

Synthesis and Spectroscopic Characterization of Seven-Coordinate Complexes of Niobium (V) and Tantalum (V) with Dibenzyl Sulphide

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Abstract

Dibenzyl sulphide forms stable complexes of composition $[MX_5(R_2S)]$ ($M=Nb/Ta$; $X=Cl/Br$; $R=C_6H_5CH_2$) and $[NbOX_3(R_2S)_2]$ ($X=Cl/Br$; $R=C_6H_5CH_2$). The compositions of the complexes have been established by elemental analysis, magnetic susceptibility measurements, conductivity, IR, UV-vis and 1H NMR spectral data. These complexes are seven-coordinate and halogen-bridged or oxygen-bridged pentagonalpyramidal dimeric structure.

Key words : Niobium, Tantalum, Pentahalides, Complexes, dibenzylsulphide.

Introduction

Dibenzyl sulphide has been used as ligand by various workers.¹⁻⁴ Trichlorotris (dibenzyl sulphide) rhodium (III) is used as catalyst for the hydrogenation of maleic acid and trans-Cinnamic acid by James *et al.*⁵ With the aim of studying niobium (V) and tantalum (V) complexes as possible catalyst,⁶⁻⁷ we have reported structural and physico-chemical investigation in our earlier communications with amide⁸, thioamide⁹⁻¹¹, S,O-donor¹² and N,O-donor¹³ ligands. The present study reports synthesis and spectroscopic characterization

of complexes of Pentahalides of niobium and tantalum with dibenzyl sulphide ligand.

Experimental

All chemicals used were of CP grade or AR grade. Dibenzyl sulphide (R_2S) ¹⁴ was prepared by refluxing benzyl chloride and sodium sulphide in the molar ratio of 2:1 in an ethanolic medium till the smell of benzyl chloride disappeared. (m.p = 48.5°C lit., mp = 49-50°C), MX_5 ($M=Nb/Ta$; $X=Cl, Br$) were commercial products of the highest purity available. Solvents were dried before use.

Niobium and tantalum were determined gravimetrically as Nb_2O_5 and Ta_2O_5 and chloride as AgCl . N, C and H were determined by microanalytical methods. The conductance of 10^{-3} M solutions of the complexes in DMF were measured using Wiss-Werkstatter Weithem obb type LBR conductivity meter. IR spectra of ligand and complexes were recorded on a Perkin-Elmer model-577 spectrophotometer in the range of $4000\text{-}200\text{ cm}^{-1}$ as KBr pellets. Magnetic measurements were made on Gouy balance using $\text{Hg}(\text{Co}(\text{SCN})_4)$ as calibrant. The electronic spectra were recorded with Ziess (Jena) Model of automatic recording system. ^1H NMR (CDCl_3) spectra of ligand and complexes were recorded with 90 MHZ NMR spectrometer using TMS as the internal indicator in the range of 0 to 10 PPM.

Preparation of $[\text{NbOX}_3(\text{R}_2\text{S})_2]$ ($X = \text{Cl}/\text{Br}$):

All complexes were prepared using our general method reported earlier.⁸ NbX_5 (1m mol) and dibenzyl sulphide (2m mol) in $\text{CCl}_4.\text{CH}_3\text{OH}$ (1:1) solvents stirred on magnetic stirrer at room temperature for 1 h and further refluxed for two hours on water-bath. The solid products were isolated on concentration, dried and stored in vacuum over fused anhydrous CaCl_2 . (yield = 82%)

Analysis

Sl. No. 1 : $[\text{NbOCl}_3(\text{R}_2\text{S})_2]$ (Cream) :

Calculated (%) for $\text{NbCl}_3\text{C}_{28}\text{H}_{28}\text{OS}$ (627.4) : C = 53.55; H = 4.46; Cl = 16.97; Nb = 14.80; **Found (%)** : C = 53.60; H = 4.60; Cl = 17.01; Nb = 14.82;

Sl. No. 2 : $[\text{NbOBr}_3(\text{R}_2\text{S})_2]$ (Yellow) :

Calculated (%) for $\text{NbBr}_3\text{C}_{28}\text{H}_{28}\text{OS}$

(760.6) : C = 44.17; H = 3.68; Br = 31.51; Nb = 12.21; **Found (%)** : C = 44.16; H = 3.72; Br = 31.68; Nb = 12.30;

Preparation of $[\text{MX}_5(\text{R}_2\text{S})]$ ($M = \text{Nb}/\text{Ta}$; $X = \text{Cl}/\text{Br}$):

MX_5 (1m mol) in CHCl_3 (100 mL) was treated with ligand (1m mol) in the same solvent. The reaction mixture was stirred on magnetic stirrer for 2 h to afford the dinuclear adducts. The resulting solid complex was filtered through a Gooch Crucible (G_3), washed with CHCl_3 and dried in VaCuO over CaCl_2 . (yield = 71%)

