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Synthesis, Characterization and X-Ray Diffraction Studies of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Schiff Base Derived from 5-nitrosalicylaldehyde and Anthranilic Acid

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Transition metal (II) complexes of the type $ML \cdot nH_2O$ [where M–Co(II), Ni(II), Cu(II) and Zn(II), L-Schiff base derived from 5-nitro salicylaldehyde and anthranilic acid, n=0,1...] have been prepared and characterized by elemental analysis, molar conductivity, IR, electronic spectra, magnetic susceptibility studies and X-ray difraction spectra. Molar conductivity measurements indicate that the complexes are non-electrolytic in nature. From the analytical and spectral data, the stoichiometry of the complexes has been found to be 1:1 (metal : ligand). IR spectral data suggests that the ligand behaves as a monobasic tridentate ligand with O:N:O donor sequence towards metal ions. Magnetic susceptibility measurements indicate paramagnetic behaviour of all the complexes except Zn-complex. X-ray diffraction studies suggest monoclinic crystal system for these complexes.

Key Words: Synthesis, 5-Nitro salicylaldehyde, Anthranilic acid, Binuclear complex, Transition metal complexes, X-ray diffraction.

INTRODUCTION

Transition metal coordination compounds constaining the Schiff base ligands have been interest for many years. These complexes play an important role in the developing of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures[1-3]. Imines are an important class of ligands in coordination chemistry and have various applicaton in analytical chemistry and in catalysis[4,5].

Schiff bases and their transition metal complexes have been used in anticancer, antituberculosis, antibacterial, antifungal, hypotensive and hypothermic reagents[6,7]. Some of the copper complexes are known to posses antiinflammetry[8] anticancer[9] properties. Schiff base can also be used as analytical reagent for epoxydation fo olefins[10]. In this paper, the synthesis, characterization and crystal lattice parameters of transition metal complexes of Schiff base derived from 5-nitrosalicylaldehyde and anthranilic acid with Co(II), Ni(II), Cu(II) and Zn(II) metal ions are reported. These metal complexes may have enhanced biological activity which may find their importance in the applied medicinal chemistry.

EXPERIMENTAL

All chemicals used for the synthesis were of AnalaR grade. 5-nitrosalicylaldehyde was obtained from Aldrich, anthranilic acid and Metal salts from SD Fine Chemicals. Distilled solvents were used through out the experiments.

The melting point of all the complexes were determined by open capillary method. Elemental analysis was carried out in the Micro-analytical Laboratory, University of Mumbai. The metal content for all the metal complexes were determined as reported in the literature[11]. The complexes were examined for solubility using various polar and nonpolar solvents. Molar conductivity of ligand and metal complexes were recorded using 1×10^{-3} M solution in DMF on Toshniwal TSM-15 conductivity meter. The electronic absorpton spectra of ligand and complexes were ercorded in the UV-Visible region using DMF as solvent on UV-Visible 2100 spectrophotometer supplied by M/s Perkin Elmer-Lambda 25. IR spectra were recorded using KBr pellets on FTIR-4200 supplied by M/s Shimadzu corporation. Magnetic susceptibility measurements were made at room temperature on Gouy's balance using $Hg[CO(SCN)_4]$ as calibrant. X-ray diffraction spectra were recorded on X-ray diffractometer supplied by M/s. Philips, Holland. The experimental results are summarized in Tables 1 and 2.

Synthesis of Schiff base: 5-Nitrosalicylaldenyde (1.6712 g, 0.01 mol) and anthranilic acid (1.3714 g, 0.01 mol) were taken in a round bottom flask. Absolute ethanol (50 mL) was added and mixture was refluxed for 5 h on water bath. The hot reaction mixture was poured in crushed ice, whereby orange precipitae was obtained. It was suction filtered, washed with distilled water and cold ethanol and dried in vaccum dessicator. The pure Schiff base was recrystallized from ethanol (m.p. 250ºC, yield 75 %).

