

X-Ray Crystallography and Biological Studies of Iron(II), Cobalt(II) and Nickel (II) Complexes Derived from Bidentate Schiff Bases

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The aldehydes, salicylaldehyde and 5-nitrosalicylaldehyde were treated with *o*-phenylenediamine for the synthesis of Schiff base. The ligands, thus formed were used to synthesize Fe(II), Co(II) and Ni(II) complexes. Elemental analysis, molar conductivity, magnetic susceptibility, IR absorption spectra, thermogravimetric analysis characterized the ligand and the metal complexes. The elemental analysis reveals the metal: ligand stoichiometry for Ni(II) and Co(II) complexes are 1 : 1, while that of Fe(II) complex is also 1 : 1 with two water molecules. The XRD data can be indexed to monoclinic system for Ni(II) and Co(II) complexes, while orthorhombic system for Fe(II) complexes. The ligand and the metal complexes were also studied for their antibacterial and antifungal activity.

Key Words: X-ray crystallography, Fe(II), Co(II), Ni(II) complexes, Biological activity.

INTRODUCTION

Literature¹⁻⁴ survey on transition metal complexes with Schiff bases revealed that major contribution of the study is based on the aromatic carbonyls and aliphatic diamines. However, aromatic diamines are not used much for the preparation of corresponding ligands and their transition metal complexes. Synthesis of the Co(II) complex of the Schiff base derived from diamine and salicylaldehyde was initially done by Bigotto *et al.*⁵ to study the extended model systems for vitamin B₁₂. Later some Co(II) complexes were characterized as the oxygen carriers⁶. Despite the fact that synthesis work on *o*-phenylenediamine and salicylaldehyde with some transition metal has been studied, but no attempt has been made to elucidate the structure of the Fe(II), Co(II) and Ni(II) complexes with the help of X-ray, TGA, magnetic susceptibility, UV, IR, NMR studies.

In the past, we have concluded lattice parameter of Pd(II) and oxovanadium complexes and are reported in literature^{7, 8}. In the present paper, an attempt is made to synthesize Fe(II), Co(II) and Ni(II) complexes of ligands derived from salicylaldehyde and 5-nitrosalicylaldehyde with *o*-phenylenediamine and investigate their crystal structure and biological studies.

EXPERIMENTAL

All the chemicals, solvents and reagents used were of LR grade. The ligand L₁ [N,N'-bis-(2-hydroxy benzylidene)-1,2-benzenediamine] and ligand L₂ [N,N'-bis-(2-hydroxy-5-nitrobenzylidene)-1,2-benzenediamine] were synthesized by treating salicylaldehyde and 5-nitrosalicylaldehyde with *o*-phenylenediamine respectively. The precipitate obtained was washed with methanol and dried in an oven at 60°C. The Schiff base was recrystallized using methanol.

The metal complexes were synthesized by using ethanolic solution of the ligand with aqueous metal solution; the complexes obtained were filtered, washed with a methanolic solution and dried in an oven at 60°C. The elemental analysis was carried out by reported methods⁹ (Table-1). The complexes were examined for solubility using various polar and non-polar solvents. Molar conductivity of ligand and metal complexes was recorded using 5×10^{-3} M solution in nitrobenzene on Toshniwal conductivity meter. The electronic absorption spectra of complexes were recorded in the UV-Visible region using tetrahydrofuran as solvent on UV-Visible 2100 spectrophotometer supplied by M/s Shimadzu Corporation while IR spectra were recorded on FTIR-4200 supplied by M/s Shimadzu Corporation using KBr pellets. The magnetic susceptibility measurements were made on Gouy's balance. The NMR spectra for the ligand and the metal complexes were recorded on VXR-300S Varian spectrophotometer. TGA-DTA analysis was carried out for the metal complexes on STA-92 Setaram TG-DTA Instrument. The X-ray diffractogram was recorded on XRD diffracto-

