



Synthesis and Characterization of Some Oxo-cations Complexes with Heterocyclic Thioamide Ligand

R.N. PANDEY* and KALPANA SHAHI

Post Graduate Centre of Chemistry, College of Commerce, Patna-800 020, India

*Corresponding author: E-mail: rameshwarnath.pandey@yahoo.com; drkalpanashahi@gmail.com

(Received: 23 November 2010;

Accepted: 24 June 2011)

AJC-10075

Mono nuclear oxo-cation complexes with 1,2,4-triazole-3(s) thione have been prepared and characterized on the basis of elemental analysis, molar conductance, spectral (IR, electronic) studies and magnetic susceptibility measurements. The ligand behaves as mononegative bidentate ligand having bonding through deprotonated imino nitrogen and thiocarbonyl sulphur. IR spectra suggest existence of *cis*-dioxo structure of VO_2^+ , MoO_2^{2+} and WO_2^{2+} species, which forces the ligand to coordinate in a non-planar fashion and allow better $\text{O}_{(\text{pr})} - \text{M}_{(\text{dpr})}$ bonding than linear arrangement would allow in octahedral geometry.

Key Words: VO_2^+ , MoO_2^{2+} , WO_2^{2+} species, Complexes, Thioamide ligand.

INTRODUCTION

Oxo-metal complexes of vanadium^{1,2}, zirconium³, molybdenum^{4,5} and tungsten^{4,5} are subject of reviews and strongly bound oxygen(s) of these oxo-cations provide additional interest for studying the complexes⁶. These oxocations are related to many biological problems⁷⁻¹² and is interesting to elucidate their structure and bonding. This work reports the synthesis, characterization and various physico-chemical investigations of VO^{2+} , VO_2^+ , ZrO^+ , MoO_2^{2+} and WO_2^{2+} complexes with 1,2,4-triazole-3(s) thione following earlier report on tetrazoles¹³ and quinazoles¹⁴ having thioamide group.

EXPERIMENTAL

All chemicals used were of AR grade or CP grade. The ligand, 1,2,4-triazole-3(s)-thione (m.p. = 220-223 °C) was prepared by the method reported in literature¹⁵. Dioxometal(V & VI)¹⁶ and oxometal(IV)¹⁷ complexes were prepared similar to our previous methods. The mixed-ligand isothiocyanato complexes were prepared using metal salts (0.001 mol), ammonium thiocyanate (0.002 mol) and ligand (0.001 mol.) suspended in methyl alcohol (50 mL) and was stirred on magnetic stirrer for 2 h and filtered. On crystallization solid complexes were obtained. The IR spectra of the ligand and complexes were recorded on a Perkin-Elmer Model-577 spectrophotometer in the range of 4000-200 cm^{-1} as KBr pellets. The magnetic measurements were made on a Gouy balance and the diamagnetic corrections for the ligand molecules were applied. The UV-VIS spectra of ligand and complexes were

recorded on a Beckmann and Carl Zeiss (Jenna) Spectrophotometer. The molar conductance of complexes (10^{-3} M) were measured in DMF using Wiss-Werkstatter Weithem obb type LBR conductivity meter.

RESULTS AND DISCUSSION

The ligand (LH) exist as thione tautomeric form with deprotonation of imino group at pH = 8 and elemental analysis data (Table-1) correspond to 1:2 metal-ligand stoichiometry for all the complexes. However, 1:1 metal-ligand ratio was observed in presence of mixed-ligand complexes with isothiocyanate ion. The molar conductance of the complexes in DMF (10^{-3} M) lies below $10\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ indicating their non-electrolytic nature. All the complexes were found to be diamagnetic as expected for d^0 -configuration of ZrO^{2+} , VO_2^+ , MoO_2^{2+} and WO_2^{2+} species. Oxovanadium(IV) complexes exhibited magnetic moment 1.70 BM for one unpaired electron and close to spin only value 1.73 BM for d^1 -configuration. The square pyramidal (C_{4v}) structure may be assumed as the magnetic moment of square pyramidal complexes are expected to be fairly close to spin only value due to lower symmetry.

