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Synthesis, Spectral Characterization, Biological Screening Study and Antifungal Activity of Oxovanadium (IV) Complexes with Schiff Bases Derived from Aromatic Amines

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ABSTRACT

The present work is concerned with synthesis and study on the nature of bonding in oxovanadium (IV) complexes. Schiff base complexes with transition metal played a prominent role in the development of coordination chemistry. Several schiff base metal complexes have been studied because of there industrial and biological application.

Key words: Antifungal activity, Oxovanadium complexes, Schiff base, Aromatic amines.

INTRODUCTION

The schiff bases 4-chlorobenzylidene-2-amino-4-chlorophenol (CBACP) and 4-dimethyl aminobenzylidene-2-aminophenol (DABAP) were prepared by Standard methods and characterised by the determination of melting point and elemental analysis. The complexes of these ligands were prepared with oxovanadium (IV) by standard methods and characterised by elemental analysis, electrical conductance, magnetic susceptibility, IR, electronic spectral measurements and TGA.

Co-ordination chemistry has become an important branch of chemistry. Co-ordination compounds are formed by the interaction of metal and the ligand. These compounds play a vital role in our life as well as in plant life. There are a variety of chemical reactions are reported to be catalysed by co-ordination compounds and provides active centers for process such as hydrosulphurisation and oxygen atom transfer reaction such as olefinic epoxidation and depoxidation[1].

Schiff base complexes with transition metal played a prominent role in the development of co-ordination chemistry[2]. Several schiff base metal complexes have been studied because of there industrial and biological application[3-5].

The present work is concerned with synthesis and study on the nature of bonding in oxovanadium (IV) complexes.

Vanadium is receiving attention as a biologically important metal[6-7] due to the existance of vanado enzyme.

Keeping in view the importance of oxovanadium complex in biological system we have synthesised and characterised the complexes of vanadium and results of study are reported here.

MATERIAL AND METHODS

All chemical used were of analytical grade. The ligands were prepared by different carbonyl and amino compounds. The carbonyl compound used were 4-chlorobenzaldehyde and 4-dimethyl aminobenzaldehyde and the amino compounds used were 2-amino 4-chloro and 4-aminophenol.

The ligands form complexes with oxovanadium (IV) by the addition of vanadyl sulphate solution in methanol to the solution of ligand in DMSO. The ppt thus obtained was washed with DMSO and dried over fused $CaCl_2$.

The elemental analysis were carried out at RSIC, CDRI, Lucknow, conductivity measurements were carried out at philips conductivity Bridge model PR 9500 with a dip type conductivity cell at Department of Chemistry in Bareilly College, Bareilly. The conductance of the complexes were measured in methanol, DMF and DMSO at 25°C. Magnetic susceptibility of the complexes were determined by Gouy method at the Deptt. of Chemistry in Bareilly College, Bareilly. The sample tube was caliberated with $CuSO_4$. The IR spectra of the complexes were recorded with Perkin Elmer spectrophotometer model 651 in KBr or nujol phase at RSIC, CDRI, Lucknow. The visible spectra were recorded with Beckmann-DU-2 spectrophotometer in the range of 750 cm^{-1} to 300 cm^{-1} at Chemistry Deptt in Bareilly College, Bareilly.

Preparation of ligandsPreparation of ligands

The schiff base were prepared by the condensation of carbonyl and amino compound. The amino compound was dissolved in ethanol and refluxed for about half an hour. Now the requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for about six hours and kept for 24 hours. The crystals of ligand were obtained and purified by recrystalisation. The purity of ligands was checked by elemental analysis and M.P.

RESULTS AND DISCUSSION

Elemental analysis reveals that the oxovanadium complexes have the compositions with CBACP $C_{26}H_{20}N_2O_4VCl_6$ and DABAP $C_{30}H_{34}N_4O_2VCl_2$. The electrolytic nature and oxovanadium complex measured in DMF, DMSO and methanol at 10^{-3} M dilution has 1:2 and the value of magnetic moment for the complexes varies from 1.69 to 1.73 B.M. Which is close to the expected value for d' system.

The electronic spectra of oxovanadium (IV) complexes exhibits three distinct absorption bands. The low intensity absorption peaks in long wave length region are possible due to first crystal field transition is spread over 13500-14100 cm^{-1} region. The second crystal field transition were observed at 18500 to 20640 cm^{-1} due to $2B_2 \rightarrow 2B_1$ ($dxy \rightarrow dx^2\text{-}y^2$). The third peak lies at 26500 cm^{-1} and is due to transition $2B_2 \rightarrow 2A_1$ ($dxy \rightarrow dz_2$).

