

Synthesis and Spectroscopic Studies of Novel Transition Metal Complexes with Schiff Base synthesized from 1,4-bis-(*o*-aminophenoxy)butane and salicyldehyde

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ABSTRACT

The new Co(II), Cu(II), Ni(II) and Zn(II) complexes of potentially N₂O₂ Schiff base ligand [N,N'-bis(salicyldehydene)-1,4-bis-(o-aminophenoxy)butane] (H₂L) prepared from 1,4-bis-(o-aminophenoxy)butane and salicyldehyde in DMF. Microanalytical data, elemental analysis, magnetic measurements, ¹H nmr, ¹³C nmr, uv-visible and ir-spectra as well as conductance measurements were used to confirm the structures. In all complexes, H₂L behaves as a tetradentate.

INTRODUCTION

The salen ligand is a versatile, widely used ligand for homogeneous transition metal mediated catalysis. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. In the area of bioinorganic chemistry, interest in Schiff base complexes has centered on the role of such complexes in providing synthetic models for the metalcontaining sites in metallo-proteins and -enzymes. Schiff base ligands and their complexes derived from the reaction of derivatives of salicylaldehyde with amines have been extensively studied in great details for their various crystallographic, structural and magnetic features¹⁻¹⁰. The simple salen ligand is synthesized by the condensation of two equivalents of salicylaldehyde with one equivalent of ethylene diamine¹¹. Transition metal complexes of salen have been known since at least 1931¹¹⁻¹⁴. Schiff bases have often been used as chelating ligands in the field of coordination chemistry for obtaining thermotropic liquid crystalline polymers and their metal complexes have been of great interest for many years. These complexes have been used as radiopharmaceuticals for cancer targeting, as dioxygen carriers and as model systems for biological macromolecules. Some metal complexes containing Schiff base ligands play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architecture. One of the typical examples is

the study of the effect of lateral hydroxyl group on mesomorphism of azobenzene derivatives¹⁵⁻²³.

In the present paper, Co(II), Cu(II), Ni(II) and Zn(II) complexes with Schiff base derived from 1,4-bis-(*o*-aminophenoxy)butane and salicyldehyde are reported. These have been characterized on the basis of analysis of the solid complexes, elemental analysis, magnetic measurements, ¹H nmr, ¹³C nmr, uv-visible and ir spectra as well as conductance studies. As far as we know, this is the first report on this ligand.

EXPERIMENTAL

Materials and instruments

All the chemicals, such as the metal salts [Co(OAc)₂·4H₂O, Cu(OAc)₂·H₂O, Zn(OAc)₂·6H₂O and Ni(OAc)₂·6H₂O] and solvents were purchased from Merck and used without purification. Conductivities of 10⁻³ M solutions of the complexes were measured in DMF at 25°C using a conductivity hand-held Meter, LF 330. The electronic spectra of the complexes in uv-vis region were recorded in DMF solutions using Shimadzu Model 160 uv-visible Spectrophotometer. The ir spectra of the complexes were recorded with Midac 1700 instrument in KBr pellets. ¹H nmr spectra were recorded on a BRUKER DPX-400 High Performance Digital FT-NMR spectrometer in DMSO-d₆. Magnetic moments were determined on a Sherwood Scientific magnetic

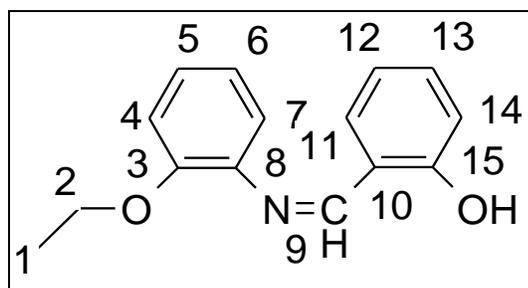
moment balance (Model N0: MK1) at room temperature (23°C) using Hg[Co(SCN)₄] as a calibrant: diamagnetic corrections were calculated from Pascal's constants²⁴. The elemental analyses were conducted on Carlo Erba instrument.

