

Synthesis and characterization of hexa, hepta and octa-coordinated Nb(V) complexes of N,N'-(substituted)-formamidino-N'-(substituted) carbamides and thiocarbamides

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Abstract. The non-electrolytic compounds of composition $MCl_n(ON_p)_{5-n}$ have been prepared by digesting the niobium pentachloride with β -naphthol in an appropriate molar ratio in carbon tetrachloride. The hexa-, hepta- and octa-coordinated derivatives of Nb(V) have been isolated by reacting Nb $(ON_p)_5$ with N,N'-diarylformamidino-N'-arylcaramides, thiocarbamides and N-benzoylformamidino-N'-arylcaramides and thiocarbamides, of the general formula Nb $(ON_p)_4(L)$; Nb $(ON_p)_3(L)_2$ and Nb $(ON_p)_2(L)_3$; (L = a molecule of bidentate ligand).

Keywords. Nb(V) naphthoxides; niobium pentachloride; carbamides, thiocarbamides

1. Introduction

Complexes of the type $NbCl_5L$ are known for L = acetophenone (Djordjevic and Katovic 1970) and 2,2-bipyridyl (Fowles and Gadd 1970). The carbonyl frequency was lower in complexes indicating the coordination through oxygen of acetophenone and benzophenone. Compared to alkoxides, very little work has been carried out on the synthesis of compounds of phenoxides and naphthoxides inspite of their utility as catalysts in many industries (Malhotra *et al* 1982; Taniguchi and Arakawa 1971). Two series of compounds of anhydrous aluminium chloride were isolated with β -naphthol (Prasad and Upadhyay 1959). Halides of titanium (IV) are known to react with phenols and naphthols to form the corresponding derivatives (Emeleus and Rao 1958) but their structural information is lacking. Naphthoxides of beryllium (II) and tungsten (V) have been isolated by reacting their halides with β -naphthol (Turova *et al* 1959).

Earlier papers have reported the complexes of Mo(V) (Srivastava and Madhok 1978a), Fe(III) (Madhok and Srivastava 1980), Ni(II) (Madhok 1982) and Mo(VI) (Srivastava and Madhok 1978b) with NO and SO donors. The present paper describes the physico-chemical studies of Nb(V) naphthoxides and their compounds with N,N'-diarylformamidino-N'-arylcaramides, thiocarbamides and N-benzoyl formamidino-N'-arylcaramides and thiocarbamides and possible structures of hexa, hepta and octa-coordinated Nb(V) complexes have been proposed.

2. Experimental

All the chemicals used were either BDH 'AnalaR' quality of E Merck G R reagent. All the

solvents were dried by appropriate drying agent and fractional distillation. NbCl_5 was Fluka, analytical grade and was used without further purification.

2.1 Preparation of Nb(V) naphthoxides

Naphthoxides of composition $\text{NbCl}_4(\text{ON}_p)$, $\text{NbCl}_3(\text{ON}_p)_2$ and $\text{NbCl}_2(\text{ON}_p)_3$, where ON_p stands for the anion of β -naphthol, were obtained by adding β -naphthol to NbCl_5 in 1:1, 2:1 and 3:1 ratio in CCl_4 with constant stirring till there was no evolution of HCl gas. The preparation of the compounds of composition $\text{NbCl}(\text{ON}_p)_4$ and $\text{Nb}(\text{ON}_p)_5$ required slow heating (not more than 70°). Slight excess of N_pOH was added beyond 1:5 ratio to ensure complete reaction. The compounds so prepared were filtered washed with benzene and finally dried under vacuum. Niobium was estimated as Nb_2O_5 and chlorine by Volhard's method.

2.2 Preparation of N -substituted-formamidino- N' -substituted-carbamides and thiocarbamides

The ligands N,N' -diphenylformamidino- N'' -phenylcarbamide (DPFPC), N,N' -diphenylformamidino- N'' -phenylthiocarbamide (DPFPTC), N,N' -diphenylformamidino- N'' -orthotolylthiocarbamide (DPF \cdot oTTC), N,N' -diphenylformamidino- N'' -paratolylthiocarbamide (DPF \cdot pTTC), N -benzoylformamidino- N' -phenylcarbamide (BFPC), N -benzoylformamidino- N' -phenylthiocarbamide (BFPTC), N -benzoylformamidino- N' -orthotolylthiocarbamide (BF \cdot oTTC), and N -benzoylformamidino- N' -paratolylthiocarbamide (BF \cdot pTTC) were prepared and purified as described earlier (Madhok 1982).

