

## Synthesis, Characterization and Antimicrobial properties of Oxovanadium(IV) Complexes Derived from Schiff Base Ligand Containing Thiosemicarbazone Moiety

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The synthesis and characterization of the complexes of oxovanadium(IV) is reported here-in of  $[\text{VOL}_1(\text{H}_2\text{O})_2]\text{SO}_4$  ( $\text{L}_1$  = Schiff bases ligands containing thiosemicarbazone moiety) *i.e.*, *bis(p-methoxybenzaldehyde)* thiosemicarbazone, *bis(N,N'-dimethyl-4-aminocinnamaldehyde)* thiosemicarbazone, *bis(pyridine-2-aldehyde)* thiosemicarbazone, *bis(p-chlorobenzaldehyde)* thiosemicarbazone, *bis(indole-3-aldehyde)* thiosemicarbazone, *bis(3-methylsalicylaldehyde)* thiosemicarbazone, *bis(5-methylsalicylaldehyde)* thiosemicarbazone, *bis(furfuryl-2-aldehyde)* thiosemicarbazone and *bis(5-bromosalicylaldehyde)* thiosemicarbazone. All the complexes of characterized by elemental analysis, molar conductivity, magnetic moments, thermal studies, EPR, IR and electronic spectra. These studies show octahedral geometry around the metal ion. These complexes were also screened for their antibacterial and antifungal activities.

**Key Words:** Synthesis, Oxovanadium(IV), Complexes, Biological studies, Thiosemicarbazones.

### INTRODUCTION

The synthesis and characterization of the complexes of oxovanadium(IV) of different ligands are of growing interest in co-ordination chemistry. The chemistry of oxocation<sup>1</sup> has been interesting because the V=O multiple bond could be used as internal molecular bond, as it provides an understanding about the nature of M-ligand bond. The pronounced biological activity<sup>2,3</sup> of the Schiff bases from the class of important compounds in medicine and pharmaceutical field. We have successfully prepared the complexes of oxovanadium(IV) of the  $[\text{VOL}_1(\text{H}_2\text{O})_2]\text{SO}_4$  ( $\text{L}_1$  = Schiff bases ligand containing thiosemicarbazone moiety). New VO(IV) complexes of schiff bases ligand containing thiosemicarbazone moiety have been synthesized and characterized.

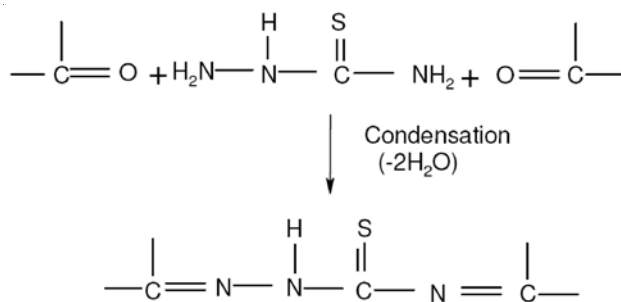
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## EXPERIMENTAL

All the chemicals used in the investigation were of AR grade. The purity of these compounds was checked by melting point determination. All the solvents were purified by standard methods, before the preparation of Schiff bases.

**Procedure:** The Schiff bases were prepared by the condensation of respective aldehyde with thiosemicarbazide in molar ratio of 2:1. The reaction mixture was refluxed, in ethanol for 0.5 h and the requisite amount of respective aldehyde was added into the reaction vessel and refluxed for *ca.* 6 h. It was allowed to stand overnight to yield the crystals of the Schiff bases having thiosemicarbazone moiety, *i.e.*, *bis(p-methoxybenzaldehyde)thiosemicarbazone* (MBATSCZ), *bis(N,N'-dimethyl-4-aminocinnamaldehyde)thiosemicarbazone* (DMABATSCZ), *bis(pyridine-2-aldehyde)thiosemicarbazone* (PATSCZ), *bis(p-chlorobenzaldehyde) thiosemicarbazone* (CBATSCZ), *bis(indole-3-aldehyde)thiosemicarbazone* (IATSCZ), *bis(3-methylsalicylaldehyde)thiosemicarbazone* (MSATSCZ), *bis(5-methylsalicylaldehyde) thiosemicarbazone* (M'SATSCZ), *bis(furfuryl-2-aldehyde) thiosemicarbazone* (FATSCZ) and *bis(5-bromosalicylaldehyde)thiosemicarbazone* (BSATSCZ) (**Scheme-I**). Purification was effected by recrystallization.



**Scheme-I**

**Preparation of oxovanadium(IV) complexes:** All the complexes were prepared by following the general procedure. To a solution of oxovanadium(IV) sulphate (0.1 mol) in methanol (*ca.* 15 mL) to the solution of ligand in DMSO (*ca.* 20 mL) were added drop-wise with constant stirring. The mixture was refluxed for 6-10 h and then the volume was reduced to *ca.* 15 mL by rota-vapour. Coloured precipitate (yellow, white, brown, orange, black) formed on addition of a small amount of ether, was filtered off, washed with DMSO and dried *in vacuo* and finally the yield was 70-75 %.