UV-VIS spectra: The UV and visible spectrum of the ligand contains two broad bands at 305 and 335 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. These bands shifted to (250-260) and (270-280) nm in all complexes of VO_2^+ , ZrO^{2+} , MoO_2^{2+} and WO_2^{2+} ions due to coordination of ligand. However, no absorption in the range of 800-400 nm indicating d^0 -configuration of these ions¹⁸.

TABLE-1
ANALYTICAL, PHYSICAL AND ELECTRONIC SPECTRAL DATA OF COMPLEXES.

Complex/(pH of isolation colour)	m.f.	Analysis (%) Found/(calcd)				λ max/(nm Assignment)
		C	H	N	M	
[VO ₂ L ₂] (8, Violet)	C ₄ H ₄ N ₆ S ₂ O ₂ V	17.02 (16.96)	1.45 (1.42)	29.75 (29.68)	18.12 (18.02)	250 (CT Band) 270 (CT Band)
[MoO ₂ L ₂] (8, Golden Brown)	C ₄ H ₈ N ₆ S ₂ O ₂ Mo	13.11 (13.18)	2.21 (2.19)	23.17 (23.07)	26.40 (26.37)	255 (CT Band) 275 (CT Band)
[MoO ₂ L(NCS) ₂] (8, Leaf Brown)	C ₄ H ₂ N ₅ S ₃ O ₂ Mo	14.02 (13.95)	0.96 (0.58)	20.51 (20.34)	28.01 (27.90)	260 (CT Band) 280 (CT Band)
[WO ₂ L ₂] (8, light yellow)	C ₄ H ₄ N ₆ S ₂ O ₂ W	11.55 (11.54)	1.10 (0.96)	20.32 (20.20)	44.28 (44.20)	260 (CT Band) 280 (CT Band)
[WO ₂ L(NCS) ₂] (8, faint yellow)	C ₄ H ₂ N ₅ S ₃ O ₂ W	11.51 (11.11)	0.82 (0.46)	16.01 (16.21)	42.68 (42.56)	256 (CT Band) 279 (CT Band)
[VO ₂ L ₂] (8, grey)	C ₄ H ₄ N ₆ S ₂ OV	18.11 (17.97)	1.50 (1.49)	31.50 (31.46)	19.12 (19.10)	280 (CT Band) 325 (CT Band) 485 (² B ₂ → E) 760 (² B ₂ → E)
[Zr(OH) ₂ L ₂] (9, faint yellow)	C ₄ H ₆ N ₆ S ₂ O ₂ Zr	14.85 (14.75)	1.95 (1.84)	25.96 (25.82)	28.14 (28.04)	260 (CT Band) 280 (CT Band)

(LH = N₃C₂H₃S)

TABLE-2
CHARACTERIZATION BANDS (cm⁻¹) OF THE IR SPECTRA OF LIGAND AND OXO-METAL COMPLEXES

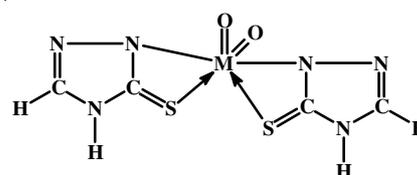
Compounds.	$\nu(\text{M}=\text{O})$	Thioamide Bands				$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
		I	II	III	IV		
(ligand)	—	1550s	1297 m, 1250 m	1050 m	840 m	—	—
[VO ₂ L ₂]	930 ms, 910 m	1530 m	1310 m, 1260 m	1020 m	800 m	450 m, 440 m	320 w
[MoO ₂ L ₂]	935 s, 915 m	1525 m	1320 m, 1260 m	1025 m	805 m	460 m, 450 m	340 w
[MoO ₂ L(NCS) ₂]	930 m, 910 m	1535 m	1310 m, 1255 m	1030 m	800 m	480 m, 470 m	350 w
[WO ₂ L ₂]	935 ms, 920 ms	1530 m	1330 m, 1260 m	1035 m	800 m	490 m, 480 m	310 w
[WO ₂ L(NCS) ₂]	930 m, 925 m	1520 m	1340 m, 1270 m	1025 m	810 m	480 m, 460 m	300 w
[VOL ₂]	970 vs	1525 m	1340 m, 1265 m	1020 m	810 m	450 m	320 w
[Zr(OH) ₂ L ₂]	—	1530 m	1320 m, 1265 m	1025 m	795 m	500 m, 480 m	320 w

