



## Synthesis and Characterization of Some Oxo and Dioxovanadium(IV & V) Chelates with Thioamide Ligands

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Some oxo and dioxovanadium(IV & V) chelates of methyl, methoxy, ethoxy, hydroxyl and chloro derivatives of 1-substituted phenyl-tetrazoline-5-thione have been prepared and characterized by elemental analysis, molar conductivity, magnetic susceptibility measurements, IR, electronic and <sup>1</sup>H NMR spectral studies. Tentative octahedral structure to dioxovanadium(V) and square pyramidal (C<sub>4v</sub>) structure to oxovanadium(IV) chelates is assigned.

**Key Words:** VO<sup>2+</sup>, VO<sub>2</sub><sup>+</sup>, Complexes, Thioamide ligands.

### INTRODUCTION

Vanadium is a physiologically important trace element that is found in cationic, anionic and neutral complexed form with various oxidation states<sup>1-3</sup>. Oxovanadium(IV) complexes are very interesting as model compounds for the clarification of several bio-chemical process<sup>4</sup>. The *bis*(maltolato) oxovanadium(IV) is reported to be first orally active insulin mimetic agent<sup>5</sup>. Moreover, several investigations into biologically relevant vanadium compounds have been made<sup>6-9</sup>. The present study describes some new *bis*-metal chelates of oxovanadium(IV) and dioxovanadium(V) with physiologically active *para*-substituted 1-phenyl tetrazoline-5-thiones<sup>10</sup>.

### EXPERIMENTAL

All chemicals used were of CP-grade or AR-grade. The ligands, *para*-substituted methyl (m.p. = 149 °C), methoxy (m.p. = 160 °C), ethoxy (m.p. = 250 °C), hydroxyl (m.p. = 161 °C) and chloro (m.p. = 157 °C) derivatives of 1-phenyl tetrazoline-5-thione were prepared by the method reported in literature<sup>11</sup>.

All complexes were prepared by reported method<sup>12</sup> at pH = 8. Carbon, hydrogen and nitrogen analysis were done at the micro-analytical section of CDRI, Lucknow (India). The magnetic moments of the complexes were measured at 300 K using gouy balance. The IR spectra of ligands and complexes were recorded by means of Perkin-Elmer 521 spectrophotometer using KBr pellets. The electronic spectra were recorded with Zeiss (Jena) model of automatic recording system. <sup>1</sup>H NMR spectra of ligands and complexes were recorded with

90 MHz NMR spectrophotometer in CDCl<sub>3</sub> solution using TMS as the internal indicator in the range of 0-10 ppm. Molar conductance of complexes were measured in DMF (10<sup>-3</sup> M) using Wiss-Werkstatter weithem obb type conductivity meter.

### RESULTS AND DISCUSSION

Elemental analyses of the metal chelates confirm their stoichiometry as indicated in Table-1. These *bis*-chelates are high melting, coloured solid and were found to be insoluble in most of solvent. The 10<sup>-3</sup>M solution of complexes (sl. no. 1 to 5) exhibited molar conductance value between 60-75 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating uni uni electrolytic nature of all dioxovanadium(V) complexes and chlorine is present in the outer sphere of complexes. All complexes were found to be diamagnetic indicating *d*<sup>0</sup>-configuration of VO<sub>2</sub><sup>+</sup> species. These observations are further supported by electronic spectra of complexes. Two strong bands in the UV region was observed (Table-2) due to intraligand charge transfer. No absorption was attributed between 400 to 800 nm as expected for metal ions with (n-1)*d*<sup>0</sup>*ns*<sup>0</sup> electronic configuration<sup>13</sup>. Barnum<sup>14</sup> and Lintvedt *et al.*<sup>15</sup> have also suggested a strong absorption at about 270-232 nm for vanadate(V) ion, which clearly originate in <sup>1</sup>t<sub>1</sub> → 2e transition.