TABLE-I
ANALYTICAL DATA OF LIGANDS AND METAL COMPLEXES

Complexes (Colour)	M (%)	Molar cond. $\times 10^{-3}$ siemens	Magnetic moment (B.M.)	Charge transfer bands (cm^{-1})	$\nu(\text{—OH})$ (cm^{-1})	$\nu(>\text{C}=\text{N})$ (cm^{-1})	D_{cal} (g/cm^3)	Temp range (°C)
L ₁ (C ₂₀ H ₁₆ N ₂ O ₂) (Orange)	—	3.76	—	—	3050 (s)	1620 (s)	—	—
L ₁ (C ₂₀ H ₁₄ N ₄ O ₆) (Yellow)	—	4.85	—	—	3100 (s)	1630 (s)	—	—
FeL ₁ ·2H ₂ O (Brown)	15.48 (15.76)	12.08	0.98	24937	3010 (w)	1610 (s)	1.1644	(i) 50–150 (ii) 150–350 (iii) 350–800
FeL ₂ ·2H ₂ O (Brown)	12.55 (11.26)	10.43	0.87	24420	3050 (w)	1610 (s)	1.4217	(i) 50–150 (ii) 150–350 (iii) 350–800
CoL ₁ (Brown)	15.93 (15.80)	10.20	3.01	25575	—	1610 (s)	1.3614	(i) 100–400 (ii) 400–650
CoL ₂ (Red)	12.95 (12.67)	9.16	3.38	26041	—	1610 (s)	0.9081	(i) 100–350 (ii) 350–700
NiL ₁ (Brick red)	16.25 (15.75)	11.64	0.98	21739	—	1610 (s)	1.0440	(i) 100–450 (ii) 450–550
NiL ₂ (Red)	12.55 (12.63)	9.68	1.20	21505	—	1615 (s)	1.3640	(i) 100–400 (ii) 400–550

gram 6000 using CuK_α radiation ($\text{CuK}_\alpha = 1.5418 \text{ \AA}$). The X-ray diffractograms were scanned in the 2θ range of $10\text{--}60^\circ\text{C}$.

RESULTS AND DISCUSSION

The results of all the above experimental findings are summarized in Table-1. The ligands L_1 and L_2 are yellow in colour having melting point 152 and 197°C respectively. The Fe(II), Co(II) and Ni(II) complexes derived from this Schiff base vary in their colour. The elemental analysis of Fe(II) complexes suggests metal : ligand stoichiometry as $1 : 1$ with two water molecules, while that of Co(II) and Ni(II) complexes is also $1 : 1$. This can be indicated by close agreement with the analytical data and theoretical molecular formula. The metal complexes are soluble in nitrobenzene and DMSO. The molar conductance value suggests that these complexes are non-electrolytic in nature.

The prominent features in the spectrum of the ligands are sharp and strong absorption bands at around $3100\text{--}3050$ and 1620 cm^{-1} , characteristic of $\nu(\text{—OH})$ and $\nu(>\text{C}=\text{N})$ respectively. However, the weak bands of $\nu(\text{—OH})$ are seen in the Fe(II) complexes at $3050\text{--}3010 \text{ cm}^{-1}$ suggesting the presence of water molecule. Thus absence of strong band of $\nu(\text{—OH})$ in the Fe(II) complexes indicates the involvement of —OH group in bond formation. Similarly, a shift in absorption band from 1620 cm^{-1} to lower frequency suggests the involvement of azomethine nitrogen in the coordination of the metal ion. Sreenivasulu and Reddy¹⁰ reported similar assignments to band appearing at around 1600 cm^{-1} in the Schiff base complexes. Critical examination of the spectra of ligands and their metal complexes in the far infrared region shows appearance of few but definite absorption bands. These new bands may be assigned to $\nu(\text{M—N})$ and $\nu(\text{M—O})$ stretching vibrations in the region $550\text{--}540 \text{ cm}^{-1}$ and $480\text{--}440 \text{ cm}^{-1}$ respectively. The infrared spectra of the ligands do not show any absorption in these regions. Nakamoto¹¹ has reported assignments of $\nu(\text{M—N})$ and $\nu(\text{M—O})$ in the same range.

