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Synthesis and Spectral Characterization of Tantalum(V) derivatives of 1-Para substituted phenyl-tetrazoline 5-thione

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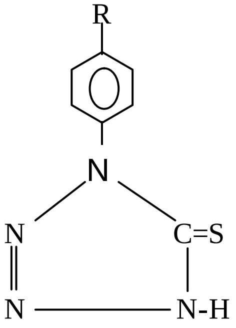
Abstract

Tantalum(V) complexes [$TaCl_5$(LH)] (where LH = 1- para substituted phenyl tetrazoline-5-thione) have been synthesised and characterised on the basis of elemental analyses, conductivity measurements, IR, UV-vis and ‘HMNR studies. The ligands behaves as neutral monodentate having bonding through thiocarbonyl sulphur of thioamide group.

Key words : Ta(V), Thiamide, structure bonding.

Introduction

In continuation of our earlier work on coordination compounds of transition metals in higher oxidation state[1-3] the present paper reports in detail the results of studies on some monomeric complexes of 1 tantalum (V) with 1-parasubstituted phenyl- tetrazoline-5-thione (IA)



(R=CH_3-, CH_3O-, CH_3CH_2O-, Cl-& OH-)

(IA)

Experimental

All the reagents, including $TaCl_5$ were commercial products (Aldrich) of the highest purity available. Solvents were dried before use. The ligands were prepared by the reaction of Para substituted aryl isothiocyanate and sodium azide in accordance with an earlier report[4]. The complexes were prepared using a general method reported in our previous Papers[2]. The analytical and physical data of complexes are given in table 1.

Carbon, hydrogen and nitrogen were analysed at CDRI, Lucknow. Tantalum was determined gravimetrically as Tantalum Pentaoxide and Chloride as silver chloride. The conductance of 10^{-3} M solution of the complexes in DMF were measured using Wiss-Werkstten wheiheim obb type LBR conductivity meter. The electronic spectra of the ligands and the complexes were recorded by Cary-17 D automatic recording Spectrophotometer. The IR spectra were recorded in the range 4000-200 cm^{-1} on a Perkin-Elmer- 783 instrument in KBr pellets. The magnetic measurements were made on a Gouy balance and ‘H NMR spectra of ligands and complexes were recorded with 90 MHZ NMR Spectrometer in $CDCl_3$ solution using TMS as the internal indicator in the range of 0 to 10 PPM.

Results and Discussion

The analytical data (Table 1) reveals a stoichiometry of 1:1, metal : ligand. The molar conductance values of 10^{-3} M solutions in DMF were in the range of 16.50-33.50 ohm^{-1} cm^2 mol^{-1}, indicating a non-electrolytic behaviour of the complexes[5]. All the products did not melt but were decomposed to black mass in all cases in the temperature range 170-185° C due to reduction of Ta(V) to black $TaCl_4$ or $TaCl_3$ by thioamide ligands. All complexes were diamagnetic indicating d° configuration of Ta(V). The ligands behaves as neutral monodentate having formula [$TaCl_5$.(ligand)] and octahedral structure to all may be proposed considering our previous observations[1-3].

Electronic and infrared Spectra :

The electronic spectra of ligands exhibit two absorption maxima at 300-305 nm and 320-335 nm assignable to p → p* and n→ p* transition respectively indicating the presence of coordinating ligands. However, no

Table 1. Analytical and physical data of complexes

Sl. No.	Complex/ (Colour)	Analysis(%)found/ Calculated					^m (ohm^{-1} cm^{2}mol^{-1})
		C	H	N	Cl	Ta	
1	[$TaCl_5$(P-CH_3-L)] (light yellow)	17.30 (17.40)	1.46 (1.45)	10.12 (10.17)	32.30 (32.24)	32.33 (32.87)	24.56
2	[$TaCl_5$(P-CH_3O-L)] (dull yellow)	17.0 1(16.44)	1.45 (1.41)	9.90 (9.88)	31.30 (31.33)	31.90 (31.95)	29.80
3	[$TaCl_5$(P-Cl-L)] (white)	14.78 (14.71)	0.91 (0.87)	9.78 (9.80)	37.50 (37.30)	31.72 (31.69)	25.75
4	[$TaCl_5$(CH_3CH_2O-L)] (dull yellow)	18.72 (18.60)	1.75 (1.72)	9.70 (9.64)	30.66 (30.57)	31.20 (31.18)	21.29
5	[$TaCl_5$(P-OH-L)] (faint yellow)	15.30 (15.20)	1.10 (1.08)	10.23 (10.13)	32.40 (32.12)	32.80 (32.76)	28.38

