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Synthesis and Spectral Characterization of Oxo- and di-Oxo-Transition Metal Chelates of 2-aminothiophenol and 2-aminophenol

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Abstract

Squarepyramidal chelates of VO^{++}, oxo-bridged octahedral chelates of VO_2^+ and octahedral cis-dioxo chelates of $MoO_2^{++}$and WO_2^{++} are prepared using 2-aminothiphenol and 2-aminophenol as chelating agents. The possible structures are deducted in the light of results from elemental analysis, magnetic susceptibility, electrical conductivity measurements, IR, UV-vis, 'H NMR and ESR Spectra. The persistent of ZrO^{++} group is lacking in octahedral bis-chelate of oxo-zirconium (iv).

Key words : VO_2^+, VO^{++}, ZrO^{++}, MoO_2^{++} and WO_2^{++} species chelates, 2-aminothiophenol, 2-aminophenol.

Introduction

Metal chelates of 2- aminothiophenol are investigated by several workers[1-3]. A perusal of the literature reveal that no work has been done on d^o-oxocations like, VO^{++}, ZrO^{++}, and which may display a great variety of coordination geometries and very interesting insights into structure and bonding[4-6]. These oxo-cations are related with several bio-chemical problems[7-9] and we have reported some novel complexes of these ions with thioamide ligands[10-12]. The present study aims at synthesis and spectral characterization of these oxo-cations with 2-aminothiophenol and 2-amino-phenol.

Experimental

The ligands, 2-aminothiophenol (Schuchardt, Munchen) and 2-aminophenol (Ward Blenkinsop, London) and other chemicals used were either of AR grade or were CP-

grade. All complexes were prepared using our general method reported earlier[10-12].

IR Spectra were recorded on a Perkin Elmer 577 Spectrometer, electronic spectra on a Backmann DV-6 Spectrometer, 'HMR ($CDCl_3$) on a JEO_2 JMS 60011 NMR Spectrometer, ESR spectra on Varian Associate Spectrophotometer using 100 KHZ, X-band (RT), Scan range 2.0 x 1 Kg and field set 3200 and molar conductance (10^{-3}M) of complexes were measured in DMF using Wiss-werkstatter Weithein obb type LBR conductivity meter. Magnetic moment was measured on a gouy balance using $Hg[Co(SCN)_4]$ as calibrant.

Analysis :

Sl.No. 1 : For $[VO(SC_6H_4NH_2)_2].4H_2O$:
Found(%) : C, 37.34; H, 5.21; N, 7.20; V, 13.20;
Calculated (%): C, 37.20; H, 5.16; N, 7.23; V, 13.17;

Sl.No. 2 :For $VO(OC_6H_4NH_2)_2].3H_2O$:
Found(%) : C, 42.68; H, 5.31; N, 8.28; V, 15.10;
Calculated (%): C, 42.72; H, 5.34; N, 8.30; V, 15.13;

Sl.No. 3 : For $[V_2O_3(S\text{-}C_6H_4\text{-}NH_2)_4]$:
Found(%) : C, 44.55; H, 4.32; N, 8.72; V, 15.68;
Calculated (%): C, 44.58; H, 4.33; N, 8.66; V, 15.78;

Sl.No. 4 : For $[V_2O_3(O\text{-}C_6H_4\text{-}NH_2)_4]$:
Found(%) : C, 49.44; H, 4.80; N, 9.72; V, 17.55;
Calculated (%): C, 49.48; H, 4.81; N, 9.62; V, 17.52;

Sl.No. 5 : For $[MoO_2(S\text{-}C_6H_4\text{-}NH_2)_2]$:
Found(%) : C, 38.12; H, 3.00; N, 7.52; Mo, 25.20;
Calculated (%): C, 38.29; H, 3.19; N, 7.44; Mo, 25.53;

Sl.No. 6 : For $[MoO_2(O\text{-}C_6H_4\text{-}NH_2)_2]$:
Found(%) : C, 38.11; H, 3.18; N, 7.52; Mo, 25.09;
Calculated (%): C, 38.29; H, 3.19; N, 7.44; Mo, 25.53;

Sl.No. 7 : For $[WO_2(S\text{-}C_6H_4\text{-}NH_2)_2]$:
Found(%) : C, 31.21; H, 2.55; N, 6.11; W, 39.55;
Calculated (%): C, 31.04; H, 2.58; N, 6.03; W, 39.64;

Sl.No. 8 : For $[WO_2(O\text{-}C_6H_4\text{-}NH_2)_2]$:
Found(%) : C, 33.21; H, 2.58; N, 6.66; W, 42.47;
Calculated (%): C, 33.34; H, 2.77; N, 6.48; W, 42.57;