The electronic absorption spectra of metal complexes display various $d\text{--}d$ transitions and charge transfer transitions in the UV-Vis region. Fe(II) complexes are brown in colour and exhibit a subnormal magnetic moment of 0.98 and 0.87 B.M. for $\text{FeL}_1 \cdot 2\text{H}_2\text{O}$ and $\text{FeL}_2 \cdot 2\text{H}_2\text{O}$ complexes respectively. The band pointed at 24937 cm^{-1} and 24420 cm^{-1} in the spectrum of $\text{FeL}_1 \cdot 2\text{H}_2\text{O}$ and $\text{FeL}_2 \cdot 2\text{H}_2\text{O}$ may be assigned to charge transfer transitions. On the colour, magnetic susceptibility data and spectral properties, low spin octahedral geometry can be assigned for Fe(II) complexes. Co(II) complexes of ligands L_1 and L_2 are red and brown in colour and exhibit a magnetic moment of 3.01 and 3.38 B.M. respectively. The Co(II) complexes exhibit bands at 25575 and 26041 cm^{-1} for CoL_1 and CoL_2 respectively, which can be assigned to charge transfer bands. Rai *et al.*¹² also observed high frequency band at 26100 cm^{-1} , which can be assigned to charge transfer transitions. Based on the above data, Co(II) complexes may be considered as crystals with distorted octahedral geometry. Ni(II) complexes of ligands L_1 and L_2 are brick red in colour and exhibit subnormal magnetic moments of 0.96 and 1.21 B.M. respectively. The absorption spectrum of NiL_1 complexes shows an

absorption band at 21739, 26350 and 32258 cm^{-1} , while NiL_2 complexes show an absorption band at 21505, 28169 and 36363 cm^{-1} . The band appearing at 21739 and 21505 may be assigned to charge transfer bands. On the basis of magnetic susceptibility and electronic spectral data Ni(II) complexes may be assigned tetrahedral geometry. Dickson and Long¹³ have interpreted such observations in favour of tetrahedral Ni(II) complexes.

The proton NMR of Fe(II) , Co(II) and Ni(II) complexes were recorded using TMS as a reference in DMSO solvent. Spectra of ligands show multiple signals in the range of 6.94–7.67 ppm, which are characteristic signals for aromatic ring protons. The signals were integrated for 12 protons. The corresponding metal chelates also show a similar multiple signal with δ value in the range of 6.40–9.75 ppm. Similarly, signals at 8.92 and 12.96 ppm were assigned to $>\text{CH}=\text{N}$ and phenolic OH group respectively. The spectra of Ni(II) and Co(II) complexes do not show any proton signal corresponding to a phenolic OH. But the spectrum of FeL_1 and FeL_2 does show a signal at 12.97 and 10.26 ppm, which is due to the coordinated water molecule in the complexes. Thus, the PMR of metal complexes suggests that phenolic oxygen participates in coordination after complete deprotonation of phenolic group. The assignments to the aromatic proton and phenolic proton were supported by literature¹⁴.

The thermal behaviour of the metal complexes was studied by recording thermogravimetric plot (Fig. 1). It can be seen that for Fe(II) complexes

