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Spectral characterization and thermal behavior of Schiff base metal complex derived from 2-aminobenzimidazole

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ABSTRACT

The Ni(II) complex of Schiff base derived from 2-Aminobenzimidazole with Salicylaldehyde has been synthesized keeping in view that some metal complexes are found to be more potent than their parent drugs. The synthesized complex has been characterized by elemental analysis, conductivity measurements, IR, UV, magnetic susceptibility and TGA studies. The molar conductance measurement of the complex in DMF indicates its weak molecular nature. The spectroscopic studies shows the presence of azomethine nitrogen in coordination to the metal ion and octahedral geometry of the metal complex has been proposed. The thermal decomposition of the complex was studied and indicates that not only the lattice water is lost but also the decomposition of ligand from the complex is necessary to interpret the successive mass loss.

Keywords: 2- Aminobenzimidazole, Schiff base, metal complex, conductivity, spectral studies.

INTRODUCTION

The field of Schiff base complexes was fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines. Many attempts were done to prepare symmetric polydentate ligands in order to achieve rare coordination number with divalent metal ions whose importance was mainly due to their ability to form metal chelates.Benzimidazole and its derivatives play an important role in analysis and in several biological reactions. Benzimidazole derivatives exhibit antibacterial, antihelmintic and insecticidal activities[1-3].Transition metal complexes containing benzimidazole are widely used as catalysts for hydrogenation, hydroformylation, oxidation and other reactions[4-6]. Even though many Schiff bases using salicylaldehyde and substituted salicylaldehydes and amines had been studied [7-10] as ligands, no work had been done with salicylaldehyde and 2-aminobenzimidazole as the basic nucleus of Schiff bases. Schiff base metal complexes had been a widely studied subject due to their industrial and biological applications[11]. The synthesis, physico-chemical characterization and biological activity of 2-aminobenzimidazole complexes with different metal ions have been reported[12]. An efficient synthesis of Schiff bases containing benzimidazole moiety catalysed by transition metal nitrates had been done[13]. The synthesis and antimicrobial activity of Cu(II), Co(II) and Ni(II) complexes with 2-aminobenzimidaole were available[14].

The crystal structure of two mononuclear cadmium and dinuclear, µ-hydroxybridged zinc macrocyclic Schiff base complexes were reported[15]. Also multidentate benzimidazole ligands were incorporated in cross linked polymeric matrices and their ligating behavior towards different metal ions to develop new types of chelating ion-exchange resin systems were studied[16]. The development of such polymeric ligands could be useful to study the reaction mechanisms in the biological systems involving imidazole and benzimidazole derivatives[17].

In the present paper, we report the synthesis and spectroscopic characterization of the Ni(II) complex with Schiff base (ABZ-SAL) derived from 2-Aminobenzimidazole (ABZ).

MATERIALS AND METHODS

Chemicals

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

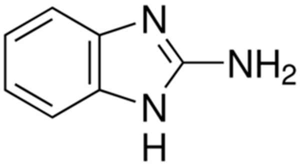


Fig. 1 Structure of pure compound (2-Aminobenzimidazole)

Synthesis of Schiff base

The Schiff base was prepared[18,19] by mixing equimolar amounts of 2-aminobenzimidazole and the aromatic aldehyde in ethanol. The mixture was refluxed for about 4 hours.Concentration of the solution was done to reduce it to one-half of its original volume and kept for 4-5 days when deep yellow crystals were formed in the reaction mixture, which were filtered,washed thoroughly with same solvent and recrystallised with acetone.The yellow Schiff base product obtained (m.p. 142°C) produced in 54% yield was subjected to analysis.

