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Synthesis and Spectral Properties of Cobalt(II) and Nickel(II) Complexes Derived from Bidentate Schiff Bases

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The Schiff bases L_1 = [N,N′-bis(2-hydroxybenzylidene)-1,2 benzenediamine] and L_2 = [N,N′-bis(2-hydroxy-5-nitrobenzylidene)-1,2-benzenediamine] have been synthesized for its characteristic parameter. The syntheses of Co(II) and Ni(II) complexes of these Schiff bases have been done by precipitation technique. The coloured metal complexes were crystallized from the methanolic solution. These complexes exhibit 1 : 1 as metal to ligand stoichiometry, which is evident from its elemental analysis. Various spectroscopic techniques were used to characterize these complexes and the spectra are used to evaluate the spectral parameters. The probable structure of metal complexes was suggested based on these spectral findings. The metal complexes are further investigated for their applied analytical and biological applications.

Key Words: Schiff bases, Co(II), Ni(II), complexes, TGA studies.

INTRODUCTION

In recent years, series of differently constituted multidentate ligands which can coordinate to metal ions have been reported[1–4]. A literature survey reveals that Schiff base containing polyfunctional group can coordinate with transition metal ions. The co-ordination of metal to ligand depends on various parameters like temperature of solution, reagents, pH of solution, solvent media, etc. These factors subsequently decide about geometry of crystalline compounds. Transition metal complexes of nitrogen donor ligand have been a subject of current interest because of their biochemical significance[5–7]. Also transition metal complexes are found to catalyze many important chemical reactions involving unsaturated organic molecules. Co(II) and Ni(II) complexes of the tetradentate schiff base ligand are shown to have aromatic dimine dependent structural features have also been reported[8].

In this communication an attempt is made to investigate the ligantional properties of the Schiff bases and utility towards the coordination with Co(II) and Ni(II) ions. The metal complexes are characterized by various spectroscopic techniques and thermal methods.

EXPERIMENTAL

All the chemicals, solvents and reagents used for the synthesis were of LR grade. The ligands [N,N′-bis(2-hydroxybenzylidene)-1,2-benzenediamine] (L_1) and [N,N′-bis(2-hydroxy-5-nitrobenzylidene)-1,2-benzenediamine] (L_2) were synthesized by treating salicylaldehyde with *o*-phenylenediamine 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 with methanol.

The metal complexes were synthesized by mixing ethanolic solution of the ligand with aqueous metal solution, solid 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 methods[9]. 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. 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 experimental findings are summarized in Tables 1–3.

RESULTS AND DISCUSSION

The analytical parameters of ligands and metal complexes are given in Table-1. The complexes are stable at room temperature as indicated by isothermal heating experiments. The elemental analysis of metal complexes suggests 1 : 1, metal to ligand stoichiometry. This interpretation was further supported by determination of molecular weight of each complex. Literatures[8, 10, 11] reveal that Co(II) and Ni(II) coordinates with bidentate Schiff base ligand in 1 : 1 stoichiometry.

These complexes were examined for solubility in various polar and non-polar solvents. It was found that complexes are freely soluble in dimethylsulphoxide, nitrobenzene and tetrahydrofuran, while they are sparingly soluble in solvents like acetonitrile, ethanol, chloroform, methanol, carbon tetrachloride, benzene and ether. The molar conductivity value of the complexes in nitrobenzene is in the range of 9×10^{-3} to 11.64×10^{-3} Siemens. Literature[12–14] has reported the complexes with low molar conductance as non-electrolytes. The non-electrolytic nature of these complexes is in accordance with their solubility test in non-polar solvents.

The magnetic behaviour of the complexes was established by determining magnetic susceptibility using Guoy's method[15]. Ni(II) complexes of ligands L_1 and L_2 exhibit sub-normal magnetic moments of 0.96 and 1.21 B.M. respectively. Figgis[16] has reported the Ni(II) complexes with magnetic moments in such a range as a tetrahedral complex. Both the complexes are brick red to red in colour. The absorption spectrum of NiL_1 complex shows an absorption band at 21739, 26350 and 32258 cm^{-1}, while NiL_2 complex shows an absorption band at 21505, 28169 and 36363 cm^{-1}. The band appearing at 21739 and 21505 may be assigned to charge transfer bands. The band appearing at 26350 and 28169 cm^{-1} may be assigned to the different *d-d* transitions from the ground state. Due to strong delocalization of aromatic ring, charge transfer band appears with weak intensity. On the basis of magnetic susceptibility and electronic spectral data Ni(II) complexes may be assigned tetrahedral geometry. Dickson and Long[17] have interpreted such observations in favour of tetrahedral Ni(II) complexes.