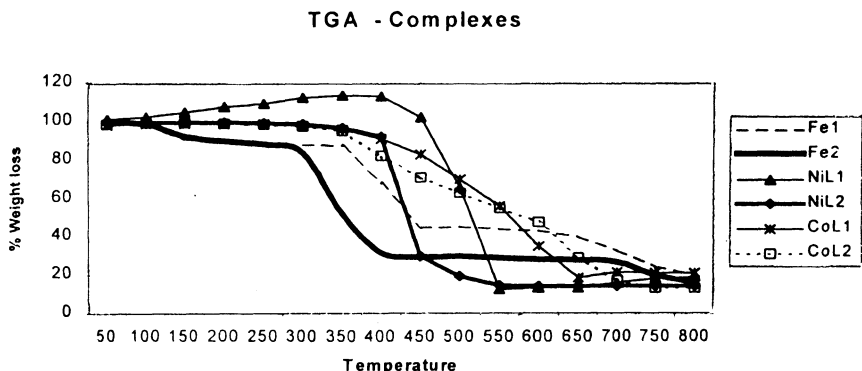


Fig. 1. TGA curves for the metal complexes

decomposition begins at 300–350°C and is completely decomposed at 800°C. The sudden weight loss at around 150°C is attributed to water molecules coordinated with Fe(II) complexes. In case of Co(II) and Ni(II) complexes decomposition begins at 450°C whereby Co(II) complexes are completely decomposed at 700°C while Ni(II) complexes are decomposed at 550°C. The percentage loss at decomposition temperature is in agreement with the calculated values. After decomposition metal oxide remains as residue.

In X-ray diffractogram of the complexes, major reflexes were measured and corresponding 'd' values were obtained using Bragg's equation. The independent indexing of major reflexes was carried out using least square method. The Miller

indices h, k, l were calculated and refined by using Back-cal program on computer. The complexes were successfully indexed to orthorhombic crystal system with $Z = 4$ for Fe(II) complexes, Co(II) and Ni(II) complexes exhibited monoclinic crystal system with $Z = 4$ for CoL₁ and $Z = 2$ for CoL₂ complexes and $Z = 4$ for Ni(II) complexes. Similar observations are reported in the literature^{15, 16}.

The lattice parameters along with 'd' values are summarized in Tables 2–7. The correctness of these values was confirmed by comparing the observed density with that calculated from the X-ray diffractogram. It may be concluded that Fe(II) complexes are low spin octahedral complexes, which crystallize in orthorhombic system with space group P_{222} . Co(II) complexes have distorted octahedral geometry which crystallize in monoclinic system with space group $P_{2/m}$ for CoL₁ complex and P_m for CoL₂ complex. Ni(II) complexes are tetrahedral complexes, which crystallize in monoclinic system with space group $P_{2/m}$. The space groups were assigned to the complexes as specified in the literature^{17, 18}.

TABLE-2
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR FeL₁

a (Å) = 9.9689 ± 0.0198	Volume (Å) ³ = 2314.1740
b (Å) = 17.2443 ± 0.1110	D_{cal} (g/cm ³) = 1.1644
c (Å) = 13.4616 ± .03273	D_{obs} (g/cm ³) = 1.2086
Std. Deviation = 0.58%	% Porosity = 2.25%
$\alpha = 90^\circ$	$Z = 4$
$\beta = 90^\circ$	Crystal system = orthorhombic
$\gamma = 90^\circ$	Space group = $P_{222} - D_{1/2}$

I/I ₀	D _{obs}	D _{cal}	h	k	l
51	5.8761	5.8689	1	2	1
39	4.0931	4.0918	1	0	3
100	3.3335	3.3229	3	0	0
41	3.0085	3.0085	3	2	1
37	2.9801	2.9801	3	0	2
23	1.9291	1.9291	2	3	6
23	1.7665	1.7665	3	3	6

The literature survey of the antimicrobial activity of Schiff bases is well known for their pronounced biological activity^{19, 20} and their metal complexes have shown that many of them are useful as bactericides and fungicides against various bacteria and fungi. These compounds were screened against various pathogenic microorganisms, viz., *Staphylococcus aureus* 209P, *E. coli* ESS 2231, *Aspergillus fumigatus*, *Candida albicans*, *Candida albicans* ATCC 10231, *Candida krusei* GO3 and *Candida glabrata* HO5. The screening was performed by using solutions of the compounds prepared in 10% DMSO in methanol. The concentrations of the compounds employed for the screening were 250 µg/mL (50 µL per well/disc). The standard agar well diffusion assay method²¹ was used for the screening. The control used for the screening was flucanazole.