The magnetic moment of oxovanadium(IV) chelates were observed between 1.66-1.68 BM, which are close to the spin value (1.73 BM) for one unpaired electron. Thus, VO<sup>2+</sup> species are monomeric nature and absence of metal-metal interaction was assumed. The electronic spectra of complexes display strong band at 11834 cm<sup>-1</sup> assigned to charge transfer and two strong bands at 11834 cm<sup>-1</sup> (<sup>2</sup>B<sub>2</sub> → <sup>1</sup>A<sub>1</sub>) and at 22471 cm<sup>-1</sup>

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF VANADIUM COMPLEXES

Sl. No.	Complex/ (Molecular Formula)	Colour/ M. Pt. (°C)	Analysis (%) : Found/(calcd)				Molar cond. $\Lambda_m^{-1}$ $\text{cm}^2 \text{mol}^{-1}$
			C	H	N	V	
1.	$\text{VO}_2(\text{P-CH}_3\text{-L})_2\text{Cl}\cdot 2\text{H}_2\text{O}$ ( $\text{V}\cdot\text{C}_{16}\text{H}_{18}\text{N}_8\text{O}_4\text{S}_2\text{Cl}$ )	Violet (302)	35.80 (35.79)	3.51 (3.35)	20.91 (20.87)	9.50 (9.99)	73.3
2.	$[\text{VO}_2(\text{P-CH}_3\text{-O-L})_2\text{Cl}\cdot 4\text{H}_2\text{O}]$ ( $\text{VC}_{16}\text{H}_{24}\text{N}_8\text{O}_8\text{S}_2\text{Cl}$ )	Violet (295)	31.82 (31.66)	4.01 (3.96)	18.52 (18.46)	8.41 (8.39)	76.2
3.	$[\text{VO}_2(\text{P-CH}_3\text{CH}_2\text{O-L})_2\text{Cl}]$ ( $\text{VC}_{18}\text{H}_{20}\text{N}_8\text{O}_4\text{S}_2\text{Cl}$ )	Violet (305)	38.56 (38.40)	3.58 (3.55)	20.01 (19.91)	9.11 (9.05)	69.8
4.	$[\text{VO}_2(\text{P-Cl-L})_2\text{Cl}]$ ( $\text{VC}_{14}\text{H}_{10}\text{N}_8\text{O}_2\text{S}_2\text{Cl}_3$ )	Violet (307)	31.01 (30.91)	1.89 (1.84)	20.72 (20.60)	9.51 (9.37)	72.3
5.	$[\text{VO}_2(\text{P-OH-L})_2\text{Cl}\cdot 2\text{H}_2\text{O}]$ ( $\text{VC}_{14}\text{H}_{16}\text{N}_8\text{O}_6\text{S}_2\text{Cl}$ )	Grey (290)	31.01 (30.97)	3.02 (2.94)	20.72 (20.64)	9.51 (9.40)	71.6
6.	$[\text{VO}(\text{P-CH}_3\text{O-L})_2]\cdot 3\text{H}_2\text{O}$ ( $\text{VC}_{16}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2$ )	Grey (300)	35.78 (35.75)	4.32 (4.10)	20.95 (20.85)	9.51 (9.48)	nc
7.	$[\text{VO}(\text{P-Cl-L})_2]\cdot 3\text{H}_2\text{O}$ ( $\text{VC}_{14}\text{H}_{16}\text{N}_8\text{O}_4\text{Cl}_2\text{S}_2$ )	Violet (295)	30.79 (30.77)	2.98 (2.93)	20.66 (20.51)	9.35 (9.33)	nc

LH=C<sub>7</sub>H<sub>6</sub>N<sub>4</sub>S (1-phenyl litrazoline-5-thione)

TABLE-2  
CHARACTERISTICS BANDS  $\text{cm}^{-1}$  OF THE IR SPECTRA AND ELECTRONIC SPECTRA OF LIGANDS AND THEIR VANADIUM COMPLEXES

