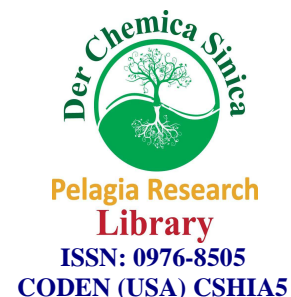




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Der Chemica Sinica, 2015, 6(7):1-6



Spectral and biological behaviour of complexes derived some bivalent metals and Schiff base

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ABSTRACT

Complexes of 2-Aminobenzimidazole-5-bromosalicylaldehyde (HL) with chlorides of nickel(II) and manganese(II) were synthesized. The molar ratio metal:ligand in the reaction of the complex formation was 1:2. It should be noticed that the reaction of the metal salts yielded bis (ligand) complexes of the general formula $M(L)_2$ ($M = Ni^{II}, Mn^{II}$). The complexes were characterized by elemental analysis, molar conductivity measurements, magnetic susceptibility measurements, IR, electronic spectra, mass and thermal studies. Both the complexes have octahedral configuration around the metal ion. In both the complexes, ligand act as tridentate (NNO donor) coordinating by participation of the imidazole nitrogen of the benzimidazole ring, nitrogen of the azomethine group and oxygen of the deprotonated hydroxyl group. The Schiff base and its metal complexes have been screened for their antifungal activity against *Candida albicans* and *Aspergillus niger*.

Keywords: 2-Aminobenzimidazole, complexes, nickel(II), manganese(II), spectroscopic studies, antifungal activity.

INTRODUCTION

Schiff bases are widely employed in synthetic organic and inorganic chemistry. They were reported to show diverse biological activity[1-4] and have many applications as ligands in coordination chemistry of transition metals[5,6]. The chemistry of metal complexes with Schiff base ligands and their application have aroused considerable attention mainly because of preparative accessibility, diversity and structural variability[7]. Schiff bases belong to a widely used group of organic intermediates important for the production of special chemicals, e.g. pharmaceuticals or rubber additives and as amino protective groups in organic synthesis[8,9]. The Schiff base synthesized from 4-Aminobenzoic acid and 5-Bromosalicylaldehyde have phototropic and thermotropic properties. Schiff bases very similar to this compound have shown microbiological activity and antifungal properties[10]. 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 [11,12]. The metal complexes from bidentate ligands have often been studied recently because of their applications in enhancement of drug action [13,14]. Transition metals are essential for normal functioning of living organisms and are, therefore, of great interest as potential drugs [15]. 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 [16, 17]. In this paper, we are reporting the synthesis, characterization and antifungal activity of metal complexes of Schiff base derived from 2-Aminobenzimidazole derived on some pathogenic fungi.

MATERIALS AND METHODS

Chemicals

All the chemicals used were of AR/GR grade. Pure sample of 2-Aminobenzimidazole (Ab), molecular formula $C_7H_7N_3$, molecular weight 133.15 g/mol, melting point 229-231°C was obtained from Himedia Pharmaceuticals Ltd. Metal salts like $NiCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ were of Merck chemicals. Solvents used were ethanol, acetone and DMF.

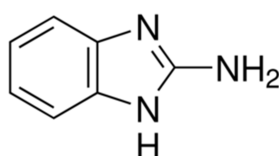


Fig. 1: Structure of Pure Compound

Synthesis of Schiff base ligand(HL)

The Schiff base was synthesized from 5-Bromosalicylaldehyde(BS) and 2-Aminobenzimidazole (Ab) by adding 500 ml of 5-Bromosalicylaldehyde ethanolic solution (1.005 g; 0.01 M) to same volume of ethanolic solution of 2-Aminobenzimidazole (0.8144 g; 0.01M), the mixture was refluxed for 2 hours and kept overnight at room temperature. The resulting solution was evaporated to 20% of its original solution and the product was collected by filtration, washed several times with ethanol and crystallized from hot ethanol and then dried. The melting point of yellow crystals was found to be 245°C.