## RESULTS AND DISCUSSION

All the complexes were found to be coloured, stable in air and non-hygroscopic. The compounds were soluble in water but sparingly soluble in other solvents. The analytical data of all the synthesized complexes are given in Table-1. The molar conductance value of oxovanadium(IV) in MeOH, DMF and DMSO reveals their 1:1 electrolytic nature<sup>4</sup>.

TABLE-1  
ANALYTICAL DATA

Compd. / colour	Metal % Found (Calcd.)	Molar conductance ( $\text{Ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$ )			$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}=\text{S})$ ( $\text{cm}^{-1}$ )	Magnetic moments (BM)	m.p. ( $^{\circ}\text{C}$ )
		MeOH	DMF	DMSO				
[(MBATSCZ) $\cdot$ 2H <sub>2</sub> O $\cdot$ VO $\text{SO}_4$ ] Light Yellow	5.9788 (5.9909)	110	66	52	1572	802	1.64	308
[(DMACATSCZ) $\cdot$ H <sub>2</sub> OVOSO <sub>4</sub> ] White	5.9545 (6.005)	95	60	50	1570	835	1.66	305
[(DMBATSCZ) $\cdot$ H <sub>2</sub> OVOSO <sub>4</sub> ] Yellow	4.6353 (5.001)	90	65	55	1646	835	1.65	290
[(PATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Brown	4.9199 (5.0980)	85	72	86	1563	850	1.67	295
[(CBATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Pale yellow	4.0553 (4.0256)	80	84	82	1565	806	1.58	275
[(FATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Yellow	7.6491 (7.3593)	90	80	55	1596	805	1.66	285
[(IATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Brownish yellow	5.9349 (5.7367)	64	87	48	1566	790	1.63	325
[(MSATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Brownish black	6.0263 (5.9788)	76	75	34	1550	774	1.64	335
[(M'ATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Orange	6.0316 (5.9788)	88	70	48	1535	780	1.69	295
[(BSATSCZ) $\cdot$ 2H <sub>2</sub> OVOSO <sub>4</sub> ] Black	5.5316 (5.3515)	60	84	39	1561	775	1.62	288

The reported complexes are paramagnetic in nature and magnetic moment values were lower than expected for  $d^1$  system (1.73) BM<sup>5,6</sup>. Such low values indicate that some anti-ferromagnetism is taking place with the neighboring molecule. The complexes display strong V=O stretching frequency in the infrared spectrum.

The thermogram run on the complexes of VO(IV) reveals interesting facts and corroborate some of the assumption made on the basis on spectral studies. The complex loses the two molecules of water at around 230  $^{\circ}\text{C}$ , which indicates that these occupy the coordinate position of the complex<sup>7</sup>.

The IR spectra of reported ligands show two important peaks between 1650-1550 and 900-750  $\text{cm}^{-1}$  which were shifted to 1646-1535 and 850-774  $\text{cm}^{-1}$ , respectively in the spectra of all the complexes indicating that the coordination occurred through N atom of  $\nu(\text{C}=\text{N})$  group<sup>8,9</sup> and S atom  $\nu(\text{C}=\text{S})$  group (Table-1). In all the complexes of VO(IV) a peak between 915-723  $\text{cm}^{-1}$  show the presence of coordinated water molecules.

The tetravalent(IV) complexes are EPR active, displaying axial spectra with well-resolved ( $I = 7/2$ ) hyperfine lines. As a representative case some of the pertinent value of EPR spectral data of VO(IV) complexes are  $g_{\parallel}$  ( $A_{\parallel}/G$ ) 1.944 (184.3),  $g_{\perp}$  ( $A_{\perp}/G$ ) 1.984 (65.7),  $g_{\text{av}}$  ( $A_{\parallel}/G$ ) 1.971 (105.2) where  $g_{\text{av}} = 1/3[2(A_{\perp} + A_{\parallel})]$ . The  $g_{\parallel}$  ( $g_{\perp}$  and  $A_{\parallel} \gg A_{\perp}$ ) relationships are the characteristic of axially compressed  $d^1_{xy}$  configuration<sup>10,11</sup>.

The electronic spectral bands of the present oxovanadium(IV) complexes show similar absorption peaks<sup>12</sup>. The three low intensity band are observed at room temperature in the spectral region of 25000-23000  $\text{cm}^{-1}$ . The band I st may be assigned to the electronic transition  ${}^2B_2 \rightarrow {}^2B_1$  and band II nd to  ${}^2B_2 \rightarrow {}^2A_1$ , respectively. The spectral band at 15150-12800  $\text{cm}^{-1}$  indicated octahedral environment for these complexes<sup>13</sup>.

A moderately intense band observed in the region of 13000-13500  $\text{cm}^{-1}$  has been assigned to un-observed band resulting from  $d_{xy} \rightarrow d_{yz}, d_{zx} ({}^2B_2 - {}^2B_1)$  transition<sup>14</sup>. The second shoulder observed at 17000-16800  $\text{cm}^{-1}$  region may be attributed to  $d_{xy} \rightarrow d_{x^2-y^2} ({}^2B_2 - {}^2B_1)$  and the third band at 25200-24400  $\text{cm}^{-1}$  may be assigned to the transition  $d_{xz} \rightarrow d_z^2 ({}^2B_2 - {}^2A_1)$ .