L = $C_7H_5N_4S$; P-CH_3-L = $C_8H_8N_4S$; P-CH_3O-L = $C_8H_8N_4SO$;
P-Cl-L = $C_7H_5N_4SCl$; CH_3CH_2O-L = $C_9H_{10}N_4SO$; P-OH-L = $C_7H_6N_4SO$;

Table 2. Major IR Spectral bands of ligands and complexes

Compd.	Thioamide Bands# (cm^{-1})				υTa-Cl	υTa-S
	Band I 1500 (m)	Band II 1280 (m)	Band III 1044 (m)	Band IV 810 (m)	-	-
[TaCl$_5$(P-CH$_3$-L)]	1505 (s)	1275 (m)	1025 (m)	780 (m)	320 (m) 325 (m)	360 w 370 w
P-CH$_3$O-L (ligand)	1505 (s)	1290 (s)	1050 (m)	800 (m)	-	-
[TaCl$_5$ P-CH$_3$O-L]	1515 (s)	1285 (s)	1020 (m)	775 (m)	315 (m) 325 (m) 330 (m)	355 (w) 365 (w)
CH$_3$CH$_2$O-L (ligand)	1510 (s)	1280 (s)	1060 (s)	805 (m)	-	-
[TaCl$_5$(CH$_3$CH$_2$O-L)]	1510 (sb)	1275 (s)	1020 (m)	780 (m)	320 (m) 330 (m) 335 (m)	360 (w) 370 (w)
P-Cl-L (ligand)	1495 (s)	1280 (s)	1055 (s)	780 (m)	-	-
[TaCl$_5$(P-Cl-L)]	1500 (sb)	1285 (s)	1030 (m)	7765 (m)	325 (m) 335 (m) 340 (m)	370 (w) 375 (w)
P-OH-L (ligand)	1510 (s)	1280 (s)	1050 (s)	790 (m)	-	-
[TaCl$_5$(P-OH-L)]	1515(sb)	1285(s)	1030(m)	775 (m)	320 (m) 330 (m)	365 (w) 370 (w)

\# Band I (δNH + δCH + υC=N); Band II (υC –N + δNH + υC=S);
Band III (υC⎓N + υCS); Band IV (υC⎓S)

absorption occurs in the range of 400-800 nm in all cases which suggest the metal ion in $(n-1)d^o ns^o$ electronic configuration[2].

The two distinct broad absorption bands around 3120-3180 cm^{-1} and 3050-3060 cm^{-1} in the spectra of thioamide ligands are assigned to superimposed bands of υNH and υCH vibrations. Rao *et al.*[6] on examining the spectra of tetrazoles (pka = 4.89) in very dilute solution assigned υNH frequency at 3145 cm^{-1}. This band blue shift to higher frequency on coordination indicating absence of bonding through iminonitrogen of ligands. This observation is further supported by blue shift of thioamide band I of ligands observed at 1500 cm^{-1} considering normal coordinate analysis (NCA) of other thioamide ligands performed by Agarwala *et al.*[7] and Suzuk[8].

Thioamide band IV, band II and band III have major contribution from υC=S[9-11]. The red shift of these bands indicate the formation of Ta-S bond and ligands act as neutral monodentate. New bands at 360-370cm^{-1} region in far-IR spectra of complexes confirms the formation of tantalum-sulphur bond and assigned to Ta-S stretching modes[12-13]. Two to three new bands between 320-325cm^{-1} in complexes suggest covalent chloride and assigned to υTa-Cl modes[12,14].

'H NMR Spectra :

The metal-ligand bonding is further substantiated by 'H NMR spectra of ligand and their complexes. All ligands display broad multiplet in the range of d7.2-7.70 PPM due to phenyl protons. The broad nature of peak may be due to large quadrupole resonance broadening effect of tetrazole nitrogen atoms[15]. These protons signals are slightly low shifted on complexations and the integrated intensities of these signals agree well with the formulation of the complexes. The methyl protons (δ2.4 PPM), methoxy protons (δ3.74 PPM) and imino proton (δ1.3-1.42 PPM) of ligands are also displayed slightly low field shift and the integrated intensities of the signals support the assigned structure. Thus, imino proton of ligands are intact and no deprotonation has occured on complexation. These observations are consistent with conclusions drawn from IR spectral data.

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