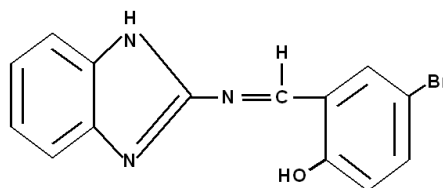


Fig.2: Structure of Schiff base

Synthesis of Complexes

For the synthesis of complexes, ligand-metal ratio was determined by conductometric titration using monovariation method on systronics conductivity meter using dip type electrode. 20 ml of the ligand (0.01 M) was diluted to 200 ml using pure ethanol and titrated against metal salts (0.02 M) solution prepared in the same solvent. Conductance was recorded after each addition of metal salt solution. Graph is plotted between corrected conductance and volume of metal salt added. From the equivalence point in the graph, it has been concluded that the complex formation of the ligand with metal salts takes place in the ratio 2:1 (L:M).

Conductometric titration supported 2:1 (L:M) ratio in the complex, which was further supported by Job's method of continuous variation[18] as modified by Turner and Anderson [19]. The solid complexes were prepared by mixing ethanolic solutions of the ligand L (0.31 g, 0.01 M) with solution of chlorides of Ni(II), (0.059 g, 0.005 M) and Mn(II), (0.049 g, 0.005 M), separately in the same solvent. The resulting solutions were checked for pH and pH was adjusted by adding few drops of N/10 NaOH solution. The solutions were refluxed for 4 hours and the refluxed solutions were kept for some days, solid crystalline complexes appeared in the solution which were filtered off, washed thoroughly with same solvent and finally with acetone, vacuo dried and weighed. Melting points of the complexes were recorded.

Analytical Procedure

Elemental analysis were carried out on Vario MICRO V2.20 Elementar Analysen Systeme GmbH, from IIM, Jammu. Metal contents were determined gravimetrically[20]. The infrared spectra were recorded on FT-InfraRed Spectrophotometer Model RZX (Perkin Elmer) using KBr pellets from SAIF, Punjab University, Chandigarh. Molar conductance measurements were made in 10^{-3} M DMF solution on a Systronics direct reading Conductivity Meter (Model 303). The melting points of the ligand and the complexes 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 magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer (VSM) from IIT, Roorkee. The mass spectra was recorded at SAIF/CIL, PU, Chandigarh by LC-MS spectrometer Model Q-ToF Micro Waters. The thermo-gravimetric analysis was carried out in nitrogen atmosphere (0.00 l/min.) with a heating rate of $10^{\circ}\text{C min}^{-1}$ at ambient pressure using Perkin Elmer TG Analyser within a temperature range from room temperature to 950°C at Department of Chemistry, University of Jammu, Jammu.

Antifungal activity

The antifungal activities of the ligand and their complexes were tested in vitro for growth inhibitory against *Candida albicans* and *Aspergillus niger* by agar well diffusion method at different concentrations compared with Griseofulvin as the positive control[21,22].

RESULTS AND DISCUSSION

Through a condensation reaction, an amino group available in the pure compound was allowed to react with 5-Bromosalicylaldehyde to form a Schiff base ligand (HL) which was subsequently, reacted with metal ions to form Schiff base metal complexes. The ligand and the metal(II) complexes were isolated pure from EtOH in good yields.

The analytical data of the complexes correspond with 1:2 (metal: ligand) stoichiometry. Thus, the general formula $[\text{M}(\text{L})_2] \cdot 2\text{H}_2\text{O}$ where (M(II) = Ni, Mn), have been assigned to the metal complexes, respectively. They are very air stable solids at room temperature without decomposition for a long time. The complexes are non-hygroscopic, insoluble in water and other common organic solvents but soluble in DMF and DMSO[23]. The magnetic moment data indicated both the complexes to be paramagnetic in nature. Thermograms of the metal complexes indicate the presence of lattice water molecules. The analytical data has been presented in Table 1.

