



REACTIONS OF SULPHAGUANIDINE WITH CHLORIDES AND BROMIDES OF NIOBIUM (V) AND TANTALUM (V)

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ABSTRACT

Reaction of sulphaguanidine with chlorides and bromides of Niobium (V) and Tantalum (V) yields seven coordinated solid complexes of composition $[MX_5L]$ ($M = Nb/Ta$; $X = Cl/Br$; $L = \text{Sulphaguanidine}$). The reaction products have been characterized by elemental analyses, magnetic measurements, conductivity, IR, UV-vis spectral studies. Sulphaguanidine behaves as neutral bidentate N, O-donor.

Key words: Sulphaguanidine, Niobium (V), Tantalum (V), Complexes, Characterization.

INTRODUCTION

We have been involved in studying the chemistry of coordination of thioamides^{1,2}, amides³ and O-donors⁴ to group 5 metal pentahalides MX_5 ($M = Nb/Ta$; $X = Cl, Br$). The present study describes some metal chelates of sulfonamide, 4-amino-N-[amino (imino) methyl] benzene sulfonamide known as sulphaguanidine (SPG) used in the treatment of bacillary dysentery.

EXPERIMENTAL

All chemicals used were of CP grade or AR grade. Niobium pentachloride and tantalum pentachloride (Fluka) and sulphaguanidine (E. Merck) were commercial products of the highest purity available. Solvents were dried and distilled before use. Nb and Ta were determined gravimetrically as pentoxide and chloride as AgCl. Nitrogen, carbon and hydrogen were determined by microanalytical methods. The conductance of 10^{-3} M solution of complexes were measured using Wiss-Werkstatter Weithem obb type LBR conductivity meter in DMF. The IR spectra were recorded on a Perkin Elmer 577 spectrometer using KBr pellets. The magnetic measurements were made on a Gouy Balance and the diamagnetic corrections for SPG molecule were applied. The UV and visible spectra of SPG

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and complexes were recorded on a Beckmann and Carl Zeiss (Jena) spectrophotometer.

Preparation of complexes

All complexes were prepared using a general method taking MX_5 and SPG in molar ratio 1 : 1 in CCl_4 and CH_3OH (1:1) solvents adopting our previous method⁵. MBr_5 were prepared by the method reported in literature⁶. The analytical data of complexes is given in Table 1.

Table 1: Analytical and conductivity data for complexes

S. No.	Complex [Empirical formula] [Formula weight]	Found (Calcd.) %					λM Ohm^{-1} $\text{cm}^2\text{mol}^{-1}$
		Metal	C	H	N	X	
1.	[$\text{NbCl}_5(\text{SPG})$] ($\text{C}_7\text{H}_{10}\text{N}_4\text{O}_2\text{SCl}_5\text{Nb}$) [484.65]	19.07 (19.17)	17.46 (17.33)	2.16 (2.06)	11.60 (11.55)	36.72 (36.62)	17.0
2.	[$\text{NbBr}_5(\text{SPG})$] ($\text{C}_7\text{H}_{10}\text{N}_4\text{O}_2\text{SBr}_5\text{Nb}$) [706.7]	13.23 (13.14)	12.01 (11.88)	1.42 (1.41)	8.01 (7.92)	56.45 (56.53)	20.0
3.	[$\text{TaCl}_5(\text{SPG})$] ($\text{C}_7\text{H}_{10}\text{N}_4\text{O}_2\text{SCl}_5\text{Ta}$) [572.74]	31.66 (31.60)	14.76 (14.66)	1.86 (1.74)	9.92 (9.77)	31.02 (30.99)	23.0
4.	[$\text{TaBr}_5(\text{SPG})$] ($\text{C}_7\text{H}_{10}\text{N}_4\text{O}_2\text{SBr}_5\text{Ta}$) [794.7]	22.66 (22.76)	10.60 (10.56)	1.20 (1.25)	7.11 (7.04)	50.12 (50.27)	22.0

(X = Cl/Br; H = Nb/Ta)

Table 2: Infrared peak assignment (KBr pellets), cm^{-1}

Compounds	$\nu\text{SO}_2/(\nu\text{SO}_2)$	$\nu\text{NH}/(\nu\text{NH})$	$\nu\text{M-N}$	$\nu\text{M-O}$	$\nu\text{M-X}$ (assignment)
SPG (ligand)	1300 (s) (1170 s)	3470 (sb) (3280 s)	-	-	-
[$\text{NbCl}_5(\text{SPG})$]	1285 (m) (1156 m)	3435 (s) (3300 m)	450 m	370	336 m (Nb-Cl)

Cont...