Band I ($\delta\text{NH} + \delta\text{CH} + \text{C}=\text{N}$); Band II ($\nu\text{C}=\text{N} + \delta\text{NH} + \delta\text{CH} + \nu\text{C}=\text{S}$); Band III ($\nu\text{C}=\text{S} + \nu\text{C}=\text{N}$) Band IV ($\nu\text{C}=\text{S}$)

The spectral bands at 760, 485, 325 and 280 nm indicate square pyramidal stereo chemistry around vanadyl ion and assigned to ²B₂ → ¹A₁, ²B₂ → E and charge transfer transition. These results are in excellent agreement with those achieved earlier¹⁹.

IR Spectra: The characteristic IR bands observed in the spectrum of the ligand²⁰, at 3060, 1550, 1297, 1050 and 840 cm⁻¹ are assigned to νNH , thioamide band I, band II, band III and band IV respectively. The systematic shift of thioamide bands of ligand (Table-2) is similar to our earlier observations^{21,22} with thioamide ligands and suggest the simultaneous formation of Metal-N and Metal-S bond in all complexes. (Table-2) The occurrence of new bands at 500-490 and 350-310 cm⁻¹ in far-IR of complexes further suggest the coordination of ligand (LH) through nitrogen and sulphur atoms assignable to M-N and M-S stretching vibrations respectively. Two non-ligand bands at 910 and 930 cm⁻¹ (VO₂⁺), 915 and 935 cm⁻¹ (MoO₂²⁺) and at 920 and 935 cm⁻¹ (WO₂²⁺) are consistent with *cis*-MO₂ configuration and assigned to $\nu_{\text{sym}}(\text{O}=\text{M}=\text{O})$ and $\nu_{\text{asym}}(\text{O}=\text{M}=\text{O})$ modes. The *cis*-MO₂ structure forces the ligand to coordinate in a non-planar fashion²³ (**str. I**) and allow better O($\rho\pi$) - M($d\pi$) bonding than linear arrangement would allow.

The absence of a band in the region 955-835 cm⁻¹ due to the $\nu(\text{Zr}=\text{O})$ stretch in the present oxozirconium(IV) complex

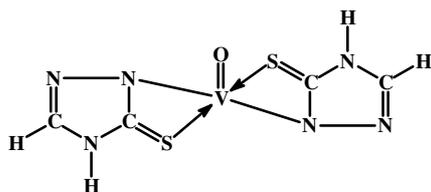


(str. I)

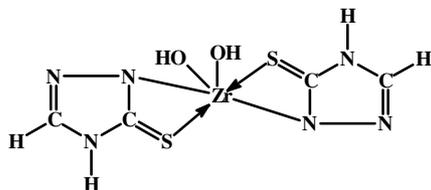
(M = V, Mo & W) (tentative octahedral structure)

suggest its formulation as [Zr(OH)₂L₂] and not as [ZrO(H₂O)L₂]. The presence of a broad band at 3440 cm⁻¹ and the appearance of a new medium intense band at 1140 cm⁻¹ due to the $\delta(\text{Zr}-\text{OH})$ bending mode also support the proposed structure (**str. III**) of the present oxozirconium(IV) complex. However, the new non-ligand band in oxovanadium(IV) complexes at 970 cm⁻¹ assigned to $\nu(\text{V}=\text{O})$ mode is indicative of monomeric VO₂⁺ -group²⁴ (**str. II**). The thiocyanate anion is N-bonded in all complexes and exhibits $\nu(\text{C}=\text{N})$ 2040 cm⁻¹, $\nu(\text{C}=\text{S})$ 780 cm⁻¹ and δ NCS 490 cm⁻¹ consistent with literature value²⁵.

