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Synthesis and Characterization of Metal Complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with Tetradentate Schiff Bases

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4-(Benzeneazo)salicylaldehyde was synthesized with aniline, sodium nitrite and salicylaldehyde. Two tetradentate ligands, N,N′-bis[4-(benzeneazo) salicylaldehyde]-o-phenylenediamine (H_2L) and N,N′-bis[4-(benzeneazo) salicylaldehyde]ethylenediamine (H_2L') were formed by the 2:1 molar condensation of 4-(benzeneazo) salicylaldehyde with o-phenylenediamine or ethylenediamine. Their Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) complexes were synthesized and characterized by elemental analysis, molar conductivity measurements, and infrared and electronic spectral data. Two ligands and their Ni(II) and Zn(II) complexes were further identified using ^{1}H NMR spectra. The results suggest that the metal is bonded to the ligand through the phenolic oxygen and the imino nitrogen.

Key Words: Synthesis, Tetradentate Schiff Base, Metal Complex, Characterization.

Introduction

Tetradentate Schiff bases with a N_2O_2 donor atom set are well known to coordinate with various metal ions, and this has attracted the interest of many authors[1−12]. Complexes of Schiff base ligands have been studied for their dioxygen untake[13] and oxidative catalysis[14]. Furthermore, complexes of transition metals(II), which involve derivatives of salicyldhyde and diamine, have received considerable attention. This is because of their potential as catalysts for the insertion of oxygen into an organic substrate[15−18].

The reaction of tetradentate Schiff bases derived from salicylaldehyde and diamine has been the subject of many studies[1−9]. The present study aimed to investigate the reaction of 2 tetradentate Schiff bases derived from the condensation of 4-(benzeneazo) salicylaldehyde with o-phenylenediamine or ethylenediamine with copper, nickel, zinc, cobalt, manganese and cadmium ions. The prepared ligands and complexes were characterized by elemental analysis, molar conductivity measurements, and infrared and electronic spectral data. Two ligands and their Ni(II) and Zn(II) complexes were further identified using ^{1}H NMR spectra.

Experimental

All reagents used were chemically pure or analytical reagent grade. C, H and N analysis data were obtained using a Perkin-Elmer 240B elemental analysis instrument. Copper, nickel, zinc, cobalt, manganese and cadmium were determined by EDTA titration. All conductivity measurements were performed in absolute dimethylformamide (DMF) using a Shanghai DDS-11A conductivity apparatus at 25 °C the concentration of the solution was 10^{-3} mol L^{-1}. Melting points were obtained using a Beijing X_4 microscopic melting point apparatus. Infrared spectra were measured in KBr pellets on a Shimadzu FTIR-8400 spectrophotometer in the range 200-4000 cm^{-1}. Electronic spectra from 200 to 800 nm were determined in DMF on a Perkin-Elmer Lambda 7 spectrophotometer. ^{1}H NMR spectra of Schiff bases and Ni(II) and Zn(II) complexes were recorded in deuterated dimethylsulfoxide using a Varian XL − 200 NMR spectrometer with TMS as internal standard.

Preparation of the ligands

A quantity of 0.05 mol of aniline was dissolved in 12 mL concentrated hydrochloric acid in a 250 mL 3–necked flask and cooled with ice water. Then 20 mL of a water solution of 4.0 g $NaNO_2$ was added dropwise to the above solution with stirring and the resulting mixture was reacted for 1 h at 0 °C. A solution of salicylaldehyde (0.05 mol) and anhydrous sodium carbonate (18 g) and water (150 mL) was added dropwise to the resulting solution with stirring and the resulting mixture was reacted for 4 h at 0 °C. The reaction mixture was acidated with hydrochloric acid. 4-(Benzeneazo) salicylaldehyde was precipitated out as light red solids. The reaction mixture was filtered. The crude product was recrystallized with ethanol. Yields $> 75‰$, m.p. 117-118 °C. Then 0.05 mol o-phenylenediamine or (ethylenediamine) was slowly added to a solution of 0.03 mol of 4-(benzeneazo) salicylaldehyde (in 30 mL ethanol). After refluxing the reaction mixture for 2 h, the precipitate was cooled and collected by filtration. The precipitate was washed several times using ethanol, followed by crystallization in ethanol and drying at 50 °C overnight. Yields $> 70‰$.