Synthesis of metal complexes: Metal complexes were synthesized by refluxation precipitation method. To the hot methanolic solution of ligand methanolic solution of metal salts in the ratio of [1:1] was added dropwise from dropping funnel with constant stirring by using magnetic stirrer. The resulting mixture was refluxed for 5 h on water bath and cooled. The pH of the solution was adjusted in the range of 6.5-8.0 by adding alcoholic ammonia. The reaction mixture was digested for 10 min. The metal complexes obtained were filtered washed with water and then with hot methanol and dried in vaccum dessicator.

TABLE-1
ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/complexes (colour)	m.w.	m.p. ($^{\circ}$C)	Stoichiometry	Molar condc-tance (S cm^2 mol^{-1})	Elemental analysis (%) Found (Calcd.) C	H	N	Metal	μ_{eff} (BM)
$C_{14}H_{10}N_2O_5$ (Orange)	286	250	-	5.80	59.36 (58.74)	3.95 (3.49)	10.65 (9.76)	- -	-
$CoC_{14}H_8N_2O_5.H_2O$ (Yellow)	361	>300	1.1	2.90	45.98 (46.54)	3.28 (2.77)	7.49 (7.75)	16.50 (16.23)	4.33
$NiC_{14}H_8N_2O_5.H_2O$ (Green)	361	>300	1.1	2.60	46.22 (46.57)	2.53 (2.77)	7.38 (7.76)	16.43 (16.18)	3.28
$CuC_{14}H_8N_2O_5$ (Green)	347.5	>300	1.1	3.10	48.64 (48.33)	2.76 (2.30)	7.55 (8.05)	17.79 (18.17)	1.87
$ZnC_{14}H_8N_2O_5.H_2O$ (Yellow)	349	>300	1.1	2.80	45.85 (45.72)	2.71 (2.72)	8.06 (7.62)	17.06 (17.70)	-

TABLE 2
UV-VISIBLE, DENSITY AND IR SPECTRAL DATA OF
LIGAND AND METAL COMPLEXES

Ligand/complexes	IR spectral data (cm^{-1})					Electronic spectral data (cm^{-1}) (E = dm^3 mol^{-1} cm^{-1} × 10^4)		
	ν(OH)	ν(C=N)	ν(C-O)	ν(M-N)	ν(M-O)	Assignment for *d-d* transition		
$C_{14}H_{10}N_2O_5$	3450	1637	1453	-	-	23171 (7.50)	28172 (5.84)	38146 (3.77)
$CoC_{14}H_8N_2O_5.H_2O$	3300	1615	1409	517	450	25529 (3.60)	37575 (3.99)	38124 (3.18)
$NiC_{14}H_8N_2O_5.H_2O$	3450	1594	1434	518	452	26158 (4.42)	37516 (3.79)	38074 (3.10)
$CuC_{14}H_8N_2O_5$	-	1595	1435	518	452	26279 (11.47)	37381 (10.24)	37627 (21.64)
$ZnC_{14}H_8N_2O_5.H_2O$	3450	1615	1407	515	452	25641 (3.31)	30025 (1.51)	37768 (2.64)

RESULTS AND DISCUSSION

Analytical data of ligand and complexes are given in the Table-1. All the complexes are coloured, stable in air and decomposes at higher temperature [>300ºC]. The elemental analyis of metal complexes suggests 1:1 [$ML\cdot nH_2O$, n = 0, 1] metal to ligand stoichiometry. The complexes are soluble in DMSO, DMF and THF, while they are sparingly soluble in solvents like ethanol, methanol, chloroform, carbon tetrachloride, petroleum ether, ethyl acetate etc. The molar conductivity values of 1×10^{-3} M solution of metal complexes in DMF falls in the range 2×10^{-3} to 6×10^{-3} S cm^{2}mol^{-1}. This value indicates their non-electrolytic behaviour[12,13].

IR spectrum of ligand shows strong band in the ergion of 3450-3200 cm^{-1} which is assigned to hydrogen bonded ν(OH) stretching vibration[14]. The spectra of complexes exhibit a broad absorption band in the region of 3400-3200 cm^{-1} with weak intensities attributed to the -OH group of the coordinated water molecule[15]. The new peak at *ca.* 841 cm^{-1} confirms the presence of coordinated water as reported in literature[16].