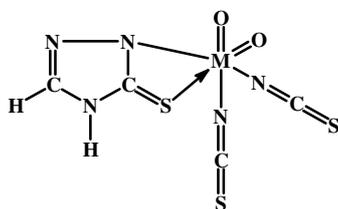
Thus, on the basis of analytical data (Table-1), valence requirements, UV-VIS and IR spectral studies square pyramidal structure to VO₂⁺ complexes and octahedral configuration to ZrO₂²⁺, VO₂²⁺, MoO₂²⁺ and WO₂²⁺ complexes may be tentatively assigned.



(str. II)
Square pyramidal structure (C_{4v})



(str. III)
Octahedral structure



(str. IV)
Octahedral structure

REFERENCES

1. D.A. Rice, *Coord. Chem. Rev.*, **37**, 61 (1981); **45**, 67 (1982).
2. J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
3. R.C. Fay, *Coord. Chem. Rev.*, **37**, 41 (1981); **45**, 41 (1982); **52**, 285 (1983).
4. C.D. Garner, *Coord. Chem. Rev.*, **37**, 117 (1981); **45**, 153 (1982).
5. F.E. Mabbs, *Coord. Chem. Rev.*, **37**, 157 (1981).
6. K.C. Dash, *J. Indian Chem. Soc.*, **66**, 562 (1989).
7. A. Butler and C.J. Carrano, *Coord. Chem. Rev.*, **109**, 61 (1991).
8. Y.H. Xing, K. Aoki and F.Y. Bai, *J. Coord. Chem.*, **57**, 157 (2004).
9. R.A.D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).
10. E.I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
11. A. Garnovskii, A.L. Nivorozhkin and V.I. Minkin, *Coord. Rev.*, **126**, 1 (1993).
12. K.H. Thompson and C. Orvig, *J. Chem. Soc., Dalton Trans.*, 2885 (2000).
13. R.N. Pandey, L.M.R. Choudhary, P. Sharma, A.N. Sahay and R.N. Sharma, *Indian J. Chem.* **32A**, 450 (1993).
14. R.N. Pandey, R.N. Sharma, L.M. Roy Choudhary and P. Sharma, *J. Indian Chem. Soc.*, **69**, 719 (1992).
15. G. Ainsorth, *J. Org. Synth.*, **40**, 99 (1960).
16. R.N. Pandey, S. Singh and A.K. Sinha, *Asian J. Chem.*, **6**, 252 (1994).
17. R.N. Pandey, S.K. Ogha and R.N. Sharma, *Int. J. Chem. Sci.*, **6**, 2073 (2008).
18. T.M. Dunn, R.S. Nyholm and S. Yamada, *J. Chem. Soc.*, 1564 (1962).
19. R.K. Narula, Y. Dong, O.J. D' Cruz, C. Navara and F.M. Uckun, *Clin. Cancer Res.*, **6**, 1546 (2000).
20. R.N. Pandey, G. Kumari and R.K. Singh, *J. Ultra Chem.*, **5**, 327 (2009).
21. R.N. Pandey, A. Anand, R.K. Singh and A. Kumar, *Asian J. Chem.*, **22**, 5601 (2010).
22. R.N. Pandey, R.K. Singh, Priya and M. Ranjan, *Asian J. Chem.*, **22**, 5595 (2010).
23. K. Dey, B.K. Maity and G.K. Bhar, *Transition Met. Chem.*, **6**, 346 (1981).
24. A.A. Osowole, B.C. Ejelolu and S.A. Balogun, *J. Ultra. Sci.*, **20**, 549 (2008).
25. J.L. Burmister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).