –NHO group [13] (Table 1).

Table 1. 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})
$C_6H_5C(O)NHOK$ (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 HL1 = ion of potassium benzohydroxamate and HL2 = ion of potassium 4-chlorobenzohydroxamate

Apart from these significant changes, the bands due to υ(C–O) phenolic and υ(Nb–O) modes in the 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 1.

1H NMR Spectra

A comparison of 1H NMR spectra of mixed-ligand complexes with that of uncoordinated benzohydroxamate ligands further supported their formation.

The 1H NMR spectra of potassium benzohydroxamate (KHL1) 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 (KHL2) 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 $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4 \cdot HL1]$ and $[Nb(OC_6H_4CH(CH_3)_2\text{-}2)_4 \cdot HL2]$ showed distinct proton resonances due to aromatic protons of the 2-isopropylphenoxy ligand and benzohydroxamate/4-Cl-benzohydroxamate ligands. The signals due to the former aromatic protons appeared in δ 6.70–7.10 ppm range in both complexes. The resonances due to aromatic protons of the ligands occurred in δ 7.42–7.86 ppm and δ 7.37–7.82 ppm range in the 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 the respective complexes (Figure 1, 2).

These observations suggested bonding through hydroxylamine oxygen and that –NH is retained in complexes (Table 2).

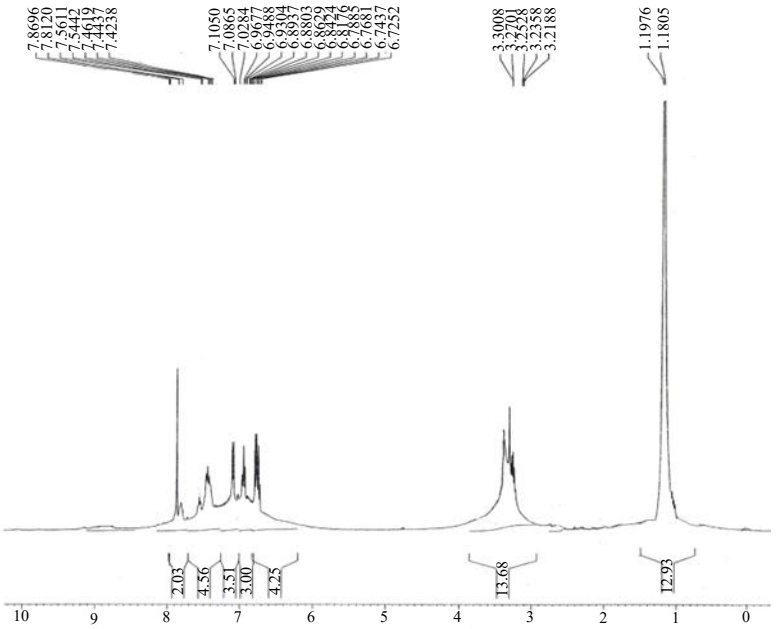


Figure 1. ^{1}H NMR spectrum of Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$·HL1.

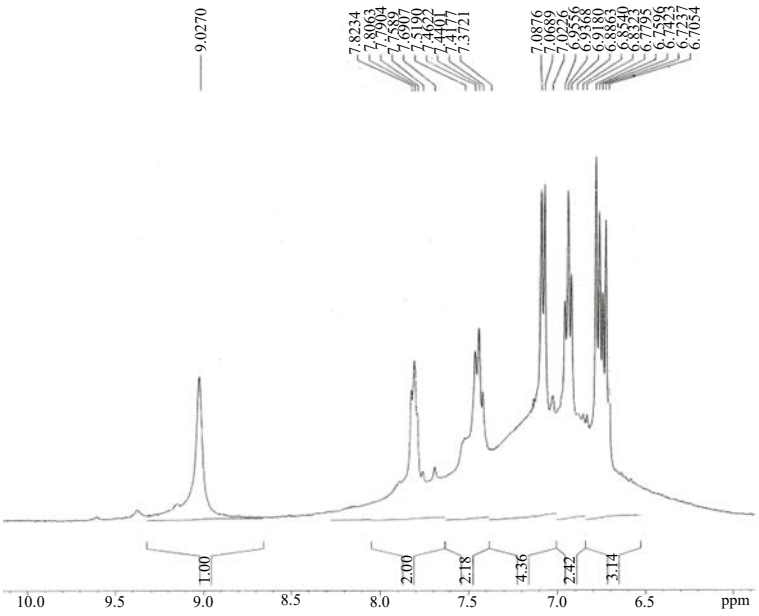


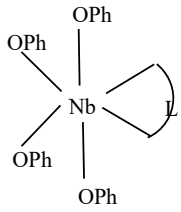
Figure 2. ^{1}H NMR spectrum of Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$·HL2.

Table 2. 1H-NMR data of reaction products of NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$ with hydroxamate ligands (ppm)

Complex	**Substituent (isopropyl protons)**		**Aromatic phenolic ring protons**	**(Ligands)**	
	-(CH$_3$)$_2$	*-CH*		*-C$_6$H$_5$*	*-NH*
NbCl(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$	1.20	3.26-3.37	6.77-7.14	---	---
Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$.HL^1	1.18-1.19	3.21-3.30	6.72-7.10	7.42-7.86	8.83
Nb(OC$_6$H$_4$CH(CH$_3$)$_2$-2)$_4$.HL^2	1.16-1.18	3.19-3.24	6.70-7.08	7.37-7.82	9.02

where HL1 = ion of potassium benzohydroxamate and HL2 = ion of potassium 4-chlorobenzohydroxamate

A deformed octahedral geometry around niobium in complexes derived from hydroxamate ligands may be tentatively assumed based on IR and 1H NMR spectrum data combined with physicochemical studies.



(where OPh = $OC_6H_4CH(CH_3)_2$-2 and L = ion of potassium benzohydroxamate/potassium 4-chlorobenzohydroxamate)

CONCLUSION

The spectroscopic studies of the newly synthesized niobium(V) complex suggest a dimeric structure formed through bridging by the 2-isopropylphenoxo group. The reaction of $NbCl(OC_6H_4CH(CH_3)_2\text{-}2)_4$ with chelating ligands such as potassium benzohydroxamate and p-chlorobenzohydroxamate results in the formation of mononuclear 1: 1 coordination complexes. It has been suggested that the niobium center in these compounds has a deformed octahedral shape based on IR and ^1H NMR spectrum data and physicochemical studies.

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