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Research Paper

Synthesis and Characterisation of Salicyaldehyde Salicyloyl Hydrazone Oxovanadium (Iv) Complex and Antimicrobial Studies

Organic chemistry

KEYWORDS : Salicyaldehyde Salicyloyl hydazone, Oxovanadium, Molar Conductance, Biological activity , Thermal analysis, IR spectra , Elemental analysis.

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ABSTRACT

Oxovanadium (IV) complex with Schiff base ligands are interesting because of their nature and biological activities. The purity and composition of the Schiff bases and the metal Salicyaldehyde Salicyloyl hydrazone Oxovanadium (IV) complex are explained by elemental analysis which formed ligand: metal ratio of 1:2 .The synthesized schiff bases and their transition metal complex are evaluated for their in vitro antibacterial activity against four gram negative and two gram positive bacterial stains by the agar well diffusion method. All the complexes have been characterized on the basis of elemental analysis, magnetic moments, spectral studies and molar conductance. On the basis of spectral studies complex of Salicyaldehyde Salicyloyl hydrazone Oxovanadium (IV) have been assigned polymeric octahedral structure.

INTRODUCTION:

Schiff bases are used as intermediate for the synthesis of amino acids or as ligands for the preparation of metal complexes having a series of different structure. Schiff bases are very important in the field of co-ordination chemistry for complexation with transition metal ions. Depending upon the nature of their donor atoms in the ligands, a large number of complexes with different transition metal ions are reported. The most of the complexes which are prepared have combination of nitrogen, oxygen and sulphur donor atoms containing ligands [1]. In the study of present literature, it appears that salicyaldehyde salicyloyl hydrazon and its related compounds have been extensively used as biological screening agents and analytical agents. Considering the above facts, author describes the behaviour of the tetradentate aromatic Schiff base ligand with various transition metal ions in this paper.

CHEMISTRY OF VANADIUM:

Vanadium is an important trace element that may be beneficial and possibly essential in humans, but certainly essential for some living organism. Vanadium, the most important ores are petronite and carnotite. It is prepared by Debore Van Arkel process. But it is generally used as Ferro-Vanadium which is an iron alloy. The important oxidation states shown by vanadium are +5, +4, +3, +2 but +5 is the most stable state. Vanadium also shows +3 oxidation and in this oxidation forms are V_2O_3,VCl_3 etc. In +2 oxidation state it forms $VSO_4.7H_2O$ &$V(CN)_2$ etc.

Chemistry of vanadium (IV):

This important oxidation state of vanadium is the most stable one under ordinary conditions. V^{III} is oxidized to V^{IV} by fairly mild reducing agents. Aside from a few compounds such as VCl4, the chemistry of V^{IV} is almost entirely of oxovanadium or vanadyl compounds. These contain the VO unit which can persist through a variety of chemical reactions. Oxovnadium (IV) compounds may depend on the nature of the ligands, cationic, neutral or anionic and be either penta or hexa co-ordinate, e.g. $[VOdiPy2Cl]^+$,$VOaca_2$,$[V(NCS)]^{2-}$.

The VO bond has been shown to be essentially a double bond V=O. Thus $VOSO_4.5H_2O$ there are four outer molecules in a plane with V-O distance 2.3A, while perpendicular to this plane is the V-O bond length 1.67A; the position trans to the oxygen is occupied by one oxygen atom of the SO_4 group. The structure of the acetylaccetonate is similar with V-O= 1.56A and the vanadium atom is above the centre of the base square. Even in VO_2, which has a distorted retile structure, one bond is conspicuously shorter, 1.76A than the others in the VO_6 unit.

All oxovanadium (IV) compounds have infrared bands in the region 900-1100cm^{-1}. Electronic esr. and vibrational spectra of the vanadyl ion are consistent with the formulation $[VO(H_2O)_5]^{2-}$. The V=O stretching frequency is quite sensitive to the trans ligand and donar which increase the electron density on the on the metal there by reduce its acceptor properties towards O and hence cause lowering of the V-O multiple bond character and stretching frequency[2-5].

This physiological effects in many cases stem from the good complexation behavior of VO^{+2} and the chemical similarity between phosphate and vanadate. The schiff bases salicyaldehyde salicyloyl hydazone Oxovanadium (IV) are prepared by standard methods and characterized by the determination of melting point and elemental analysis.

MATERIALS AND METHODS:

All chemical used are of A. R. grade. Melting points were determined using open glass capillaries and are uncorrected. Micro analysis for C, H and N were performed on perkin Elmer C, H, N analyzer. Mass spectra are obtained on Shimadzu GCMS –QP-2000 Mass spectra. Magnetic susceptibility measurements of the metal complexes in the solid state are determined by a Gouy balance at room temperature.

