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Synthesis, Characterization and Antimicrobial Activity of Some Transition Metal Complexes with Schiff Base Ligand

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ABSTRACT

Transition metal complexes of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Fe(III) have been synthesized with the Schiff base ligand prepared by the condensation reaction between 5-methyl isooxazol-3-yl amine and salicylaldehyde. Elemental analysis of these complexes suggests that these metal ions forms complexes of type $ML_2(H_2O)_2$ *stoichiometry for Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Fe(III). The ligand behaves as bidentate and forms coordinate bonds through O and N atoms. Magnetic susceptibility, IR, mass and ESR spectral studies suggest that Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Fe(III) complexes posses octahedral geometry. The complexes were tested for their antimicrobial activity against the bacterial strains Staphylococcus aureus, Bacillus subtilis, and Klebsiella pneumoniae.*

Keywords: Schiff base, transition metal complexes, antimicrobial activity, ESR.

INTRODUCTION

Schiff bases have played a vital role as chelating ligands in transition metal coordination chemistry [1-2], especially when a functional group like OH is present close to the azomethine group so as to form five or six membered ring with the metal ion. Schiff bases can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming an imine. Schiff bases of the general formula RR′C=NR{Prime} that are obtained typically by condensation of an aldehyde or ketone with a primary amine(as aniline) with elimination of water[3], that usually polymerize readily if made from aliphatic aldehydes, and that are used chiefly as intermediates in organic synthesis and in some cases as dyes[4].
The metal complexes of Schiff base have been studied extensively due to synthetic flexibility and their selectivity as well as sensitivity towards the central metal atom [5-6]. A large number of Schiff bases and their complexes have been studied because of their interesting and important properties like catalytic property and transfer of amino group [7] and complexing ability towards toxic metals [8]. Metal complexes of Schiff bases containing nitrogen donor ligands are of interest in different field like industry, pharmacy and biology [9-11]. Heterocyclic compounds are very widely distributed in nature and are essential to many fields of material science and biological systems.
In view of the above facts we prepared the ligand by using 5-methyl isoxazol – 3 – yl amine with salicylaldehyde and its Cu(II), Ni(II), Zn(II), Cd(II), Co(II) and Fe(III) metal complexes were synthesised.

These metal complexes were characterized by the spectroscopic and analytical methods and the antimicrobial activities of complexes are evaluated.

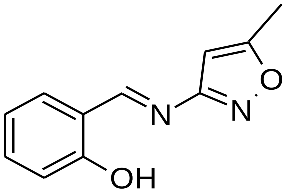


Figure 1: Structure of Ligand

MATERIALS AND METHODS

Analytical grade metal chloride salts, viz. $NiCl_2$. $CoCl_2$, $CuCl_2$, $FeCl_3$, $ZnCl_2$, $CdCl_2$ are used. The chemicals used are of analytical grade and solvents are used after distillation. Molar conductivities of 10^{-3}M solutions were carried out using EM 183 EC conductivity meter. ESR spectra were recorded on a Varian USA E112 spectrophotometer. Elemental analysis results for the prepared complexes are obtained from microanalysis of Carbon, Hydrogen, Nitrogen and Oxygen using Thermo Finnigan FLASH EA 1112 CHNS analyzer. Melting points for the prepared complexes are obtained from Electric melting point apparatus Tempo make. FT - IR spectra were recorded on a Thermo Nicolet Avatar FTIR-ATR spectrometer with 4 cm^{-1} resolution in the frequency range 400 – 4000 cm^{-1} and ^1H NMR spectra of the was recorded in DMSO-d6 solvent and the spectrum were recorded on a DSX- 300/AV-III 400/DRX-500/AV-III500/AV-700 NMR spectrometer at IISc, Bangalore. The magnetic susceptibility was measured at room temperature using Gouy balance. Mass spectra were recorded on a JEOL SX 102/DA 6000 Mass spectrophotometer using argon/xenon(6 kV, 10 mA) as the FAB gas. Antimicrobial activity studied against the bacterial strains viz. *Staphylococcus aureus Bacillus subtilis, Klebsiella pneumoniae* obtained from Institute of Microbial Technology, Chandigarh and maintained on Potato Dextrose Agar [12-13].