Synthesis of ligand [N,N'-bis(salicyldehyde)-1,4-bis-(*o*-aminophenoxy)butane]

A solution of salicyldehyde (20.00 mmol, 2.44 g) in 50 mL absolute ethanol was added dropwise over 2 hours to a stirred solution of 1,4-bis(*o*-aminophenoxy)butane (10.00 mmol; 2.72 g) dissolved in 50 mL warm absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol, ether and subsequently dried over anhydrous CaCl₂ in a desiccator. This ligand is little soluble in all common organic solvents, *viz.*, acetone, alcohol, benzene, etc. and soluble in polar organic solvents *viz.* DMF and DMSO. The yellow imines were purified by recrystallization from DMF-Absolute Ethanol, m.p. 264-266°C; yield: 4.13 g (86 %).

Spectral characterization of ligand

Characteristic ir bands (KBr cm⁻¹): 3058(arom. C-H), 2954 (aliph. C-H), 2705 (intramolecular hydrogen bonded -OH), 1614 (-C=N), 1255 (phen. C-O). Characteristic ¹H-nmr spectra (ppm, in DMSO-d₆): δ = 13.89 (s, 2H, -OH), δ = 8.72 (s, 2H, -HC=N-), δ = 7.39-6.90 (m, 16H, aromatic H), δ = 4.16 (t, 4H, J = 5.2 Hz, O-CH₂-), δ = 2.12 (p, 4H, J = 4 Hz, -CH₂-). Characteristic ¹³C-nmr spectra (ppm, in DMSO-d₆): δ = 26.4 (-CH₂-), δ = 68.2 (-OCH₂-), δ = 113.0, 117.4, 118.7, 119.4, 120.8, 127.9, 131.9, 132.8 (Aromatic), 161.6 (C=N).



Synthesis of Co(II), Cu(II), Ni(II) and Zn(II) complexes

A solution of metal acetate in DMF (2 mmol) was mixed with the Schiff base ligand in DMF (2 mmol, 0.96 g) in a 1:1 molar ratio. The contents were refluxed in 100 mL of DMF in an oil-bath for two to three hours. The refluxed solution was then poured into ice cold water when a colored solid separated out. The product was isolated by filtration, washed with ether, recrystallized from dimethyl sulfoxide and dimethyl formamide and dried over anhydrous CaCl₂ in vacuo at room-temperature. The yield was 73-86 % in all the complexes with respect to the ligand. They decompose at 219-300 °C and are almost insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they are slightly too fairly soluble in polar organic solvents (dimethyl sulfoxide and dimethyl formamide).

Spectral Characterization of complexes

Characteristic ir bands for Co(II) complex (KBr cm⁻¹): 3041 (arom. C-H), 2931 (aliph. C-H), 1610 (-C=N), 1244 (phen. C-O), 588 (M-N) and 457 (M-O). Characteristic ir bands for Cu(II) complex (KBr cm⁻¹): 3006 (arom. C-H), 2909 (aliph. C-H), 1606 (-C=N), 1244 (phen. C-O), 564 (M-N) and 456 (M-O). Characteristic ir bands for Ni(II) complex (KBr cm⁻¹): 3037 (arom. C-H), 2931, 2872 (aliph. C-H), 1609 (-C=N), 1234 (phen. C-O), 539 (M-N) and 487 (M-O). Characteristic ¹H-nmr spectra for Zn(II) (ppm, in DMSO-d₆): δ = 9.71 (s, 2H, -HC=N-), δ = 8.22-7.30 (m, 16H, aromatic H), δ = 4.38 (t, 4H, J = 4.1 Hz, O-CH₂-), δ = 2.36 (p, 4H, J = 4 Hz, -CH₂-). Characteristic ir bands for Zn(II) complex (KBr cm⁻¹): 3043 (arom. C-H), 2930, (aliph. C-H), 1623 (-C=N), 1243 (phen C-O), 564 (M-N) and 458 (M-O).