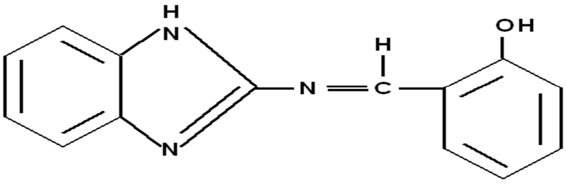


Fig. 2 Structure of Schiff base

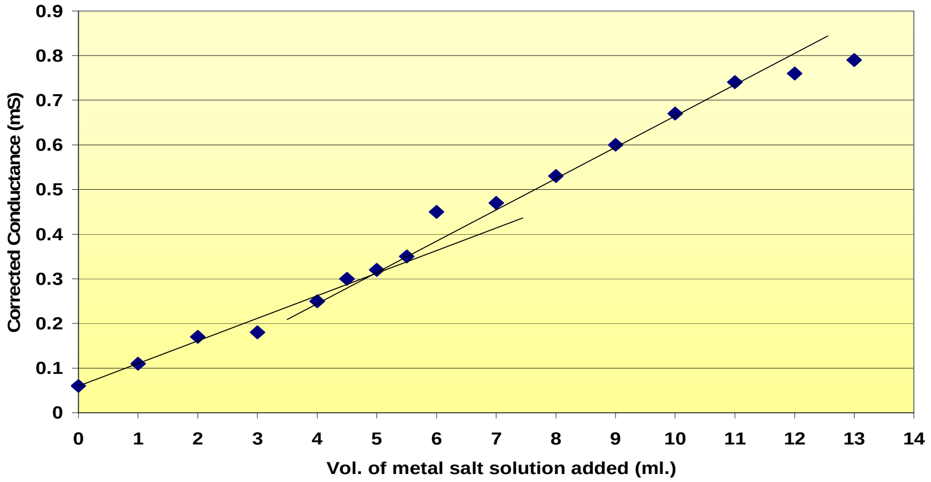


Fig. 3. Conductometric titration (Monovariation method) 2-Aminobenzimidazole-salicylaldimine (Ab-S) Schiff base with metal salt

Synthesis of the complex

For the synthesis of complex[20,21], ABZ-SAL-Ni, ligand-metal ratio was determined by conductometric titration using monovariation method on systronics conductivity meter using dip type electrode. 20ml of the ligand (0.01M) was diluted to 200ml using pure ethanol and titrated against $NiCl_2.6H_2O$ (0.02M) solution prepared in the same solvent. Conductance was recorded after each addition of metal salt solution. Graph is plotted (fig. 3) 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 the metal 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[22] as modified by Turner and Anderson[23](Fig. 4).

