Synthesis and Characterization of Antimicrobial Activities of some Transition Metal Complexes of Asymmetrical Tetradentate Ligands

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Abstract

The Schiff bases have been prepared by reacting dehydroacetic acid with 6-methyl 1,3,5-triazine 2,4- diamine and 2'-hydroxy acetophenone. The Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been prepared by reacting metal nitrate with those Schiff bases in alcoholic medium. The Complexes are electrolytes in DMSO. All the complexes were characterized by elemental analysis, ^1H -NMR, FT-IR, UV-VIS, magnetic susceptibility, conductance measurements studies. The IR spectral data suggest that the ligand behaves as a tetradentate ligand with NNNO donor atoms sequence towards central metal ion. From the microanalytical data, the stoichiometry of the complexes was found to be 1:1 (metal : ligand). X-ray diffraction and screened for their antibacterial activity against bacterium Staphylococcus aurious, B.subtilis (Gram positive) and Escherichia coli, K. pneumonae (Gram negative). The result indicated that the complexes exhibited good antibacterial activities.

Keywords: Unsymmetrical schiff bases, transition metal complexes, powder X-ray diffraction, biological activity.

Introduction

Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspecta[1]. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in analytical, industrial, biological, clinical, biochemical, antimicrobial, anticancer, antibacterial, antifungal and antitumor activity[2-5] in addition with important roles in ranging from anticorrosion, soil treatment agents and medicinal agents[3,5-10]. Metal complexes make the compounds effective as a stereo specific catalyst towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry. Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carries. [4,11-13] However a brief survey of literature reveal that not much work has been carried out on the chelating tendency of Schiff bases derived from dehydroacetic acid, heterocyclic diamine and 2'-hydroxy acetophenone with transition metal ions. In view of the above observations it appeared worthwhile to study the synthesis, characterization and antimicrobial activity of unsymmetrical metal complexes.

Material and Methods

Experimental: All chemicals used were of the analytical grade (AR) Dehydroacetic acid, 6-methyl 1,3,5-triazine 2,4- diamine and 2'-hydroxy acetophenone were used for the complex preparation. IR spectra were recorded on FTIR(ATR)-BRUKER -TENSOR37 spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. ^1H- NMR varian mercury 300MHZ spectra of ligand were measured in CDCl$_3$ using TMS as internal standard. XRD were recorded on BRUKER D8 Advance. The carbon, hydrogen and nitrogen contents were determined on Elementar model vario EL-III. The UV-visible spectra of the complexes were recorded on UV-1800, SHIMADZU spectrometer. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-4} M solution in DMSO. Magnetic susceptibility measurements of the metal complex were done on Gouy balance at room temperature using Hg[Co(SCN)$_4$] as a calibrant.

Synthesis of ligand: 6-methyl 1,3,5-triazine 2,4- diamine (0.05M) was dissolved in ethanol to which Dehydroacetic acid (0.05M) was added and mixture was refluxed for 4 hours. The yellow mono- Schiff base product formed was filtered and washed with ethanol. Mono-Schiff base thus formed was then refluxed with 2'-hydroxy acetophenone (0.05M) to prepare asymmetric ligand. Asymmetric Schiff base thus formed was cooled to room temperature and recrystalized in ethanol. Purity of the compound was checked by TLC. (Yield: 69-71%).

Synthesis of metal complexes: Equimolar amount of metal and the ligands were mixed in 1:1 molar ratio using required quantities of ethanol were mixed together under constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for 3 hours at room temperature on water bath. On cooling, colored solid metal complexes were precipitated out. The products were filtered, washed with warm methanol, warm ethanol, petroleum ether and Chloroform and dry at room temperature.
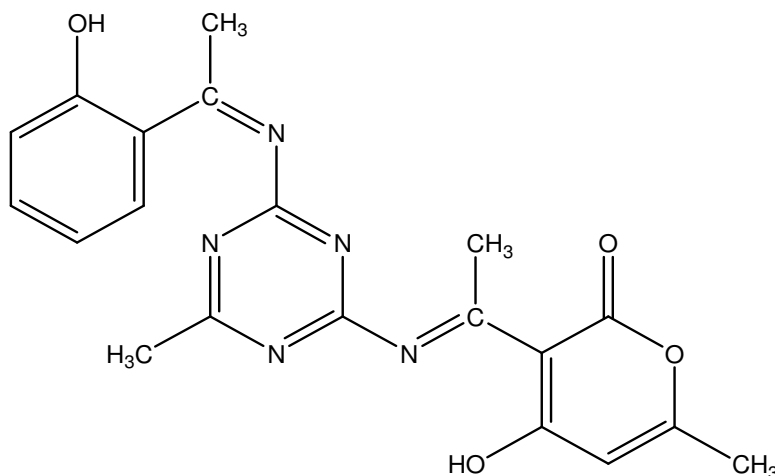
Figure-1
Structure of ligand

