Mixed Ligand Schiff Base Complexes: Synthesis, Spectral Characterization and Antimicrobial Activity

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ABSTRACT

The mixed ligand chelates of Cu(II), Co(II), Mn(II) and Ni(II) derived from L_1 (4- chloroaniline & salicylaldehyde), L_2(benzaldehyde & 2-aminophenol) and L_3(4-nitroaniline & 2-hydroxyacetopheone) have been synthesized and investigated by different Physicochemical techniques. The resulting complexes were characterized by elemental analysis, molar conductance, IR, Electronic spectra and cyclic voltammogram. The Schiff base acts as bidentate monobasic ligand, coordinated through deprotonated phenolic oxygen and azomethine nitrogen atom. Their low electrical conductance values indicate that all the complexes are non-electrolytes. The electrochemical behavior, the anodic, cathodic potential and the number of electron transfer have been calculated using cyclic voltammogram. The synthesized chelates were assayed for antibacterial activity against some pathogenic bacteria: Staphylococcus aureus, Escherichia coli, Klebsilla pneumonia and Bacillus subtilis using paper disc method and placing the chelates on surface at nutrient agar. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base because of chelation.

Keywords: 4-chloroaniline, 2-hydroxyacetophenone, benzaldehyde, 2-aminophenol, Salicylaldehyde & Antimicrobial activity.

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INTRODUCTION

The literature reveals that the Schiff base ligands are excellent coordinating ligands. It forms a stable complex with different transition metal ions. In particular, the transition metal complexes have been the subject for thorough investigation because of their extensive application in wide ranging areas from material science to biological sciences [1,2]. The study of mixed ligand complexes formation were relevant in the field of analytical chemistry, where the use of mixed ligand complexes allows the development of methods with increased selectivity, sensitivity and has also great important in the field of biological and environment chemistry [3]. The pharmacological activity have been found to be highly dependent on the nature of the metal ion and the donor sequence of the ligands, different ligand shows different biological properties, though they may vary only slightly in their molecular structure [4].

The present investigation is to prepare some Schiff base mixed ligand complexes derived from L_1 (4- chloroaniline & salicylaldehyde), L_2 (benzaldehyde & 2-aminophenol) and L_3 (4-nitroaniline & 2-hydroxyacetopheone), to elucidate their geometrical structures and to show their biological activity on some pathogenic bacteria.

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EXPERIMENTAL SECTION

All chemicals used in this work were reagent grade (Aldrich) including 4-chloroaniline, 4-nitroaniline, benzaldehyde, 2-aminophenol and 2-hydroxyacetophenone and metal salts.

The Schiff base ligands were prepared by the condensation of the aldehyde and amine in the 1:1 molar ratio by refluxing in ethanol [5].The mixture of ethanolic solution of 4-chloroaniline and ethanolic solution of salicylaldehyde was stirred for 1hr. The resulting solution was then cooled below room temperature. The product (L_1) obtained was filtered and dried. L_2 ligand was obtained from benzaldehyde and 2-aminophenol by refluxing for 3 hrs in ethanolic medium and similarly L_3 ligand was obtained from 4-nitroaniline and 2-hydroxyacetophenone.The Schiff base mixed ligand complexes were prepared by mixing the appropriate molar quantities of the Schiff base ligand and the metal salts using the following procedure. The hot ethanolic solution of the metal salt was added slowly with constant stirring to the ethanolic solution of Schiff base ligand (L_1), it was then followed by the addition of L_2 ligand [6].The mixture was then refluxed for 3hrs on a water bath and the solution was cooled to room temperature. The solid obtained was filtered and dried. Similarly all the complexes of [ML_1L_3] were prepared.

Metals like Cu(II), Co(II), Ni(II) and Mn(II) complex were determined by Spectrophotometer method and Nitrogen was estimated by Kjeldhal's method. UV-Visible absorption spectra were recorded in the range of 200-800 nm using shimadzu instrument. IR spectra were recorded in 400-4000 cm^{-1} using shimadzu spectrometer. Conductivity of the complexes in DMF was measured using simple conductivity bridge and Redox nature of the complex in DMF was measured using CHI -760 Electrochemical Analyser.