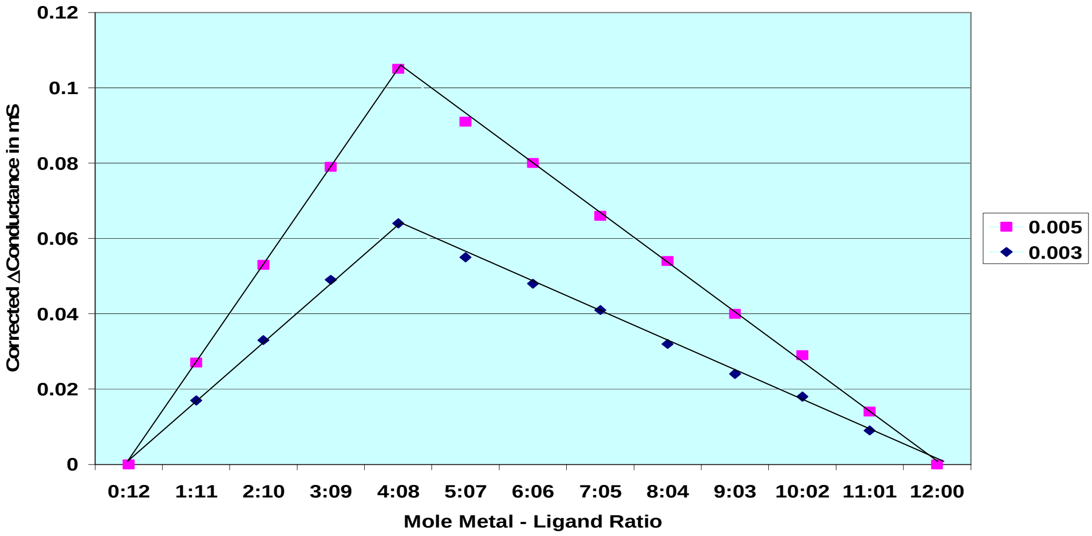


Fig. 4 Modified Job's method

The metal complex was prepared by mixing 50ml of Schiff base (0.05M) solution in the appropriate metal salt $NiCl_2.6H_2O$ (0.025M) in 50ml ethanol solution. The resulting solution was checked for pH and the pH was adjusted by adding few drops of N/10 NaOH solution. This solution was refluxed for 2 and 1/2 hours and the refluxed solution was kept for 2-3 days. Solid crystalline compound appeared in the reaction mixture which were filtered, washed with same solvent and dried over fused $CaCl_2$.

Physical measurements

Elemental analysis were carried out on VarioMICRO V2.20 Elementar Analysen Systeme GmbH, from IIIM, Jammu. Metal content was determined gravimetrically. The infrared spectra was recorded on FT-InfraRed Spectrophotometer Model RZX (Perkin Elmer) using KBr pellets, from SAIF, Panjab University, Chandigarh. Molar conductance measurement was made in 10^{-3}M DMF solution on a Systronics direct reading Conductivity Meter (Model 303). The melting points of the ligand and the complex were recorded in open capillaries on a capillary melting point apparatus. Electronic spectra was 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 thermo-gravimetric analysis was carried out in nitrogen atmosphere (0.00 l/min.) 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 800^oC at Department of Chemistry, University of Jammu, Jammu. The mass spectra of a Schiff base and its metal complex in this study were recorded at SAIF/CIL, Panjab University, Chandigarh by (LC-MS Spectrometer Model Q-ToF Micro Waters).

RESULTS AND DISCUSSION

The synthesis of Schiff base (HL) is schematically represented in fig. 2. Elemental analysis indicated 2:1 (L:M) ratio in the synthesized metal complex. The complex is non-hygroscopic, yellow in colour and stable at room temperature. The lower value of molar conductance 17.5 $ohm^{-1} cm^2 mol^{-1}$, measured in 10^{-3} M DMF of the complex indicates its non-electrolytic nature[24,25]. The low conductivity value is in agreement with low solubility of the complex in water, ethanol, chloroform, acetone and most organic solvents. On the other hand, complex is soluble in DMSO and DMF and decomposed at higher temperature. Elemental analysis data, formula weight, magnetic moment and melting point of the ligand and the complex are given in Table 1.

Table 1: Physico-chemical and Analytical data of schiff base and its complex

Ligand/ Complex	L-M Ratio	Colour (Yield%)	$^{\mu}$eff /B.M	ohm^{-1} cm^{2} mol^{-1}	M.Pt.(^{o}C)	Elemental Analysis % Found (Calcd.)			
						C	H	N	M
(L) $C_{14}H_{11}N_3O$ (237.25)	----	Yellow (54)	---	---	142	70.87 (70.30)	4.67 (4.40)	17.71 (17.3)	---
$[Ni(L)_2].2H_2O$ $C_{28}H_{24}N_6O_4Ni$ (567.21)	2:1	Yellowish green (52)	2.85	17.5	250 (Decomp.)	61.0 (59.29)	4.02 (4.27)	13.94 (14.82)	10.15 (10.35)

