

Synthesis, characterization and antimicrobial properties of oxovanadium (IV) complexes derived from Schiff base ligands containing semicarbazone moiety

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ABSTRACT

The synthesis & characterization of the complexes of oxovanadium (IV) are reported here-in of $[VO L_1 (H_2O)_2] SO_4$ (L_1 = Schiff bases ligands containing semicarbazone moiety). Complexes of oxovanadium (IV) with *bis(p-methoxybenzaldehyde)* semicarbazone (MBASCZ), *bis(N, N'-di-methyl-4-aminocinnamaldehyde)* semicarbazone (DMABASCZ), *bis(pyridine-2-aldehyde)* semicarbazone (PASCZ), *bis(p-chlorobenzaldehyde)* semicarbazone (CBASCZ), *bis(indole-3-aldehyde)* semicarbazone (IASCZ), *bis(3-methylsalicylaldehyde)* semicarbazone (MSASCZ), *bis(5-methylsalicylaldehyde)* semicarbazone (M'SASCZ), *bis(furfuryl-2-aldehyde)* semicarbazone (FASCZ) and *bis(5-bromosalicylaldehyde)* semicarbazone (BSATCZ) have been synthesized and 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 anti-bacterial and anti-fungal activities.

Keywords: Oxovanadium (IV), Schiff bases, semicarbazone, antibacterial & antifungal action.

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 Oxocation¹ 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^{2, 3} 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 $[VO L_1 (H_2O)_2] SO_4$. (L_1 = Schiff bases ligand containing semicarbazone moiety). New VO (IV) complexes of schiff bases ligand containing semicarbazone moiety have been

synthesized and characterized by elemental analysis, molar conductivity, magnetic moment, thermal studies, EPR, IR spectra and electronic spectra. These studies indicate octahedral geometry around the metal ion. These complexes were also screened for anti-bacterial and anti-fungal activity.

MATERIAL AND METHODS

All the chemicals used in the investigation were of A.R. 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 semicarbazide in molar ratio of 2:1. The reaction mixture was refluxed, in ethanol for half an hour and the requisite amount of respective aldehyde was added into the reaction vessel and refluxed for around six hours. It was allowed to stand over-night to yield the crystals of the Schiff bases. Purification was effected by recrystallization.

Preparation of Oxovanadium(IV) complexes:

All the complexes were prepared by following the general procedure. Thus to a solution of Oxovanadium(IV) sulphate (0.1mol) in methanol (~15ml) to the solution of ligand in DMSO (~20ml) were added drop-wise with stirring. The mixture was refluxed for 6-10 hours and then the volume was reduced to ~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 molar conductance value of Oxovanadium (IV) in MeOH, DMF and DMSO reveals their 1:1 electrolytic nature⁴.

The reported complexes are paramagnetic in nature and magnetic moment values were lower than expected for d¹ system (1.73) B.M.^{5,6} 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

Table 1: Analytical data, conductance, magnetic moments and m.p. (s) of complexes

Compound/Colour	Metal % Found / Calcd.	Molar Conductance ($\text{Ohm}^{-1}\text{cm}^{-1}\text{mol}^{-1}$)			$\nu\text{C=N}$ (cm^{-1})	Magnetic Moments In B.M.	m.p. °C
		MeOH	DMF	DMSO			
[(MBASCZ).2H ₂ O.VOSO ₄] Light Yellow	6.2119 (5.009)	95	54	36	1572	1.67	325
[(DMACASCZ).H ₂ OVOSO ₄] White	5.2200 (4.005)	80	65	46	1570	1.68	305
[(DMBASCZ).H ₂ OVOSO ₄] Yellow	5.8419 (4.006)	110	75	52	1646	1.70	312
[(PASCZ). 2H ₂ OVOSO ₄] Brown	7.2340 (5.0980)	115	80	48	1563	1.67	219
[(CBASCZ). 2H ₂ OVOSO ₄] Pale yellow	6.0786 (5.006)	120	76	52	1565	1.64	305
[(FASCZ). 2H ₂ OVOSO ₄] Yellow	8.1346 (7.7155)	55	72	35	1596	1.69	265
[(IASCZ). 2H ₂ OVOSO ₄] Brownish yellow	6.7392 (5.9509)	65	75	42	1566	1.70	297
[(MSASCZ). 2H ₂ OVOSO ₄] Brownish black	7.6246 (6.2119)	85	80	45	1550	1.68	305
[(M ASCZ). 2H ₂ OVOSO ₄] Orange	7.5003 (6.2119)	75	74	37	1535	1.65	315
[(BSASCZ). 2H ₂ OVOSO ₄] Black	6.6318 (5.5374)	87	83	50	1561	1.73	309

molecules of water at around 230°C, which indicates that these occupy the coordinate position of the complex⁷.