RESULTS AND DISCUSSION

The elemental analysis indicates that all the metal complexes have 1:1:1 stoichiometry with respect to L_1:L_2:M similarly L_1:L_3:M [where M= Co(II), Cu(II), Mn(II) and Ni(II)].

Molar Conductance
The molar Conductance of the synthesized mixed ligand complexes were measured using 10^{-3} M DMF solvent at room temperature. The Conductivity values are in the range of 10-30 ohm^{-1}mol^{-1} cm^2.These values are too low to account for any dissociation of the complexes in DMF and the obtained values were taken as a good evidence for the existence of a non-electrolytic in nature of the complexes [7].

Infrared Spectra
The IR spectra provides a valuable information regarding the nature of functional group attached to the metal atom [8].The important IR frequencies exhibited by the Schiff base ligands L_1,L_2,L_3 and their corresponding mixed ligand complexes are tabulated in table 1.2. The ligands shows broad band at around 3410-3440 cm^{-1} due to the phenolic hydroxyl group in free ligands, which shows shift in frequency in complexes, indicating the coordination through metal atom [9, 10]. The band in the range 1610-1620 cm^{-1} are observed due to ν(C=N) which has been shifted towards lower region at around 1580-1610 cm^{-1} in the complexes indicating the participation of the azomethine group in the complexes formation [11,12], this shift is also due to the reduction of double bond character of carbon-nitrogen bond of azomethine group [13] .The Schiff base ligand shows a medium intensity band at around 1271 cm^{-1}& 1327 cm^{-1} due to phenolic ν(C-O) is shifted to higher region indicating the coordination through the phenolic oxygen atom [11,12,14] and also due to the conversion of hydrogen bonded structure into a covalent metal bonded structure. The coordination through nitrogen of azomethine and oxygen of ν(C-O) of ligand are further evidenced by the appearance in the complexes of non-ligand bands around 417-465 cm^{-1}and 497-545 cm^{-1} are due to M-N and M-O bonds respectively [14,15].

Electronic Spectra
The electronic spectra of the Schiff base ligand and their complexes have been measured in DMF solution between 200-800 nm at room temperature. The spectral data of the ligands and its complexes are tabulated in table 1.3. In the spectra of the Schiff base ligands, the absorption band observed at 280 nm were assigned to a benzene $\pi\rightarrow\pi$*transition and the band at 380 nm were assigned due to n$\rightarrow\pi$* transition associated with the azomethine chromophore (-C=N) [16]. The new bands observed near 390-450 nm can be assigned to L$\rightarrow$M Charge transfer band. The newly synthesized Schiff base ligands gives colored complexes with metal ions that have a series of overlapping absorption bands in the UV part of the spectrum as well as in the visible part. In such cases the d-d transition may be

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completely overwhelmed and essentially impossible to observe [17] because of limited solubility of the complexes. Mostly d-d transition occurs in the region of 450-550 nm. Based on these data, a distorted square planar geometry has been proposed for all the complexes.

Cyclic Voltammogram

The redox behavior of these complexes has been investigated by cyclic voltammogram in DMF using 0.1 M Tetrabutylammoniumperchlorate (TBAP) as supporting electrolyte. The electrochemical data obtained at a glassy carbon electrode in DMF solution are recorded. The copper complexes are redox active and show a cyclic voltammogram response in the potential range 0.7-1.7V [18-20] assigned to the Cu(II)/Cu(I) couple. The non-equivalent current intensity of cathodic and anodic peaks (i_c/i_a=0.6 V) indicates a quasi reversible behavior [21]. It has been shown that the formal redox potential of Cu(II)/Cu(I) couple is dependent on factors such as coordination number, hard/soft nature of the ligands and bulkiness of the ligands [22]. The cobalt complexes exhibit one electron quasi reversible transfer process with a peaks at Epa= 0.6 V, Epc=1.5 V and ΔEp= 0. 9 V. This gives evidence for quasi reversible Co(II)/Co(I) couple .The cyclic voltammogram of Nickel complexes shows well defined redox process corresponding to the formation of the quasi-reversible Ni(II)/Ni(I) couple. The anodic peak at Epa= 0.5 V and the associated cathodic peak at Epc=1.6 V corresponds to Ni(II)/Ni(I) couple [23]. The one electron cyclic response for Manganese complexes were observed at Epc=1.6 V and Epa=0.5 V. This corresponds to Mn(II)/Mn(I). The table1.3 also shows the redox nature of the other Schiff base mixed ligand complexes.

