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Metal Complexes of 2-Aminobenzimidazole Derived Schiff Base: Preparation, Characterization and Biological Evaluation

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ABSTRACT

A new series of vanadium and copper complexes of tridentate Schiff base derived from the condensation of 1H-Benzimidazol-2-amine with 2-hydroxybenzaldehyde were prepared and characterized. Physical (molar conductance, magnetic moment, thermal), spectral (IR, UV-Vis, mass) and analytical data have established the structures of synthesized Schiff base and its complexes. From the elemental analyses data, the complexes are proposed to have the general formulae $[M(HL)_2]$; $[M = V(III)]$ *and* $[M(HL)Cl].2H_2O$; $[M = Cu(II)]$. *The molar conductance data reveal that all the metal chelates are non-electrolytes. IR spectra show that the Schiff base is coordinated to the metal ions in a neutral tridentate manner with NNO donor sites of the imidazole nitrogen of the benzimidazole ring, nitrogen of the azomethine group and oxygen of the deprotonated hydroxyl group. From the magnetic and electronic spectra, octahedral and square planar geometry is proposed for V(III)) and Cu(II)) complexes respectively. The thermal behavior of these complexes is studied using thermogravimetric analysis (TGA) technique. The results obtained show that the hydrated complexes lose water molecules of hydration immediately followed by decomposition of the anions and the ligand molecules in the successive unseparated steps. The pure compound, its Schiff base and the metal complexes have been screened invitro for their antifungal activity against Candida albicans and Aspergillus niger fungal strains by agar well-diffusion method.*

Keywords: Schiff base, complex, spectroscopy, non-electrolyte, Thermal analysis.

INTRODUCTION

Schiff bases are the compounds derived from an amine and any aldehyde or ketone, which on coordination with metal ions through the azomethine nitrogen form good chelating agents[1]. Benzo[b]furan derivatives are an active and important class of organic compounds known to be present in many natural products and possess physiological activity [2]. It is an effective synergist for rotenone- pyrethrum against houseflies, mosquitoes, aphids and many other insects [3]. Over the years, Schiff bases have drawn much attention of the chemists due to their vast biological and chemical properties. It is now well known that some drugs get increased activity when administered as metal complexes [4,5]. A variety of Schiff bases containing various donor sites have been tried for complexation and the structures were deduced with the help of spectral and magnetic data [6,7]. The increasing interest in transition metal complexes containing a

Schiff base ligand is derived from their well-established role in biological systems as well as their catalytic and pharmaceutical applications [8-11]. The metal complexes from bidentate ligands have often been studied recently because of their applications in enhancement of drug action [12,13]. Transition metals are essential for normal functioning of living organisms and are, therefore, of great interest as potential drugs [14]. The coordination chemistry of nitrogen donor ligands is an active area of research. Schiff bases derived from salicylaldehyde are well known for their interesting ligational properties and exclusive applications in different fields [15-17].

MATERIALS AND METHODS

Materials and reagents: All the chemicals used were of analytical reagent (AR) grade and of highest purity available. These include 2-minobenzimidazole (Himedia Pharmaceuticals Ltd.) and metal salts of vanadium and copper (Merck chemicals). Organic solvents used included absolute ethyl alcohol, acetone, DMF and DMSO.

Instruments: The molar conductance of solid complex in 10^{-3}M DMF solution was measured on a Systronics direct reading Conductivity Meter (Model 303). Elemental microanalysis of the separated solid chelates was performed at IIIM, Jammu using Vario MICRO V2.20 ElementarAnalysenSysteme GmbH. The metal content was determined gravimetrically [18]. Infrared spectra were recorded on FT-Infrared Spectrophotometer Model RZX (Perkin Elmer) in the region 4000-400 cm^{-1}. The spectra were recorded as KBr pellets from SAIF, Punjab University, Chandigarh. The melting points of the ligand and the complex were recorded in open capillaries on a capillary melting point apparatus. Electronic spectra were recorded on a UV-VIS-NIR-Spectrophotometer Model Lambda 750 Perkin Elmer from SAIF, PU, Chandigarh. The molar magnetic susceptibility was measured on Vibrating Sample Magnetometer (VSM) from IIT, Roorkee. The mass spectra were recorded at SAIF/CIL, PU, Chandigarh by LC-MS spectrometer Model Q-TOF MicroWaters. The thermogravimetric analysis was carried out in dynamic nitrogen atmosphere with a heating rate of 10^oC min^{-1} at ambient pressure using Perkin Elmer TG Analyser within a temperature range from room temperature to 1000^oC at Department of Chemistry, University of Jammu, Jammu.