Results and Discussion

All the metal complexes are colored solids, stable to air and soluble in polar solvents like DMF and DMSO. The physical Characteristics, analytical and molar conductance data of the ligands and metal complexes are given in tables-1 and 2. The molar conductance values of all the metal complexes in DMSO at the concentration of 10^{-4} M are very low indicating their non electrolytic nature. The analytical data indicate 1:1 metal: ligand stoichiometry for the Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

1H-NMR spectra of ligand: The ^{1}H-NMR. spectra of ligand was recorded in CDCl$_3$. It shows following signals at 2.18 δ (s, 3H, C$_6$-CH3), 2.49 δ(s, 3H, C$_6$ methyl H 6-methyl-1,3,5-triazine-2,4-diamine), 2.50 δ (s, 3H, N=C-CH3), 6.28 δ (s, 1H, phenolic OH), 6.95 to 7.67 δ (m,4H, Aromatic H$_a$, H$_b$, H$_c$, H$_d$ protons of phenyl ring).

IR Spectra: The IR spectral frequencies (cm^{-1}) of ligands and their complexes are shown in table-3. The IR spectrum of the free ligands show a broad weak band 3279 cm^{-1} attributed to intramolecular bonding ν(OH). The bands 1662-1232 cm^{-1} are assigned to ν (C=N) (azomethine), ν (C=C) (Aromatic double bond), ν (C-N) (aryl azomethine) and ν (C-O) (enolic) stretching modes, respectively. The disappearance of IR band at 3100-3300 cm^{-1} (intramolecular hydrogen bonding) in the spectra of all the complexes indicates deprotonation of enolic oxygen and azomethine nitrogen in coordination to the metal ion. It is further supported by a downward shift in ν (C-O) in all complexes[14]. A downward shift in ν (C=N) indicates participation of azomethine nitrogen in complex formation[15]. The IR spectra of the metal complexes showed new bands in the 510-612 cm^{-1} and 469-541 cm^{-1} region, which can be assigned to ν (M-O) and ν (M-N) vibrations respectively[16-18].

Table-1
Physical characterization, analytical and molar conductance data of compounds

Compound Molecular formula	Mol. Wt.	M.P. Decomp temp. ^{0}C	Colour	Molar Conduc. Mho Cm^{2}mol^{-1}
L	393.40	>300	White	----
L Cr	445.39	>300	Gray	14.02
L Fe	449.24	>300	Brown	31.26
L Co	452.33	>300	Pink	21.04
L Ni	452.09	>300	Green	26.55
L Cu	456.94	>300	Blue	14.22
L Zn	458.79	>300	White	38.07

Table-2
Elemental Analysis of Zn(II) Complex

Compound	Found (Calculated)			
	C	H	N	M
L	60.90 (61.06)	4.39 (4.86)	17.67(17.80)	0
L-Zn	52.29 (52.35)	4.19 (4.17)	15.30 (15.26)	14.29 (14.25)

Magnetic measurements and electronic absorption spectra: The electronic spectral studies of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complex in DMSO solution. The absorption spectrum of the Cr(III)complex shows band at 37878 cm^{-1} attributed to charge transfer transition respectively in an octahedral field[19]. Fe(III) complex exhibits electronic spectral band at 29411 cm^{-1} which can be assigned to charge transfer in an octahedral field[20]. The absorption spectrum of the Co(II)complex shows bands at 18248 and 38314 cm^{-1} attributed to $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and charge transfer in an octahedral field[21]. Ni(II) complex exhibits electronic spectral bands at 12886 and 29411 cm^{-1} which can be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) and charge transfer in an octahedral field [22]. The absorption spectrum of the Cu(II) complex shows band at 39062cm^{-1} attributed to charge transfer respectively in an octahedral field[23]. Zn(II) complex exhibits electronic spectral band at 38910 cm^{-1} which can be assigned to charge transfer in an octahedral field[24]. All the Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes were diamagnetic in nature.

X-ray powder diffraction: The x-ray diffractogram of metal complexes Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) of L was scanned in the range 20-80° at wavelength 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Cr(III) complex of L had eighteen reflections with maxima at 2θ = 14.74° corresponding to d value 3.02Å. The diffractogram of Fe(III) complex of L had eighteen reflections with maxima at 2θ = 14.74° corresponding to d value 3.02Å. The diffractogram of Co(II) complex of L had twenty one reflections with maxima at 2θ = 14.86° corresponding to d value 3.00Å. The diffractogram of Ni(II) complex of L had sixteen reflections with maxima at 2θ = 10.71° corresponding to d value 4.14Å. The diffractogram of Cu(II) complex of L had nineteen reflections with maxima at 2θ = 14.84° corresponding to d value 3.00Å.The diffractogram of Zn(II) complex of L shows twenty two reflections with maxima at 2θ = 10.68° corresponding to d value 4.14Å.. The X-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer program.[25] The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cr(III) complex of L yielded values of lattice constants, a=10.9942 Å, b=10.0016Å, c = 14.8995 Å and unit cell volume V=1418.85Å^3. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β=90^0 ≠γ required for Monoclinic. The unit cell of Fe(III) complex of L yielded values of lattice constants, a=10.5883 Å, b=8.5768Å, c = 19.6346Å and unit cell volume V=1544.22 Å^3. In concurrence with these

