

SYNTHESIS AND CHARACTERIZATION OF NEW OXOVANADIUM (IV) AND VANADIUM (III) COMPLEXES WITH ALDIMINES ON THE BASIS OF SOME PHYSICOCHEMICAL STUDIES

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ABSTRACT

Complexes of oxovanadium (IV) and vanadium (III) with aldimines, p-chlorobenzophenone-sulfisoxazole, p-chlorobenzophenone-4-aminophenazone, N, N'dimethyl-p-aminobenzaldehyde-sulfisoxazole, N, N'dimethyl-p-aminobenzaldehyde-4-amino-2-nitrotoluene, acetophenone-sulfisoxazole, N,N'dimethyl-p-aminocinnamaldehyde-sulfisomidine, have been synthesized. These were characterized on the basis of some physicochemical parameters like elemental analyses, molar conductance, magnetic moment, IR spectra and thermogravimetric studies. The molar conductance values of vanadyl complexes in DMSO indicate 1:1 electrolytic nature while those of V(III) complexes as 1:1, 1:2 & 1:3 electrolytic nature of complexes. The spectral studies support square pyramidal geometry of VO (IV) complexes and octahedral geometry of V (III) complexes as predicted on the basis of these parameters.

INTRODUCTION

Aldimines possess strong ability to form metal complexes and related complexes have played a prominent role in the development of coordination chemistry. Because of diverse chemical activity, broad spectrum of biological and pharmacological properties, such as analgesic, antipyretic, anti-inflammatory, anticancerous, bactericidal and fungicidal has made the study of aldimine-metal complexes a viable source to signify and magnify the observations and results for the betterment of human life.

In view of the above, some chelating aldimines derived from sulfisoxazole, sulfisomidine, antipyrine have been chosen and attempts made to synthesize and characterize their oxovanadium (IV) and vanadium (III) chelates.

MATERIALS AND METHODS

With all precaution. Sulfisomidine (Sigma, USA), Sulfisoxazole (Sigma, USA), Antipyrine (E. Merck), N, N'dimethyl-p-amino cinnamaldehyde (Leico, USA), N, N' dimethyl-p-amino benzaldehyde (BDH, England), p-chlorobenzophenone (NCL, Poona), Acetophenone (BDH, India), Vanadyl Sulphate pentahydrate (BDH, India), Vanadium (III) Chloride (BDH, India) were used as supplied.

The complexes of vanadyl (IV) were prepared by the addition of methanolic solution of vanadyl sulphate to the solution of aldimine in ethanol while complexes of vanadium (III) were prepared by adding ethanolic solution of vanadium trichloride to ethanolic solution of aldimine. The mixture was refluxed for about 10-12 hours over a water bath. The

precipitated complex was filtered, washed with dry ethanol and dried over anhydrous calcium chloride under reduced pressure.

Measurement of physicochemical parameters

Metal ions and anions were analysed by standard methods. Carbon, hydrogen and nitrogen analysis were done at SAIF, CDRI, Lucknow. Conductance measurements in DMSO and DMF were carried out at 25°C using conductivity meter, TCM-15 model with a dip type conductivity cell at department of chemistry, Bareilly College, Bareilly. The IR spectra of complexes were recorded with Perkin-Elmer spectrometer model 651 in KBr as well as Nujol phase from 4000 cm^{-1} to 200 cm^{-1} at SAIF, CDRI, Lucknow. Magnetic susceptibility was determined by Gouy's method and molecular weights were determined by cryoscopic method using Beckmann's thermometer at department of chemistry, Bareilly College, Bareilly.