Antibacterial Activity

The Paper disc technique was used to evaluate the antibacterial activity of the synthesized complexes**.** The results of the bactericidal screening of the synthesized complex are recorded. The Schiff base ligand has less activity in comparison with their complex against staphylococcus aureus, klebshellia, E-coli, bacillus substilis. This is due to the fact that the metal chelates have more antibacterial activity than uncomplexed ligand because of ChelationTheory [24], the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups further it increases the delocalization of π- electrons over the whole chelate ring and enhances the lipophilicity of the complexes. Thus inhibiting the growth of bacteria more potent than the parent Schiff base [25-29]. The Co(II) Schiff base mixed complexes have higher Antimicrobial activity than the other because of electron releasing group present in the complexes.% of inhibition was shown in table 1.4 and also calculated by using the formula

$$\% \text{ Inhibition} = \frac{(C-T)\,X100}{C}$$

Where C = Colony Diameter (mm) of the control plate;
T = Colony Diameter (mm) of the test plate.

Table 1.1: Analytical data of the Schiff base ligands and its complexes

Compound	Molecular formula	Molecular weight	colour	Yield %	Melting Point (º)	% of Nitrogen		% of Metal	
						Cal	Exp	Cal	Exp
SALCA(L₁)	C₁₃H₁₀NOCl	232	Yellow	80	116	6.04	6.02	-	-
SALAP(L₂)	C₁₃H₁₁NO	197	Brown	70	88	7.10	7.12	-	-
NAHAP(L₃)	C₁₄H₁₂N₂O₃	256	Brown	75	140	10.9	10.8	-	-
[CuL₁L₂]	Cu[C₂₆H₁₉ N₂O₂Cl]	490	Dark green	70	148	5.71	5.73	12.9	12.7
[CoL₁L₂]	Co[C₂₆H₁₉ N₂O₂Cl]	486	Black	75	154	5.77	5.76	12.1	12.0
[NiL₁L₂]	Ni[C₂₆H₁₉ N₂O₂Cl]	486	Green	75	110	5.76	5.77	12.0	12.1
[MnL₁L₂]	Mn[C₂₆H₁₉ N₂O₂Cl]	481	Black	65	90	5.81	5.82	11.4	11.3
[CuL₁L₃]	Cu[C₂₇H₂₀ O₄N₃Cl]	549	Blackish Green	70	138	7.64	7.63	11.5	11.5
[CoL₁L₃]	Co[C₂₇H₂₀ O₄N₃Cl]	545	Brown	70	104	7.71	7.73	10.8	10.7
[NiL₁L₃]	Ni[C₂₇H₂₀ O₄N₃Cl]	545	Green	65	140	7.72	7.70	10.8	10.7
[MnL₁L₃]	Mn[C₂₇H₂₀ O₄N₃Cl]	541	Light green	65	94	7.76	7.74	10.1	10.3