Magnetic measurements

The magnetic moment data are presented in Table 1. The Ni(II) complex showed magnetic moment values of 2.95 B.M. slightly higher than the spin only (2.83 B.M.) value, indicating an octahedral environment around Ni(II) ion[24]. The Mn(II) complex showed a value of 5.42 B.M., which is slightly lower than the spin only value of 5.92 B.M. for high spin octahedral Mn(II) complexes[25].

Electronic spectra

The electronic spectra of the complexes were recorded in the solution state. The energies of the observed spin allowed bands in all the complexes agreed with the octahedral geometry. The electronic spectrum of paramagnetic Mn(II) complex shows four weak bands at bands at 600 nm, 441 nm, 408 nm, and 382 nm which can be assigned to ${}^6\text{A}_{1g} \rightarrow {}^6\text{T}_{1g}(\text{G})^v_1$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})^v_2$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})^v_3$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})^v_4$, respectively, for an Mn (II) ion in an octahedral field[26]. The electronic spectrum of the Ni(II) complex displayed three bands at 655 nm, 540 nm and 440 nm, assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})^v_1$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})^v_2$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})^v_3$ transitions, respectively, which indicate octahedral geometry[27] of the Ni(II) complex.

IR spectral studies

The comparison of the IR spectra of Schiff base (HL₂) and its metal complexes indicated that the ligands are principally coordinated to the metal ions in three ways, thus acting as tridentate ligands. The band appearing at $\sim 1603\text{ cm}^{-1}$ due to azomethine linkage [28] in the ligands is shifted by $\sim 33\text{--}40\text{ cm}^{-1}$ in the complexes, indicating the participation of the azomethine nitrogen in interaction with the metal ion [29]. The band at $\sim 1563\text{ cm}^{-1}$, assigned to the nitrogen of the imidazole ring (C=N), is shifted to lower frequency by $\sim 7\text{--}12\text{ cm}^{-1}$, which was indicative of the involvement of the imidazole ring N in the coordination with metal ions[30]. A broad band appearing at $\sim 3200\text{ cm}^{-1}$ assigned to hydroxyl group in the Schiff base, was no longer found in the spectra of the investigated metal complexes[31,32] and instead, appearance of a new band at $\sim 1265\text{--}1305\text{ cm}^{-1}$ due to (C-O)stretching vibrations, indicated deprotonation[33] and coordination of the hydroxyl oxygen to the metal ion. Further conclusive evidence of coordination of these Schiff bases with the metal ions was shown by the appearance of low frequency new bands at 440 cm^{-1} and 463 cm^{-1} and at 620 cm^{-1} and 635 cm^{-1} . These were assigned to the metal-nitrogen (M-N) and metal-oxygen (M-O) vibrations, respectively and were observed in the spectra of the investigated metal complexes and not in the spectra of the uncomplexed Schiff bases, thus confirming participation of the O and N atoms in the coordination[34,35]. The appearance of bands at 3366 and 3325 cm^{-1} are due to lattice water molecules[36] which

were further confirmed by the appearance of new bands at 831 and 836 cm^{-1} frequencies due to $\nu\text{OH}_{(\text{rocking})}$. The bands at 544, 535 and 539 cm^{-1} are due to $\nu\text{C-Br}$ stretching vibrations in the Schiff base and the respective metal complexes.

Mass spectra

The mass spectrum of $[\text{Mn}(\text{C}_{28}\text{H}_{22}\text{N}_6\text{Br}_2\text{O}_4)]$ shows molecular ion peaks at m/z value 720.10 due to $[\text{Mn}(\text{L})_2]^+$, which is in accordance with the proposed formula of the complex. The other peaks at m/z values of 403.7, 308.7, 267.9, 132.0, 271.9, 170.8 and 100.9 may be due to the different fragments. The base peaks at m/z 132.0 may be due to the metal Mn linked to the donor atoms of the ligand. Such type of fragmentation pattern has been reported by many workers [37,38].