Analysis

Sl. No. 3 : $[\text{NbCl}_5(\text{R}_2\text{S})]$ (Yellow) :

Calculated (%) for $\text{NbCl}_5\text{C}_{14}\text{H}_{14}\text{S}$ (484.5) : C = 34.67; H = 2.88; Cl = 36.63; Nb = 19.17; **Found (%)** : C = 35.01; H = 2.89; Cl = 36.72; Nb = 19.22;

Sl. No. 4 : $[\text{NbBr}_5(\text{R}_2\text{S})]$ (Yellow) :

Calculated (%) for $\text{NbBr}_5\text{C}_{14}\text{H}_{14}\text{S}$ (706.4) : C=23.78; H = 1.98; Br = 56.55; Nb = 13.15; **Found (%)** : C=23.88; H=2.01; Br= 56.34; Nb = 13.10;

Sl. No. 5 : $[\text{TaCl}_5(\text{R}_2\text{S})]$ (Light yellow) :

Calculated (%) for $\text{TaCl}_5\text{C}_{14}\text{H}_{14}\text{S}$ (572.5) : C = 29.34; H = 2.44; Cl = 31.00; Ta = 31.51; **Found (%)** : C=29.44; H= 2.45; Cl = 31.21; Ta = 31.44;

Sl. No. 6 : $[\text{TaBr}_5(\text{R}_2\text{S})]$ (Yellow) :

Calculated (%) for $\text{TaBr}_5\text{C}_{14}\text{H}_{14}\text{S}$ (793.94) : C=21.16; H = 1.76; Br = 50.31; Ta = 22.72;

Found (%) : C=21.26; H=1.51; Br= 50.20; Ta = 22.69;

Results And Discussion

The reaction between MX_5 ($\text{M} = \text{Nb}/\text{Ta}$; $\text{X} = \text{Cl}/\text{Br}$) and dibenzyl sulphide in CHCl_3 under dry, oxygen free conditions in equimolar ratio affords to the adducts $[\text{MX}_5(\text{R}_2\text{S})]$. At room temperature no evidences for the formation of O-abstraction products were found. However, O-abstraction products were formed in $\text{CHCl}_3:\text{CH}_3\text{OH}$ (1:1) solvents heating on reflux. Baradley *et al.*¹⁵ and others¹⁶⁻¹⁷ have observed that niobium (V) halides have greater tendency of oxygen abstraction. It is therefore possible that in present reactions oxygen abstraction has occurred during complexation. The products did not melt but were decomposed to blue- black mass in all cases in the range of 230-265°C probably due to reduction of Nb (V) to a blue Nb (III) ion by sulphide ligand. These observations are consistent with our previous report.¹¹ The nature of reactions products between pentahalides of Nb (V) and Ta(V) and dibenzyl sulphide depends on the stoichiometry of reacting species, nature of solvents and temperature. All the solid products were insoluble in common organic solvents indicating their polymeric nature. However, fair solubility was attributed in DMF and DMSO. The molar conductance values of 10^{-3} M solution of complexes were found in the range 10.62 – 15.32 $\text{cm}^2 \text{mol}^{-1}$ consistent with value suggested for non-electrolyte in literature.¹⁸ All complexes were found to diamagnetic as expected for d^0 -configuration $[\text{Nb}(\text{V}) \& \text{Ta}(\text{V})]$. However, Nb (V) complexes showed a slight paramagnetism 0.35 – 0.41

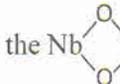
BM which is in agreement with results reported earlier¹⁹ and due to temperature independent second order Zeeman-effect as suggested by Fowles *et al.*²⁰ Electronic spectra complexes exhibited a very broad band at 365 nm assigned due to charge transfer. However, no complex absorbs between 800–400 nm as might be expected for metal ions with $(n-1)d^0ns^0$ electronic configuration.⁹

IR Spectra :

The IR spectra of dibenzyl sulphide (R_2S) indicate that νCS band of the ligand (R_2S) shift from 720 cm^{-1} to $690\text{-}695 \text{ cm}^{-1}$ on complexation, suggesting bonding through sulphur.²¹⁻²³ New band 365 cm^{-1} (Nb) and 368 cm^{-1} (Ta) are assigned due to Nb-S and Ta-S stretching modes confirms the bonding through sulphur. The other non-ligand bands at 335 cm^{-1} and 260 cm^{-1} are assigned to $\nu\text{Nb-Cl}$ and $\nu\text{Nb-Br}$ and at 320 cm^{-1} and 225 cm^{-1} due to $\nu\text{Ta-Cl}$ and $\nu\text{Ta-Br}$ modes. These observations are in good agreement for seven-coordinated complexes reported in literature.²⁴⁻²⁵