Synthesis of Schiff base ligand: 10 mL of isoxazol – 3 – yl amine is mixed with 10 ml of salicylaldehyde in a round bottom three necked flask and then ethanol is added as solvent and about two drops of conc. HCl is added. This mixture is refluxed on a water bath maintained at about 60^0C for about two hours. Then the contents of the flask are added to ice water. Then the obtained yellow solid is separated by filtration and dried in electric oven. Yield: 80%

Synthesis of metal complexes: The metal complexes were prepared by mixing of 50 mL of 2.5 mmol ethanolic solution of $CoCl_2.6H_2O$ / $NiCl_2.6H_2O$ / $CuCl_2.6H_2O$ / $ZnSO_4.7H_2O$ / $CdCl_2$. $6H_2O$ / $FeCl_3$ with 50 mL of 5 mmol ethanolic solution of the Schiff base ligands in 1:2 (metal: ligand) ratio. The resulting mixture was refluxed on water bath for about 4-5 h. A colored product appeared on standing and cooling the above solution. The precipitated complex was filtered and recrystallized with ethanol and then dried in an electric oven at $50^0 – 70^0$ C. Yield: 60-70% [14-15] .

RESULTS AND DISCUSSION

The analytical data of complexes and their molar conductance values are given in table 1 [16-17]. All these complexes are analysed. The stoichiometry of the ratio 1:2 of the type $ML_2(H_2O)_2$. Molar conductance and values of these metal complexes are too low and this reveals that complexes are non – electrolytic in nature.

Table 1. Elemental analysis, colour, melting point and conductance data of ligand and metal complexes

Sl. No.	Compound	Elemental analysis, found(calculated)					Colour	Melting Point (^{O}C)	Molar conductivity (Scm^2mol^{-1})
		C	H	O	N	M			
1	L	65.00 (65.02)	5.45 (5.42)	15.71 (15.76)	13.82 (13.79)	----	Yellow	143	-----
2	$CoL_2(H_2O)_2$	52.66 (52.70)	5.13 (5.19)	19.11 (19.16)	11.15 (11.18)	11.73 (11.76)	Brown	220	10.23
3	$NiL_2(H_2O)_2$	52.66 (52.72)	5.11 (5.19)	19.10 (19.17)	11.12 (11.18)	11.60 (11.72)	Yellow Green	> 300	18.98
4	$CuL_2(H_2O)_2$	52.18 (52.22)	5.16 (5.14)	18.95 (18.98)	11.03 (11.07)	12.50 (12.56)	Dark	> 300	9.23
5	$ZnL_2(H_2O)_2$	52.00 (52.03)	5.08 (5.12)	18.88 (18.92)	11.00 (11.03)	12.80 (12.88)	Yellow	> 300	8.98
6	$CdL_2(H_2O)_2$	47.54 (47.61)	4.58 (4.68)	17.26 (17.31)	10.03 (10.10)	20.50 (20.57)	Yellow	>300	8.40
7	$FeL_2(H_2O)_2$	53.00 (53.02)	5.16 (5.22)	19.19 (19.28)	11.20 (11.24)	11.19 (11.21)	Red	300	15.98

^{1}H NMR spectral data of ligand: In order to identify structure of the ligand, the ^{1}HNMR spectra were recorded and the chemical shifts observed at 9.2 is assigned to the proton of the imine group (CH=N) as a singlet. The OH resonance in the ^{1}H-NMR spectra appears as a singlet at 12.00 ppm. The observation of the absorption phenolic OH proton at lower frequency can be explained by strong intermolecular hydrogen bonding. The aromatic protons of salicylaldehyde side of the ligand, appear as multiple peaks at 6.98-7.38 ppm [18-19].

IR spectral data: IR spectral studies of the ligand shows the hydrogen bonded phenolic OH stretching frequency of the ligand at 3125.7 cm^{-1}. The C – H streching frequency was observed at 3008.3 cm^{-1} and the charecteistic steching frequency of C=N is at 1604.5 cm^{-1}. The IR spectral data and assignments of metal complexes are listed in table 2. The IR spectra of complexes indicates that the ligand behaves as bidentate and the metal coordinates via C = N and C – O groups(Figure 3). The imine group of C=N stretching frequency observed at 1604 cm^{-1} in the free ligand. So upon complexation C=N stretching frequency is shifted to lower frequency side by 10 – 30 cm^{-1}. This shift in stretching frequency shows that the in the complex the N of imine group acts as donor atom. The C – O stretching frequency is observed at 1370 cm^{-1} in the ligand, during the formation of metal complexes O atom coordinates through metal ion due to deprotonation of phenolic group. In the complexes ν_{M-O} and ν_{M-N} vibrations occur in the region 446 – 485 cm^{-1} and 498 to 523 cm^{-1} respectively [20-23].