Thermal Studies

The TGA for the complex was carried out within a temperature range from room temperature to 950 $^{\circ}\text{C}$. The TG studies indicate that complex showed a slight depression at 20-100 $^{\circ}\text{C}$. The weight loss at this temperature range is found to be equivalent to two water molecules for the complex indicating to be the lattice water. Thereafter, the complex showed rapid decomposition of the organic constituents. The decomposition continues upto 920 $^{\circ}\text{C}$ and finally metal oxide gets formed in addition to other organic constituents [39]. The complete result of thermal analysis is shown in fig.3

Antimicrobial Activity

For antifungal activity, the ligand and its metal complexes were screened against *Candida albicans* and *Aspergillus niger* and the findings are given in Table 3. These complexes showed higher activity with 13.45–17.00 mm inhibition than the ligand which showed only 11.48 mm inhibition at the same concentration as that of the test compound for *Candida albicans*. However, ligand and their complexes showed lower activity as compared to standard drug griseofulvin with 19.38 mm inhibition at the same concentration.

Antifungal activity studies of ligand and its complexes against *Aspergillus niger* showed that all the complexes with 14.33–21.22 mm inhibition showed higher activity than the ligand which showed only 10.38 mm inhibition only. Ni(II) complex showed higher activity than standard drug which showed 18.22 mm inhibition at the same concentration as that of the test drug. It is known that chelation tends to make the ligand act as more powerful and potent antimicrobial agent, thus inhibiting more of the microbes than the parent ligand[40,41].

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. ($^{\circ}\text{C}$)	λ_m $\text{Scm}^2\text{mol}^{-1}$	μ^{eff} (B.M.)
		C	H	N	M				
[HL ₂] (C ₁₄ H ₁₀ N ₃ BrO)	316.14	54.21 (53.18)	3.55 (3.19)	13.7 (13.29)	-	Yellow (58)	245	-----	
[Ni(C ₂₈ H ₁₈ N ₆ Br ₂ O ₂)] \cdot 2H ₂ O (Ab-BS-Ni)	725.0	47.03 (46.38)	3.00 (3.05)	10.70 (11.6)	8.07 (8.10)	Yellow (53)	205	17.1	2.95
[Mn(C ₂₈ H ₁₈ N ₆ Br ₂ O ₂)] \cdot H ₂ O (Ab-BS-Mn)	721.23	46.70 (46.63)	3.03 (3.07)	12.10 (11.7)	7.85 (7.62)	Olive (50)	230 (Decomposition)	16.4	5.42

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

Ligand / Complexes	$\nu\text{CH=N}$	$\nu\text{C=N}$	νOH	$\nu\text{H}_2\text{O}$	$\nu\text{M-O}$	$\nu\text{M-N}$	$\nu\text{C-Br}$
(C ₁₄ H ₁₀ N ₃ BrO)	1281 s	1603 s	S 3200 b	----	----	----	544 b
(C ₂₈ H ₁₈ N ₆ Br ₂ O ₂ Ni)	1265 s	1636 m	----	3366 s	620 m	440 s	535 b
(C ₂₈ H ₁₈ N ₆ Br ₂ O ₂ Mn)	1302 s	1643 s	---	3325 s	635 s	463 s	539 s

Table-3: Antifungal activity of ligand and its metal complexes

Ligands/complexes	Antifungal zone of inhibition (in mm)	
	<i>Candida albicans</i>	<i>Aspergillus niger</i>
(C ₁₄ H ₁₀ N ₃ BrO)	11.48	10.38
[Ni(C ₂₈ H ₁₈ N ₆ Br ₂ O ₂)] \cdot 2H ₂ O	17.00	21.22
[Mn(C ₂₈ H ₁₈ N ₆ Br ₂ O ₂)] \cdot 2H ₂ O	13.45	14.33
Grisofulvin	19.38	18.22

