

Synthesis and Characterization of Reaction Products of Thioacetic acid and thioacetamide with Chlorides of Niobium (V) and Tantalum (V)

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Abstract

Reactions between niobium(V) and tantalum(V) chlorides with thioacetic acid and thioacetamide have been examined. Thioacetic acid yielded dinuclear but mononuclear solid products with thioacetamide was isolated. The probable structure of all new products were deduced by elemental analysis, conductivity measurements, IR and UV-vis, spectral studies.

Key words: Niobium(V), Tantalum(V), Thioacetic acid, Thioacetamide, O-abstraction.

Introduction

The coordination chemistry of group 5 metal pentahalides of niobium and tantalum with acetic acid, haloacetic acids and their related anhydrides are reported by Marchetti *et al.*¹ and with aryl carboxylic acid by Brown and Co-workers². The complexes of oxo-chlorides of niobium and tantalum ligated by RCOOH are also highlighted in literature³⁻⁶. However, acid derivatives having thioamide group are comparatively less studied. In continuation⁷⁻⁹ of our previous work on the

Penta halides of niobium and tantalum, we report some solid and stable reaction products of thioacetic acid and thioacetamide. The metal-ligand vibrations in far- IR Spectra are located and analysed.

Experimental

All the chemicals used were AR-grade or CP-grade Thioacetamide, thioacetic acid and MCl_5 ($M = Nb/Ta$) were commercial products of the highest purity available. Solvents were dried before use. The complexes were prepared using a general method:

*Preparation of Niobium(V) Complexes:**Sl. No. 1 :***[NbCl₅(CH₃CSNH₂)] (light yellow)**

Niobium Pentachloride (0.270 g, 0.001 mol.) in Chloroform (20 ml) was reacted with thiocetamide (0.0012 mol) in Methanol (80 ml). The reaction mixture was stirred at room temperature for 2h. The volume of the mixture was reduced to ~15 ml on water bath and the resulting solid complex was filtered through a Gooch Crucible (G₃), washed with Chloroform and dried in vacuo over CaCl₂ (yield 65%).

Calculated (%) for **NbC₂H₅NSCl₅** : C = 6.96; H = 1.45; N = 4.06; Cl = 51.53; Nb = 26.97; Found (%) : C = 6.65; H = 1.80; N = 4.12; Cl = 51.62; Nb = 26.89;

*Sl. No. 2 :***[Nb(NCS)₅(CH₃CSNH₂)] (Yellow):**

A suspension of NbCl₅ (0.001 mol), NH₄SCN (0.005 mol.) in equimolar mixture of CHCl₃ and CH₃OH (100 ml) was stirred at room temperature and ligand (0.001 mol.) solution in methanol was added. The solution mixture was concentrated on water bath and yellow solid was obtained and dried in vacuo over CaCl₂.

Calculated (%) for **NbC₇H₅N₆S₆** : C = 18.34; H = 1.09; N = 18.34; Nb = 20.30; Found (%) : C = 18.32; H = 1.19; N = 18.35; Nb = 20.43;

*Sl. No. 3 :***[NbO(NH₃)₄(CH₃CSNH₂)]Cl₃ (White):**

A suspension of Niobium pentachloride (0.001 mol.) and ligand (0.001 mol.) in Chloroform : CH₃OH (1:1) was stirred on magnetic stirrer for 1 hr. and pH of the mixture was made, using conc. HCl and Conc. NH₃ solution. On concentration of mixture white solid was obtained (yield = 72%).

Calculated (%) for **NbC₂H₁₇N₅OSCl₃** : C = 6.69; H = 7.74; N = 19.52; Cl = 29.70; Nb = 25.94; Found (%) : C = 6.62; H = 7.80; N = 19.82; Cl = 29.75; Nb = 26.01;

*Sl. No. 4 :***[Nb₂Cl₈(CH₃CSO)₂] (Faint yellow) :**

This compound was prepared by a procedure analogous to that described for Sl. No. 1 by reacting NbCl₅ (0.001 mol.) and thiocetic acid (0.001 mol.) for 2h. (yield = 68%) :

Calculated (%) for **Nb₂Cl₈C₄H₆S₂O₂** : C = 7.74; H = 0.96; Cl = 45.80; Nb = 30; Found (%) : C = 7.78; H = 1.01; Cl = 45.92; Nb = 30.01;

*Preparation of Tantalum (V) Complexes :**Sl. No. 5 :***[TaCl₅(CH₃CSNH₂)] (White)**

This compound was prepared by a procedure analogous to that described for Sl. No. 1 by reacting TaCl₅ (0.001 mol.) and

CH_3CSNH_2 (0.001 mol.) in CHCl_3 : CH_3OH mixture (1:1)

Calculated (%) for $\text{Ta}_2\text{H}_5\text{NSCl}_5$: C = 5.53; H = 1.53; N = 3.22; Cl = 40.94; Ta = 41.73; Found (%) : C = 5.55; H = 1.55; N = 3.12; Cl = 41.01; Ta = 41.75;

Sl. No. 6 :

$[\text{Ta}_2\text{Cl}_8(\text{CH}_3\text{CSO}_2)_2]$: (Light yellow)

This compound was prepared by a procedure analogous to that described for Sl. No. 1 by reacting TaCl_5 (0.001 mol.) and CH_3CSOH (0.001 mol.) in CHCl_3 and CH_3OH mixture (1:1)

Calculated (%) for $\text{Ta}_2\text{C}_4\text{H}_6\text{O}_2\text{S}_2\text{Cl}_8$: C = 6.03; H = 0.75; Cl = 35.67; Ta = 45.47; Found (%) : C = 6.13; H = 1.01; Cl = 35.68; Ta = 45.57;

Niobium tantalum and chloride contents in the complexes were determined gravimetrically as Nb_2O_5 , Ta_2O_5 and AgCl respectively. Elemental analysis, IR, UV-vis, magnetic measurements and molar conductance data (10^{-3} M) in DMF = were obtained as our previous paper⁹.