The ir spectra of 4-chloro benzylidine-2-amino-4-chloro phenol vanadium (IV) and its ligands reveals that a medium intensity band appearing at 1620 cm^{-1} has shifted to 1600 cm^{-1} in the spectra of the complex. This suggests co-ordination of the metal with azomethine nitrogen.

A strong band in the spectrum of ligand appears at 1370 cm^{-1} (8) may be assigned to phenolic OH (deformation). This band has been found to be absent in the spectrum of the complex, this suggests deprotonation and co-ordination of phenolic oxygen to the metal ion. The chelation of phenolic oxygen is supported by upward shift of υC=O (phenolic) in the spectrum of the complex[9-11].

The appearance of broad band around 3200 cm^{-1} in the spectrum of the complex may be due to associated lattic water molecule. This is further supported by the percent weight loss for two water molecules at 160°C on the thermogram of complex.

The ir spectra of 4-dimethyl amino benzylidine-2-amino phenol vanadium (IV) shows a band at 1581 cm^{-1} due to co-ordination through azomethine nitrogen and another important band appears at 1307 cm^{-1} due to co-ordination through

Table 1: Physical and Analytical data of Complexes

S. No.	Name of complex	Molecular formula	Colour	M.P.	% Composition				Solubility	Magnetic moment in B.M.
					C	H	N	Cl		
1.	4-Chloro benzilidine -2-amino-4-chloro phenol oxovanadium	$C_{30}H_{30}N_2O_2VCl_6$	Deep	365°C	45.35 (45.22)	2.90 (2.74)	4.07 (4.01)	30.96 (30.96)	DMSO	1.69
2.	4-dimethyl amino benzylidin-1-amino phenol oxovanadium	$C_{30}H_{34}N_2O_2VCl_2$	Black	290°C	62.5 (62.12)	5.90 (5.68)	4.86 (4.72)	12.32 (12.11)	DMSO	1.73

azomethine nitrogen and another important band appears at 1307 cm^{-1} in the spectrum of the ligand which may be assigned to phenolic OH. This suggests deprotonation and subsequent co-ordination of phenolic group. This is further supported by upward shift of υC=O from 1260 cm^{-1} to 1270 cm^{-1} in the spectrum of the complex may be due to associated lattice water molecule. This is further supported by TGA data. The thermogram shows percent weight loss of two water molecules at 170°C [12-13].

Biological screening studyBiological screening study

The *in vitro* biological screening effects of the investigated compounds were tested against several bacteria like. *Bacillus subtilis, Klebsiella pneumoniae, Pseudomonas aeruginosa* and two fungi *Aspergillus niger* and *Rhizoctonia* bacteria. The measured zone of inhibition against the growth of various micro-organisms.

A comparative study of ligands and their complexes indicates that most of the metal chelates exhibits higher antimicrobial activity than that of the antifungal activity of metal chelates with increase in the antifungal activity of metal, chelates with increase in concentration is due to the effect of metal ion on the normal cell process. Such increased activity of metal chelates can be explained on the basis of overtone's concept[14] and chelation theory[15].

According to overtones concept of cell permeability of the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which liposolubility has important factor which control the antimicrobial activity. On chelation the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups. Further it increases the delocalisation of p electrons over the whole chelate ring and enhances the lipophilicity of the complex. This again enhances the penetration of complexes in to lipid membrane and blocking the metal binding sites on enzymes of micro organisms. These complexes also disturbs the respiration process of the cell and thus block the synthesis of proteins which restrict the further growth of the organism[16].

Table 2: Spectroscopic data of complexes

S. No.	Name of complex	Important peaks in ir spectra		
		υC=N	**Co-ordinated H_2O molecule**	**υC=O phenolic mode**
1.	4-Chloro benzilidine-2-amino-4-chloro phenol oxovanadium	1600 cm^{-1}	3200 cm^{-1}	1410 cm^{-1}
2.	4-dimethyl amino benzylidin-1-amino phenol oxovanadium	1580 cm^{-1}	3260 cm^{-1}	1340 cm^{-1}

Antifungal activity

The antifungal activity of the compounds was evaluated by the well diffusion method against the fungi *Aspergilus niger* and *Rhizoctonia bataicola*. Cultured on potato dextrose agar as medium. Acetonitrile was used as the solvent and the drug amphotericin as control. In a typical procedure, as well as made on the agar medium inoculated with micro organisms. The well was filled with the test solution using a micropipette and the plates were incubated test at 35°C for 72 hours. During this period the test solution was diffused and affected the growth of the inoculated micro-organisms. A zone was developed on the plate and the inhibition zone were measured.

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