Table 1.2: Infrared spectral data of the Schiff base ligand and its complexes

| Compound	Free-OH (cm^{-1})	-CH=N (cm^{-1})	C-O (cm^{-1})	M-O (cm^{-1})	M-N (cm^{-1})
L$_1$	3420	1610	1271	-	-
L$_2$	3480	1626	1287	-	-
L$_3$	3481	1631	1327	-	-
[CuL$_1$L$_2$]	-	1583 1606	1296 1323	528 586	424 490
[CoL$_1$L$_2$]	-	1583 1604	1301 1350	516 538	459 495
[NiL$_1$L$_2$]	-	1600 1614	1296 1334	520 549	455 501
[MnL$_1$L$_2$]	-	1570 1614	1280 1346	516 532	462 497
[CuL$_1$L$_3$]	-	1604 1629	1298 1381	534 590	414 489
[CoL$_1$L$_3$]	-	1600 1629	1300 1392	534 590	430 489
[NiL$_1$L$_3$]	-	1598 1630	1298 1390	534 632	424 489
[MnL$_1$L$_3$]	-	1600 1630	1300 1394	516 534	372 489

Table 1.3: Electronic Spectral data, Molar conductance and Cyclic Voltammetric data of Schiff base mixed ligand metal complexes.

Compound	Electronic spectra (nm)			CV Data (V)		Molar Conductance Scm^{2}mol^{-1}
	$\pi\rightarrow\pi*$	$n\rightarrow\pi*$	L$\rightarrow$M	Epc	Epa	
L$_1$	274	346	-	1.6	0.5	-
L$_2$	265	360	-	0.2	0.4	-
L$_3$	271	371	-	1.5	1.2	-
[CuL$_1$L$_2$]	261	372	400	1.5	0.6	5.3
[CoL$_1$L$_2$]	263	356	450	0.8	0.4	7.3
[NiL$_1$L$_2$]	271	353	468	1.6	0.5	12.7
[MnL$_1$L$_2$]	271	338	424	0.7	0.5	22.8
[CuL$_1$L$_3$]	259	359	430	1.6	0.6	9.9
[CoL$_1$L$_3$]	260	355	400	1.5	0.6	6.5
[NiL$_1$L$_3$]	261	346	390	1.3	0.6	4.8
[MnL$_1$L$_3$]	269	360	400	1.6	0.5	12.6

Table 1.4: Antimicrobial activity of Schiff base ligands and its complexes

Samples	Diameter of inhibition zone (mm)			
	Bacillus subtilis	*Staphylococcus aureus*	*E-Coli*	*Klebsilla pneumonia*
L$_1$	10	8	10	7
L$_2$	8	10	9	10
L$_3$	10	8	9	8
[CuL$_1$L$_2$]	15	12	17	14
[CoL$_1$L$_2$]	23	19	21	19
[NiL$_1$L$_2$]	19	17	13	18
[MnL$_1$L$_2$]	16	15	17	19
[CuL$_1$L$_3$]	19	20	17	16
[CoL$_1$L$_3$]	22	18	21	19
[NiL$_1$L$_3$]	14	13	16	16
[MnL$_1$L$_3$]	18	16	19	17

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Proposed Structure of the Schiff Base Mixed Ligand Complexes:
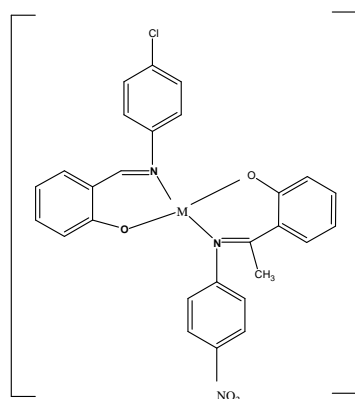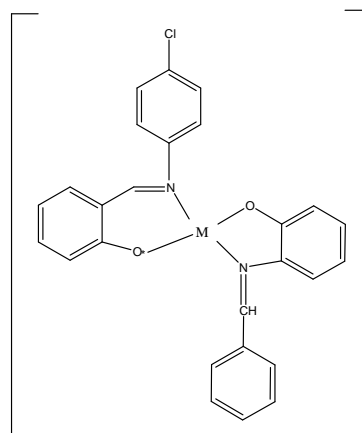
[ML₁L₃]   [ML₁L₂]

M=Cu(II), Co(II), Ni(II) & Mn(II)

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