TABLE-3
CELL DATA AND CRYSTAL LATTICE PARMETERS FOR CoL₁

a (Å) = 8.6065 ± 0.0117	Volume (Å) ³ = 1818.79
b (Å) = 20.2815 ± 0.0836	D _{cal} (g/cm ³) = 1.3614
c (Å) = 10.61436 ± 0.0389	D _{obs} (g/cm ³) = 1.2784
Std. deviation = 0.44%	% Porosity = 6.49%
α = 90°	Z = 4
β = 100.99°	Crystal system = monoclinic
γ = 90°	Space group = P _{2/m} - C _{1/2h}

I/I ₀	D _{obs}	D _{cal}	h	k	l
38.41	7.8070	7.7990	1	1	0
100.00	4.9418	4.9527	1	3	1
66.73	4.2101	4.2038	2	0	1
97.20	3.7906	3.8004	1	2	-2
25.71	3.5140	3.5051	1	3	-2
43.82	2.6426	2.6382	0	5	3
41.98	2.3113	2.3113	3	4	-1
36.68	2.2983	2.3007	3	0	-2
27.16	1.9688	1.9707	4	1	3

TABLE-4
CELL DATA AND CRYSTAL LATTICE PARMETERS FOR NiL₁

a (Å) = 8.9938 ± 0.0195	Volume (Å) ³ = 2369.0240
b (Å) = 20.5700 ± 0.0955	D _{cal} (g/cm ³) = 1.044
c (Å) = 13.2995 ± 0.0510	D _{obs} (g/cm ³) = 1.2926
Std. deviation = 0.83%	% Porosity = 19.23%
α = 90°	Z = 4
β = 105.68°	Crystal system = monoclinic
γ = 90°	Space group = P _{2/m} - C _{1/2h}

I/I ₀	D _{obs}	D _{cal}	h	k	l
4.03	8.6527	8.6597	1	0	0
100.00	8.2886	8.2868	1	0	1
6.08	5.9808	5.9776	1	0	2
0.60	5.4419	5.4355	1	2	2
4.83	5.2668	5.2828	1	3	1
1.01	4.6599	4.6796	0	3	2
7.74	4.1568	4.1434	2	0	2
4.03	4.0352	4.0352	1	4	-1

TABLE-5
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR FeL₂

a (Å) = 9.9958 ± 0.02580	Volume (Å) ³ = 2315.6810
b (Å) = 17.2976 ± 0.06856	D _{cal} (g/cm ³) = 1.4217
c (Å) = 13.3878 ± 0.05717	D _{obs} (g/cm ³) = 1.3841
Std. deviation = 1.0%	% Porosity = 2.71%
α = 90°	Z = 4
β = 90°	Crystal system = orthorhombic
γ = 90°	Space group = P ₂₂₂ - D _{1/2}

I/I ₀	D _{obs}	D _{cal}	h	k	l
14	6.2695	6.2427	0	1	2
24	5.8761	5.8773	1	2	-1
100	5.0026	4.9997	2	0	0
26	3.5915	3.6348	2	2	-2
29	3.2020	3.1793	3	1	1
14	2.1749	2.1794	2	6	-3
14	2.0913	2.0875	1	8	1
17	1.9250	1.9281	5	2	1
14	1.6729	1.6737	0	5	7
14	1.5159	1.5139	4	9	-1
14	1.5014	1.5014	6	5	0
14	1.4761	1.4750	5	6	4

TABLE-6
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR CoL₂

a (Å) = 8.3018 ± 0.0335	Volume (Å) ³ = 1699.7630
b (Å) = 20.9121 ± 0.1065	D _{cal} (g/cm ³) = 0.9081
c (Å) = 10.3225 ± 0.0501	D _{obs} (g/cm ³) = 1.2334
Std. deviation = 0.99%	% Porosity = 26.37%
α = 90°	Z = 2
β = 102.85°	Crystal system = monoclinic
γ = 90°	Space group = P _m - C _{1/s}

I/I ₀	D _{obs}	D _{cal}	h	k	l
52.16	6.0809	6.0316	1	2	1
44.44	4.9052	4.9137	1	0	2
100.00	3.5339	3.5560	2	3	1
60.49	3.2753	3.2674	2	1	-1
46.95	2.9982	2.9965	2	1	3
100.00	2.0785	2.0774	1	8	3
66.39	2.0699	2.0740	1	6	4
35.12	1.9642	1.9665	2	9	2
35.12	1.5347	1.5362	5	3	0