Ultra violet spectra are recorded on a Hitachi U-2000 double beam spectrophotometer. IR spectra of the synthesized complexes are recorded using Shimadzu spectrometer in the range 4000-500cm^{-1} using KBr pellet. The molar conductivity of the complexes (10-3) is measured for the freshly prepared solution of the complexes in DMSO using DCM 900 [6]. The Visible spectra is recorded with Beckmann DU-2 spectrophotometer in the range of 750cm^{-1} to 300 cm^{-1}. Thermogravimetric analyses of the compounds are studied in the temperature range 40-700^{0}C on Perkin Elmer TG-2 thermobalance in ambident air with a heating rate of 10^{0}C min^{-1}.

SYNTHEZIATION OF SCHIFF BASE:

Salicylaldehyde salicyloyl hydrogen was prepared by the method as reported in literature, by reacting together ethanolic solution of salicyloyl hydrazide (1.52gm 10mmol in 50ml) and Salicyaldehyde (1.22gm 10mmol in 50ml) as in Fig.1 . The crude product was recystalized from hot ethanolic solution.

CHARACTERIZATION OF SCHIFF BASE:

The melting point of the ligands was determined. These were characterized by elemental analyses for C, H, N & S. The IR Spectra of the ligand were recorded. The data is given in the Table 1.

SYNTHESIS OF METAL COMPLEXES:

The metal complexes were prepared by adding the solution of the ligand in appropriate solvent to the solution of the respective metal. To this solution was added drop wise, the solution of the respective metal salt. The reaction mixture was refluxed on water bath for about 1h & then cooled to room temperature. Precipitate obtained was separated by filtration, washed with distilled water, followed by ethanol & then dried in vccum desi-

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cator [5-6].

CHARACTERIZATION OF METAL COMPLEXES OR ANALYSIS:

The complexes so obtained show satisfactory elemental analyses in Table 1. Their infrared spectra (in KBr) show sharp, symmetric Vv=o bands in Table 2. Electronic spectra of oxovanadium (IV) complexes should exhibit three d-d bands corresponding to dxy→dyz, dxx→ dx^2-y^2 and dz^2 transition respectively. Spectroscopic data of complex is given in Table 3. The gravimetric estimation of the metal indicate that the metal reacts with the ligand in 1:1.The colours of the complexes were noted and melting points were determine by open capillary method and were uncorrected. The molar conductance was measured at 10^{-3}M dilution at room temperature. Their magnetic properties were also studied by Gouy's method using $CuSO_4$.$5H_2O$ as calibrate [7-8].

RESULT & DISCUSSION:

The elemental analyses for C, H & N and the gravimetric estimation of the metal indicate that the metal reacts with ligand in 1:1 molar ratio. The molecular formula of the complex, therefore comes out to be $(C_{14}H_9N_2O_3).3H_2O.VO$.

There was difference in the melting points of the ligands and the complex suggesting the formation of the complex. The molar conductance of the complex in DMSO at 10-3 dilution indicates non electrolytic nature of the complex [9]. The magnetic moments of the complex were found to be 1.64 BM which is somewhat higher for d^1 system like vanadium. The electronic spectrum of the complex has charge transfer origin at ~ 25,000, ~36,000 and ~ 40,000 cm^{-1}. The ligand field absorption occur mainly at ~12,000, ~17,000, and ~23,000 cm^{-1} from dxy →dyz , dxx→dx^2-y^2 and dz^2 transition respectively. The band positions in methanol are slightly different from those in nujol and this is may be due to slight participation of the solvent in co-ordination sphere in the former case. The new band in the complex occurs at lower frequency. This shift may be due to hexa co-ordination [10-12].

The infrared spectra of the ligand and the complex were recorded in the KBr phase. The I.R.spectrum of the ligand shows bands at 3280, 1670, 1620, 1580, 1360 and 1000 cm^{-1}, which have been attributed to ν (N-H), amide-II, amide-III and ν(N-N) respectively. All the amide and ν(N-H), bands seem to disappear in the I.R. spectrum of the complex indicating distruction of the >C=O group and loss of NH protons via enolization. Further, some new peaks appeared in the spectra of the complex viz-a sharp band at 1610 cm^{-1} due to (>C=N-N=C<) group and medium intensity bands at 1530 and 1400 cm^{-1} due to ν (NCO^-) vibration. This indicates that the co-ordination is occurring through one of the nitrogen atom and the two oxygen atoms of the deprotonated of hydroxyl groups. It appears therefore the ligands is behaveing in dinegative tridentate manner[13-15].

The comparison of the I.R.spectra of the ligand and the complex indicate that the infrared spectrum of the complex show modified ligand absorption bands. A shift of ν(O-H) band by 50 cm^{-1} to lower frequency at 3300 cm^{-1} and the appearance of band in region ~860 cm^{-1} indicate the presence of co-ordinated water molecules.This is further supported by the loss of water at 140^{0}C in thermogram[16-18]. The bonding sites of the ligand actually involved in co-ordination were determined by comparing the ^{1}HNMR spectra of the ligand with those of the complex. The –NH and the phenolic –OH proton signals of the ligand appearing at 11.7 and 12.1δ respectively, disappear in complex indicating deprotonation consquentupon co-ordination with the metal ion. All the ring proton signals of the ligand appearing in the region 7-8δ get slightly shifted to 6.5-7.9δ in the complex. The aliphatic –CH proton signal of the ligand (at 8.8δ) shifts to slightly higher magnetic field (to-8.4δ) in the complex. A broadpeak appearing at 3.4δ in the in the complex is assigned to the protons of water molecules [19-21].