Synthesis of Schiff base ligand [HL]: A mixture of 1H-Benzimidazol-2-amine (0.1 mol) with 2-Hydroxybenzaldehyde (0.1 mol) in 30 mL ethanol was refluxed on water bath for about 8h with the addition of few drops of glacial acetic acid with occasional shaking of the solution. The product, which was separated out as a crystalline solid on cooling, was collected and recrystalized from ethanol [19,20].

Synthesis of metal complexes: The metal complexes were prepared by the addition of solution of the appropriate metal chloride salts (VCl_3, 0.01 M) and ($CuCl_2 \cdot 2H_2O$, 0.02 M) in ethanol to the solution of ligand (0.02 M) in the same solvent . The resulting mixtures were stirred under reflux for 4 h whereupon the complexes precipitated. They were collected by filtration, washed with same solvent and recrystalized with acetone.

Biological activity: All the metal complexes and the ligand (HL) were screened against selected fungi to examine their anti-fungal activities. The susceptibility of the bacteria and fungi towards complex compounds were tested by measuring zone of inhibition (in mm) and compared with the parent ligand (HL). All the complexes show medium sensitivity against the fungal strains. The obtained results were compared with the standard drug Griseofulvin (10 μg mL^{-1}). In general, metal complexes are moderately more active than the ligands because metal complexes may serve as a vehicle for activation of ligands as the principle cytotoxic species [21-23] with a concentration of 3.45 μg mL^{-1} and 3.95 μg mL^{-1}.

RESULTS AND DISCUSSION

The physical appearance and analytical results show that the complex of V(III), possesses 1:2 stoichiometry whereas that of Cu(II) possesses 1:1 stoichiometry. Lower molar conductance values show that the complexes are non-electrolytes. Both the complexes are colored, stable and non-hygroscopic in nature having high melting points. The complexes are soluble in DMF and DMSO and the results have been given in Table 1.

Table-1: Analytical and physico-chemical data of Schiff base and its complexes.

Ligand / Complexes	**Mol. Wt.**	**Elemental Analysis Found (calcd.) (%)**				**Colour (yield%)**	**M.Pt. (^{o}C)**	**λ_m Scm^2 mol^{-1}**	**$^{\mu}$eff (B.M.)**
		C	**H**	**N**	**M**				
(HL) $C_{14}H_{11}N_3O$	237.25	70.87 (70.30)	4.67 (4.40)	17.71 (17.3)	--- ---	Yellow (54)	142	----	----
$[V(HL)_2]$ $C_{28}H_{20}N_6O_2Cl_2V$	594.33	65.10 (64.2)	3.60 (3.85)	15.20 (16.06)	9.00 (9.73)	Olive (60)	265 (Decomposition)	12.5	1.69
$[Cu(HL)Cl]{\cdot}2H_2O$ $C_{14}H_{14}N_3O_3ClCu$	371.26	45.10 (45.28)	4.00 (3.80)	13.70 (11.32)	16.95 (17.11)	Olive green (61)	180	16.65	1.44

IR spectral studies: A comparative interpretation of IR spectral data (Table 2) suggests that ligand (HL) acts as a tridentate ligand in the investigated complexes, using phenolic oxygen and azomethine nitrogen and imidazole nitrogen as donor atoms. The IR spectrum of the ligand shows a strong band at 1609 cm^{-1} attributed to $\nu_{(-HC=N)}$ stretching vibrations of the azomethine group[24], which gets shifted to higher frequencies in the complexes indicating involvement of the nitrogen atom of azomethine group. The band at 1569 cm^{-1} is due to the $\nu_{(C=N)}$ stretch and this frequency shifted to a lower value in the complexes confirming the involvement of the (C=N) in the coordination with the metal ions [25]. The stretching vibrational band C-O of the ligand lies at 1273 cm^{-1} frequency [26]. This band shifts to the higher frequency side in both the complexes. This suggests the coordination of the phenolic oxygen group with metal ions. Further the bonding is supported by the appearance of new bands in the 501,520, 614 and 593 cm^{-1} regions which are assigned to ν(M-N) and ν(M-O) vibrations respectively[27]. This indicates that carbonyl oxygen, azomethine nitrogen and imidazole nitrogen atoms are involved in coordination.

Table-2: Important IR spectral bands (cm^{-1}) of the ligand and its complexes.