2.3 Reaction of $\text{Nb}(\text{ON}_p)_5$ with the title ligands

To a weighed amount of $\text{Nb}(\text{ON}_p)_5$ dissolved in 50 ml of dry anhydrous benzene, calculated amount of ligand was swiftly added. The contents was refluxed in a fractionating column for 10–15 hr and the progress of the reaction ascertained by estimating the β -naphthol and excess of ligand (Bradley *et al* 1950), a modification of the one developed by Adams and Nicholls (1919). The excess solvent was pumped out and dried under vacuum for 4 hr at 30 – 50°C . The melting points of the coloured complexes of Nb(V) so obtained were determined in an open capillary tube on a Unimelt temperature apparatus and are uncorrected.

IR spectra of the complexes were recorded on a double grating infrared spectrophotometer (Perkin Elmer 237B and 621) in KBr pellets. Molar conductance of the complex compounds was determined in freshly distilled dimethylformamide and nitrobenzene at a concentration of about 10^{-3} M, with conductivity meter (type LBR of Wassenschaftlich Technisch, Werkstatin, Germany) using dip type cell.

The magnetic measurements of the compounds were made on a Guoy's magnetic balance at room temperature (30°C) by applying a field strength of about 4.5×10^3 G.

Thermogravimetry was analysed on Perkin Elmer TGS-2 model attached with UU-1 temperature programmer autobalance coupled with weight suppression assembly AR-2 recording balance and first derivative computer FDC-1, and a second generation system. A heating rate of $5^\circ\text{C}/\text{min}$ was employed for all the runs. Absorption spectra of Nb(V) complexes were measured by the standard method using Perkin Elmer UV-visible spectrophotometer model 139 in appropriate solvent.

3. Results and discussions

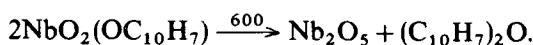
3.1 Nb(V) naphthoxides

The reaction of NbCl₅ with β-naphthol in CCl₄ was slow but became facile on digestion. All attempts to isolate a solvate of β-naphthol with niobium pentachloride, at room temperature were unsuccessful, possibly because of the greater lability of the proton of β-naphthol. Niobium gave dull orange crystals. Stoichiometric composition of these compounds was established by elemental analysis and the results reported in table 1. All these compounds are moisture sensitive but are sufficiently stable in dry air. Compounds are insoluble in most organic solvents except slightly in benzene, nitrobenzene and dimethylformamide.

Low values of molar conductance in 10⁻³ M nitrobenzene solution suggest that the compounds are non-ionic in nature. The negative values of magnetic susceptibilities (-0.182 to -0.232 × 10⁻⁵) suggest that the compounds are diamagnetic suggesting thereby that there is no further reduction of metal to the lower oxidation state.

The composition of the complexes suggested on the basis of their analytical data is further confirmed by their infrared vibrational frequencies. In molecules like β-naphthol the intensity of hydrogen bonded phenolic-hydroxyl group ν(O-H) at 3400 cm⁻¹ is missing in the complexes indicating the absence of phenolic hydroxyl group. This is supported by the observation that hydrogen chloride gas was liberated during the course of their preparation. There is no change in the position and intensity of ν(C-H) band (3075 cm⁻¹) in β-naphthol and complexes. A shift to lower spectral region in the (C-O) stretching mode of β-naphthol (45 cm⁻¹) on complexation is attributed to the drainage of electrons from the ring to the metal through C-O bond (Szymanski 1964). Intense band around 570-580 cm⁻¹ in niobium compounds may be assigned to IR active terminal (M-O) stretching modes (Barraclough 1959 and Clark 1965). A sharp intense band at 340 cm⁻¹ is assigned to ν(Nb-Cl) vibrations and is in agreement with the assignment by Djordjevic (1965) for the ν(Nb-Cl) vibrations and for similar octahedral complexes by others (Adams *et al* 1963).