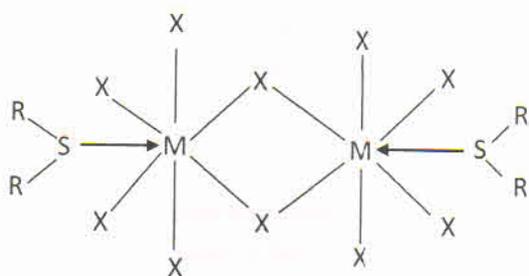
The bands observed in the region (Sl. No. 1 & 2) $490\text{-}475 \text{ cm}^{-1}$ correspond to


NbNb moiety. These complexes also exhibited two bands $620\text{-}610 \text{ cm}^{-1}$ and $480\text{-}460 \text{ cm}^{-1}$ due to antisymmetric and symmetric vibrations of

the  Nb bridge bond (Str. I). However,

the absence bands in the $555\text{-}560 \text{ cm}^{-1}$ region may be taken as the absence of Nb-O linkage.²⁶

The possibility of bridging halides, can not be rule out which falls below 200 cm^{-1} .²⁷ However, considering poor solubility and observed molecular weight of complexes halogen bridge structure (Str. II) may be proposed.

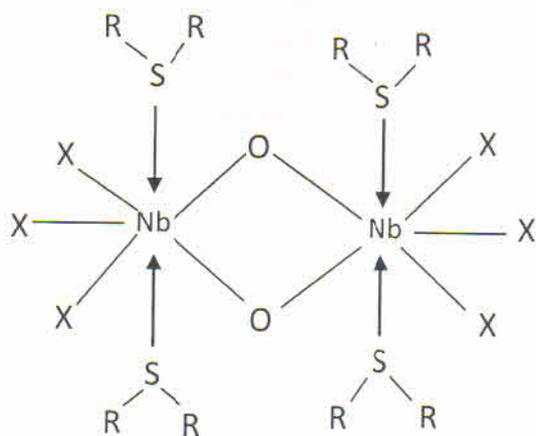


(Str. I)

 $(M = \text{Nb/Ta}; X = \text{Cl/Br})$ $R = \text{C}_6\text{H}_5\text{CH}_2$

Pentagonal bipyramidal structure

(Sl. No. 3 to 6)



(Str. II)

 $(R = \text{C}_6\text{H}_5\text{CH}_2; X = \text{Cl, Br})$

Pentagonal bipyramidal Structure

¹H NMR Spectra :

The ¹H NMR spectrum of dibenzyl sulphide shows its phenyl protons at δ 7.2 PPM and CH₂ protons at δ 3.5 PPM and a complex small peak at δ 4.45 PPM. The two CH₂ peaks may be due staggered and eclipsed conformations of ligands. All $[\text{MCl}_5(\text{R}_2\text{S})]$ ($M = \text{Nb/Ta}; R = \text{C}_6\text{H}_5\text{CH}_2$) complexes exhibits a complex peak at δ 7.10 – 7.02 PPM corresponding to aromatic protons and two peaks centred at δ 4.30 PPM and δ 3.18 PPM due to methylene protons. The shifting of CH₂ protons signals to lower fields indicate the formation of Metal (V) – S bond.²⁸ The other $[\text{NbOX}_3(\text{R}_2\text{S})_2]$ ($X = \text{Cl/Br}; R = \text{C}_6\text{H}_5\text{CH}_2$) complexes exhibit phenyl protons signal in the range of δ 7.1 – 7.18 PPM and CH₂ sharp singlet at δ 3.54 PPM and small complex peaks in the region δ 4.11 – 3.82 PPM. This change in two CH₂ peaks indicates larger interaction in $[\text{NbOX}_3(\text{R}_2\text{S})_2]$ as compared to $[\text{NbX}_5(\text{R}_2\text{S})]$.

Thus, considering elemental analysis, conductivity, observed molecular weight, IR and ¹H NMR spectral data pentagonal bipyramidal structure may be deduced for all seven-coordinate complexes.

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Table 1. IR and ¹H NMR spectral data of ligand and complexes

Compounds	IR (cm ⁻¹)			¹ H NMR (δ PPM)	
	νCS	νM-S	νM-X	Arene Protons	CH ₂ Protons
R ₂ S (ligand)	720 s	-	-	7.2	3.564.45
[NbOCl ₃ (R ₂ S) ₂]	690 m	365 w	355 m	7.10	3.544.11-3.82
[NbOBr ₃ (R ₂ S) ₂]	692 m	360 w	335 m	7.18	3.504.10-3.80
[NbCl ₅ (R ₂ S)]	695 m	360 w	365 m	7.10-7.02	4.303.18
[NbBr ₅ (R ₂ S)]	690 m	360 w	332 m	7.01-7.10	4.263.16
[TaCl ₅ (R ₂ S)]	690 ms	368 w	320 m	7.00-7.12	4.163.10
[TaBr ₅ (R ₂ S)]	695 ms	370 w	225 m	6.98-7.10	4.223.30

(R = C₆H₅CH₂, X = Cl, Br; M = Nb, Ta)

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