The magnetic susceptibility of Co(II) complexes of ligands L_1 and L_2 is 3.01 and 3.38 B.M respectively. Sreenivasulu and Reddy[8] have reported such low magnetic moments for Co(II) complexes. These Co(II) complexes are red and brown in colour which are typical colour criteria for distorted octahedral geometry. 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.*[18] also observed high frequency band at 26100 cm^{-1}, which can be assigned to charge transfer transitions. The other *d-d* transitions appeared in the range 32000 cm^{-1}. The poor quality of electronic spectra prevents to assign *d-d* transitions with authenticity. These complexes may be considered as crystals with distorted octahedral geometry.

The salient features of infrared spectral findings are presented in Table-2. The spectra of ligands show broad absorption bands at 3100 cm^{-1} which can be assigned to ν(OH) stretching vibrations. This band is absent in corresponding Ni(II) and Co(II) complexes indicating that phenolic oxygen is involved in the complex formation. This is further supported by the appearance of ν(CO) stretching vibrations at lower frequency in the spectra of metal complexes. The Schiff base ligands exhibit ν(CO) stretching vibrations at around 1620 cm^{-1}. However these stretching vibrations appear at lower frequency in the range 1615–1610 cm^{-1}, which indicates the participation of azomethine nitrogen atom, in complex formation. Several authors[19, 20] have predicted lowering of ν(C═N) frequency during chelation. Critical examination of the spectra of ligands and their metal complexes in the far infrared region show appearance of few but definite absorption bands. These new bands may be assigned to ν(M—N) and ν(M—O) stretching vibrations in the range 540 and 440 to 480 cm^{-1} respectively. The infrared spectra of the ligands do not show any absorption in these regions. Nakamoto[21] has reported assignments of ν(M—N) and ν(M—O) in the similar range.

The proton NMR of Ni(II) and Co(II) complexes were recorded using TMS as a reference in DMSO solvent. Data related to various protons is summarized in Table-3. Each spectrum of ligand shows multiple signals in the range of 6.94 to 7.67 ppm, which are characteristic signals for aromatic ring protons. The signals were integrated for 12 protons. The corresponding metal chelates also show similar multiple signals with δ value in the range of 6.40 to 8.73 ppm. Similarly signals at 8.92 and 12.96 ppm were assigned to >CH═N and phenolic OH group respectively. The spectra of metal complexes do not show any proton signal corresponding to a phenolic OH range. Similar observation was made with respect

TABLE-1

ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/Complex	m.w.	m.p. (°C)	Colour	Stoichio-metry	Molar cond. × 10^{-3} (siemens)	Elemental analysis (%): Found (Calcd.)				Magnetic moment (B.M.)
						C	H	N	M	
$C_{20}H_{16}N_2O_2$	316.00	152	Orange	—	3.76	76.71 (75.94)	5.57 (5.06)	8.45 (8.86)	—	—
$C_{20}H_{16}N_4O_6$	408.00	197	Yellow	—	4.85	59.15 (58.82)	4.38 (3.92)	13.62 (13.72)	—	—
$NiC_{20}H_{14}N_2O_2$	372.71	285	Brick red	1 : 1	11.64	63.95 (64.38)	3.67 (3.75)	7.60 (7.51)	16.25 (15.75)	0.98
$NiC_{20}H_{14}N_4O_6$	464.71	>300	Red	1 : 1	9.68	52.24 (51.64)	2.75 (3.01)	13.28 (12.05)	12.55 (12.63)	1.20
$CoC_{20}H_{14}N_2O_2$	372.93	291	Brown	1 : 1	10.20	64.35 (64.38)	4.95 (3.75)	9.75 (7.50)	15.93 (15.80)	3.01
$CoC_{20}H_{14}N_4O_6$	464.93	>300	Red	1 : 1	9.16	50.89 (51.64)	2.85 (3.01)	12.75 (12.05)	12.95 (12.67)	3.38

TABLE-2

UV-VIS AND IR SPECTRAL DATA OF LIGAND AND COMPLEXES

Ligand/Complex	IR Spectral data (cm^{-1})					Electronic spectral data (cm^{-1}) ($\varepsilon = dm^3\ mol^{-1}\ cm^{-1} \times 10^4$) Assignments for *d-d* transitions			
	ν(—OH)	ν(>C═N)	ν(C—O)	ν(M—N)	ν(M—O)				
$C_{20}H_{16}N_2O_2$	3050	1620	1280	—	—	—	29851 (2.1)	37037 (2.7)	42553 (2.7)
$C_{20}H_{16}N_4O_6$	3100	1630	1300	—	—	—	29585 (1.7)	32258 (1.9) 33955 (2.1)	42372 (2.8)
$NiC_{20}H_{14}N_2O_2$	—	1610	1260	540	440	20725 (1.0) 21739 (1.0)	26350 (3.1)	32258 (2.0) 34246 (2.1)	—
$NiC_{20}H_{14}N_4O_6$		1615	1270	540	480	21505 (0.5)	28169 (1.5)	36363 (1.7)	46189 (2.1)
$CoC_{20}H_{14}N_2O_2$	—	1610	1240	540	450	—	25575 (1.7)	32000 (2.2)	47169 (3.4)
$CoC_{20}H_{14}N_4O_6$	—	1610	1270	540	450	—	26041 (3.3)	—	46948 (2.6)