The relative strength of bonds in niobium naphthoxides and the mode of decomposition have been inferred from the weight changes noted from thermograms. In the compound NbCl₄(ON_p)₄ a molecule of chloronaphthalein is lost at 160° leaving behind niobium oxytrichloride which decomposes further at about 270°C, followed by subsequent disproportionation to the pentoxide and pentachloride (Fairbrother 1967) at about 600°C. In fully substituted naphthoxide Nb(ON_p)₅, the major intermediate products are dinaphthyl ether and niobiumoxytrinaphthoxides as shown below:



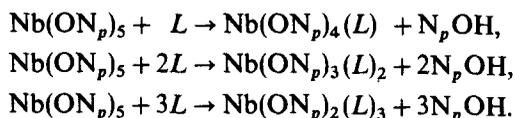
The final product in all the naphthoxides was Nb₂O₅. Formation of these intermediates is supported by earlier reports on the mode of decomposition of alkali metal (Fischer 1919) and transition metal phenoxides (Malhotra *et al* 1982). It can thus be concluded that these naphthoxides have sufficient thermal stability.

Table 1. Analytical data and principal IR bands (cm^{-1}) of the isolated niobium naphthoxides.

Compound	Colour	Nb	% Found (reqd)				IR absorption bands					
			Cl	C	H	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$	$\nu(\text{C-H})$		
N_pOH	—	—	—	—	—	—	3400	1260	—	—	—	3075
$\text{Nb}(\text{ON}_p)_5$	Red	11.0 (11.5)	—	76.0 (74.53)	4.4 (4.34)	—	—	1195	535, 575	—	—	3074
$\text{NbCl}(\text{ON}_p)_4$	Brick red	12.9 (13.32)	4.9 (5.07)	69.0 (68.5)	3.86 (3.9)	—	—	1215	545, 578	348	—	3075
$\text{NbCl}_2(\text{ON}_p)_3$	Deep orange	14.82 (15.7)	11.56 (12.0)	60.0 (60.71)	3.62 (3.54)	—	—	1210	547, 572	352	—	3075
$\text{NbCl}_3(\text{ON}_p)_2$	Orange	18.5 (19.15)	22.2 (21.97)	49.18 (49.4)	2.9 (2.88)	—	—	1200	542, 567	349	—	3076
$\text{NbCl}_4(\text{ON}_p)$	Orange	25.0 (24.14)	36.85 (37.05)	31.5 (31.7)	1.9 (1.85)	—	—	1205	540	340	—	3075

3.2 Niobium (V) complexes

The reaction of $\text{Nb}(\text{ON}_p)_5$ with N,N'-diarylformamidino-N''-arylcarbamides, thiocarbamides and N-benzoylformamidino-N'-arylcarbamides and thiocarbamides, in 1:1, 1:2, 1:3 molar ratios, in anhydrous benzene have resulted in the formation of products as shown below:



where L stands for bidentate ligand. These reactions are quite facile and comparatively the reaction rate of the thiocarbamides is faster to that of the corresponding carbamides due to thioenolization in the thiocarbamides.

All the resulting complexes are coloured solids, mostly insoluble in all common organic solvents, except in benzene, chloroform DMF and DMSO. The analytical data are represented in table 2. The 1:4 reaction was also attempted but even on prolonged refluxing, only three molecules of ligands could react. The excess of ligand was washed quantitatively with ethanol and recrystallized for estimation. After washing and drying the stoichiometry of the Nb derivative obtained is 1:3. The resulting derivatives are moisture sensitive, coloured solids.

Cryoscopic determination of molecular weights in benzene shows the monomeric nature of these derivatives.

The molar conductance values of the complexes in dry DMF are below $12 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating their nonelectrolytic nature. The negative values of magnetic susceptibility (-0.50 to -0.62×10^{-5}) suggest that the complexes are diamagnetic.

The UV and visible spectra of DAFATC, DAFAC, BFATC and BFAC show three bands at 240, 290 and 395 nm, probably due to $\phi - \phi^*$ (benzenoid) and $\pi - \pi^*$ and $n - \pi^*$ electronic transitions within the thiocarbamide and carbamide groupings. The blue shift of 35–42 nm in the last two bands in the metal complexes is due to the coordination of nitrogen and sulphur to the metal atom (Ahmed and Mandal 1967).

