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Synthesis and Characterization of Some Transition Metal Complexes Derived from 5-Nitro salicylaldehyde and *p*-Anisidine

B.H. MEHTA* and P.S. MORE
Department of Chemistry, University of Mumbai, Vidyanagari
Santacruz (E), Mumbai- 400 098, India
E-mail: bipin_281050@yahoo.com

Transition metal(II) complexes of the type ML_1 [where M = Co(II), Ni(II), Cu(II) and Zn(II), L_1 = Schiff base derived from 5-nitro salicylaldehyde and *p*-anisidine] have been prepared characterized by elemental analysis, molar conductivity, IR, electronic spectra, magnetic susceptibility studies and X-ray diffraction spectra. Molar conductivity measurements indicate that the complexes are non-electrolytic in nature. The analytical data indicates that the metal to ligand ratio in all the complexes is [1:2]. IR spectral data suggests that the ligand behaves as a bidentate O, N donar system. Magnetic susceptibility measurements indicates paramagnetic behaviour of all the complexes except Zn-complex. X-ray diffraction studies suggests monoclinic crystal system for these complexes.

Key Words: Transition metal complexes, 5-Nitrosalicylaldehyde, *p*-Anisidine, X-Ray diffraction.

INTRODUCTION

Transition metal complexes containing the Schiff base ligands have been of interest for years[1-4]. These complexes play an important role in the development of coordination chemistry related catalysis and enzymatic reaction, magnetism and molecular architectures[5-8]. Bidentate ligands containing imine groups have also been used as the modulators of structural and electronic properties of transition metal centers[9].

In the area of bioinorganic chemistry, Schiff base complexes have been used as synthesis model for the metal containing sites in metallo-protiens and enzymes[10,11]. The Schiff bases and its transition metal complexes are used as catalyst for number of catalytic process such as oxidation, epoxidation and polymerization of alkene[12-14].

In this paper we describe the synthesis, characterization and crystal lattice parameters of the complexes of Schiff base derived from 5-nitro salicylaldehyde and *p*-anisidine with Co(II), Ni(II), Cu(II) and Zn(II) metal ions. 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 AR grade 5-nitrosalicylaldehyde was obtained from Aldrich, *p*-anisidine from S.D. Fine Chemicals. Metal salts from S.D. Fine chemicals. Distilled solvents were used throughout the experiments.

Synthesis of Schiff base: 5-Nitro salicylaldehyde [1.671 g, 0.01 mol] and *p*-anisidine [1.23 g, 0.01 mol] were taken in a round bottom flask. 50 mL of absolute ethanol was added and the mixture was refluxed for 5 h on water bath. The resulting solution was concentrated and then cooled, where by yellow crystals were 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 165ºC, yield 78 %]

Synthesis of metal complexes: To hot methanolic solution of ligand, methanolic solution of the corresponding metal salts in the ratio of [1:2] was added dropwise with constant stirring 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 distilled water and then with methanol and dried in vaccum dessicator.

Physical measurements: The melting point of all the complexes were determine 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[15]. The complexes were examined for solubility using various polar and non polar 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 absorption spectra of ligand and complexes were recorded 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.

RESULTS AND DISCUSSION

Analytical parameters of ligand and complexes are given in the Table-1. All the complexes are coloured, stable in air and decomposes at higher temperature [> 300ºC] except Zn-complex which decompose at 290ºC.

TABLE-1
ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Complex (Colour)	m.w./ m.p. (ºC)	Molar conductance (S cm^2 mol^{-1})	Elemental analysis: Found (calcd.) %				μ_{eff} (BM)
			C	H	N	Metal	
$C_{14}H_{12}N_2O_4$	272	12.5	62.19	4.74	10.50	–	–
(Yellow)	(165)		(61.76)	(4.41)	(10.29)		
$CoC_{28}H_{22}N_4O_8$	600.93	16.2	55.62	4.12	9.82	9.80	4.49
(Dark brown)	(>300)		(55.91)	(3.66)	(9.31)	(10.01)	
$NiC_{28}H_{22}N_4O_8$	600.69	16.3	55.43	3.98	9.63	9.77	4.63
(Yellowish brown)	(>300)		(55.93)	(3.66)	(9.32)	(10.56)	
$CuC_{28}H_{22}N_4O_8$	605.55	16.3	55.42	4.19	9.88	10.16	2.10
(Yellowish brown)	(>300)		(55.48)	(3.63)	(9.24)	(10.49)	
$ZnC_{28}H_{22}N_4O_8$	607.39	13.2	55.12	3.85	9.72	10.76	–
(Yellow)	(290)		(55.31)	(3.62)	(9.21)	(11.77)	