TABLE-3

^{1}H NMR SPECTRAL DATA AND TGA DATA OF LIGAND AND METAL COMPLEXES

Ligand/Complex	^{1}H NMR spectral data (ppm)			TGA data for the complexes		
	δ (aromatic)	δ (CH=N)	δ (phenolic)	Temp. range (°C)	% Loss of mass	Probable assignments
$C_{20}H_{16}N_2O_2$	6.94–7.67 (12 H)	8.92 (2 H)	12.96 (2 H)	—	—	—
$C_{20}H_{16}N_4O_6$	6.31–8.78 (10 H)	8.82 (2 H)	10.29 (2 H)	—	—	—
$NiC_{20}H_{14}N_2O_2$	6.64–8.17 (12 H)	8.8 (2 H)	—	(I) 100–450 (II) 450–550	80.15 (79.96)	$Ni(L_1) \rightarrow NiO$
$NiC_{20}H_{14}N_4O_6$	6.41–8.75 (10 H)	8.99 (2 H)	—	(I) 100–400 (II) 400–550	85.32 (85.64)	$2[Ni(L_2)] \rightarrow Ni_2O$
$CoC_{20}H_{14}N_2O_2$	6.40–8.73 (12 H)	8.82 (2 H)	—	(I) 100–400 (II) 400–650	78.32 (79.91)	$Co(L_1) \rightarrow CoO$
$CoC_{20}H_{14}N_4O_6$	6.75–8.76 (10 H)	8.84 (2 H)	—	(I) 100–350 (II) 350–700	86.17 (85.61)	$2[Co(L_2)] \rightarrow Co_2O$

to ligand L_2 where phenolic OH was assigned to a singlet appearing at 10.29 ppm. The PMR of the metal complexes suggests that phenolic oxygen participates in coordination, after complete deprotonation. The assignments to the aromatic proton and phenolic proton were supported by literature[22].

The thermal behaviour and decomposition pattern of the metal complexes was established by recording TGA and DTA curves. These curves are reproduced in Fig. 1. It can be seen that the metal complexes are stable up to 200°C, as indicated by no weight loss during isothermal heating. It also suggests that compounds are anhydrous in nature. The nature of TGA curve indicates that Ni(II) and Co(II) complexes are decomposed gradually in one stage.

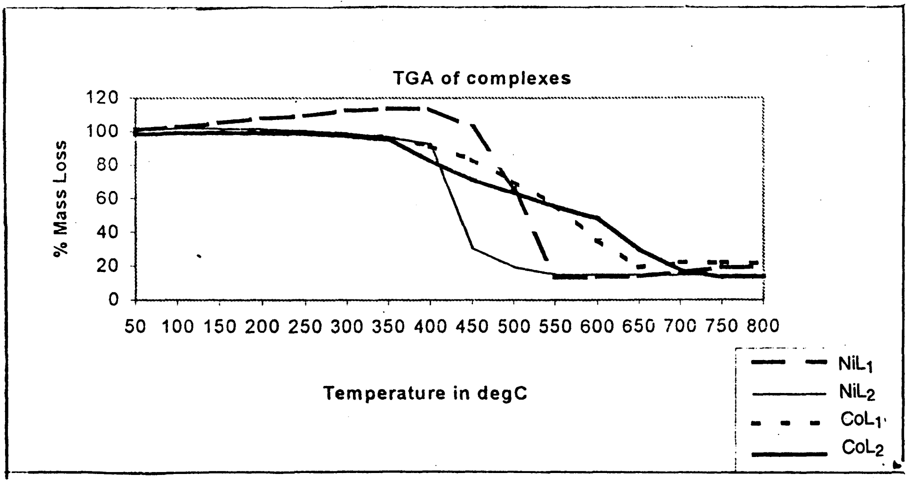
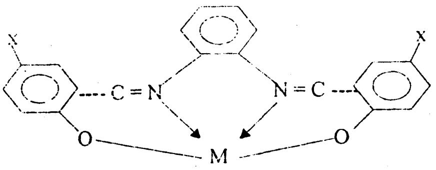


Fig. 1. TGA Traces for the Metal Complexes

The decomposition begins at around 450° and it is completely decomposed at 550°C, in case of Ni(II) complexes, while Co(II) complexes are decomposed at around 700°C. The percentage loss at decomposition temperature is in agreement with the calculated values. After decomposition metal oxide remains as a residue.

Conclusively these coloured Ni(II) and Co(II) complexes have tetrahedral or distorted octahedral geometry with good thermal stability. The complexes may be structurally depicted as follows. It is expected that these complexes may have better value towards biological activity.



Structure of metal complexes, where M = Ni(II), Co(II) and X = H, NO_2

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