

Synthesis, characterization of some transition metal complexes of unsymmetrical tetradentate schiff base

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ABSTRACT

Neutral tetradentate complexes of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized using a unsymmetrical Schiff base formed by the condensation of Dehydroacetic acid, 3-nitrobenzaldehyde and 6-methyl-1,3,5-triazine-2,4-diamine (L) in alcohol medium. All the complexes were characterized on the basis of their micro analytical data, molar conductance, magnetic susceptibility, IR,UV-Vis, ¹H NMR, X-ray diffraction, thermogravimetric analysis. The ligand and its complexes were screened for their antibacterial activity against bacterium *Staphylococcus aureus*, *B.subtilis* (Gram positive) and *Escherichia coli*, *K.pneumoniae* (Gram negative). The result indicated that the complexes exhibited good antibacterial activities.

Keywords: Dehydroacetic acid, Unsymmetrical Schiff bases, Transition metal complexes, Thermal analysis, Powder X-ray diffraction.

INTRODUCTION

Schiff bases play important role in co-ordination chemistry as they easily form stable complexes with most transition metal ions. Many biologically important Schiff bases and their complexes have been reported in literature possessing, analytical, industrial, biological, clinical, biochemical, antimicrobial, anticancer, antibacterial, antifungal and antitumor activity[1-4] in addition with important roles in ranging from anticorrosion, soil treatment agents and medicinal agents [2,4,5]. Schiff bases and their metal complexes have been used as carries in the preparation of potentiometric sensors of determining cations and anions, catalysts in several industrial redox process, oxidation reaction, vitamin B₆, Metal alkoxides. It's important and diversified roles in biological systems. The role of chlorophyll, hemoglobin, carbonic anhydrase, vitamin B₁₂, xanthine oxides and haemocyanin, illustrates the intimate linkage between inorganic chemistry and biology[6-12]. A search of literature reveals that no work has been done on the transition metal complexes of the asymmetrical Schiff bases derived from 6-methyl-1,3,5-triazine-2,4-diamine, dehydroacetic acid and 3-nitrobenzaldehyde. In this communication we report the synthesis of asymmetrical tetradentate Schiff bases formed by the condensation of 6-methyl-1,3,5-triazine-2,4-diamine, dehydroacetic acid and 3-nitrobenzaldehyde (Fig.1). The solid complexes of Cr(III), Fe(III), Co (II), Ni(II), Cu(II) and Zn(II) with these ligands have been prepared and characterized by different physico-chemical methods.

MATERIALS AND METHODS

Reagents and solvents

3-nitrobenzaldehyde, 6-methyl-1,3,5-triazine-2,4-diamine, metal nitrate of AR grade and Dehydroacetic acid obtained from Merck was used for synthesis of ligand and complex .

Synthesis of ligand

The ligand was prepared by a modification of the reported methods [13-19]. Asymmetric tetradentate Schiff base ligand has been synthesized via a stepwise approach. In the first step mono-Schiff base compound was prepared by refluxing 50 ml solution of 10 mmol of dehydroacetic acid and 20 mmol 6-methyl-1,3,5-triazine-2,4-diamine in super dry ethanol for about 4 h. Mono-Schiff base thus formed was then refluxed with 10mmol 3-nitrobenzaldehyde to prepare asymmetric ligand. Asymmetric Schiff base thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol. (Yield: 74%).

Synthesis of metal complexes

To a hot ethanol solution (25ml) of the ligand (0.005mol), methanolic solution (25ml) of metal Nitrate (0.0025mol) was added with constant stirring. The pH of reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 3 h. The precipitated solid metal complex was filtered off in hot condition and washed with hot methanol, ethanol, petroleum ether (40°-50°) and dried over calcium chloride in vacuum desiccator.(yield: 57%)

Physical Measurement

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. X-RD were recorded on BRUKER D8 Advance. TGA- DTA were recorded on Shimadzu. The carbon, hydrogen and nitrogen contents were determined on Elementar model vario EL-III. The UV-visible spectra of the complexes were recorded on model 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 chelates were done on a Guoy balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant.