Compd.	IR Bands ( $\text{cm}^{-1}$ )					Electronic spect. Bands (Assignment, $\text{cm}^{-1}$ )	
	vNH	Thioamide Bands $\nu$ (V=O)					
		I	II	III	IV		
Ligand (P-CH <sub>3</sub> -LH)	3080 (mb)	1504(s)	1286(s)	1060m	790(m)	(—)	32780 ( $\pi \rightarrow \pi^*$ ) 31250 ( $n \rightarrow \pi^*$ )
Complex (Sl. No.1)	—	1485(s)	1310(m)	1035(m)	765(m)	830(s)	33333 (CT Band) 31250 (CT Band)
Ligand (P-CH <sub>3</sub> O-LH)	3070 (mb)	1504m	1286(m)	1050m	790(m)	—	33003 ( $\pi \rightarrow \pi^*$ ) 31740 ( $n \rightarrow \pi^*$ )
Complex (Sl. No. 2)	—	1478(s)	1325 (m)	1025m	770(m)	845(s)	31645 (CT Band) 30760 (CT Band)
Ligand (P-CH <sub>3</sub> CH <sub>2</sub> O-LH)	3095 (mb)	1510m	1280(m)	1020(m)	780(m)	845(s)	33890 ( $\pi \rightarrow \pi^*$ ) 30303 ( $n \rightarrow \pi^*$ )
Complex (Sl. No. 3)	—	1485(s)	1315(m)	1010(m)	770(m)	840(s)	207050 (SB) (CT Band)
Ligand (P-Cl-LH)	3090 (mb)	1500(s)	1280m	1055(m)	810(m)	(—)	33445 ( $\pi \rightarrow \pi^*$ ) 31545 ( $n \rightarrow \pi^*$ )
Complex (Sl. No. 4)	—	1485(s)	1320(s)	1035(m)	790(m)	840(s)	37000 (sb) (CT Band)
Ligand (P-OH-LH)	3072 (mb)	1510(s)	1290(m)	1060(m)	805(m)	(—)	33550 ( $\pi \rightarrow \pi^*$ ) 32250 ( $n \rightarrow \pi^*$ )
Complex (Sl. No. 5)	—	1577(s)	1340(m)	1045(m)	785(m)	835(s)	43280 (sb) (CT Band)
Complex (Sl. No. 6)	—	1478(s)	1310(m)	1030(m)	780(m)	930(s)	27173 (CT Band) 22471 ( ${}^2\text{B}_2(\text{p}) \rightarrow \text{E}$ ) 11834 ( ${}^2\text{B}_2 \rightarrow {}^1\text{A}_1$ )
Complex (Sl. No. 7)	—	1480(s)	1325(m)	1035(s)	775(m)	940(s)	31250 (CT Band) 20833 ( ${}^2\text{B}_2 \rightarrow \text{E}$ ) 13157 ( ${}^2\text{B}_2 \rightarrow {}^1\text{A}_1$ )

LH=1-phenyl tetrazoline-5-thione; Sl. No. indicate complexes listed in Table-1

${}^2\text{B}_2(\text{p}) \rightarrow \text{E}$ ) are in agreement with square pyramidal configuration achieved earlier<sup>16,17</sup>.

**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 V-S and V-N bonding in all complexes. The  $\nu(\text{SH})$  and  $\nu(\text{N-H})$  bands of ligands disappears on complexation indicating deprotonation of imino protons and formation of vanadium-N bond. Oxovanadium(IV & V) cation are a class-'A' cation<sup>3</sup> and interacts with N-donor ligands with deprotonation in basic medium (pH = 8).

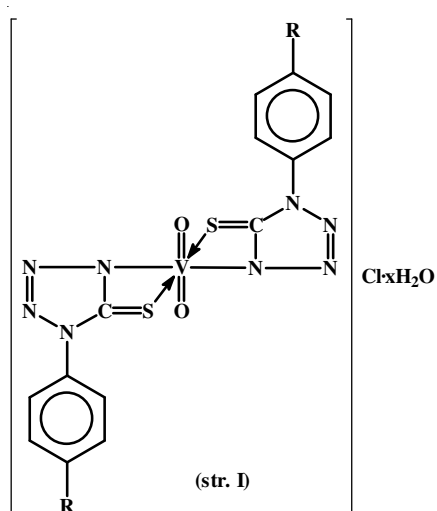
Agarwala *et al.*<sup>18</sup> and Suzuki<sup>19</sup> have performed normal coordinate analysis (NCA) of thioamide ligands. Thioamide ligands give rise to four characteristic thioamide bands<sup>20-22</sup> in the region of 1500  $\text{cm}^{-1}$  (band I), 1300  $\text{cm}^{-1}$  (band II), 1000  $\text{cm}^{-1}$  (band III) and 800  $\text{cm}^{-1}$  (band IV). These bands are mixed