cell parameters, the condition such as a ≠ b ≠ c and α = β=90^0 ≠γ required for sample to be Monoclinic. The unit cell of Co(II) complex of L yielded values of lattice constants, a=8.9162 Å, b=9.9679 Å, c = 14.5956Å and unit cell volume V=1123.41Å^3.In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠ γ required for sample to be monoclinic. The unit cell of Ni(II) complex of L yielded values of lattice constants, a=8.9621 Å, b=10.5908Å, c = 16.6019Å and unit cell volume V=1364.68Å^3.In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β=90^0 ≠γ required for sample to be monoclinic. The unit cell of Cu(II) complex of L yielded values of lattice constants, a=10.0120 Å, b=10.0120Å, c = 14.7903Å and unit cell volume V=1363.89Å^3. In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = β = 90° ≠γ required for sample to be monoclinic. The unit cell of Zn(II) complex of L yielded values of lattice constants, a=8.9568Å, b=9.8841 Å, c = 16.8813Å and unit cell volume V=1294.28Å^3.In concurrence with these cell parameters, the condition such as a ≠ b ≠ c and α = γ = 90° ≠ β required for sample to be monoclinic were tested and found to be satisfactory.

Hence it can be concluded Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complex of L has monoclinic crystal system. The experimental density values of the complexes were determined by using specific gravity method[26] and found to be 1.02, 1.06, 1.2, 1.04, 0.96 and 1.12 gcm^{-3} for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively. By using experimental density values, molecular weight of complexes, Avogadro's number and volume of the unit cell were calculated. Number of molecules per unit cell were calculated by using equation ρ = nM/NV and was found Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively. With these values, theoretical density were computed and found to be 1.02,1.06, 1.2, 1.04, 0.96 and 1.12 gcm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error[27].

Antibacterial activity: The antibacterial activities of ligand and its metal complexes were screened against bacteria such as *E. Coli, B.Subtilis*, *S. Aurious And K.Pneumonae* by paper disc plate method[28]. The compounds were tested at the concentration 1250ppm 2500ppm 5000ppm and 10000ppm. DMSO and compared with known antibiotics *viz Tetracyclin*. From Table 4and 5, it is found that the inhibition by metal chelates is higher than that of a ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes[29].

Table-3
Characteristic IR frequencies (cm^{-1}) of the ligands and their complexes

Compound	ν (C=N)	ν (C=C)	ν (C-N)	ν (C-O)	ν (M-O)	ν (M-N)
L	1662	1553	1391	1232	--	--
L-Ni	1624	1537	1260	1067	612	541
L-Cu	1645	1540	1269	1071	510	469

Table-4
Antibacterial activity of Ligand

Bacterium	Diameter of inhibition zone (mm)			
	(Ligand)			
	1250 ppm	2500 ppm	5000 ppm	10000 ppm
E. coli	07	05	06	02
S. *Aurious*	09	11	08	06
B.Subtilis	13	06	05	06
K.Pneumonae	09	04	07	07

Table-5
Antibacterial activity of Co(II) Complex

Bacterium	Diameter of inhibition zone (mm)				*Tetracyclin*
	(Ligand-Co)				
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
E. coli	15	12	10	07	25
S. *Aurious*	19	17	13	11	29
B.Subtilis	22	16	14	12	40
K.Pneumonae	14	14	14	13	25
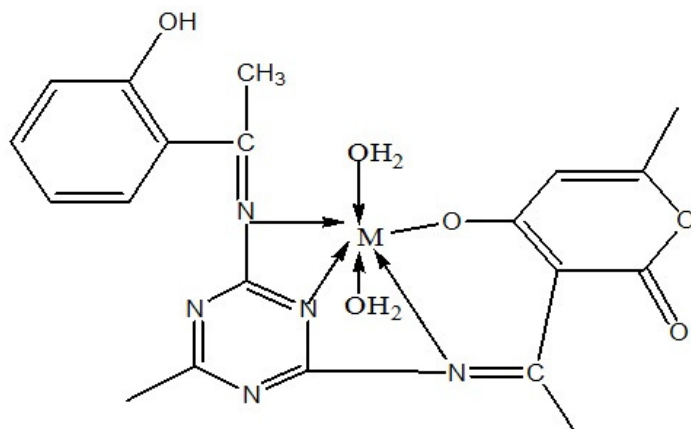
Figure-2
The proposed Structure of the complexes

When M= Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)

Conclusion

Metal complexes of octahedral geometry for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. On the basis of the physico-chemical and spectral data discussed above, one can assume that the ligand behave as dibasic, NNNO tetradentate, co-ordinating via phenolic oxygen and imino nitrogen as illustrated in figure-2. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. The X-ray study suggests monoclinic crystal system for Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes.

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