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Synthesis and Characterization of Mono Nuclear Complexes of Mn^{2+}, Ni^{2+} and Cu^{2+} with Tetradentate N_3O Schiff Base

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An unsymmetrical Schiff base ambsalen, [1-(2-aminobenzylideneiminato)-2-(salicylaldiminato) ethane] derived by the condensation of ethylenediamine with equimolar amounts of *o*-aminobenzal-dehyde and salicylaldehyde was synthesized and was characterized. The copper(II), nickel(II) and manganese(II) complexes of the ligand ambsalen were also synthesized and characterized by elemental analysis, conductivity, ^{1}H NMR, UV-Vis, IR, EPR spectral studies and cyclic voltammetry. The molar conductivity data of the mononuclear complexes showed them to be 1:1 electrolytes. The tetradentate nature of the ligand is concluded from the IR spectral studies. The electronic spectral data suggest planar geometry for all the complexes. The antibacterial activities of the ligand and their metal complexes have been screened *in vitro* for their antibacterial and antifungal activities.

Key Words: Synthesis, Characterization, Schiff base, Metal complexes.

INTRODUCTION

The coordination complexes of Schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological processes[1]. Eventhough a lot of work has been done with Schiff base ligands prepared by the condensation of aliphatic diamines with the aromatic or aliphatic aldehydes, the unsymmetrical Schiff base ligands and their metal complexes are relatively few in number. Recently, metal complexes with unsymmetrical Schiff base ligands have become of interest in connection with a design of synthetic models for biological systems involving metal ions[2,3]. Hence an attempt has been made to synthesis and characterize a new N_3O type schiff base ligand and their metal complexes.

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EXPERIMENTAL

All the chemicals used were of AR grade and used without further purification. Perkin Elmer FTIR-8300 model spectrometer was used for recording the infrared spectra of the complexes in the range 4000-400 cm^{-1}. The spectra were taken suitably as potassium bromide discs of the compounds. Hitachi UV-2001 spectrophotometer was used for recording the electronic spectra of the complexes. The spectra were recorded in spectroscopic grade acetonitrile and the pure solvent was used as the reference. ^{1}H NMR spectra were recorded at 400 MHz on Bruker AMX 400 MHz spectrophotometer using DMSO as solvent and TMS as internal standard. The mass spectrum was recorded on a VG analytical 7070E instrumentation equipped with VG-250 data acquisition system. The conductivity studies were carried out using a Systronics direct reading conductivity bridge provided with conventional dip type platinized platinum electrodes. The ESR spectra of the complexes were recorded on the Jeol-spectrometer operating at X-band frequencies. The spectra were recorded at room temperature in ethanol. Cyclic voltammetric studies were carried out using a model ECDA-001, basic electrochemistry system. HPLC grade acetonitrile was used as solvent with 0.1 M tetrabutyl ammonium perchlorate as supporting electrolyte. A three electrode configuration was used, comprising glassy carbon or platinum working electrode, platinum wire counter electrode and Ag/AgCl reference electrode and oxygen free atmosphere was provided by bubbling purified nitrogen through the solution before starting the experiment. For the antibacterial and antifungal activity assay, the *in vitro* filter paper disc diffusion method[4] was adopted. The ligand and the metal complexes were tested against five bacterial strains *viz.*, *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Klebsiella pneumoniae* and three fungi *viz.*, *Aspergillus fumigates*, *Mucor* and *Microsporum gypsium*.

Synthesis of ligand: The Schiff base, ambsalen [1-(2-aminobenzylideneiminato)-2-(salicylaldiminato)ethane] was prepared by first blocking one of the amine groups of 1,2-diaminoethane by converting it into an ammonium ion by treatment with an equimolar amount of hydrochloric acid. To this, equimolar amount of salicylaldehyde was added and refluxed for 1 h. The solution was allowed to cool and then neutralized with the requisite volume of standard NaOH solution to exactly neutralize the HCl present in the solution. To this, 2-aminobenzaldehyde was added and refluxed for 1 h. The solution was poured in ice and the Schiff base formed as yellow flakes was filtered and recrystallized from ethanol.

Preparation of metal complexes: Cu(II), Ni(II) and Mn(II) complexes of the Schiff base ambsalen were prepared by refluxing the ligand ambsalen with equimolar amounts of copper perchlorate hexahydrate, nickel perchlorate hexahydrate and manganese chloride tetrahydrate respectively in 30 mL of ethanol for 1.5 h. The solution was cooled, filtered and left in a petri dish to allow the solvent to evaporate slowly. The crystalline complexes formed were recrystallized from ethanol.