Table-2
UV-VISIBLE AND IR SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Complex	IR spectral data (cm^{-1})					Electronic spectral data (cm^{-1}) ε = 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		
$C_{14}H_{12}N_2O_4$	3436	1624	1485	–	–	22988 (2.95)	27932 (3.85)	31545 (2.74)
$CoC_{28}H_{22}N_4O_8$	–	1609	1461	544	447	25839 (14.42)	26525 (17.32)	31545 (8.71)
$NiC_{28}H_{22}N_4O_8$	–	1618	1468	541	449	23041 (3.90)	26666 (7.34)	31948 (3.66)
$CuC_{28}H_{22}N_4O_8$	–	1618	1467	541	449	20533 (4.54)	26666 (11.00)	31545 (6.11)
$ZnC_{28}H_{22}N_4O_8$	–	1614	1464	544	472	22883 (4.92)	26665 (8.18)	31545 (8.50)

The elemental analysis of metal complexes suggests 1:2 $[ML_1]$ metal to ligand stoichiometry. The elemental analysis of metal complexes suggests 1:2 $[ML_1]$ 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 12-17 S cm^2 mol^{-1}. These values indicate their non-electrolytic behaviour[16].

IR spectrum of ligand show strong band in the region of 3400 cm^{-1} which is assigned to hydrogen bonded ν(OH) stretching vibration[17].

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

a (Å) = 18.1802 ± 0.0111
b (Å) = 18.3926 ± 0.0431
c (Å) = 37.0650 ± 0.0743
Standard deviation = 0.32 %
$\alpha = 90°$; $\beta = 87.38°$; $\gamma = 90°$

Volume $(Å)^3$ = 12381.05
D_{cal} = 1.2892 g/cm^3
D_{obs} = 1.5968 g/cm^3
Z = 16
Crystal system = Monoclinic
Space group = $P_2/_m$; Porosity (%) = 19.26

I/I_0	D_{obs}	D_{cal}	h	k	l
45.84	5.9290	5.9315	3	0	-1
100.00	5.4138	5.4253	3	1	-2
82.13	3.8554	3.8636	4	1	5
19.14	3.6073	3.5954	5	0	2
35.25	3.4776	3.4771	3	0	9
53.19	3.3245	3.3215	5	0	5
13.29	3.2500	3.2524	3	2	9
13.29	2.9536	2.9548	4	2	9
11.11	2.8899	2.8866	5	1	8
25.00	2.8070	2.8057	6	1	-4
12.54	2.7883	2.7855	5	2	8
11.11	2.7756	2.7800	6	2	4
14.85	2.7319	2.7276	6	1	-5
11.11	2.5954	2.5964	7	0	1
11.82	2.5634	2.5709	7	1	1
11.11	2.5308	2.5289	6	4	1
13.29	2.3039	2.3023	7	3	5
11.11	1.7789	1.7776	9	3	-7
11.11	1.4671	1.4668	7	10	6

No band in the region 3400-3200 cm^{-1} in the metal complexes indicates absence of coordinated H_2O molecule which is further confirmed by TGA analysis.