IR Spectra

The comparative analysis of the IR spectra of the free ligand and the complex (Table 2) revealed that the absorption band characteristic of the stretching vibrations of ^{v}(C=N-), azomethine group is shifted towards lower number from 1609 cm^{-1} in the spectrum of ligand to 1606 cm^{-1} in the complex[26,27]. This indicates the coordination of the nitrogen of this group with the metal ion. Further, the coordination of metal to azomethine nitrogen is confirmed by a new band at 437 cm^{-1} due to ^{v}(M-N). In addition, the ligand exhibits a band at 1569 cm^{-1} due to ^{v}cyclic (C=N) of the imidazole nitrogen (N_3). This band is shifted to 1436 cm^{-1} in the complex, indicating the involvement of imidazole nitrogen atom in complex formation. Conclusive evidence regarding the binding of oxygen to the metal ion is provided by the occurrence of a band at 583 cm^{-1}(M-O) [28]. The phenolic C-O stretch band is observed at 1273 cm^{-1}in the free ligand[29]. In the complex, this band appears at lower wave number at 1268 cm^{-1}, showing a strong peak, confirming the involvement of phenolic group in the complex formation[30]. The ligand shows a strong band at 3566 cm^{-1} due to phenolic -OH group. This band is absent in the complex indicating the involvement of this group in complex formation[31].

Table-2: IR Spectral data (cm^{-1}) of ligand and its complex

Ligand/ Complex	$^{v}{}_{C-O}$	$^{v}{}_{C=N}$	$^{v}{}_{Cyclic(C=N)}$	$^{v}{}_{M-N}$	$^{v}{}_{M-O}$	$^{v}{}_{OH}$	$^{v}{}_{H2O}$(str.)	$^{v}{}_{H2O(-OH)}$ (rocking)	$^{v}{}_{Chelate\ ring}$
$C_{14}H_{11}N_3O$	1273	1609	1569	----	----	3566 s	----	---	---
$C_{28}H_{24}N_6O_4Ni$	1268	1606	1436	437	583	----	3432 b	846 s	1333 s

Electronic Spectra

Ni (II) complex shows magnetic moment at 2.85 B.M. corresponding to two unpaired electrons[32]. The solid reflectance spectrum of Ni (II) complex is consistent with the formation of an octahedral geometry with the appearance of three bands 20800, 18577 and 12500 cm^{-1} corresponding to the transitions $^{3}A_{2g\,(F)} \rightarrow {}^{3}T_{1g}$ (P), $^{3}A_{2g\,(F)} \rightarrow {}^{3}T_{1g}$ (F) and $^{3}A_{2g} \rightarrow {}^{3}T_{2g\,(F)}$ [33,34].

Thermal Studies

The TG for the complex was carried out within a temperature range from room temperature to 800^{o}C. The water molecules are present as lattice water and are usually eliminated at higher temperatures than those of hydration viz. less than 150^{o}C. The decomposition temperature ranges, percent mass losses and the residue leaving behind are given[35-37]. The Ni(II) complex of the general formula $[Ni(L_2)].2H_2O$ gives a six-stage decomposition process. The first stage from 20-200^{o}C may represent loss of water molecules of hydration (Calcd. mass loss 6.3%, found5.6%). The second stage from 200-350^{o}C, the third from 350-500^{o}C, the fourth from 500-570^{o}C, fifth from 570-700^{o}C and sixth from 700-800^{o}C stages may be due to the decomposition of two ligand molecules leaving nickel oxide as the residue. The mass losses for these temperature ranges are 14.25% (found 13.9%), 12.94% (found 13.0%), 41.46% (found 39.3%), 16.1% (found 15.8%) , 4.0% (found 2.9%) and 9.8% (found 9.5%), respectively.

Mass spectral studies

Mass spectrometry is a micro-analytical technique requiring only a few nano moles of the sample to obtain characteristic information pertaining to the structure and molecular weight of the analyte. It is unlike the other forms of spectroscopy, in that it is not concerned with non-destructive interactions between molecules and electromagnetic radiation. Instead, it involves the production and separation of ionized molecules and their ionic decomposition products and finally the measurement of the relative abundances of different ions produced.