RESULTS AND DISCUSSION

Schiff bases of 6-methyl-1,3,5-triazine-2,4-diamine and its complexes have a variety of applications including biological, clinical and analytical .The Co-ordinating possibility of 6-methyl-1,3,5-triazine-2,4-diamine has been improved by condensing with a variety of carbonyl compounds. An attempt has been made to synthesize asymmetric Schiff bases from 6-methyl-1,3,5-triazine-2,4-diamine and dehydroacetic acid with 3-nitrobenzaldehyde.

Physical characteristics, micro analytical, and molar conductance data of ligand and metal complexes are given in Table 1 and 2. The analytical data of complexes reveals 2:1 molar ratio (metal:ligand) and corresponds well with the general formula $[\text{ML}(\text{H}_2\text{O})_2]$ (where M = Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)). The magnetic susceptibilities of Cr(III), Fe(III), Co (II), Ni(II), Cu(II) and Zn(II) complexes at room temperature are consistent with high spin octahedral structure with two water molecules coordinated to metal ion. The presence of two coordinated water molecules was confirmed by TG-DT analysis. The metal chelate solutions in DMSO show low conductance and supports their non-electrolyte nature.(Table 1)

^1H -NMR spectra of ligand

The ^1H -NMR. spectra of free ligand at room temperature shows the following signals. 2.14 δ (s, 3H, $\text{C}_6\text{-CH}_3$), 2.50 δ (s, 3H, Methyl hydrogen's bonded to azomethine carbon), 4.33 δ (s, 1H, phenolic OH), 6.95-7.59 δ (m, 4H, Aromatic H_a , H_b , H_c , H_d protons of phenyl ring).

IR Spectra

The IR spectra of the complexes are compared with that of the ligand to determine the changes that might have taken place during the complexation. The bands at 3277, 1663, 1551, 1463, 1395 and 1177 cm^{-1} assignable to ν OH (intramolecular hydrogen bonded), ν C=C(aromatic), ν C=N (azomethine), ν C-N (aryl azomethine) and ν C-O (phenolic) stretching modes respectively[20-23] The absence of a weak broad band in the 3200-3400 cm^{-1} region, in

the spectra of the metal complexes suggests deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of phenolic oxygen to the metal ion. This is further supported by downward shift in ν C-O (phenolic) [24] with respect to free ligand. On complexation, the ν (C=N)[25] band is shifted to lower wave number with respect to free ligand, denoting that the nitrogen of azomethine group is coordinated to the metal ion. The ν C-N band is shifted to lower wave number with respect to free ligand. The IR spectra of metal chelates showed new bands in between the 500-800 and 400-500 cm^{-1} regions which can be assigned to ν M-O and M-N[26] vibrations respectively. The IR spectra of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) show a strong band in the 3050-3600 cm^{-1} region, suggesting the presence of coordinated water in these metal complexes. The presence of coordinated water is further confirmed by the appearance of non-ligand band in 830-840 cm^{-1} region, assignable to the rocking mode of water. The presence of coordinated water is also established and supported by TG/DT analysis of these complexes. Hence it is concluded that the coordination takes place via phenolic oxygen and azomethine nitrogen of ligand molecule.