RESULTS AND DISCUSSION

All the complexes of VO (IV) and V (III) are stable, crystalline, and non hygroscopic. They are insoluble in common organic solvents but soluble in DMSO and DMF without undergoing any solvolysis reactions. On the basis of analytical data (Table-1), the metal chelates were found to have 1:2 (complex-1) and 1:1 (complex-2 to 10) Metal: Ligand stoichiometry. The molar conductance values of vanadyl complexes in DMSO at 10⁻³M concentration are in the range of 27.66-54.68 $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ indicating that they are 1:1 electrolytes². The molar conductance values of V(III) complexes lies in the range 31.04 - 46.47 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating 1 : 1 electrolytic nature, 109.6 $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ indicating 1:2 electrolytic nature and 220 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating 1:3 electrolytic nature of complex.

The magnetic moments of oxovanadium (IV) complexes lies in the range 1.66-1.69 B.M. confirming the presence of one unpaired electron and hence 3d¹ configuration of oxovanadium (IV) ion. The magnetic moments of vanadium (III) complexes lies in the range 2.72-2.79 B.M. indicating that metal remain in +3 oxidation state (3d² system) even on complexation.

The M.P. and decomposition temperatures of the complexes determined in the laboratory are recorded in Table - 1. These values are close to those observed in the thermograms.

In oxovanadium (IV) complexes, thermogram shows an inflection in the range 80°C-90°C, which corresponds to percent weight loss of one lattice water molecule. Inflection in the range 100°C-110°C corresponds to percent weight loss of two lattice water molecules. The inflection in the range 170°C-180°C and 200°C - 210°C corresponds to percent weight loss of one and two co-ordinated water molecules respectively. Inflection in the range 250°C-450°C indicate loss of different parts of ligand and finally metallic oxide is formed which remains unaffected at temperature above than 500°C.

The comparison of IR spectra of ligand and the complex gave valuable informations regarding complexation sites of ligand. The spectra of all the VO (IV) complexes show a sharp absorption band in the region 1570-1620 cm^{-1} which was attributed to $\nu(\text{C}=\text{N})$ azomethine vibration³. The appearance of band in the region 970 - 990 cm^{-1} could be assigned to $\nu(\text{V}=\text{O})$ vibrations⁴. The presence of ionic sulphate in complexes was confirmed by appearance of bands in the region 1100-1130 cm^{-1} and 580-640 cm^{-1} .⁵

The aldimines having sulfoxazole amine, exhibit sharp band in the region 1150 cm^{-1} -1170 cm^{-1} due to $\nu(\text{S}=\text{O})$, the observed low energy shift of this band in complexes (1110 cm^{-1} - 1130 cm^{-1}) indicate the involvement of oxygen of (S=O) in co-ordination⁵. The presence of bands in the region 3300-3420 cm^{-1} may be assigned to $\nu(\text{OH})$ vibrations of co-ordinated water molecules⁶.

The appearance of sharp band in the region 650 cm^{-1} -680 cm^{-1} in ligands spectra is indicative of $\nu(\text{C}-\text{Cl})$ stretching vibration. The observed low energy shift of this band suggests the involvement of chloro atom in co-ordination⁷.

In vanadium (III) complexes, ligand N, N' dimethyl-p-amino cinnamaldehyde sulfoxazole behaved in tridentate manner while rest of the ligands behaved in bidentate manner. The major absorption peaks in the IR spectra of aldimines as well as complexes are given in Table-2.