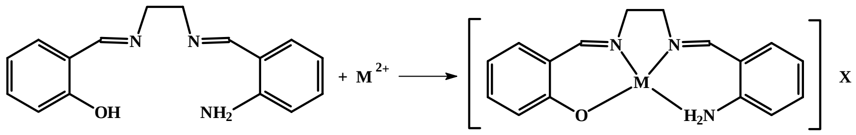
RESULTS AND DISCUSSION

The analytical data for the ligand ambsalen and all the metal complexes are given in Table-1.

TABLE-1
ANALYTICAL DATA OF AMBSALEN AND ITS METAL COMPLEXES

Compound	m.f.	Metal (%)		Nitrogen (%)	
		Found	Calculated	Found	Calculated
Ambsalen	$C_{16}H_{17}N_3O$	-	-	15.13	15.74
Cu-ambsalen	$[Cu(C_{16}H_{16}N_3O)]ClO_4$	14.13	14.81	9.35	9.79
Ni-ambsalen	$[Ni(C_{16}H_{16}N_3O)]ClO_4$	13.79	13.84	9.81	9.91
Mn-ambsalen	$[Mn(C_{16}H_{16}N_3O)]Cl$	14.87	15.42	10.80	11.79

The ligand has four ligating sites, one hydroxyl, one amine and two azomethine groups and hence binds to the metal ion through these four ligating atoms. The reactions in the synthetic route followed for the preparation of mononuclear transition metal complexes can be represented as follows.



where M = Ni^{2+} or Cu^{2+}, X = ClO_4; M = Mn^{2+}, X = Cl

In the metal complexes, only the -OH moiety group is deprotonated to form a covalent bond with metal and the amine group binds to the metal through its lone pair of electrons. The molar conductance of the metal complexes (10^{-3} M) in acetonitrile at room temperature are in the range 127-148 S cm^2 mol^{-1}, thereby showing the 1:1 electrolytic nature of these complexes according to the ranges suggested by Geary[5]. This is in agreement with the formula, $[M(C_{16}H_{16}N_3O)]X$ where M = Cu^{2+} or Ni^{2+}/Mn^{2+}; X = ClO_4^- or Cl^-, proposed for the metal complexes on the basis of the analytical data.

In the infrared spectra of the ligand, the ν(N-H) band[3] appears as a medium intensity band at 3456 cm^{-1}. The unsymmetrical nature of this broad band may be due to the overlapping of -OH band with the -NH_2 band. This

-NH_2 band is shifted to lower frequency in the spectra of the complexes (3440-3433 cm^{-1}) suggesting coordination through the NH_2 group to the metal atom[6]. The band at 1635 cm^{-1} in the free ligand is assigned to the ν(C=N) mode. This undergoes a shift towards lower frequency (1621-1605 cm^{-1}) in the complexes indicating that the nitrogen of azomethine group is involved in the coordination. The -NH_2 band expected in the 1600-1550 cm^{-1} region appears at 1596 cm^{-1} in the free ligand and it appears as a shoulder merging with the azomethine band for the complexes. The strong band appearing at 1282 cm^{-1} in the free ligand, assigned to valence vibration of the phenolic C-O group[7], is shifted in the complexes towards higher energies (1304, 1295 cm^{-1}) indicating that the oxygen atom is involved in bonding.

A broad intense band was observed for the Cu(II) and Ni(II) mononuclear complexes at 1084 and 1092 cm^{-1}, respectively and also a band of 622 and 626 cm^{-1} which is typical for a perchlorate ion. This is in agreement with the 1:1 electrolytic behaviour observed in the conductivity studies.

In the low frequency region, all the complexes exhibit two bands at 492-485 cm^{-1} and 417-404 cm^{-1} which are assigned to ν(M-N) and ν(M-O), respectively[8]. Lever and coworkers[9] have empirically observed that for octahedral complexes ν(M-N) occurs below 400 cm^{-1} and for square planar complexes it occurs in the range 500-400 cm^{-1}. Hence a square planar geometry is indicated for the complexes under study.

The UV-Vis spectra of the metal complexes showed characteristic bands suggesting square planar geometry for the complexes.

^{1}H NMR spectrum of the ligand ambsalen recorded in DMSO. The broad singlet appearing at downfield at δ 13.38 ppm is assigned to the -OH proton which is least shielded. The signal for the azomethine proton (-CH=N) appears as a sharp singlet at δ 8.59 ppm. The aromatic protons were observed as a multiplet in the region δ 6.52-7.43 ppm. The signal for the -CH_2 protons appear at δ 3.34 and 3.92 ppm and this may be due to the *cis* and *trans* form of the ligand by the free rotation around $-CH_2$-CH_2- bond. The broad signal at δ 2.50 ppm is assigned to the -NH_2 proton.