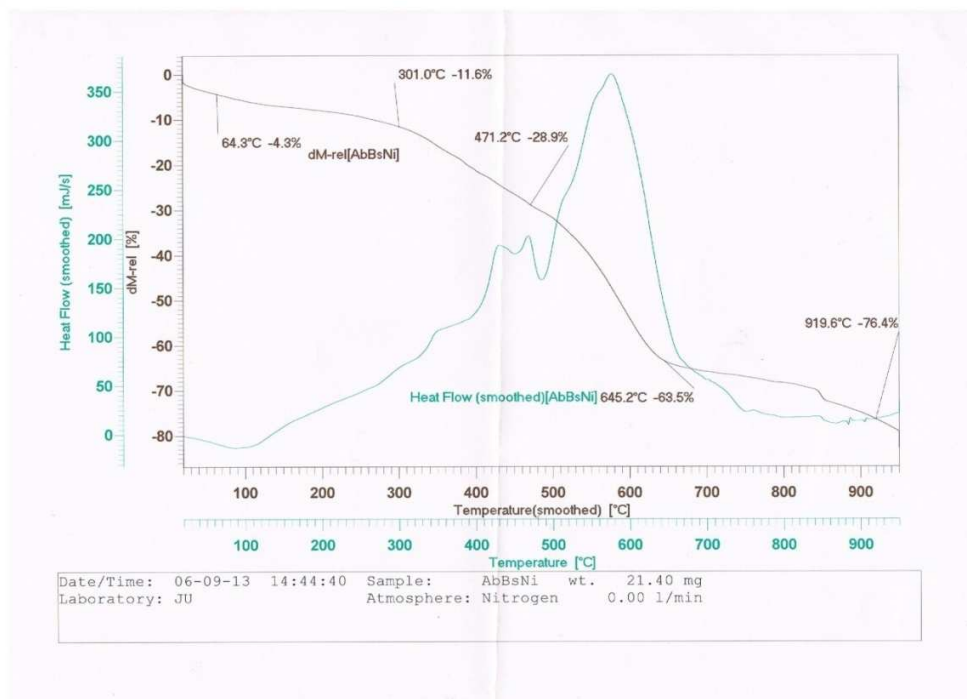


Fig. 3. TGA Spectrum of Ab-BS-Ni Complex

CONCLUSION

Based on stoichiometry and analytical data it can be concluded that the ligand is neutral, tridentate coordinating through the 'N', 'N' and 'O' of the azomethine, imidazole and phenolic groups, respectively. Both the complexes possess 1 : 2(M : L) stoichiometry. Based on analytical and spectral data, octahedral structures have been proposed for the complexes. The ligand and the complexes showed good activity against the selected microbes.

Hence, the proposed structure for the metal complexes is given as below in Fig.4:

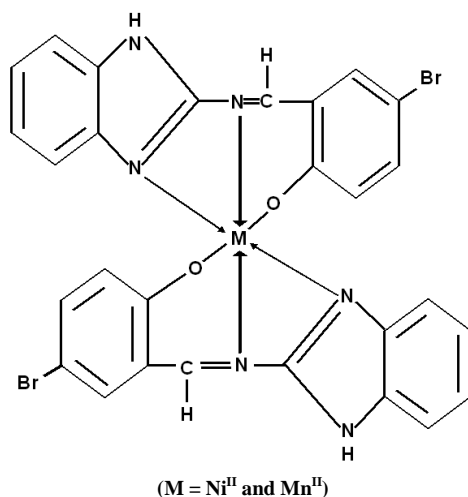


Fig.4. Structure of metal complexes

Acknowledgements

The authors are thankful to Principal, Sadhu Vaswani College, Bairagarh, Bhopal for providing necessary facilities for research work, DST for granting FIST program to the college and UGC for sanctioning Minor Research Project to Dr. Suman Malik, one of the Co-authors.

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