Table 1: Physico-Chemical Parameters of VO (IV) AND V(III) COMPLEXES

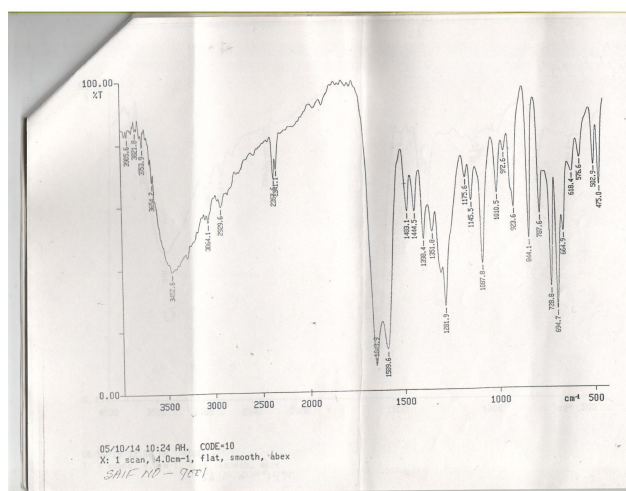
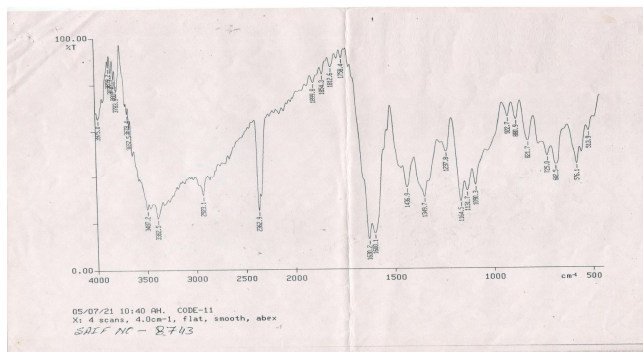
S. No.	Complex	Found (Calcd. %)					V	Δ_M (mho cm ² mol ⁻¹)	m.p.(⁰ C) Colour	$\mu_{\text{eff.}}$ (B.M.)
		C	H	N	S	Cl				
1.	[VO (C ₁₉ H ₁₉ N ₃ O ₃ S) ₂ (H ₂ O)] SO ₄ .4H ₂ O	45.79 (46.02)	3.78 (4.84)	8.15 (8.48)	9.48 (9.69)	- -	5.02 (5.14)	29.37	220 ⁰ C (Light green)	1.69
2.	[VO (C ₂₄ H ₂₀ N ₃ O ₃ SCI) (H ₂ O) ₂]SO ₄ .3H ₂ O	39.91 (40.09)	4.10 (4.17)	5.45 (5.84)	8.70 (8.91)	- -	6.93 (7.08)	31.69	>250 ⁰ C (Light brown)	1.66
3.	[VO(C ₂₀ H ₂₂ N ₄ O ₃ S)(H ₂ O) ₂]SO ₄ .3H ₂ O	36.38 (36.87)	4.81 (4.92)	8.51 (8.60)	9.62 (9.83)	- -	7.59 (7.82)	27.73	>250 ⁰ C (Reddish brown)	1.68
4.	[VO(C ₂₂ H ₂₄ N ₄ O ₃ S)(H ₂ O) ₂] SO ₄ .3H ₂ O	38.79 (39.00)	4.91 (5.02)	7.98 (8.27)	9.18 (9.45)	- -	7.41 (7.52)	27.66	>250 ⁰ C (Dark brown)	1.69
5.	[VO (C ₂₃ H ₂₅ N ₅ O ₂ S)(H ₂ O) ₂]SO ₄ .3H ₂ O	40.02 (40.12)	4.98 (5.09)	9.89 (10.17)	9.11 (9.30)	- -	7.25 (7.40)	32.63	>250 ⁰ C (Dark brown)	1.67
6.	[VO(C ₂₄ H ₂₀ N ₃ OCl)(H ₂ O) ₂]SO ₄ .3H ₂ O	43.75 (44.01)	4.39 (4.58)	6.10 (6.42)	- -	4.58 (4.89)	7.61 (7.78)	54.68	>250 ⁰ C (Brown)	1.69
7.	[V(C ₁₉ H ₁₉ N ₃ O ₃ S) (Cl) ₂ (H ₂ O) ₂]Cl	40.54 (40.72)	4.09 (4.21)	7.46 (7.89)	- -	18.94 (19.07)	9.06 (9.20)	46.47	110 ⁰ C (Reddish brown)	2.72
8.	[V(C ₂₄ H ₂₀ N ₃ OCl)(Cl) ₂ (H ₂ O) ₂]Cl	48.41 (48.78)	4.03 (4.12)	7.06 (7.15)	- -	23.87 (23.98)	8.56 (8.69)	31.04	88 ⁰ C (Reddish brown)	2.76
9.	[V(C ₂₂ H ₂₄ N ₄ O ₃ S) (H ₂ O) ₃]Cl ₃	41.55 (41.67)	4.72 (4.83)	8.81 (8.93)	- -	16.76 (16.85)	8.01 (8.15)	220	180 ⁰ C (Dark brown)	2.79
10.	[V(C ₁₆ H ₁₇ N ₃ O ₂) (Cl) (H ₂ O) ₃]Cl ₂ .2H ₂ O	36.20 (36.31)	5.09 (5.15)	7.92 (7.98)	- -	20.08 (20.18)	9.59 (9.67)	109.6	>250 ⁰ C (Dark green)	2.79