IR spectrum of ligand show a very strong band at 1624 cm^{-1} which is assigned to ν(C=N) azomethine. The lowering of ν(C=N) azomethine group by 5-15 cm^{-1} in all the complexes indicates the participation of azomethine nitrogen atom during chelation[18]. The ligand exhibits ν(C-O) stretching vibration at 1485 cm^{-1}. In the metal complexes ν(C-O) phenolic absorption band appears at 1468-1461 cm^{-1} which is 20-25 cm^{-1} lowers than the corresponding ν(C-O) vibration of free ligand. This indicates bonding of phenolic oxygen to the metal ion[19]. The additional bands around 541 and 447 cm^{-1} are assigned to ν(M-N) and ν(M-O) stretching vibration, respectively[20-23].

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

a (Å) = 18.1998 ± 0.0240
b (Å) = 18.5485 ± 0.1202
c (Å) = 37.0925 ± 0.2057
Standard deviation = 0.70 %
$\alpha = 90^\circ$; $\beta = 87.42^\circ$; $\gamma = 90^\circ$

Volume $(Å)^3$ = 12509.04
D_{cal} = 1.2754 g/cm^3
D_{obs} = 1.5788 g/cm^3
Z = 16
Crystal system = Monoclinic
Space group = $P_2/_m$; Porosity (%) = 15.41

I/I_0	D_{obs}	D_{cal}	h	k	l
13.53	6.7994	6.8031	1	2	-3
9.28	5.9290	5.9386	3	0	-1
27.35	5.7846	5.7296	3	1	1
85.62	5.5228	5.5688	3	1	2
15.27	5.3154	5.3084	3	1	3
9.63	4.3562	4.3614	4	1	-1
11.50	3.8325	3.8296	4	2	-3
27.96	3.7379	3.7419	4	0	6
100.00	2.9508	2.9475	4	1	-9
6.99	2.6728	2.6733	6	0	-6
5.02	2.4026	2.4014	7	2	5
35.04	2.3606	2.3624	7	3	-2
7.61	2.3417	2.3420	7	3	4
9.63	2.3073	2.3067	7	3	5
4.05	2.0731	2.0696	8	2	7
20.1	1.9662	1.9683	9	1	-3
5.02	1.9223	1.9219	9	3	1
3.38	1.8490	1.8504	9	4	2

Electronic spectrum showed three high intensity bands lying at 22983, 27913 and 31595 cm^{-1} assigned to n-π^* and σ-σ^* transitions, respectively in ligand. The electronic absorption spectrum of Co(II) complex showing a band in the visible region at 25853 cm^{-1} is assignable to the transition $^4A_2 \rightarrow {}^4T_{1(P)}$ which is the characteristics of tetrahedral geometry. The spectrum also showed an intense sharp band at 31579 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 4.49 BM[24].

The electronic absorption spectrum of Ni(II) exhibits bands at 23068 and 26690 cm^{-1} which may be assigned to the $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ transitions. The spectrum also showed an intense sharp band at 31916 cm^{-1} which is attributed to ligand to metal charge transfer transition as observed in most of the tetrahedral complexes. The magnetic moment of 4.63 BM is attributed to the tetrahedral structure. The observed magnetic moment value of Ni(II) complex is slightly higher than the spin only value may be due to spin or orbit coupling[25].

The electronic absorption spectrum of Cu(II) complex exhibits band at 20547, 26656 and 31595 cm^{-1} which are assigned to $^4A_2 \rightarrow {}^4T_{1(P)}$ and remaining two transitions are attributed to charge transfer transition. The magnetic moment of 2.10 BM is attributed to tetrahedral structure[25].

The Zn(II) complex is diamagnetic and its electronic absorption spectrum does not have *d-d* transition bands. The Zn(II) complex may be assigned square planar geometry.

The crystal lattice parameters of the complexes of Co(II), Ni(II), Cu(II) and Zn(II) were found out by X-ray diffraction powder method. The X-ray diffractogram of complexes were recorded in the range 5° to 60° 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 Tables 3-6. The data indicates the monoclinic crystal system for all the complexes. Jejurkar *et al.*[26] have reported monoclinic system for such metal complexes.