The IR spectra of reported ligands show important peak between 1630-1535 cm⁻¹ which was shifted to 1646-1535 cm⁻¹ in the spectra of all the complexes indicating that the coordination occurred

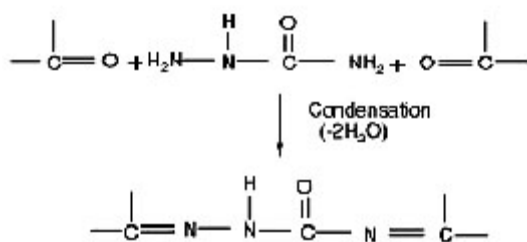


Fig. 1

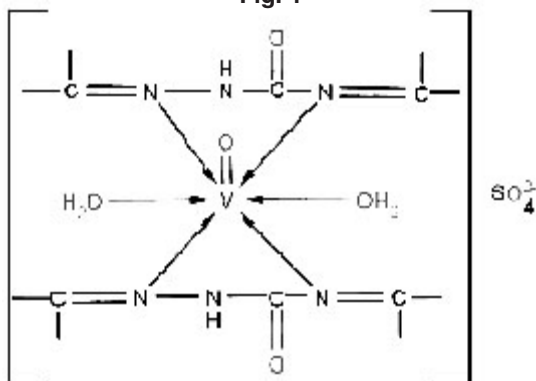


Fig. 2

through N atom of n (C=N) group^{8,9} and S atom. In all the complexes of VO (IV) a peak between 915-730 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_{||} (A_{||} / G) 1.944 (184.3), g_⊥ (A_⊥ / G) 1.985 (65.7), g_{av} (A_{||} / G) 1.971 (105.2) where g_{av} = 1/3[2 (A_⊥ + A_{||})]. The g_{||} (g_⊥ and A_{||} >> A_⊥) relationships are the characteristic of axially compressed d¹_{xy} configuration^{10, 12}.

Table 2: Antibacterial activity at 2 µg disc (Zone formation in mm)

S. No	<i>S. Aureous</i>	<i>E. Coli</i>	<i>B.Subtills</i>
1	10	08	07
2	11	07	06
3	10	08	07
4	10	08	07
5	10	07	06
6	11	08	07
7	10	07	06
8	09	06	06
9	10	08	08
10	11	09	09

Table 3: Response of the test compound (1mg/mL) against fungi

Compounds	<i>Candida Albicans</i>	<i>Rhizopus Species</i>	<i>Phytothera Intestans</i>	<i>Aspergillus Species</i>	<i>Saccharomyces Species</i>
1	-	-	±	+	-
2	-	±	±	+	-
3	-	-	±	+	-
4	-	-	±	+	-
5	-	-	±	+	-
6	-	-	+	+	-
7	-	-	±	+	-
8	-	-	±	+	-
9	-	-	±	+	-
10	±	-	±	+	-

(+) Indicate non-active. (-) Indicate active.(±) Indicate moderatlyactive

The electronic spectral bands of the present Oxovanadium (IV) complexes show similar absorption peaks.¹³ The three low intensity band are observed at room temperature in the spectral region of 25000-23000 cm^{-1} . The band Ist may be assigned to the electronic transition ${}^2B_2 - {}^2B_1$ and band IInd to ${}^2B_2 - {}^2A_1$ respectively. The spectral and at 15150-12800 cm^{-1} indicated octahedral environment for these complexes.¹⁴

A moderately intense band observed in the region of 13000-13500 cm^{-1} has been assigned to un-observed band resulting from $d_{xy} \rightarrow d_{yz}$, d_{zx} (${}^2B_2 - {}^2B_1$) transition¹⁵. The second shoulder observed at 17000-16800 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 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.

Antibacterial and antifungal activities of VO(IV) complexes

Schiff bases and their metal complexes have been reported as anticancer¹⁶, antifungal¹⁷, antitumor¹⁸ and antituberculosis compounds. All the VO (IV) complexes were screened for antibacterial and antifungal activity and the inhibition zone diameter in mm arc presented table. (2,3).

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