RESULTS AND DISCUSSION

Synthesis

The new Schiff base N,N'-bis(salicyldehyde)-1,4-bis-(*o*-aminophenoxy)butane (H₂L) was synthesized by the condensation of 1,4-bis-(*o*-aminophenoxy)butane²⁵ and salicyldehyde. The preparation of the above Schiff base is described by the scheme in Fig. 1.

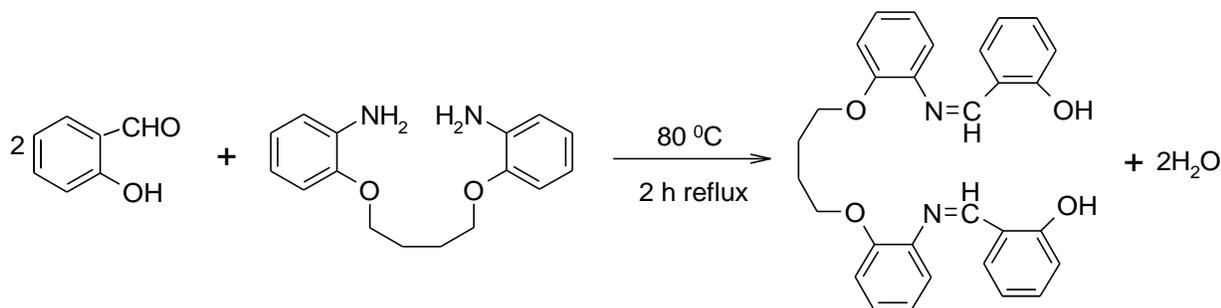
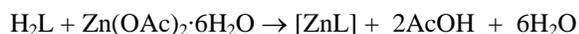
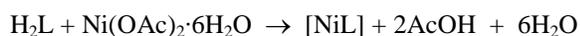
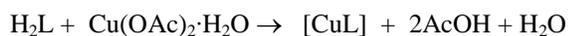


Fig. 1 Synthesis Scheme for the Preparation of the Ligand (H_2L).

Microanalytical, molar conductance and magnetic susceptibility data of the ligand and its complexes are given in Table 1. The stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductance measured in DMF of 10^{-3} M solutions of these complexes fall in the range $4.6\text{--}8.1\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ that indicates their non-electrolytic behaviour¹⁷⁻²³.

The reactions of the transition metal salts with the Schiff base are indicated by the following equations:-



The metal/ligand mole ratio was found to be 1:1 according to elemental analysis (Figure 2). The observed magnetic moment of Cu(II) complex, 1.3 B.M., suggested square planar stereochemistry of complex. The room temperature magnetic moments of the copper(II) complexes of tetra- and hexadentate ligands are paramagnetic with μ_{eff} values of 1.3-2.29 B.M., corresponding to the presence of one unpaired electron. There is a small but significant increase in magnetic moment due to an increased D_{4h} distortion²⁶.

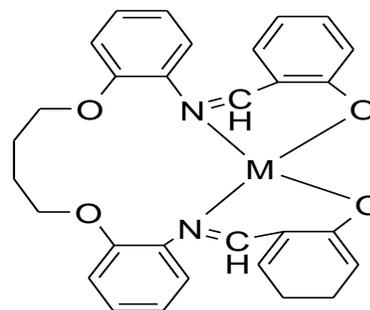


Fig. 2: Suggested structure of the tetrahedral Co(II), Ni(II) and Zn(II) and square-planar Cu(II) complexes of the ligand H_2L

The observed magnetic moment of Co(II) complex, 3.5 B.M., suggested tetrahedral stereochemistry of complex. The observed magnetic moment of Zn(II) complex, diamagnetic, suggested tetrahedral stereochemistry of complex. The observed magnetic moment of Ni(II) complex, 2.4 B.M., suggested tetrahedral stereochemistry of complex^{17-23, 27-30}. The complexes give fine powders and we could not manage to prepare single crystals to obtain appropriate X-rays data.