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

a (Å) = 18.1421 ± 0.0400
b (Å) = 18.6386 ± 0.1332
c (Å) = 37.4381 ± 0.4380
Standard deviation = 0.76 %
$\alpha = 90°$; $\beta = 87.02°$; $\gamma = 90°$

Volume $(Å)^3$ = 12642.74
D_{cal} = 1.2721 g/cm^3
D_{obs} = 1.2924 g/cm^3
Z = 16
Crystal system = Monoclinic
Space group = $P_2/_m$; Porosity (%) = 1.57

I/I_0	D_{obs}	D_{cal}	h	k	l
15.90	6.9921	6.9688	2	1	3
100.00	5.2793	5.3174	3	1	3
8.11	4.6611	4.6675	3	1	5
12.12	3.9065	3.9046	2	4	-3
7.41	3.7179	3.7156	3	1	8
34.73	2.9403	2.9329	6	1	3
8.48	2.3532	2.3559	7	3	-2
4.36	2.2187	2.2117	8	1	4
10.01	1.9612	1.9588	9	2	3
4.10	1.9117	1.9151	9	3	0

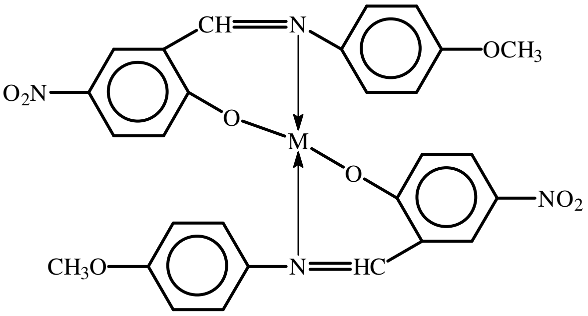
TABLE-6
CELL DATA AND CRYSTAL LATTICE PARAMETERS
FOR Zn-COMPLEXES

a (Å) = 18.1848 ± 0.0202
b (Å) = 18.4115 ± 0.0892
c (Å) = 37.4329 ± 0.2095
Standard deviation = 0.65 %
$\alpha = 90^\circ$; $\beta = 87.32^\circ$; $\gamma = 90^\circ$
Volume $(\text{Å})^3$ = 12519.27
D_{cal} = 1.2885 g/cm^3
D_{obs} = 1.5738 g/cm^3
Z = 16
Crystal system = Monoclinic
Space group = $P_2/_m$; Porosity (%) = 18.12

I/I_0	D_{obs}	D_{cal}	h	k	l
5.55	6.3728	6.4067	2	2	1
27.96	5.8976	5.3130	3	0	-1
100.00	5.3505	5.3130	3	1	3
7.99	4.8089	4.8046	3	1	-4
22.20	4.0307	4.0305	4	2	-1
25.79	3.8980	3.9200	4	2	3
52.96	3.8407	3.8242	4	2	-3
23.71	3.5829	3.5979	5	0	2
25.79	3.4458	3.4409	5	0	4
33.62	3.3251	3.3295	5	0	5
5.55	3.0351	3.0242	4	4	-4
4.84	2.9474	2.9575	4	1	-9
22.70	2.8023	2.8752	6	1	-3
7.13	2.7335	2.7251	6	2	5
10.89	2.5150	2.5171	7	0	-3
4.39	2.4948	2.4904	7	2	2
2.99	2.3817	2.3837	7	3	2
7.13	2.3417	2.3399	7	3	4
5.80	2.3017	2.3026	7	2	7
3.17	2.2557	2.2557	8	1	1
5.07	2.1978	2.1948	8	2	-1
5.31	2.1060	2.1020	8	0	-6
4.61	2.0806	2.0809	8	0	8
2.99	1.8870	1.8852	9	2	-5
2.99	1.8605	1.8595	9	0	-7

Conclusion

On the basis of magnetic susceptibility measurements, crystal lattice parameters, analytical and spectral data cobalt(II), nickel(II) and copper(II), exhibits tetrahedral structure where as zinc(II) complex exhibits square planar structure as shown in the following figure.



where, M = Co(II), Ni(II) and Cu(II)
Tetrahedral complexes and Zn(II) square planar complex

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