On an examination of infrared spectra of ligands and their metal chelates it can be seen that these ligands exhibit a C=O stretching band of medium intensity in the region $1698-1735 \text{ cm}^{-1}$ which is observed to be stronger than the usual keton C=O band (Scheinmann 1970). On chelation with the metal the carbonyl absorption frequency is shifted to lower value ($15-20 \text{ cm}^{-1}$) with comparatively weak intensities. As there is almost no change in the benzoic carbonyl frequency on complexation, the benzoic C=O group cannot be considered as a site for coordination. A peak at $1400-1485 \text{ cm}^{-1}$ is due to mixed band of (C-N) stretch, N-H bend and C=S bend.

The strong bands at $3355-3400 \text{ cm}^{-1}$ in DSFSTC and DSFSC are attributed to N-H stretching of secondary amines (-NH). In complexes either this peak is missing or a broad peak covering a range of $3300-3262 \text{ cm}^{-1}$ of comparatively low intensities is obtained. The IR spectra of ligand show that BFPTC, BF . σ TTC, BF . ρ TTC, DPFPTC, DPF . σ TTC and DPF . ρ TTC exhibit a C=S band of medium intensities at frequencies $716-799 \text{ cm}^{-1}$ which is lowered ($10-25 \text{ cm}^{-1}$) on complexation. All these observations show that coordination in BFPTC, BF . σ TTC, BF . ρ TTC, DPFPTC, DPF . σ TTC and DPF . ρ TTC is through sulphur and nitrogen (of =NH) while in DPFPC and BFPC complexes the coordination is through oxygen and nitrogen.

Table 2. Physical properties of Nb(V) complexes of carbamides and thiocarbamides.

Ligand	Complex compound	Colour	mp (°C)	% Found (Calc.)					Molecular weight Found (Calc.)
				Nb	S	C	H		
1.	2.	3.	4.	5.	6.	7.	8.	9.	
DPFFTC	Nb(OC ₁₀ H ₇) ₄ (C ₂₀ H ₁₈ N ₄ S)	Red	280	9.24 (9.32)	3.17 (3.16)	70.2 (71.7)	4.52 (4.5)	1000 (1013.5)	
	Nb(OC ₁₀ H ₇) ₃ (C ₂₀ H ₁₈ N ₄ S) ₂	Brick red	278	7.72 (7.71)	5.29 (5.28)	69.8 (69.1)	4.62 (4.6)	1190 (1214.5)	
	Nb(OC ₁₀ H ₇) ₂ (C ₂₀ H ₁₈ N ₄ S) ₃	Light red	270	6.6 (6.59)	6.75 (6.77)	68.9 (69.13)	4.8 (4.72)	1395 (1417.5)	
DPFPC	Nb(OC ₁₀ H ₇) ₄ (C ₂₀ H ₁₈ N ₄ O)	Brownish	279	9.3 (9.39)	—	73.0 (72.32)	4.58 (4.62)	940 (995.5)	
	Nb(OC ₁₀ H ₇) ₃ (C ₂₀ H ₁₈ N ₄ O) ₂	Light red	275	7.9 (7.91)	—	70.2	4.7	1099 (1182)	
	Nb(OC ₁₀ H ₇) ₂ (C ₂₀ H ₁₈ N ₄ O) ₃	Light brown	296	6.9 (6.82)	—	71.5 (70.1)	5.02 (4.96)	1300 (1369.5)	
DPF.OTTC	Nb(OC ₁₀ H ₇) ₄ (C ₂₁ H ₂₀ N ₄ S)	Brown	250	9.2 (9.11)	3.3 (3.18)	72.5 (71.42)	4.7 (4.68)	1020 (1025.5)	
	Nb(OC ₁₀ H ₇) ₃ (C ₂₁ H ₂₀ N ₄ S) ₂	Light red	251	7.5 (7.52)	5.15 (5.15)	70.2 (69.56)	5.0 (4.91)	1235 (1242.5)	
	Nb(OC ₁₀ H ₇) ₂ (C ₂₁ H ₂₀ N ₄ S) ₃	Dark red	246	6.39 (6.4)	6.6 (6.57)	—	—	1448 (1459.5)	
DPF.PTTC	Nb(OC ₁₀ H ₇) ₄ (C ₂₁ H ₂₀ N ₄ S)	Brown	252	9.05 (9.11)	3.1 (3.11)	—	—	1000 (1025.5)	
	Nb(OC ₁₀ H ₇) ₃ (C ₂₁ H ₂₀ N ₄ S) ₂	Red brown	250	7.5 (7.52)	5.16 (5.15)	—	—	1265 (1242.5)	
	Nb(OC ₁₀ H ₇) ₂ (C ₂₁ H ₂₀ N ₄ S) ₃	Brick red	247	6.5 (6.4)	6.6 (6.57)	—	—	1480 (1459.5)	
BFTTC	Nb(OC ₁₀ H ₇) ₄ (C ₁₄ H ₁₄ N ₄ SO)	Red	270	9.9 (9.82)	3.34 (3.36)	75.8 (76.96)	4.46 (4.41)	960 (951.5)	