Ir spectra and uv-vis studies

The important features for the Schiff base and its complexes may be summarized as follows (Table 2):

Table 1

The Colours, Formulas, Formula Weight, Yields, Melting Points, and Elemental Analyses Results of the Ligand and the Complexes

Compounds	F.W.(g /mole)	M.pt. (° C)	Yield (%)	Elemental analyses (%)			μ_{eff} (B.M.)
				calculated	found		
				C	H	N	
Ligand (H ₂ L) (Yellow)	480.6	149-152	86.0	75.00	5.83	5.83	-
C ₃₀ H ₂₈ N ₂ O ₄				(75.50)	(5.30)	(5.70)	
[CoL] (Red)	536.9	>300	73.0	67.05	4.85	5.21	3.50
C ₃₀ H ₂₆ N ₂ O ₄ Co				(67.49)	(4.80)	(5.38)	
[CuL] (Red)	541.5	219	82.0	66.48	4.80	5.17	1.3
C ₃₀ H ₂₆ N ₂ O ₄ Cu				(66.00)	(4.50)	(5.10)	
[NiL] (Light brown)	536.7	>300	78.0	67.08	4.84	5.22	2.4
C ₃₀ H ₂₆ N ₂ O ₄ Ni				(67.50)	(4.80)	(5.10)	
[ZnL] (Yellow)	543.4	>300	78.0	66.25	4.79	5.15	Dia
C ₃₀ H ₂₆ N ₂ O ₄ Zn				(66.90)	(4.80)	(5.10)	

^aohm⁻¹ mol⁻¹ cm²(measured in 10⁻³ M solution in DMF).

The broad band that appeared in the ir spectrum of the Schiff base at 2705 cm⁻¹ is assigned to the stretching vibration of the intramolecular hydrogen bonded -OH in the molecule. Similar bands were observed at the same frequency in the ir spectra of salicylideneanilines. This band disappeared in the ir spectra of the complexes¹⁷⁻²³. The band at 1255 cm⁻¹ in the i-spectrum of ligand is ascribed to the phenolic C-O stretching vibration according to the assignment made by Kovacic³¹ in case of salicylideneanilines. This band is found in the region 1244-1234 cm⁻¹ in the ir-spectra of the complexes. These changes suggest that the *o*-OH group of this Schiff base moiety has taken part in complex formation. The

solid state ir spectra of the complexes compared with those of the ligand indicate that the C=N band, 1614 cm⁻¹, is shifted to lower values for complexes except for Zn(II)^{17-23, 27-30}. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 457-487 cm⁻¹ and 588- 539 cm⁻¹ assigned to (M-O) and (M-N) stretching vibrations that are not observed in the spectra of the ligand²⁷⁻³⁰.

The electronic spectra of all the complexes were recorded in 10⁻³ M DMF at room temperature. The absorption spectra of the Schiff base are characterized by two absorption bands in the region

275–395 nm. In the spectra of the Schiff-base ligand, the aromatic bands at 221–280 nm are attributed to a benzene $\pi \rightarrow \pi^*$ transition. The band at 450 nm is assigned to the imino $\pi \rightarrow \pi^*$ transition. The longer wavelength band is assigned to intramolecular charge transfer while the shorter wavelength is due to $\pi \rightarrow \pi^*$ transitions within the C=N bands influenced by CT interaction¹⁷⁻²³.

Magnetic properties

The Co(II), Cu(II) and Ni(II) complexes are paramagnetic and their magnetic moments are 3.50, 1.3 and 2.4 BM, respectively. Since the Co(II), Cu(II) and Ni(II) complexes are paramagnetic¹⁷⁻²³, their ¹H nmr spectra could not be obtained. The Zn(II) complex is diamagnetic and ¹H nmr spectra were obtained.

TABLE 2: Some ir frequencies (cm⁻¹) of Schiff base and Its complexes

Ligand (H ₂ L)	CoL	CuL	NiL	ZnL	Assignment
2705	-	-	-	-	Phenolic -OH (O—H [⋯] O)
1614	1610	1606	1609	1623	Central C=N stretching
1255	1244	1244	1635	1243	Phenolic C-O stretching
-	588	564	539	564	ν (M-N)
-	457	456	487	458	ν (M-O)

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