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Synthesis and Characterization of Niobium (V) and Tantalum(V) Chelates with 2-aminothiophenol and 2-aminophenol

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ABSTRACT

Niobium(V) and Tantalum(V) Complexes $[MLX_4]$ (where M = Nb/Ta; X = Cl/NCS; L = 2-aminothiophenol or 2-aminophenol) have been synthesised and characterised on the basis of elemental analysis, conductivity measurements, Ir, UV-vis and ‘H NMR studies. The ligands behaves as mononegative bidentate donor. The value of magnetic moment of 0.35 – 0.43 BM is a consequence of combined effects of spin-orbit coupling and distortions of the ligand field from a full octahedral symmetry.

Key words : Nb(V), Ta(V), Six Coordinate, Iso-structural.

INTRODUCTION

Niobium (V) and Tantalum(V) are class-a metal but a NMR study of ^{93}Nb has shown that the SCN ligand yields a series of N-bonded isothiocyanato and s-bonded thiocyanato complexes[1]. These d°-complexes have no stereochemical preferences and exhibit a variety of coordination numbers[2-4] having very interesting insights into structure and bonding[5-7]. Some hexa-coordinate complexes with thioamide ligands are reported in our earlier paper[8-11]. The present study aims at synthesis and spectral characterization of some metal chelates with NS- and NO-donars 2-aminothiophenol and 2-aminophenol which are used as ligands by various workers[11-13].

EXPERIMENTAL

Niobium and tantalum pentachlorides were obtained from Fluka and other chemicals 2-aminothiophenol (Schuchardt, Munchen), 2-aminophenol (Ward Blenkinsop, London) were CP grade. Solvents were dried and distilled before use. Niobium and tantalum were determined gravimetrically as Penta oxide and chloride as silver chloride. Nitrogen, Carbon and hydrogen were determined by microanalytical methods. The conductance of 10^{-3} M solutions of the complexes in DMF were measured using Wiss-Werkstatter Weithein obb type LBR conductivity meter. The IR spectra were recorded on a Perkin Elmer 577 spectrometer, electronic spectra on a Beckmann

DV-6 spectrometer 'H NMR ($CDCl_3$) on a JE O_2 JMS 60011 NMR spectrometer and magnetic moment was measured on a gouy balance using $Hg[Co(SCN)_4]$ as calibrant.

Synthesis of Nb(V) Complexes

Niobium (V) Chloride (0.01 mol) in chloroform (100 ml) was treated with a ligand (0.01 mol) in the same solvent. The reaction mixture was stirred on magnetic stirror for 1 hr and further refluxed for two hrs. on waterbath till evolution of HCl(g) ceases. Light yellow coloured solid were obtained on concentration. It was filtered under suction and washed with dry chloroform. The complexes were then dried and stored in vacuum over fused $CaCl_2$(yield 78%).

Preparation of Isothiocyanato complexes of Niobium(V)

This complex was isolated with filterate of $[Nb(S\text{-}C_6H_4\text{-}NH_2)Cl_4]$ following our previous method(10).

Preparation of Tantalum(V) complexes

All Tantalum(V) complexes were isolated similar to our previous method[10].

Analysis

S.No. 1 :	For $[Nb(S\text{-}C_6H_4NH_2)Cl_4]$:	Found(%): C, 20.20; H, 1.68; N, 3.52; Nb, 25.70, Calculated (%) : C, 20.11; H, 1.67; N, 3.91; Nb, 25.69;
S.No. 2 :	For $[Nb(O\text{-}C_6H_4NH_2)Cl_4]$:	Found(%) : C, 21.01; H, 1.75; N, 4.01; Nb, 26.80; Calculated (%):C, 20.99; H, 1.74; N, 4.08; Nb, 26.82;
S.No. 3 :	For $[Nb(S\text{-}C_6H_4NH_2)(NCS)_4]$:	Found(%) : C, 26.74; H, 1.35; N, 15.56; Nb, 20.69; Calculated (%):C, 26.72; H, 1.33; N, 15.59; Nb, 20.71;
S.No. 4 :	For $[Nb(O\text{-}C_6H_4NH_2)(NCS)_4]$:	Found(%) : C, 27.69; H, 1.35; N, 16.18; Nb, 21.42; Calculated (%):C, 27.71; H, 1.38; N, 16.16; Nb, 21.47;
S.No. 5 :	For $[Ta(S\text{-}C_6H_4NH_2)Cl_4]$:	Found(%) : C, 16.20; H, 1.35; N, 3.15; Ta, 40.50; Calculated (%):C, 16.10; H, 1.34; N, 3.13; Ta, 40.48;
S.No. 6 :	For $[Ta(O\text{-}C_6H_4NH_2)Cl_4]$:	Found(%) : C, 16.72; H, 1.90; N, 3.24; Ta, 41.95; Calculated (%):C, 16.70; H, 1.99; N, 3.24; Ta, 41.98;

RESULTS AND DISCUSSION

The analytical data reveals a stoichiometry of 1:1, metal : ligand. The molar conductance value of 10^{-3} M solution in DMF were in the range of 16.60-30.90 ohm^{-1} cm^{-2} mol^{-1}, indicating a non-electolytic behaviour of the complexes[14]. The ligands behaves as mononegative bidentate and the formula of complexes may be proposed to be $[ML\ X_4]$ (M = Nb/Ta; LH = 2-aminothiophenol or 2-aminophenol; X = Cl/NCS). The value of paramagnetism between 0.35 BM- 0.50 BM is probably due to temperature independent second order Zeeman effect agreement with Fowles *et al.,*[15] and Nyholm and co-workers[16]. The value of magnetic moment (0.35 BM- 0.43 BM) is assumed due to consequence of the combined effects of spin-orbit coupling and distortion of the ligand field from full octahedral symmetry.