^{1}H NMR spectrum of the complex $[Ni(C_{16}H_{16}N_3O)]ClO_4$ is devoid of signal at δ 13.38 ppm suggesting deprotonation of $-$OH of the salicylidene moiety and subsequent involvement in coordination. This is in agreement with its 1:1 electrolytic nature shown by the conductivity study. The azomethine proton signal undergoes a slight upfield shift and appears at δ 7.93 ppm indicating that the azomethine nitrogen is involved in bonding[10]. The signal for the aromatic protons were seen in the region δ 6.51-7.29 ppm. The spectrum is devoid of signal at δ 3.92 ppm which indicates that the rotation around $-CH_2$-CH_2- bond is restrictred in the complex molecule. The other $=N{-}CH_2$ band for the complex is shifted downfield to δ 3.44 ppm which indicates that the azomethine nitrogen is the site of coordination.

The mass spectrum of Schiff base ambsalen shows a peak at (m/z) 268 which corresponds to the (M+1) isotopic peak of the molecular ion. The other prominent peaks are observed at (m/z) 175, 148, 134, 120 and 107. The peak at (m/z) 77 is the base peak. The most abundant ions arise from the C-C and C-N fission of the $N\text{-}CH_2\text{-}\ CH_2\text{-}N$ moiety.

The cyclic voltammogram of $[Cu(ambsalen)]ClO_4$ shows two quasi-reversible reduction peaks with the cathodic peak potentials, E_{pc} = -0.490 and -0.656 V and the anodic peak potentials, E_{pa} = -0.395 and - 0.580 V at the scan rate of 200 mV s^{-1} and the voltammogram changes in shape when the scan rate is changed. The cathodic reduction wave with E_{pc} = -0.490 V is assigned as due to the reduction of copper ion from Cu(II) → Cu(I) and the wave at E_{pc}= -0.656 V is assigned to the reduction of Cu(I) → Cu(0). In the anodic potential range, the wave observed at E_{pa} = -0.580 V is assigned to the redissolution of copper from Cu(0) → Cu(I). The quasi-reversibility of the two step reduction of the complex is evident from the following observations: ΔE_p values vary with the scan rate and these values were found to be more than 60 mV s^{-1} and the ratio of cathodic and anodic currents were not equal. The cyclic voltammograms of the complexes show no oxidation wave over the range of 50-250 mV s^{-1}.

The cyclic voltammogram of $[Ni(ambsalen)]ClO_4$ in acetonitrile shows a well defined reduction wave with E_{pc} = -1.618 V and E_{pa} = -1.528 V which corresponds to the one electron transfer redox reaction of nickel ion from Ni(II) → Ni(I). The reduction is quasi-reversible and the ΔE_p value vary with the scan rate and it changes its shape with increasing scan rates. The reduction potentials are more negative in the nickel complex than in the copper complex owing to the higher stability when in square planar geometry. The nickel(II) complex exhibits an oxidation wave with E_{pc} = 0.913 V is assigned to the quasi-reversible oxidation of nickel ion from Ni(II) → Ni(III).

The cyclic voltammogram of Mn(II) complex shows a quasi-reversible oxidation wave at E_{pc} = 1.351 V and E_{pa} = 1.484 V with a peak different (ΔE_p) of 0.133 V. This appears consistently in all the complexes and hence can be attributed to the oxidation of the Schiff bases[10]. On the reduction side, the Mn(II) complex shows a reduction peak at E_{pc} = -0.328 V owing to the reduction of manganese from Mn(II) → Mn(I).

At room temperature, the ESR spectrum of Mn(II) complex shows six hyperfine lines for the manganese nucleus with the g values of $g_{\parallel}$ = 2.0236 and $g_{\perp}$= 2.0041 and the hyperfine coupling constant value is $A_{\parallel}$ = 9.70 mT, confirming the presence of Mn(II) ion in the complex. Also, the ESR spectrum of the Cu(II) complex is consistent with a square planar geometry.

Results reveal that the ligand ambsalen and its metal complexes, exhibit antibacterial activity against the tested microorganisms. Compounds show higher activity against the Gram negative bacteria (*Pseudomonas aeruginosa*, *Escherichia coli* and *Klebsiella pneumoniae*) than the Gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*). On comparison, the metal complexes showed more inhibitory effects than the parent ligand against almost all bacteria. The enhanced activities of the metal complexes compared to free ligand can be ascribed to increased lipophilic nature of these complexes arising due to chelation[11]. Also, the results reveal that the ligand ambsalen does not exhibit antifungal property against the tested fungi, where as the metal complexes show antifungal activity to some extent.

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