Thermogravimetric analysis

The dynamic TGA with the percentage mass loss at different steps have been recorded. The simultaneous TG/DT analysis of Co(II) and Ni(II) was studied from ambient temperature to 1000 $^{\circ}\text{C}$ in nitrogen atmosphere using α -Al₂O₃ as reference. An analysis of the thermogram of the complexes indicated that Co(II) complexes shows two step decomposition. The first weight loss 7.58%, in between temp. 41-190 $^{\circ}\text{C}$ could be correlated with the loss of two coordinated water (calculated 8.24%). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 190-790 $^{\circ}\text{C}$, with 77.95% mass loss corresponds to decomposition of the complex (calcd. 76.63%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide CoO obs. 14.88% (calcd. 15.55%). An analysis of the thermogram of the complexes indicated that Ni(II) complexes shows two step decomposition. The first weight loss 7.16%, in between temp. 41-75 $^{\circ}\text{C}$ could be correlated with the loss of two coordinated water (calculated 7.16%). The anhydrous compound does not remain stable at higher temperature, it undergoes rapid decomposition in the range 75-765 $^{\circ}\text{C}$, with 74.81% mass loss corresponds to decomposition of the complex (calcd. 76.23%) in second step. The decomposition is completed leading to the formation of stable residue of metal oxide NiO obs. 18.02% (calcd. 18.57%). kinetic and thermodynamic viz the energy of activation (E_a), frequency factor (Z), entropy change ($-\Delta S$) and free energy change (ΔG) for the non-isothermal decomposition of complexes have been determined by employing Horowitz-Metzger method [27] and Coats-Redfern method [28] and values are given in Table 3. The Calculated values of the given activation energy of the complexes are relatively low, indicating the autocatalysis effect of metal ion on the thermal decomposition of the complex. The negative value of activation entropy indicate that the activated complexes were more ordered than the reaction were slow. The more ordered nature may be due to the polarization of bonds in the activated state, which might occur through charge transfer transitions[29].

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

Compound	Molecular formula	Mol.Wt.	M.P. Decomp temp. $^{\circ}\text{C}$	Colour	Molar Conduc. Mho $\text{Cm}^2\text{mol}^{-1}$
L		408.37	>300	Yellow	----
L Cr		460.36	>300	Gray	32.56
L Fe		464.21	>300	Brown	45.79
L Co		467.3	>300	Pink	35.47
L Ni		467.06	>300	Green	35.07
L Cu		471.91	>300	Blue	13.92
L Zn		473.76	>300	White	42.08

Table 2. Elemental Analysis of Ni(II) Complex

Compound	Found (Calculated)			
	C	H	N	M
L	55.4	4.07	19.82	0
	-55.88	-3.94	-20.57	
L-Ni	48.8	3.42	18.02	12.6
	-48.86	-3.45	-17.99	-12.56

Magnetic measurements and electronic absorption spectra

The electronic spectral studies of metal complexes of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases were carried out in DMSO solution. The absorption spectrum of the Cr(III) complex shows bands at 17513 and 37878 cm^{-1} attributed to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and charge transfer transition respectively in an octahedral field [30]. Fe(III)

complex exhibits electronic spectral bands at 26246 cm^{-1} which can be assigned to charge transfer in an octahedral field[31]. The absorption spectrum of the Co(II)complex shows bands at 18796 and 30395 cm^{-1} attributed to ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$ and charge transfer in an octahedral field[32]. Ni(II) complexes shows bands at 13175 cm^{-1} and 27472 cm^{-1} are assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ and charge transfer transitions. The absence of band below 10,000 cm^{-1} and All Ni(II) complexes were diamagnetic in nature indicates octahedral geometry[33]. The absorption spectrum of the Cu(II)complex shows bands at 36630 cm^{-1} attributed to charge transfer respectively in an octahedral field[34]. Zn(II) complex exhibits electronic spectral bands at 38314 cm^{-1} which can be assigned to charge transfer in an octahedral field[35]. All the Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes were diamagnetic in nature.

Molar Conductivity Measurements

The metal(II) and (III) complexes were dissolved in DMSO and the molar conductivity of 10^{-4}M of their solution at room temperature were measured. The lower conductance values of the complexes support their non-electrolytic nature of the compounds.