Ligand/ Complex	$^{\nu}$**HC=N**	$^{\nu}$**CyclicC=N**	$^{\nu}$**CyclicC-N**	$^{\nu}$**C-O**	$^{\nu}$**M-N**	$^{\nu}$**M-O**
HL	1609 s	1569 s	1439 s	1273 s	---	---
$C_{28}H_{20}N_6O_2Cl_2V$	1644 s	1480 s	1463 s	1282 b	501 m	614 w
$C_{14}H_{14}N_3O_3ClCu$	1639 m	1545 m	1469 s	1279 s	520 m	593 m

Mass spectral studies: In the present investigation, the LC mass spectrum of ligand (HL) shows the formation of the molecular ion (M+1) peak at m/z (237.25) and it is in good agreement with its suggested empirical formula as indicated from elemental analyses (Table 1) which supports the formation of the ligand (HL).

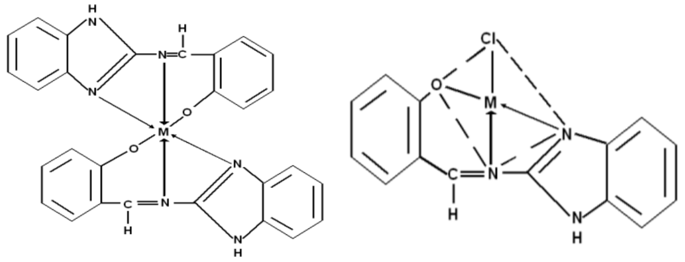
The mass spectrum of $[Cu(C_{14}H_{10}N_3OCl)]$ shows a molecular ion peak at m/z 379.09 due to $[Cu(HL)]^{+\cdot}$ which suggests the monomeric nature of the complex. The other intense peaks were found at m/z 306, 249, 238, 183 and134. The relative intensities of these peaks give an assessment of the stabilities of the various fragments. Such type of fragmentation patters have been reported by many workers [28,29].

Magnetic properties: Magnetic susceptibility measurements at room temperature exhibit paramagnetism for both the complexes and as listed in table 1. The vanadium complex exhibits magnetic moment value of 1.69 B.M. suggesting octahedral geometry [30,31]. The Cu (II) complex shows the magnetic moment value 1.44 B. M, indicating a square planar environment [32].

Electronic spectral studies: The electronic spectra of the metal complexes were recorded for freshly prepared solutions in DMF (10^{-3} M) at room temperature. The electronic spectra of the V(III) complex show three bands at 21739,17094 and 13986 cm^{-1} which are assigned to $^2B_2\rightarrow{}^2A_1(\nu1)$, $^2B_2\rightarrow{}^2B_1(\nu2)$ and $^2B_2\rightarrow{}^2E$ ($\nu3$) transitions, respectively in an octahedral environment[33]. The copper complex exhibits broad asymmetric band in the region $21650cm^{-1}$**.** The broadness of the band indicates the transition $^2B_{1g}\rightarrow{}^2A_1g$ [34,35].

Thermal analysis: In the present investigation, the weight loss for the chelate complex is calculated within the corresponding temperature ranges. The $[Cu(C_{14}H_{14}N_3Cl\ O_3)$ complex is thermally decomposed in three decomposition steps within the temperature range of 50-900°C. The first decomposition step with an estimated mass loss 7.9 % (found 6.7 %) within a temperature range 50-180°C may be attributed to the liberation of two water molecules of hydration[40,41].Second step ranges within 180-550°C and third step from 550-900°C. In the last step, decomposition of ligand moiety take place leaving CuO as residue.

Structural Interpretation: On the basis of above studies following structures of metal complexes have been proposed:



(M = V(III)) (M = Cu(II))

Fig.2. Structures of metal complexes

APPLICATIONS

Biological activity screening

Antifungal activity: All the metal complexes and the ligand (HL) were screened against selected fungi to examine their anti-fungal activities [36-39]. The susceptibility of the fungi towards complex compounds were tested by measuring zone of inhibition (in mm) and compared with the parent ligand (HL) with a concentration of 3.45μg mL^{-1} and 3.95μg mL^{-1} and the results have been given in table 3.In general, metal complexes are found to be moderately more active than the ligands.

Table 3: Antifungal activity of 2-aminobenzimidazole (Ab), its Schiff base (HL) and metal complexes

Compounds / Complexes (100 µg/ml)	Diameter of growth of inhibition zone (mm)	
	Candida albicans	*Aspergillus niger*
Ab	-	-
Ab-S (HL)	1.35	1.15
$[V(HL)_2]$	2.1	1.65
[Cu(HL)Cl]	3.20	3.41
Griseofulvin (10 µg/ml)	3.45	3.95

CONCLUSIONS

On the basis of above results we conclude that the newly synthesized Schiff base acts as a neutral tridentate ligand coordinating through the oxygen of the phenolic group, nitrogen of the azomethine group and imidazole nitrogen. Based on analytical and spectral investigations octahedral and square planar geometries are proposed to V(III) and Cu(II) complexes respectively.

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