Electronic and infrared Spectra

The electronic spectrum of 2-aminothiophenol exhibit two absorption maxima at 32260 cm^{-1} and 30485 cm^{-1}, assignable to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively. The strong absorption band at 27770 – 27700 cm^{-1} in the spectra of complexes is assigned to $L\rightarrow M$ charge transfer transition. No absorption bands are absorbed above 25000 cm^{-1} which indicates d°-configuration of complexes.

IR Spectra

A comparison of spectra of ligands and corresponding complexes indicate deprotonated ligands having Metal-S and Metal-N bonding with 2-aminothiophenol(ATP) and Metal-O and Metal-N bond with 2-aminophenol(AP). The uSH (2530 cm^{-1}) band of ATP and **u**OH (3480 cm^{-1}) of AP were found to be absent from the spectra of complexes.

Table 1: Major IR and 'H NMR Spectral data of ligands and complexes

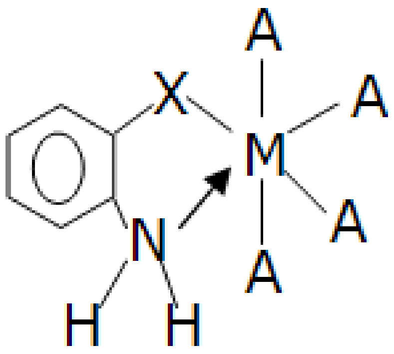
Compds.	IR (cm^{-1})					'H NMR (dPPM)		
	uasym NH_2/ υsym NH_2)	υM-N	υM-O	υM-S	υM-Cl	Amino Proton	Phenyl Proton	Thiol Proton
ATP (ligand)	3460 m (3340 m)	-	-	-	355 m	3.68	6.64-7.32 (multiplet)	3.66
(Sl. No. 1)	3400 m (3300 m)	490 m	-	320 w	350 m	3.54	6.62-7.10 (multiplet)	-
(Sl. No. 3)	3400 m (3310 m)	495 m	-	310 w	440 m	3.55	6.42-6.68 (multiplet)	-
(Sl. No. 5)	3415 m (3310 m)	500 m	-	315 w	-	3.58	6.40- 6.92 (multiplet)	-
AP (ligand)	3380 m (3300 m)	-	-	-	-	4.40	6.42-6.68 (multiplet)	-
(Sl. No. 2)	3365 m (3285 m)	480 m	580 m	-	345 m	4.11-4.41 (splat)	6.32 – 6.88 (multiplet)	-
(Sl. No. 4)	3360 m (3280 m)	490 m	590 m	-	335 m	4.20 – 4.40 (splet)	6.31 – 6.92 (multiplet)	-
(Sl. No. 6)	3370 m (3280 m)	485 m	685 m	-	460 m	4.20 – 4.42 (splet)	6.32 – 6.98 (multiplet)	-

The non-ligand bands at 315-320 cm^{-1} (ATP) and 680-685 cm^{-1} (AP) in complexes assigned to Metal-S and Metal-O stretching modes. The **u**asym(NH_2)(3460cm^{-1}) & υsym(NH_2)(3340cm^{-1}) of free 2-aminothio-phenol (ATP) red shifts to lower frequency and observed at 3400-3360 cm^{-1} and 3300-3280 cm^{-1} respectively on complexation indicating coordination through amino nitrogen of ligand. This observation is further supported by non-ligand bands at 490-500 cm^{-1} of medium intensity and assigned to metal-N stretching modes[17]. The new bands in the spectra of the complexes in the region 330-355 cm^{-1} (Nb) 446- 460 cm^{-1} (Ta) are assigned to υM-Cl modes[18-19].

N-bonded isothiocyanato group in complexes (Sl. No. 3 & 4) was confirmed by the new bands at 2040 cm^{-1}(υCN), 785 cm^{-1} (υCS) and 490 cm^{-1} (δ NCS) considering previous literature[20].

'H NMR Spectra

The 'H NMR spectra ($CDCl_3$) of ligands and complexes were recorded to substantiate further mode of bonding. The free ligands, ATP and AP exhibits signals at δ 8.92 PPM and δ 3.68 PPM respectively due to intramolecularly hydrogen bonded phenolic and thiol protons. These protons disappeared from the spectra of complexes indicating their replacement by metal ion during



Str. - I

Octa-hedral Str. of $[M(X\text{-}C_6H_4\text{-}NH_2)A_4]$

M = Nb/Ta; A = Cl/ NCS; X = O/S

complexation[21]. The aromatic protons signals are observed in the range of δ6.42-6.68 PPM(AP) and δ6.64 – 7.30 PPM(ATP) as complex multiplet are slightly low field shifted and the integrated intensities of these signals agree well with the formulation of the complexes. The amino protons of ligands observed at δ4.40 PPM (AP) and δ3.68 PPM(ATP) are low field shifted on complexation and the integrated intensities of the signals agree well with the proposed structures of complexes (Str.- I).

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