	Nb(OC ₁₀ H ₇) ₃ (C ₁₄ H ₁₄ N ₄ SO) ₂	Light red	262	8-53 (8-54)	5-86 (5-85)	—	—	1090 (1094-5)
	Nb(OC ₁₀ H ₇) ₂ (C ₁₄ H ₁₄ N ₄ SO) ₃	Light red	260	7-6 (7-55)	7-8 (7-75)	—	—	1210 (1237-5)
BFPC	Nb(OC ₁₀ H ₇) ₄ (C ₁₄ H ₁₄ N ₄ O ₂)	Light brown	262	9-95 (9-99)	—	70-4 (69-28)	4-4 (4-38)	940 (935-5)
	Nb(OC ₁₀ H ₇) ₃ (C ₁₄ H ₁₄ N ₄ O ₂) ₂	Light brown	261	8-8 (8-79)	—	64-2 (63-33)	4-42 (4-46)	1070-5 (1062)
	Nb(OC ₁₀ H ₇) ₂ (C ₁₄ H ₁₄ N ₄ O ₂) ₃	Brown	260	8-56 (8-58)	—	67-95 (68-32)	5-2 (5-14)	1099 (1089-5)
BFOTC	Nb(OC ₁₀ H ₇) ₄ (C ₂₁ H ₂₀ N ₄ S)	Red	250	9-1 (9-11)	3-2 (3-12)	72-0 (71-27)	4-68 (4-61)	995-8 (1025-5)
	Nb(OC ₁₀ H ₇) ₃ (C ₂₁ H ₂₀ N ₄ S) ₂	Red	243	7-61 (7-52)	5-2 (5-15)	70-88 (69-56)	5-0 (4-91)	1250 (1242-5)
	Nb(OC ₁₀ H ₇) ₂ (C ₂₁ H ₂₀ N ₄ S) ₃	Light red	240	6-4 (6-4)	6-6 (6-57)	68-0 (68-28)	5-0 (5-07)	1450 (1459-5)
BF · pTTC	Nb(OC ₁₀ H ₇) ₄ (C ₂₁ H ₂₀ N ₄ S)	Brown	250	9-2 (9-11)	3-22 (3-12)	—	—	1018 (1025-5)
	Nb(OC ₁₀ H ₇) ₃ (C ₂₁ H ₂₀ N ₄ S) ₂	Red	244	7-62 (7-52)	5-21 (5-15)	—	—	1242-5 (1242-5)
	Nb(OC ₁₀ H ₇) ₂ (C ₂₁ H ₂₀ N ₄ S) ₃	Red	239	6-5 (6-4)	6-49 (6-57)	—	—	1447-8 (1459-5)

In the IR spectra of complexes, several bands of relatively medium intensities occurring in the region 605–540 and 540–510 cm^{-1} may be assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively.

The central metal ion probably acquires coordination number six, seven and eight in the mono, di, and tri-substituted derivatives $\text{Nb}(\text{ON}_p)_4(L)$, $\text{Nb}(\text{ON}_p)_3(L_2)$ and $\text{Nb}(\text{ON}_p)_2(L_3)$ respectively.

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