Sl.No. 9 : For $[ZrO(H_2O)(S\text{-}C_6H_4\text{-}NH_2)_2].2H_2O$:
Found(%) : C, 35.12; H, 4.33; N, 6.68; Zr, 22.11;
Calculated (%): C, 35.18; H, 4.39; N, 6.84; Zr, 22.29;

Sl.No. 10 : For $[ZrO(H_2O)(O\text{-}C_6H_4\text{-}NH_2)_2].3H_2O$:
Found(%) : C, 36.16; H, 4.98; N, 6.89; Zr, 23.10;
Calculated (%): C, 36.43; H, 5.06; N, 7.08; Zr, 23.08;

Results and Discussion

Elemental analysis of the metal chelates confirmed their proposed stoichiometry given experimental section. These bis-chelates of all oxo-cations were found to be insoluble in most of solvents. However, they were fair soluble in DMF and DMSO. The 10^{-3} M solution

of complexes exhibited molar conductance less than 10 ohm^{-1} cm^2 mol^{-1} indicating their non-electrolytic nature and anions are present in the inner sphere of the complexes. All complexes were found to be diamagnetic indicating d^o-configuration of VO_2^+, ZrO^{++}, MoO_2^{++}, and WO_2^{++} species. The magnetic moment of oxo-vanadium (iv) chelates were observed between 1.66-1.67 BM, which are close to the spin value (1.73 BM) for one unpaired electron. The magnetic moment value suggested their monomeric nature and absence of metal-metal interaction was assumed. The electronic spectra of oxo-vanadium (iv) complexes exhibited three bands at 12315 cm^{-1} ($^2B_2 \rightarrow {}^2E$), 17670cm^{-1} ($^2B_2 \rightarrow {}^2B_1$) and 23255 cm^{-1} ($^2B_1 \rightarrow {}^2A_1$) suggesting Squarepyramidal structure (Str. II) of five-coordinated complexes. The Squarepyramidal Stereochemistry of these oxo-vanadium (iv) complexes are in good agreement with those achieved earlier[13-15]. Other bands of high intensity in ultra-violet region are assigned to intraligand charge transfer.

All diamagnetic complexes of VO_2^+, ZrO^{++}, MoO_2^{++} and WO_2^{++} cations exhibits no absorption bands between 12500cm^{-1} to 25000cm^{-1} as expected for metal ions with $(n-1)d^ons^o$ electronic configuration[16]. However, two strong bands in the UV region was observed due to intraligand charge transfer.

IR Spectra :

The IR bands of interest of the ligands and complexes are discussed here. A comparison of spectra of ligands and complexes indicate the simultaneous Metal-S and Metal-N (ATP) and Metal-O and Metal-N (AP) bonding in all complexes. The υsH (2530 cm^{-1}) band of 2-aminothiophenol (ATP) and υo-H (3480cm^{-1}) band of 2-aminophenol (AP) was abscent from the spectra of complexes and deprotonation of thiol hydrogen and phenolic –OH of ligands on complexation was assumed[17]. The ligand, 2-aminophenol shows sharp υsym NH_2 (3300cm^{-1}) and υasym NH_2 (3380 cm^{-1}), υ C-O (1220 cm^{-1}) and out of plane CH bending mode (740cm^{-1}) are observed at 3285 cm^{-1}, 3370 cm^{-1}, 1200 cm^{-1} and 745 cm^{-1} on complexation respectively and coordination through amino nitrogen and phenolic oxygen was assumed[1]. New bands at 460-445 cm^{-1} and at 515-510 cm^{-1} in the Spectra of complexes due to stretching mode also supported the formation of metal –N and Metal –O bond respectively.

The bands at 3340 cm^{-1} (υsym NH_2), 3460 cm^{-1} (υ asym NH_2) and at 2560 cm^{-1} (υSH) in the Spectrum of 2-aminothiophenol displayed major change. The first two bands red shift to lower frequency about 40-50 cm^{-1} and 60-65 cm^{-1} and third band was not observed in the Spectra of all complexes indicating the formation of M-N and M-S bonds[17].

The dioxo-vanadium(v) complexes exhibited non-ligand medium intensity broad band in the region 3485-3415 cm^{-1} along with a medium band at 840 cm^{-1} assigned for the V-O-V stretching vibration which suggest the formation of H-oxo-bridged vanadium(v) complex[18]. 2-aminothiophenol also forms oxo-bridging Fe-O-Fe system in Fe(III) complex and two sharp but weak bands at 866 and 846 cm^{-1} are reported by Singh *et al.*[1].