Results and Discussion

The suspension of MCl_5 (M = Nb/Ta) reacts with thioacetic acid to afford dinuclear adducts in 65-70% yield.



The products are characterized by means of elemental analysis and IR Spectra. The reaction with NbCl_5 was observed to be faster than TaCl_5 and the solid products were insoluble in common organic solvents. The dinuclear adducts with acetic acid, haloacetic acids, acetic anhydride, haloacetic anhydrides and haloacetyl halides are distorted octahedrally coordinated¹. However, thioacetamide forms mononuclear products with MCl_5 (M = Nb/Ta). The molar conductance values of 10^{-3} M solutions in DMF were in the range of 16.32-33.25 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating a non-electrolytic behaviour of the complexes¹⁰. But Molar conductance values of $[\text{NbO}(\text{NH}_3)_4(\text{CH}_3\text{CSNH}_2)]\text{Cl}_3$ was found to be 240 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ suggesting chloride ion in the outer sphere of complex. The presence of ionic chlorides was further supported by chemical analysis of sodium extract solution of complex¹¹.

All complexes were diamagnetic as expected for d^0 -ions (Nb(V) & Ta(V). Electronic Spectra of the complexes show no absorption peak in the visible region. However, in UV region strong and broad peak at 280-290 nm was observed due to $L \rightarrow M$ charge transfer.

The $\nu_{\text{asym}} \text{NH}_2$ (3300 cm^{-1}) and $\nu_{\text{sym}} \text{NH}_2$ (3100 cm^{-1}) of thioacetamide¹¹ red shift to lower frequency and formation of metal-N bond was assumed. Thioamide bands of this ligand are mixed bands¹² having contributions from δNH , $\nu\text{C} \cdots \text{N}$, $\text{C} \cdots \text{S}$ and δCH . The red shift of thioamide band I and thioamide band II to lower frequencies with lower

Table 1.
Major IR Bands (cm^{-1}) of ligand (CH_3CSNH_2) and Complexes :

Compd.	$\nu_{\text{asym}} \text{NH}_2 /$ $\nu_{\text{sym}} \text{NH}_2$	Thioamide Bands				$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
		Band I	Band II	Band III	Band IV		
CH_3CSNH_2 (ligand)	3300 m (3100 ms)	1490 s	1310 m	980 m	730 s	-	-
$[\text{NbCl}_5(\text{CH}_3\text{CSNH}_2)]$	3285 m (3085 m)	1465 m	1290 m	985 m	735 m	500 m	335 m
$[\text{Nb}(\text{NCS})_5(\text{CH}_3\text{CSNH}_2)]$	3280 mb (3090 m)	1475 m	1287 m	983 m	735 s	495 m	340 m
$[\text{NbO}(\text{NH})_4(\text{CH}_3\text{CSNH}_2)]\text{Cl}_3$	3282 mb (3085 m)	1470 m	1280 m 1290 m	980 m	740 m	500 m	345 m
$[\text{TaCl}_5(\text{CH}_3\text{CSNH}_2)]$	3278 mb (3080 m)	1473 m	1285 m	985 m	745 m	505 m	350 m

ψ mixed bands, Band I ($\delta\text{NH} + \nu \text{C} \equiv \text{N}$), Band II ($\nu\text{C}=\text{S} + \nu\text{C}=\text{N} + \delta\text{CH}$)

Band III ($\text{C} \equiv \text{N} + \text{C} \equiv \text{S}$) & Band IV ($\text{C} \equiv \text{S}$)

intensities clearly suggest bonding through nitrogen atom of thioacetamide¹³. The presence of new non ligand bands at 495-505 cm^{-1} also support the formation of Metal- N band and assigned to $\nu_{\text{M-N}}$ mode¹⁴.

The coordinated isothiocyanato group bounding through nitrogen was indicated by bands at 2040 cm^{-1} (ν_{CN}), 705 cm^{-1} (ν_{CS}) and 480 cm^{-1} (δ_{NCS}) agreement with previous report¹⁵. The evidence for the formation of O-abstraction¹⁶⁻¹⁷ by NbCl_5 was verified by new band at 995 cm^{-1} due to $\text{Nb}=\text{O}$ stretching mode.

The free thioacetic acid ligand exhibits δCH_3 (1466 cm^{-1} & 1430 cm^{-1}) and $\delta\text{C}=\text{S}$ (760

cm^{-1}) remain unchanged on complexation indicating absence of bonding through thiocarbonyl Sulphur. However, $\nu_{\text{O-H}}$ (3230 cm^{-1}) band of free ligand was not observed in the spectra of complexes indicating deprotonation of O-H group and formation of metal-O bond. New bands at 370-420 cm^{-1} due to $\nu_{\text{M-O}}$ confirmed the formation of metal-O bond. The metal-Cl stretching mode in complexes was observed at 335-350 cm^{-1} in good agreement with previous value¹⁸.

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