Table 3 The kinetic parameter of metal complexes calculated by the methods Horowitz-Metzger (HM) and Coats-Redfern (CR)

Complex	Step	N	Method	Decomp. Temp.($^{\circ}\text{C}$)	Ea (kJmole $^{-1}$)	Z (S^{-1})	ΔS (JK $^{-1}$ mole $^{-1}$)	ΔG (kJmole $^{-1}$)	Correlation Coefficient
L-Ni	I	0.4	HM	300	6.29	1.05×10^1	-163.49	17.55	0.977
			CR		5.46	1.83×10^1	-75.44	10.65	0.991
	II	0.9	HM	610	14.93	2.39×10^1	-153.06	31.18	0.994
			CR		18.92	5.4×10^1	-67.53	26.09	0.997
L-Co	I	0.76	HM	150	20.56	1.15×10^{-2}	-107.79	26.04	0.9991
			CR		96.47	1.85×10^{-14}	2.64×10^{-21}	96.46	0.914
	II	0.58	HM	610	14.93	2.39×10^1	-153.06	31.18	0.9925
			CR		19.68	1.91	-248.61	46.08	0.9922

Table 4: Antibacterial activity of compounds

Bacterium	Diameter of inhibition zone (mm)				
	(L)				Tetracyclin
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	10	10	7	9	15
<i>S. Aurious</i>	11	9	9	6	12
<i>B.Subtilis</i>	10	8	5	5	16
<i>K.Pneumoniae</i>	8	9	9	9	14

Table 5: Antibacterial activity of compounds

Bacterium	Diameter of inhibition zone (mm)				
	(LM)				Tetracyclin
	1250 ppm	2500 ppm	5000 ppm	10000 ppm	1000 ppm
<i>E. coli</i>	20	17	14	14	27
<i>S. Aurious</i>	19	15	13	10	30
<i>B.Subtilis</i>	21	15	13	10	42
<i>K.Pneumoniae</i>	14	13	13	13	25

Powder x-ray diffraction

The x-ray diffractogram of Cr(III), Fe(III), Co (II), Ni(II), Cu(II) and Zn(II) complexes of L was scanned in the range 20-80 $^{\circ}$ at wavelength 1.543 \AA . 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 twenty six reflections with maxima at $2\theta = 6.31^{\circ}$ corresponding to d value 7.00 \AA . The diffractogram of Fe(III) complex of L had twenty two reflections with maxima at $2\theta = 10.15^{\circ}$ corresponding to d value 4.37 \AA . The diffractogram of Co(II) complex of L had twenty two reflections with maxima at $2\theta = 11.74^{\circ}$ corresponding to d value 3.78 \AA . The

diffraction pattern of Ni(II) complex of L had twenty reflections with maxima at $2\theta = 10.59^\circ$ corresponding to d value 4.18Å. The diffraction pattern of Cu(II) complex of L had eighteen reflections with maxima at $2\theta = 14.96^\circ$ corresponding to d value 2.98Å. The diffraction pattern of Zn(II) complex of L shows twenty one reflections with maxima at $2\theta = 4.14^\circ$ corresponding to d value 10.65Å. 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 programmed [36]. 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, $a=9.9810 \text{ \AA}$, $b=11.0411 \text{ \AA}$, $c = 11.9679 \text{ \AA}$ and unit cell volume $V=1142.18 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = 90^\circ \neq \gamma$ required for sample to be Monoclinic were tested and found to be satisfactory. Hence it can be concluded that Cr(III) complex has Monoclinic crystal system. The unit cell of Fe(III) complex of L yielded values of lattice constants, $a=8.9613 \text{ \AA}$, $b=16.4365 \text{ \AA}$, $c = 14.6594 \text{ \AA}$ and unit cell volume $V=2124.32 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ required for sample to be orthorhombic. The unit cell of Co(II) complex of L yielded values of lattice constants, $a=9.5686 \text{ \AA}$, $b=10.3999 \text{ \AA}$, $c = 11.3720 \text{ \AA}$ and unit cell volume $V=986.81 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = 90^\circ \neq \gamma$ required for sample to be monoclinic. The unit cell of Ni(II) complex of L yielded values of lattice constants, $a=10.4862 \text{ \AA}$, $b=9.3621 \text{ \AA}$, $c = 10.6713 \text{ \AA}$ and unit cell volume $V=907.29 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma \neq \beta$ required for sample to be monoclinic. The unit cell of Cu(II) complex of L yielded values of lattice constants, $a=8.9601 \text{ \AA}$, $b=10.6921 \text{ \AA}$, $c = 16.1230 \text{ \AA}$ and unit cell volume $V=1337.70 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = 90^\circ \neq \gamma$ required for sample to be monoclinic. The unit cell of Zn(II) complex of L yielded values of lattice constants, $a=7.3625 \text{ \AA}$, $b=9.1491 \text{ \AA}$, $c = 11.7875 \text{ \AA}$ and unit cell volume $V=719.34 \text{ \AA}^3$. In concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \gamma = 90^\circ \neq \beta$ 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 [32] and found to be 1.12, 1.04, 1.12, 0.72, 1.04 and 1.3 g cm^{-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 $\rho = nM/NV$ 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 1.12, 1.04, 1.12, 0.72, 1.04 and 1.3 g cm^{-3} for respective complexes. Comparison of experimental and theoretical density shows good agreement within the limits of experimental error [37].