The absence of a band in the region 840-950cm^{-1} due to υZr=O stretch in zirconium (iv) complex suggests its formulation as [Zr(OH)$_2$(S-C$_6$H$_4$-NH$_2$)$_2$] and not as [ZrO(H$_2$O)(S-C$_6$H$_4$-NH$_2$)$_2$]. This observation is further supported the presence of a broad band at 3445 cm^{-1} and the appearance of a new band of medium intensity at 1140 cm^{-1} due to the δZr-OH banding[19] mode support the Str. I of the present ZrO(iv) complexes.

All the MoO_2^{++} and WO_2^{++} complexes exhibited two bands (900 and 865cm^{-1}) and (890 & 860 cm^{-1}) assignable to the two Mo=O and W=O stretching modes respectively. The presence of two bands is consistent with the cis-dioxo structure of the MoO_2^{++} and WO_2^{++} groups[10-11,19] (Str. IV).

'H NMR Spectra :

The 'H NMR Spectra ($CDCl_3$) of ligands and oxo-vanadium (iv) complexes were recorded to investigate further mode of metal-ligand bonding. The free ligands, 2-amino-phenol and 2-amino thiophenol displayed signals at δ8.92 and δ3.68 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 complexation[20]. The aryl proton 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 filed shifted on complexation and the integrated intensities of the signals agree well with structure (Str. II). Thus, these observations are consistent with the conclusion drawn from IR Spectral data.

ESR Spectra :

The X-band ESR Spectra of Oxo Vanadium(iv) Complexes with room temperature (300 k) in DMSO solution shows normal eight lines isotropic features revealing hyperfine splitting of the ^{51}V nucleus I=7/2 which indicate that a single vanadium is present in the molecule and monomer. The magnetic and bonding parameters deducted from spectra are in table 2.

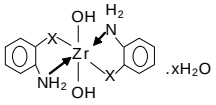
Table 2.
ESR spectral data of ATP-VO(iv) and AP-VO(iv) complexes.

Parameters	ATP-VO(iv)	AP-VO(iv)
g_{II}	1.9712	1.9702
g_I	1.9886	1.98873
g_{av}	1.9802	1.9810
α^2	0.54	0.53

The observed data indicated that g_{II} and g_I values are close to 2 and $g_{II}<g_I<2$ show that the unpaired electron (d^1) is in the dxy orbital localized on the metal with Square Pyramidal geometry[21]. The shape of ESR lines, ESR data together with the electronic Spectral data and magnetic moment value suggest Square Pyramidal geometry for both Oxo-vanadium(iv) Complexes (Str. II).

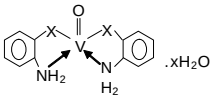
Table 1
Major IR and 'H NMR Spectral data of ligands and complexes

Compds.	IR (cm^{-1})				'H NMR (δPPM)	
	υSH	υa NH_2/ (υs NH_2)	υ M=O	Amino Proton (-NH_2)	-OH/ (-sH)	Phenyl Proton
ATP (ligand)	2560 w	3460 m (3340 m)	-	3.68	- 3.66	6.64-7.30 (multiplet)
VO(iv)-complex (Sl. No. 1)	-	3405 m (3310 m)	820 m	3.54	- (-)	6.62-7.11 multiplet
VO_2^+ - complex (Sl. no.-3)	-	3400 (m) (3310 m)	810 m	-	- (-)	-
MoO_2^{++} -complex (Sl. no.-5)	-	3400 m (3300 m)	900 m 860 m	-	- (-)	-
WO_2^{++}- complex (Sl. no.-7)	-	3410 m (3310 m)	890 m 865 m	-	- (-)	-
ZrO^{++-} complex (Sl. no.-9)	-	3400 m (3305 m)	-	-	- (-)	-
AP (ligand)	-	3380 mb 3300 mb	-	4.40	- (-)	6.42-6.68 multiplet
VO^{++-} complex (Sl. no.-2)	-	3370 m 3290 m	830 m	4.12-4.41 (split)	- (-)	6.32-6.88
VO_2^+ - complex (Sl. no.-4)	-	3360 m 3280 m	840 m	-	- (-)	-
MoO_2^{++}-complex (Sl. no.-6)	-	3350 m 3270 m	900 m 860 m	-	- (-)	-
WO_2^{++}- complex (Sl. no.-8)	-	3370 m 3265 m	880 m 850 m	-	- (-)	-



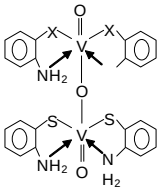
(x = 0/s)
(Str. I)

(Octa-hedral-Structure)



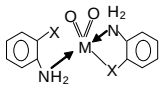
(x = 0/s)
(Str. II)

(Square Pyramidal Structure)



(x = 0/s)
(Str. III)

(Oxo-bridged-VO_2^+-complex)



(x = 0/s; M = Mo/w)
(Str. IV)

(Cis-dioxo-MO_2^{++}-complex)

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