IR spectrum of ligand shows a very strong band at 1637 cm^{-1} assigned to ν(C=N) azomethine. The lowering of ν(C=N) azomethine group to the extent of 20-40 cm^{-1} in all the complexes indicates the participation of azomethine nitrogen. The ligand atom during chelation[17]. Exhibits ν(C-O) stretching vibration at 1453 cm^{-1}. In the metal complexes ν(C-O) phenolic absorption band appears at 1435-1407 cm^{-1} which is 15-45 cm^{-1} lower than the corresponding ν(C-O) vibration of free ligand. This indicates bonding of phenolic oxygen to the metal ion[18]. The additional bands around 518 and 452 cm^{-1} are assigned to ν(M-N) and ν(M-O) stretching vibration respectively[19-22].

Electronic spectrum of ligand showed three high intensity bands lying at 23171, 28172, 38146 cm^{-1} assigned to $n\rightarrow\pi^*$ and σ-σ^* transition respectively in ligand. The electronic absorption spectrum of Co(II) complex showing a band in the visible region at 25529 cm^{-1} is assignable to the transition $^4A_2 \rightarrow {}^4T_1$ (p) which is the characteristic of tetrahedral geometry. The spectrum also shows an intense sharp band at 37576 cm^{-1} which is attributed to the ligand to metal charge transfer transition as observed in most of the tetrahedral complexes[23]. This is further supported by the magnetic moment value found to be 4.33 BM[24-26].

The electronic absorption spectrum of Ni(II) complex exhibits bands at 26158 and 38074 cm^{-1} which are assigned to $^3T_1 \rightarrow {}^1T_2$ and ligand to metal charges transfer transition respectively, on the basis of tetrahedral geometry[27]. The magnetic moment of Ni(II) complex is 3.28 BM[28] which is attributed to tetrahedral structure. The observed magnetic moment value of Ni(II) complex is slightly higher than the spin only value may be due to spin orbit coupling[29].

The elctronic absorption spectrum of Cu(II) complex exhibits bands at 25419, 26279 and 37381 cm^{-1} which are assigned to $^4A_2 \rightarrow {}^4T_1$ (p) and remaining two transition are attributed to charge transfer transition. The magnetic moment value of Cu(II) complex is 1.87 BM which supports Cu(II) complex as dimer. These results may be explained on the basis of a non-planar bridged structure for their complex[30].

Zn(II) complex is diamagnetic in nature and its electronic absorption spectrum does not have *d-d* transition bands The Zn(II) complex may be assigned square planar geometry. The TGA analysis of the complexes confirmed the presence of coordinated water molecule. All complexes have one water molecule coordinated to the metal except Cu-metal complex. The crystal lattice parameters of the complexes of Co(II), Ni(II), Cu(II), Zn(II) were found out by X-ray difraction powder method. The X-ray diffractogram of complexes were recorded in the range 5º to 60º 2θ value. The major refluxes were measured and the corresponding d-values were obtained. An independent indexing for each of these refluxes were carried out by least square method. The Miller indices (hkl) were calculated and refined using Back - cal program by computational method and data has been summarized in Table 3-6. The data indicates the monoclinic crystal system for all the complexes. Jejurkar *et al.*[31] have reported monoclinic system for such metal complexes.

TABLE-3
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR Co-COMPLEX

a(Å) = 18.1466 ± 0.0157
b(Å) = 18.4137 ± 0.0559
c(Å) = 37.4442 ± 0.5329
Standard Deviation : 0.29%
$\alpha = 90^\circ$, $\beta = 87.05$, $\theta = 90^\circ$
Volume (Å)^3 = 12498.6
D_{cal} = 1.0456 g/cm^3
D_{obs} = 1.0836 g/cm^3
Z = 32, Crystal System = $P_{2/m}$
% Porosity = 3.50

I/I_o	D_{obs}	D_{cal}	h	k	l
100.00	4.4011	4.3932	4	1	1
74.80	3.3733	3.3726	5	2	1
79.55	2.2343	2.2372	8	0	-2
79.55	2.1657	2.1642	8	1	-4
74.80	1.9743	1.9764	9	1	4
74.80	1.5222	1.5220	8	8	9
74.80	1.4341	1.4347	9	9	2