Table 2. IR spectral data(cm^{-1}) of ligand and its complexes

Sl. No.	Ligand / Complexes	ν_{N-H}	$\nu_{C=N}$	ν_{C-O}	ν_{M-O}	ν_{M-N}
1	$C_{11}H_{11}O_2N_2$	3390	1604.5	1370.4	--	--
2	$Co(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	3420	1588	1340.4	460	510
3	$Ni(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	3422	1576	1365.0	472	500
4	$Cu(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	3410	1586.2	1330.6	450	520

5	$Zn(C_{11}H_{11}O_2N_2)_2 (H_2O)_2$	3367	1591.9	1392.4	468.6	498
6	$Cd(C_{11}H_{11}O_2N_2)_2 (H_2O)_2$	3358	1574.6	1433.6	485	515
7	$Fe(C_{11}H_{11}O_2N_2)_2 (H_2O)_2$	3424.2	1574	1324.6	446	523

Magnetic Susceptibility data: Cobalt (II) complex shows magnetic moment of 4.85 BM. The spin free octahedral complex of cobalt(II) is reported to exhibit magnetic moment in the range 4.46 to 5.53 B.M. Hence the observed moment for the cobalt(II) complex indicates that it has an octahedral geometry. Nickel (II) complex shows magnetic moment of 2.98 BM. The spin free octahedral complex of nickel (II) is reported to exhibit magnetic moment in the range 2.82 to 3.4 B.M. Hence the observed moment for the nickel (II) complex indicates that it has an octahedral geometry. Copper (II) complex shows magnetic moment of 1.88 BM. The spin free octahedral complex of copper (II) is reported to exhibit magnetic moment in the range 1.82 to 2.32 B.M. Hence the observed moment for the copper (II) complex indicates that it has an octahedral geometry [24-25].

ESR spectra: The 'g' values obtained from the ESR spectra are represented in table 3. When the monomeric species changes into dimeric species having axial symmetry and identical sites, the 'g' values also changed due to the change in symmetry[16]. From the observed 'g' values $g_{\parallel} > g_{\perp} > g_e$ it is evident that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital of copper(II) ion. The $g_{\parallel} > g_{\perp} > g_e$ (2.004) observed in the 'g' values suggest that the unpaired electron present in the $d_{x^2-y^2}$ orbital. The values of the σ – bonding parameter, α^2 shows appreciable covalent character of the metal – ligand bond. Based on these observations copper(II) complex may have octahedral geometry [26-28].

Table 3: ESR spectral data of copper(II) complex

Sl. No.	Complex	$g_{\parallel}$	g_e	$g_{\perp}$	g_{av}	G	α^2
1	$CuL_2 (H_2O)_2$	2.10	2.004	2.04	2.072	1.80	0.38

Mass spectra:

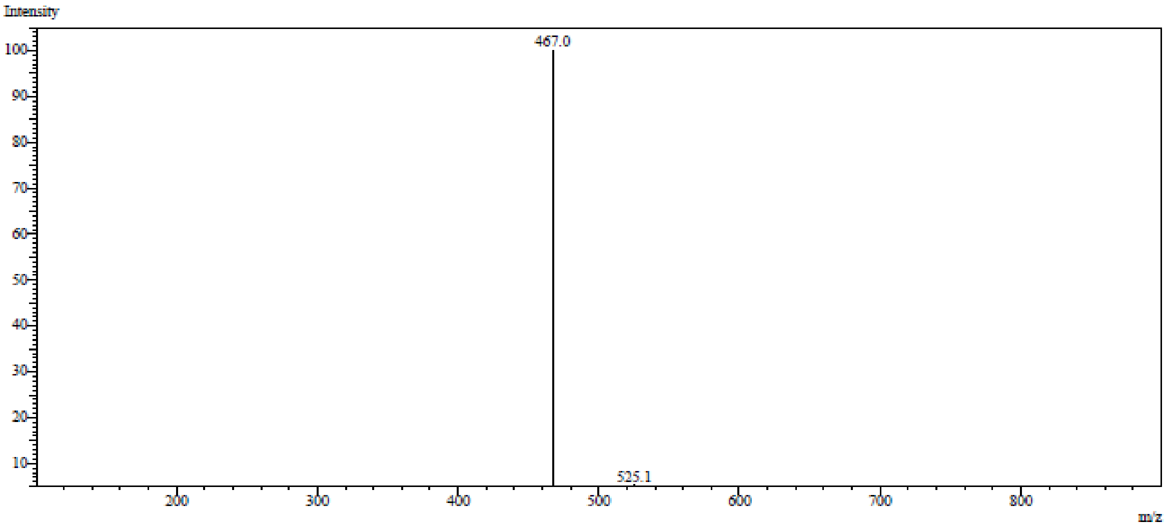


Figure 2: Mass spectra of $[CoL_2(H_2O)_2]$ complex

The mass spectra of metal complexes show that all the complexes have a monomeric nature. These complexes show molecular ion peaks in good agreement with empirical formula suggested by elemental analysis. The mass spectra of $[CoL_2(H_2O)_2]$ complex(Figure 2) shows a characteristic molecular ion peak at m/z = 467.0, which corresponds to molecular weight of complex for a monomeric structure. The mass spectrum shows multiple peaks representing successive degradation of complex molecule by the formation of different fragments. The peaks of appreciable intensity have been observed at m/z values observed(calculated) – 525.1(528), 467(468) suggesting the fragmentation pattern. The m/z value 467.0 corresponds to the nearest composition of $[CoL_2(H_2O)_2]$ [29-30].