band having contributions from  $\nu(\text{C}=\text{S})$ ,  $\nu(\text{C}=\text{N})$ ,  $\delta(\text{C-H})$ ,  $\delta(\text{NH})$  modes. The blue shift of thioamide band II (30-35  $\text{cm}^{-1}$ ), red shift band I (20  $\text{cm}^{-1}$ ) band III (20-30  $\text{cm}^{-1}$ ) and band IV (30-40  $\text{cm}^{-1}$ ), suggest simultaneous (V-N) and (V-S) bonding on complexation<sup>20-22</sup>. These observations are further supported by new bands at 455  $\text{cm}^{-1}$   $\nu(\text{V-N})$  and at 310  $\text{cm}^{-1}$   $\nu(\text{V-S})$  in far-IR spectra of complexes<sup>23</sup>.

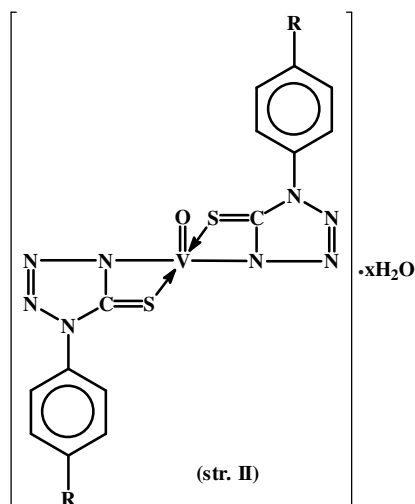
The presence of strong single band at 840-830  $\text{cm}^{-1}$  in all dioxovanadium(V) complexes indicate two oxogroups are at transposition in octahedral configuration<sup>12</sup>. However, oxovanadium(IV) complexes display strong band at 940-930  $\text{cm}^{-1}$  assigned to  $\nu(\text{V}=\text{O})$  mode<sup>12</sup> in monomeric complexes.

**<sup>1</sup>H NMR Spectra:** To substantiate further bonding in the complexes, <sup>1</sup>H NMR spectra of ligands and some complexes (Sl. No. 1, 6 & 7) were recorded in  $\text{CDCl}_3/\text{TMS}$ . The broad multiplet in the region  $\delta 7.42$ -7.81 ppm are observed in these

complexes due to phenyl protons. The broad nature of peak may be due to large quadrupole resonances broadening effect of tetrazole nitrogen atoms<sup>24</sup>. The resonances due to imino proton in the ligands observed at  $\delta$ 1.25-1.28 ppm is absent in the spectra of complexes suggesting the formation of V-N bond and deprotonation of N-H group on complexation<sup>25</sup>. The methoxy protons observed as a sharp singlet at  $\delta$ 3.70 ppm in complexes coincides with that of methoxy group protons in literature<sup>26</sup>. The methyl protons of coordinated ligands are observed at  $\delta$ 2.45 ppm<sup>26</sup>.



Tentative octahedral structure of dioxovanadium(V) chelates  
(R=CH<sub>3</sub>, CH<sub>3</sub>O, CH<sub>3</sub>CH<sub>2</sub>O, OH, Cl)



Tentative square pyramidal structure of oxovanadium(IV) chelates  
(R=CH<sub>3</sub>, CH<sub>3</sub>O, CH<sub>3</sub>CH<sub>2</sub>O, OH, Cl)

Thus, on the basis of aforesaid observations, octahedral structure to dioxovanadium(IV) (str. I) and square pyramidal (C<sub>4v</sub>) structure to oxovanadium(IV) (str. II) chelates may be assigned.

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