On the basis of available evidences octahedral geometry has been proposed for all VO(IV) complexes (Fig. 1).

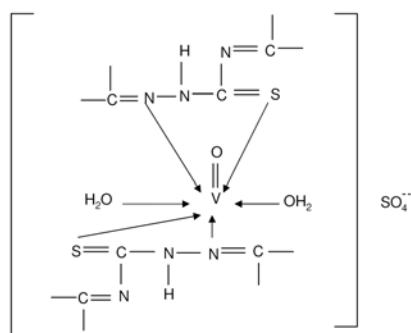


Fig. 1.

**Antibacterial and antifungal activities of VO(IV) complexes:** Schiff bases and their metal complexes have been reported as anticancer<sup>15</sup>, antifungal<sup>16</sup>, antitumor<sup>17</sup> and antituberculosis compounds. Thiosemicarbazide and thiosemicarbazones possess -N-C=S group which is an essential structural feature responsible for biocidal properties<sup>18,19</sup>. All the VO(IV) complexes were screened for antibacterial and antifungal activity and the inhibition zone diameter in mm are presented in Tables 2 and 3.

TABLE-2  
ANTIBACTERIAL ACTIVITY AT 2  $\mu\text{g}/\text{disc}$  (ZONE FORMATION IN mm)

S. No.	<i>S. aureus</i>	<i>E. coli</i>	<i>B. licheniformes</i>	<i>B. subtilis</i>	<i>B. brevis</i>	<i>P. aeruginosa</i>	<i>K. aeruginosa</i>
1	10	8	10	7	7	–	12
2	11	7	11	6	6	–	12
3	10	8	10	7	5	–	10
4	10	8	11	7	5	–	9
5	10	7	10	6	7	–	4
6	11	8	9	7	6	–	12
7	10	7	11	6	5	–	10
8	9	6	12	6	7	–	12
9	10	8	10	8	8	–	11
10	11	9	11	9	6	–	12

TABLE-3  
RESPONSE OF THE TEST COMPOUND (1 mg/mL) AGAINST FUNGI

Compd.	Penicillin species	<i>Candida albicans</i>	<i>Rhizopus</i> species	<i>Phytothera</i> intestans	<i>Aspergillus</i> species	<i>Saccharomyces</i> species
1	+/-	-	-	+/-	+	-
2	-	-	+/-	+/-	+	-
3	-	-	-	+/-	+	-
4	-	-	-	+/-	+	-
5	-	-	-	+/-	+	-
6	-	-	-	+	+	-
7	-	-	-	+/-	+	-
8	+/-	-	-	+/-	+	-
9	-	-	-	+/-	+	-
10	-	+/-	-	+/-	+	-

(+) Indicate non-active, (-) Indicate active, (+/-) Indicate moderately active

## REFERENCES

1. J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
2. E.M. Hodnett and W.J. Dunn, *J. Med. Chem.*, **13**, 768 (1970).
3. A.Z. Halve and A. Goyal, *Orient. J. Chem.*, **12**, 87 (1996).
4. M.S. Patil, H.D. Deora, M. Kulkarni and J.R. Shah, *J. Indian Chem. Soc.*, **60**, 817 (1983).
5. A. Syamal, S. Ahmad and B.K. Gupta, *Rev. Chim. Minor.*, **20**, 181 (1983).
6. S. Patil, A. Kulkarni and H. Vasant, *Inorg. Chim. Acta*, **95**, 195 (1984).
7. G. Venkatanaryana, S.J. Swamy and P. Lingaiah, *J. Indian Chem. Soc.*, **67**, 108 (1990).
8. B.L. Singh and U. Agarwala, *Inorg. Chem.*, **8**, 2341 (1969).
9. U. Agarwala and B.L. Singh, *J. Inorg. Chem.*, **31**, 2575 (1969).
10. P. Basu, S. Pal and A. Chakraworty, *J. Chem. Soc. Dalton Trans*, 3217 (1991).
11. C.R. Cornmann, J. Kampf, M.S. Lal and V.L. Pecoraro, *Inorg. Chem.*, **31**, 2035 (1992).
12. L. Singh, U. Singh and U.P. Singh, *Asian J. Chem.*, **13**, 1427 (2001).
13. C.J. Ballhausen and A.B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
14. L.G. Vonguickenborne and S.P. McGlynn, *Inorg. Chim. Acta*, **9**, 390 (1968).
15. S.K. Chakrabarti and B.K. Dey, *J. Indian Chem. Soc.*, **50**, 137 (1937).
16. E.M. Hodnett and W.J. Dunn, *J. Med. Chem.*, **15**, 399 (1972); *Chem. Abstr.*, **76**, 149141 (1972).
17. M. Raghwan, *Curr. Sci.*, **21**, 10 (1952).
18. V.K. Mishra and S.C. Bahel, *J. Indian Chem. Soc.*, **60**, 867 (1989).
19. H. Singh and L.D.S. Yadav, *Agric. Biol. Chem.*, **40**, 759 (1976).

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