ANTIMICROBIAL STUDY

The antimicrobial screening of the Schiff basses have been carried out against Escherichia coli, Aeromonas hydropila and salmonella typhi using a nutrient agar medium by disc diffusion method [18, 19]. The sterilized (autoclaved at 121^{0}C for 15 min) medium (40-50^{0}C) was poured into the petri dishes to give a depth of 3-4 mm and allowed to solidify. The suspension of the microorganism then streaked on plates. The plates were pre-incubated for 1hat room temperature and incubated at 37^{0}Cfor 24h. The variation in the effectiveness of different compounds against different organism depends either on impermeability of cells or the microbe of difference in ribosome of microbial cells [22-23]. Antimicrobial Activity of Ligand & Metal complex are given in Table 4.

CONCLUSION:

On the basis of above mentioned facts the complex appear to have octahedral geometry, three co-ordination sites are occupied by tridentate ligand molecule and the remaining three by water molecules. The structure of the complex may therefore be represented as in Fig. 2;

Figures:

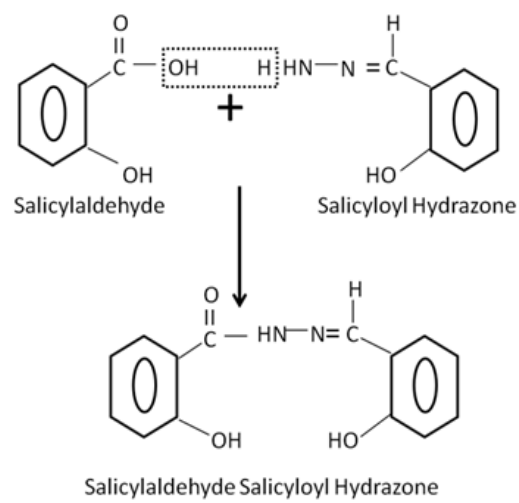

Fig. 1: Prepraion of Salicylaldehyde Salicyloyl hydrazone

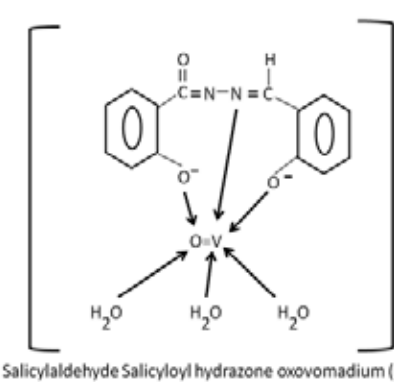

Fig. 2: Structure of Salicylaldhyde salicyloyl hydrazone oxovanadium (IV)

Tables:

Table 1: Ligand Characterization detail

S.No.	Name of the ligands	Molecular formula	Colour	M.P /D.T.	Percentage Composition				Solubility
					% of C	% of H	% of N	% of O	
1.	Salicyaldehyde Salicyloyl hydrazon	$C_{14}H_{12}N_2O_3$	RedishYellow	190^{0}C	65.64 (64.40)	4.60 (4.72)	10.90 (9.90)	18.75 (17.75)	Ethanol

Table 2: Characteristics and analytical data of the complex

Name of the ligands	Salicyaldehyde Salicyloyl hydrazon Oxovanadium (IV)				
Molecular formula	$[C_{14}H_9N_2O_3].3H_2O.VO$				
Colour	Yellow				
M.P/D.T.	415				
Percentage Composition	% of C	% of H	% of N	% of O	% of M
	45.04 (44.50)	4.02 (3.45)	7.50 (6.75)	6.95 (6.48)	13.40 (12.20)
Molar Conductance	Methanol	DMF	DMSO		
	4.2	5.6	6.0		
Magnetic Moment μ_{eff}(BM)	1.64				

Table-3 Spectroscopic data of complex

S. No.	Name of complex	Important Peaks of IR Spectra		
1	Salicyaldehyde Salicyloyl hydrazon Oxovanadium (IV)	$\nu_{co-ordination\ water\ molecule}$	$\nu_{C=N}$	ν_{N-N}
		3300	1620	1000

Table 4: Antimicrobial Activity of Ligand & Metal complex.

S. No.	Ligand/Complex	Antifungal activity zone of inhibition(mm) A.awamore
1	Salicylaldehyde salicyloyl hydrazone	19
2	Salicylaldehyde salicyloyl hydrazone Oxovanadium (IV)	13

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