TABLE-4
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR Ni-COMPLEX

a(Å) = 18.1276 ± 0.0346
b(Å) = 18.7410 ± 0.2104
c(Å) = 37.1394 ± 0.3405
Standard Deviation : 0.52%
$\alpha = 90^\circ$, $\beta = 86.53^\circ$, $\theta = 90^\circ$
Volume(Å)^3 = 12594.4
D_{cal} = 1.5213 g/cm^3
D_{obs} = 1.680 g/cm^3
Z = 32, Crystal System = P_2/m
% Porosity = 9.52

I/I_o	D_{obs}	D_{cal}	h	k	l
22.92	8.0771	8.0500	2	1	1
39.40	5.3186	5.3252	3	1	3
100.00	4.9228	4.9211	3	0	-4
27.17	4.0598	4.0735	4	2	1
20.93	3.6029	3.5928	5	0	2
47.82	3.4682	3.4699	5	1	3
30.60	3.583	3.3547	5	2	2
35.49	3.1385	3.1398	5	2	5
26.08	2.9743	2.9821	6	1	1
19.02	2.7098	2.7083	6	3	2

TABLE-5
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR Cu-COMPLEX

a(Å) = 18.1833 ± 0.0634
b(Å) = 18.5805 ± 0.2158
c(Å) = 37.4784 ± 0.6684
Standard Deviation : 0.76%
$\alpha = 90°$, $\beta = 87.28°$, $\theta = 90°$
Volume $(\text{Å})^3$ = 12648.12
D_{cal} = 1.5352 g/cm^3
D_{obs} = 1.5938 g/cm^3
Z = 32, Crystal System = $P_{2/m}$
% Porosity = 2.30

I/I_o	D_{obs}	D_{cal}	h	k	l
24.39	8.1067	8.0433	2	1	1
36.60	5.3139	5.3188	3	1	3
100.00	4.9295	4.9454	3	2	2
16.60	4.0543	4.0742	4	2	1
35.12	3.5986	3.5980	5	0	2
60.49	3.4676	3.4707	5	1	3
36.60	3.3589	3.3551	5	2	2
30.86	3.1423	3.1419	4	2	8
32.25	2.9699	2.9720	6	1	2
16.60	2.3102	2.3089	7	3	5
16.60	1.5745	1.5735	9	7	-4

TABLE-6
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR Zn-COMPLEX

a(Å) = 18.1358
b(Å) = 18.4371
c(Å) = 37.3275
Standard Deviation :
$\alpha = 90°$, $\beta = 87.55°$, $\theta = 90°$
Volume $(\text{Å})^3$ = 12470.01
D_{cal} = 1.5650 g/cm^3
D_{obs} = 1.5938 g/cm^3
Z = 32, Crystal System = Monoclinic
Space group = $P_{2/m}$, % Porosity = 1.8070

I/I_o	D_{obs}	D_{cal}	h	k	l
12.61	7.3540	7.3509	2	1	-2
78.83	5.7921	5.8190	3	0	2
15.41	4.1584	4.1444	4	0	4
100.00	3.8604	3.8660	3	3	-4
13.98	3.3996	3.4006	3	3	7
10.70	2.4280	3.4244	7	2	-3
13.98	2.1354	2.1331	6	6	3

Conclusion

On the basis of magnetic susceptibility measurements, crystal lattice parameters, analytical and spectral data Co(II), Ni(II) complexes exhibit tetrahedral structure whereas Zn(II) complex exhibits square planar structure Fig. (a) and Cu(II) exhibits a binuclear structure Fig. (b).

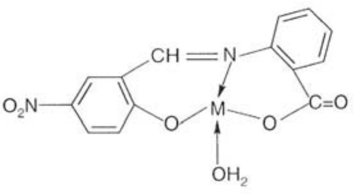

Fig. a [Co (II), Ni(II), Zn(II)]

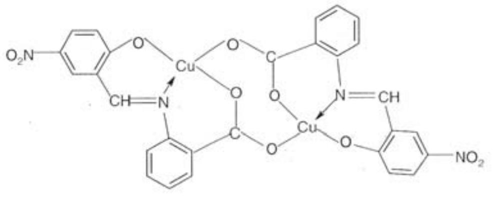

Fig. b [Cu (II)]

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