Compounds	$\nu_{\text{SO}_2}/(\nu_{\text{SO}_2})$	$\nu_{\text{NH}}/(\nu_{\text{NH}})$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-X}}$ (assignment)
[NbBr ₅ (SPG)]	1280 (m) (1150 s)	3445 (s) (3205 m)	490	385	265 m (Nb-Br)
[TaCl ₅ (SPG)]	1290 (m) (1150 m)	3440 (s) (3200 mb)	410 m	370 m	325 m (Ta-Cl)
[TaBr ₅ (SPG)]	1285 (sb) (1150 mb)	3435 (sb) (3200 mb)	400 m	360 m	225 (Ta-Br)

RESULTS AND DISCUSSION

The elemental analysis shows that all the complexes have 1:1 stoichiometry. The complexes are yellow to faint yellow in colour and insoluble in common organic solvents such as methanol, ethanol, benzene, acetone and carbon tetrachloride, but are soluble in DMF and DMSO. The observed molar conductance values of the complexes fall in the range 11.0-22.0 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that all of them are non-electrolytes^{7,8}. The magnetic moment of Nb(V) complexes were found 0.35-0.55 BM probably due to temperature independent second order Zeeman effect as suggested by Fowles et al.⁹ and Kepert and Nyholm¹⁰ and is in agreement with results reported earlier¹¹. All complexes did not melt but were decomposed to blue-black mass in the temperature range 178-225°C due to reduction of Nb (V) to a blue Nb (III) and Ta (V) to black Ta (III) by SPG.

UV-Vis spectra

The electronic spectrum of SPG exhibit absorption maxima at 235 nm due to $\pi \rightarrow \pi^*$ transition and red shift at 220-225 nm in complexes. A very strong new band at 265-270 nm is also observed in complexes is assigned to a L \rightarrow M charge transfer transition and intra ligand bands^{12,13}. However, the distinction between intra-ligand and charge transfer could not be made. The presence of coordinated ligand in all complexes was assumed and no absorption was observed in the range 400-800 nm in all complexes, which suggests the metal ion in (n-1) d^0ns^0 , electron configuration.

IR Spectra

The IR spectra of sulphaguanidine (SPG) is examined by Baxter et al.¹⁴ The bands at 3470 cm^{-1} , 3220 cm^{-1} , 3260 cm^{-1} and 3200 cm^{-1} are assigned as $\nu_{\text{as}} \text{NH}$, $\nu_{\text{sym}} \text{NH}$, $\nu_{\text{SO}_2}\text{-NH}$ and $\nu_{\text{C=N}}$ of guanidine group, respectively¹⁵. Wang and Ma¹⁶ reported NH stretching bands in the region 3365-3374 cm^{-1} and guanidine C=N stretching bands in the region 1598-1638 cm^{-1} .

These bands are red shift 15-20 cm^{-1} on complexation and appeared as broad band suggesting the coordination through NH_2 group. The antisymmetric and symmetric stretching modes of $-\text{SO}_2$ group appear at 1300 cm^{-1} and 1170 cm^{-1} in free SPG red shifts about 35-50 cm^{-1} on coordination indicating bonding through SO_2 - oxygen atom¹⁷. Chohan et al.¹⁸ reported SO_2 stretching modes at 1345 and 1110 cm^{-1} for sulphonamide derivatives. Rodriguez and co-workers¹⁹ have also reported the νSO_2 bands in the range of 1242-1394 cm^{-1} . These observation are also supported by new bands due to $\nu \text{Nb-O}$ (370-385), $\nu \text{Nb-N}$ (450-490 cm^{-1}), $\nu \text{Ta-O}$ (360-370 cm^{-1}) and $\nu \text{Ta-N}$ (400-410 cm^{-1}) in the spectra of complexes.

The absence of a strong absorption in the 850-950 cm^{-1} region ruled out the existence of $\text{Nb} = \text{O}/\text{Ta} = \text{O}$ species and absence of water molecules. The far IR spectra of complexes also exhibits new bands at 335-340 ($\nu \text{Nb-Cl}$), 260-265 ($\nu \text{Nb-Br}$), 320-325 ($\nu \text{Ta-Cl}$), 225-230 ($\nu \text{Ta-Br}$) due to metal-chlorine/metal-bromide stretching modes agreement with previous literature²⁰.

CONCLUSION

The analytical data of the complexes suggest the formulae of the complexes as MX_5L ($\text{M} = \text{Nb}/\text{Ta}$ & $\text{X} = \text{Cl}/\text{Br}$). The molar conductance values show the non-electrolytic nature of the complexes. The IR & UV-Vis spectral studies indicate neutral bidentate behaviour of sulphaguanidine coordinating through the $-\text{NH}_2$ and $-\text{SO}_2$ groups. Based on the above studies, a coordination number seven was suggested for examined Nb (V) and Ta (V) complexes.

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