Antibacterial activity

Synthesized Schiff bases and their metal complexes were screened against bacteria such as *E. Coli*, *B.Subtilis*, *S. Aurios* And *K.Pneumoniae* by paper disc plate method [38]. The compounds were tested at the concentrations 1250ppm, 2500ppm, 5000ppm and 10000ppm. DMSO and compared with known antibiotics viz *Tetracyclin*. From (Table 4 and 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 [39].

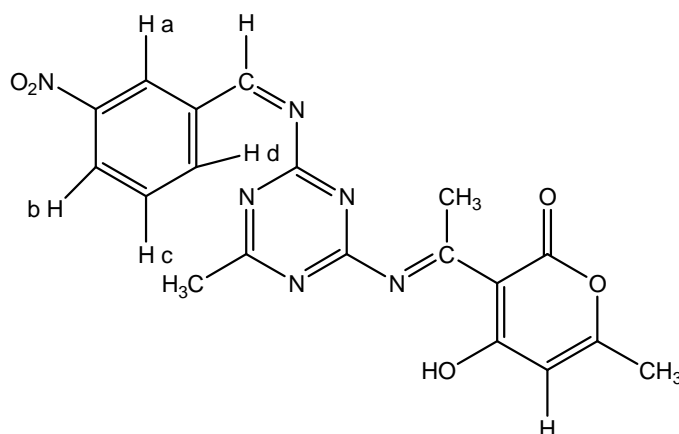


Figure 1. Structure of ligand

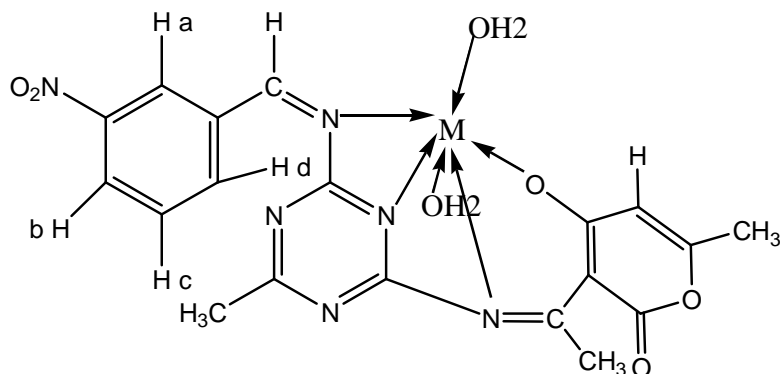


Figure 2. The proposed Structure of the complexes
when $M = \text{Cr(III)}, \text{Fe(III)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II)

CONCLUSION

In the light of above discussion we have proposed 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, coordinating via phenolic oxygen and imino nitrogen as illustrated in Fig.2. The complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Thermal study reveals thermal stability of complexes. 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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