APPLICATIONS

Antimicrobial activity: Antimicrobial activity of Schiff base and complexes were investigated against bacterial strains *Staphylococcus aureus(NCIM 2492), Bacillus subtilis(NCIM 2439),* and *Klebsiella pneumoniae (NCIM 2719)* were inoculated using a loop onto plates containing Nutrient Agar (NA) media and incubated at 32^{o}C for 24 hours. To carry out agar diffusion assay the bacterial suspensions were prepared in sterile distilled water. The modified agar well diffusion method was employed. The bacterial suspensions were inoculated on to nutrient agar media by spread plate technique. Once it is dried, 4 mm diameter wells were punched onto the media into which 25, 50 and 75 microlitres of each compound were added. The plates were sealed and incubated at 32^{0}C for 24 hours. Tetracycline was used as a standard antibiotic (0.5 mg ml^{-1}). 0.5g ml^{-1} of different synthesized compounds were dissolved in DMSO (Dimethyl Sulphoxide), which did not affect microorganisms growth, according to our control experiment. Antimicrobial activities were evaluated by measuring inhibition zone diameter in mm. All the experiments were conducted in quadruplicates. The antimicrobial activities of metal complexes against *Staphylococcus aureus*, *Bacillus subtilis* and *Klebsiella pneumoniae* are shown in table 4. It has shown that concentration dependent antimicrobial activity in all the assays.

Table 4: Antimicrobial activity of compounds

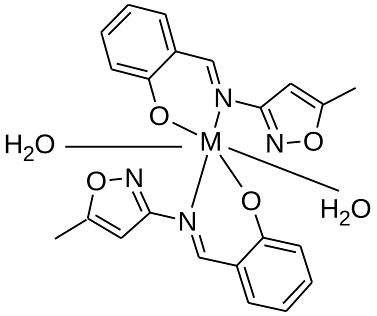
Sl. No.	**Compound**	**Inhibition zone diameter in mm****								
		Staphylococcus aureus			***Bacillus subtilis***			***Klebsiella pneumoniae***		
		25 µl	50 µl	75 µl	25 µl	50 µl	75 µl	25 µl	50 µl	75 µl
1	$C_{11}H_{11}O_2N_2$ (Ligand)	4	6	8	3	5	6	4	5	6
2	$Co(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	8	10	15	5	7	11	6	10	11
3	$Ni(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	10	12	14	6	9	10	9	12	13
4	$Cu(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	5	6	12	4	5	6	4	5	6
5	$Zn(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	10	12	14	5	6	9	7	9	10
6	$Cd(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	8	12	13	7	9	10	9	11	12
7	$Fe(C_{11}H_{11}O_2N_2)_2\ (H_2O)_2$	14	15	16	10	12	13	14	15	16
8	Tetracycline 0.5 mg/ml	18			20			20		

*Tetracycline was used as a standard antibiotic (0.5 mg/ml), *Concentration of Complexes**:** 25 µl, 50 µl, 75 µl. ****** Each value in the table was the average of quadruplicates.

It has shown that concentration dependent antimicrobial activity in all the assays showed good inhibition zone for *Staphylococcus aureus Bacillus subtilis and Klebsiella pneumoniae*. All the compounds exhibited good antimicrobial activity when compared to ligand against *Staphylococcus aureus Bacillus subtilis, Klebsiella pneumoniae.*

CONCLUSIONS

The Schiff base and their metal complexes have been synthesized using 5-methyl isooxazol-3-yl amine and salicylaldehyde and characterized by elemental analysis, conductance, magnetic susceptibility measurements, mass, IR, ^{1}H NMR and ESR data. From these results We tentatively propose the octahedral structure for Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Fe(III) complexes (Figure 3). The DC electrical conductivity data reveals that these complexes act as insulators at room temperature, however as the temperature increases the conductivity increases indicating a semiconducting behavior.



Where M – Co (II), Ni (II), Cu (II), Zn(II), Cd(II), Fe(III).

Figure 3: structures of complex

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