TABLE-7
CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR NiL₂

a (Å) = 8.5098 ± 0.0141	Volume (Å) ³ = 2262.2790
b (Å) = 20.4441 ± 0.0404	D_{cal} (g/cm ³) = 1.3640
c (Å) = 13.7105 ± 0.0354	D_{obs} (g/cm ³) = 1.3339
Std. deviation = 0.43%	% Porosity = 2.25%
α = 90°	Z = 4
β = 108.52°	Crystal system = monoclinic
γ = 90°	Space group = P2 ₁ m - C ₁ /2h

I/I_0	D_{obs}	D_{cal}	h	k	l
100.00	8.1290	8.1047	1	0	1
27.59	6.3455	6.3507	1	2	1
45.80	5.1129	5.1110	0	4	0
29.75	4.3488	4.3500	1	1	3
24.50	4.0407	4.0523	2	0	2
94.03	3.3739	3.3719	2	2	3
29.75	3.0265	3.0257	2	0	-2
25.51	2.9141	2.9150	2	4	-1

The results of the screening are presented in Table-8. Two different types of bacteria, viz., *Staphylococcus aureus* 209P and *E. coli* ESS 2231 were used for determining the activity of ligands and metal complexes. It was seen that ligand L₁ and its iron complex, i.e., FeL₁ were active to *Staphylococcus aureus* 209P and *E. coli* ESS 2231, whereas ligand L₂ is active only to *E. coli* ESS 2231 type of bacteria but its cobalt and iron complexes were active to both types of bacteria.

TABLE-8
ANTIMICROBIAL IN VITRO TESTING OF LIGAND AND METAL COMPLEXES

Sr. No.	Sample code	<i>Staph. aureus</i> 209 p	<i>E. coli</i> ESS 2231	<i>Aspergillus fumigatus</i>	<i>Candida albicans</i>	<i>Candida albicans</i> ATCC 10231	<i>Candida krusei</i> GO3	<i>Candida glabrata</i> HO5
1.	L ₁	10	16	—	—	—	—	—
2.	L ₂	sl	11	—	17	—	—	—
3.	CoL ₁	—	—	15	20	24	22	11
4.	CoL ₂	11	13	—	—	18	—	—
5.	FeL ₁	12	16	—	—	18	—	—
6.	FeL ₂	sl	10	—	—	14	—	—
7.	NiL ₁	—	—	—	—	—	—	—
8.	NiL ₂	—	—	—	—	—	—	—
9.	Fluconazole 0.5 mg/mL	—	—	—	29h	25h	19	15
10.	10% DMSO in methanol	—	—	—	—	—	—	—

Five types of fungus, namely *Aspergillus fumigatus*, *Candida albicans*, *Candida albicans* ATCC 10231, *Candida krusei* GO3, *Candida glabrata* HO5 were used to determine the antifungal activity. It was seen that only ligand L₂ was active against *Candida albicans*. Cobalt complex of ligand L₁ was active towards all types of fungi. Co(II) complex of ligand L₁ was active to all type of fungi, while iron complex of ligands L₁, L₂ and cobalt complexes of ligand L₂ are also good antifungal agents. Nickel complexes of both the ligands were found to be inactive towards bacteria as well as fungus.

Conclusively, these coloured Fe(II), Co(II) and Ni(II) complexes are thermally stable as indicated by TGA. Orthorhombic system is assigned to Fe(II) complexes and monoclinic system assigned to Co(II) and Ni(II) complexes. All the complexes showed slight decrease in bacterial activity after complexation. The activity of some complexes seems to be positive as compared to ligands, when tested for antifungal activity. Ligands did not show any activity toward fungus. It can be clearly depicted from the results that all the complexes except Ni(II) were active toward *Candida albicans* ATCC 10231. The use of Fe(II) and Co(II) complexes as strong antifungal agents is recommended.

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