The mass spectrum of the ligands ($C_{14}H_{11}N_3O$) shows a molecular ion peak ($m^{+\cdot}$) at m/z 238.1 due to $(L)^{+\cdot}$ that corresponds to the molecular weight of the Schiff base. Besides this peak, the Schiff base showed a fragment ion peak at m/z 134.1 that corresponds to $C_7H_5N_3)^{+\cdot}$, one part of the ligand (i.e. 2-Aminobenzimidazole).

The mass spectrum of [Ni($C_{28}H_{24}N_6O_4$)] shows a molecular ion peak ($m^{+\cdot}$) at m/z 567.65(I) due to $[Ni(L)_2]^{+\cdot}$ which suggests the monomeric nature and confirms the molecular weight and the proposed formula for the complex. Besides this peak, the complex showed the fragment ion peak at m/z 267.9 (IV) corresponding to $L^{+\cdot}$ with other atoms $(C_{14}H_{10}N_4O_2)^{+\cdot}$. Other peaks of appreciable intensity have been observed at m/z values 100.9, 104.9, 132.0, 170.8, 231.1, 308.7 and 403.7 that indicates the fragmentation pattern. The peaks observed at m/z 403.7(II) due to loss of $(C_7H_9N_3O_2)^{+\cdot}$ from (I) indicative of 2-aminobenzimidazole ring with two water molecules, at 308.7 (III) due to loss of $(C_7H_5)^{+\cdot}$ from (I) and at m/z 231.9 (V) due to loss of $[(C_8H_6N_3O_2)Ni]^{+\cdot}$ from (I). Intense peaks at 170.8 (VI) is due to loss of $(CH_2N_2O)^{+\cdot}$ from (V) and at m/z 132.0 (VII) due to loss of $(C_7H_5N_3)^{+\cdot}$ from (II) indicating the loss of second molecule of 2-aminobenzimidazole ring. The peaks at m/z 104.9 (VIII) due to loss of $(C_7H_5O)^{+\cdot}$ from (II) and base peak at 100.9 (IX) due to metal ion linked to the donor atoms, $[Ni(NNO)]^{+\cdot}$. The relative intensities of these peaks give an idea of the stabilities of the various fragments.

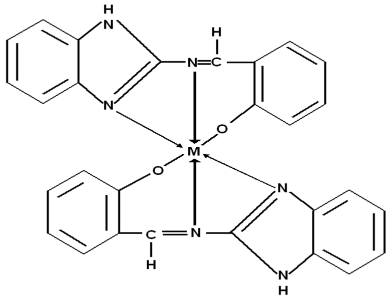
^{1}H NMR Studies

NMR spectroscopy study enables us to record differences in the magnetic properties of the various magnetic nuclei present and to deduce in large measure what positions of these nuclei are within the molecule. It can also be used to determine how many different kind of environments are there in the molecule and also which atoms are present in neighboring groups. By knowing all this, much help is achieved in structure elucidation of the molecule. The ^{1}H NMR spectra have been recorded for Schiff base only because the Ni^{2+} ion is paramagnetic in nature due to presence of odd electrons that are unshared pair of electrons.

^{1}H NMR spectrum of the ligand (Ab-S) shows a signal at 12.39 ppm as singlet due to phenolic –OH. In the ligand, the signal at 9.63 ppm as singlet is due to proton of azomethine group. The signals obtained for the ligand at 8.16-6.84 ppm are due to protons of aromatic rings (8H, Ar-H) thus further supporting the IR spectral observations.

CONCLUSION

The present work describes the synthesis of nickel complex from tridentate (NNO donor) Schiff base derived from the condensation reaction of 2-aminobenzimidazole with salicylaldehyde. The physical (molar conductance, magnetic measurements and TGA), spectral (UV-Vis, IR and mass) and analytical data for the complex clearly suggest that the Schiff base is coordinated to metal ion through its azomethine nitrogen, nitrogen of imidazole ring and oxygen of the deprotonated phenolic group. On the basis of above studies, octahedral structure is proposed for the complex.



(M=Ni ^{II})

Fig. 5 Structure of Schiff base metal (ABZ-SAL-Ni) complex

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