Table 2: Infrared spectral data (cm⁻¹) of aldimines and VO (IV), V(III) complexes

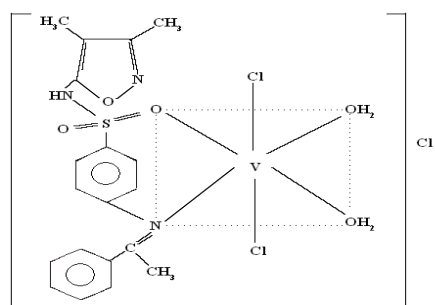
S. No.	Coordination through azomethine \square (C=N) group		\square (V=O) (cm ⁻¹)	Coordination through 3 ^o nitrogen	Coordination through water molecules \square (OH)	Wagging mode of water molecules	Coordination through free chloride	Coordination through (S=O)	
	Ligand	Complex						Ligand	Complex
1	1631.4	1597.8	$\square\square\square\square\square$	-	3381.7	769.2	-	1165.6	1123.6
2	1624.9	1595.0	$\square\square\square\square\square$	-	3408.9	768.8	-	1165.6	1121.4
3	1630.2	1600.8	$\square\square\square\square\square$	1351.6	3376.6	768.2	-	1164.5	1120.1
4	1626.6	1604.8	$\square\square\square\square\square$	1360.8	3412.1	767.4	-	1161.9	1122.4
5	1624.2	1594.6	$\square\square\square\square\square$	1356.4	3362.8	768.4	-	1162.3	1140.0
6	1625.5	1601.3	$\square\square\square\square\square$	-	3452.6	774.6	-	1165.6	1139.9
7	1631.4	1598.0	\square	-	3404.3	769.6	342.0	-	-
8	1633.2	1594.2	\square	-	3365.3	727.3	351.2	-	-
9	1626.6	1594.1	\square	1359.2	3406.2	772.0	-	1161.9	1138.2
10.	1619.4	1596.2	\square	1351.8	3432.1	766.5	-	-	-

Thus, based on the analytical and spectral data, the tentative structures of the complexes were proposed. (Structure (1) & (2))

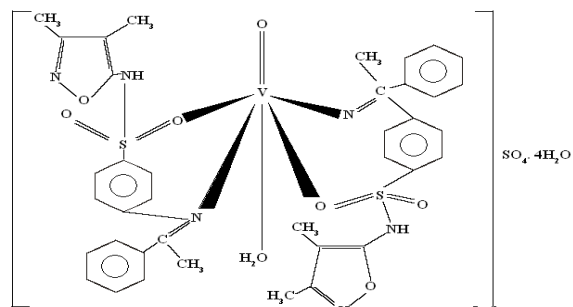
**Infra red spectra of aldimine
(N, N'dimethyl-p-aminobenzaldehyde- sulfisoxazole)**



**Infra red spectra of complex
(N, N'dimethyl-p-aminobenzaldehyde-
sulfisoxazole oxovanadium (IV) sulphate)**



$[V(C_{13}H_{17}N_2O_2S)(Cl)_2(H_2O)_2]Cl$
Structure(2)



$[VO(C_{13}H_{17}N_2O_2S)_2(H_2O)]SO_4 \cdot 4H_2O$
Structure (1)

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