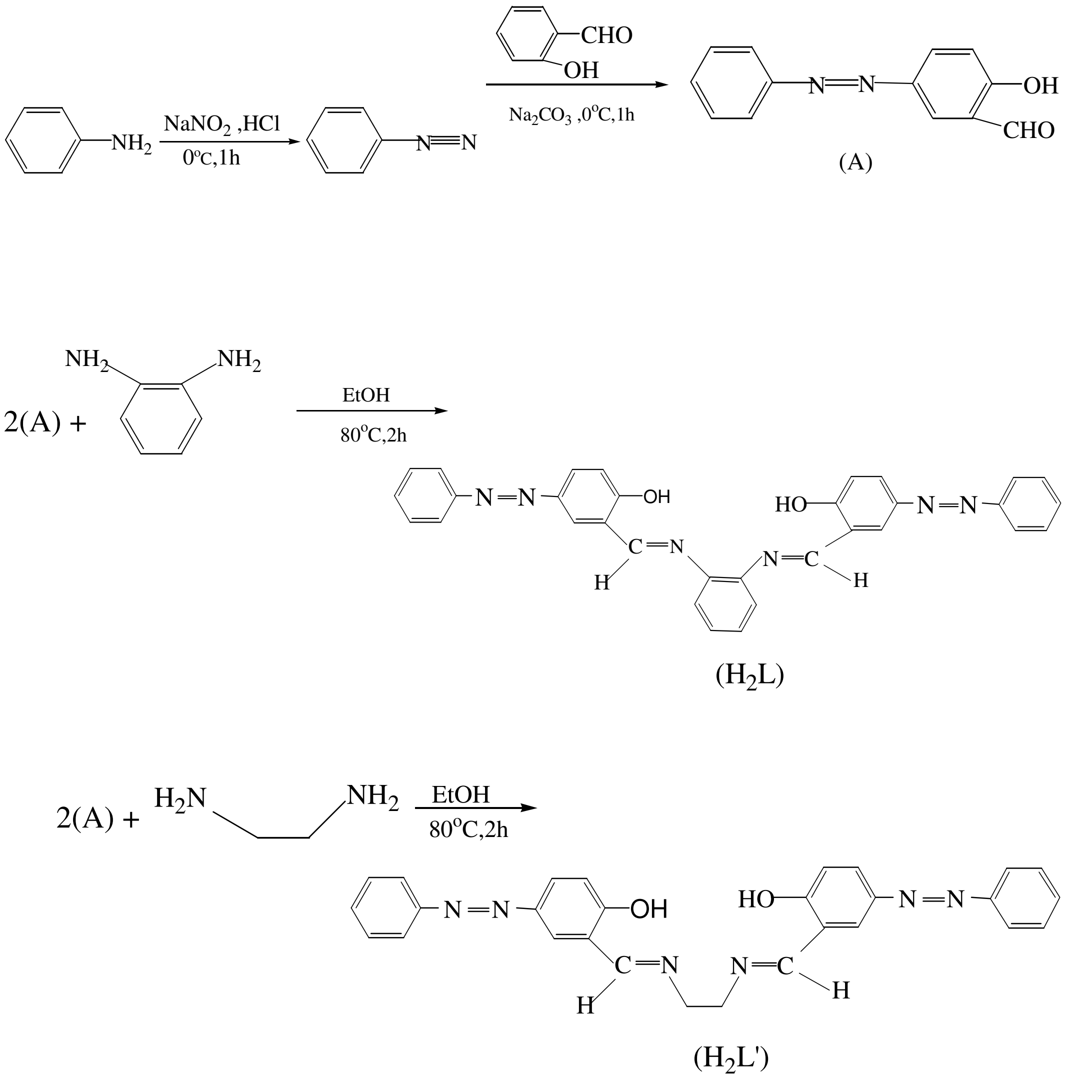
Preparation of the complexes

Cu(II), Ni(II), Zn(II), Co(II), and Mn(II) complexes were prepared by the addition of 1 mmol of $Cu(CH_3COO)_2.H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Co(CH_3COO)_2.4H_2O$, $Zn(CH_3COO)_2.2H_2O$, or $Mn(CH_3COO)_2.4H_2O$, which were dissolved in about 5-10 mL of water, into a hot ethanol solution of 1 mmol of the ligand. The mixture was then refluxed for 2 h. The precipitated solids were filtered off from the ice-cooled reaction mixture. The solids were washed with ethanol and then diethylether, followed by drying at 50 °C overnight.

Cd(II) complex was obtained in a similar way to the preparation of Cu(II), Ni(II), Zn(II), Co(II), and Mn(II) complexes described above. Cd(II) complex was prepared by the addition of 1 mmol $Cd(NO_3)_2$ and 2 mmol CH_3COONa, which were dissolved in 10 mL of water, into a hot ethanol solution of 1 mmol of the ligand.

Results and Discussion

Preparation of the ligands is represented in Scheme 1.



Scheme 1. Preparation of 2 ligands.

Reactions of (Cu-, Ni-, Zn-, Co- and Mn acetate) with tetradentate Schiff base ligands H_2L and H_2L' in 1:1 molar ratio in ethanol are represented in Scheme 2.

$$M(CH_3COO)_2 + H_2L(H_2L') \xrightarrow[2h]{EtOH,80^{o}C} ML(ML') + 2CH_3COOH$$

Scheme 2. Reaction of (Cu-, Ni-, Zn-, Co- and Mn acetate) with tetradentate Schiff base ligands.

The reaction of $Cd(NO_3)_2$ with tetradentate Schiff base ligand H_2L and CH_3COONa in 1:1:2 molar ratio in ethanol is represented in Scheme 3.

$$Cd(NO_3)_2 + H_2L + 2CH_3COONa \xrightarrow[2h]{EtOH,80^{o}C} CdL + 2NaNO_3{+}CH_3COOH$$

Scheme 3. Reaction of $Ca(NO_3)_2$ with tetradentate Schiff base ligand H_2L.

The complexes are air-stable, non-hygroscopic, colored solids, insoluble in water, partly soluble in ethanol and methanol, and soluble in DMSO and DMF. Decomposition occurs with conc. nitric acids, and the resultant solution was used after suitable dilution for metal analysis. The elemental analysis data of the Schiff bases and their complexes (given in Table 1) are consistent with the calculated results from the empirical formula of each compound. The results of molar conductivity measurements (Table 1) suggest that all compounds are non-electrolytes in DMF[19].

Table 1. Analytical data and some physical properties of the Schiff bases and their complexes.

Formula		Color	Yield (%)	Found (Calcd)%				Conductivity Cohm^{-1}.cm^{2}.mol^{-1}
				C	H	N	M	
H_2L	$C_{32}H_{24}N_6O_2$	Orange	85.6	73.15 (73.26)	4.62 (4.61)	16.00 (16.03)		
CuL	$C_{32}H_{22}N_6O_2Cu$	Red	78.6	65.51 (65.57)	3.80 (3.78)	14.34 (14.34)	10.87 (10.84)	5.3
NiL	$C_{32}H_{22}N_6O_2Ni$	Red	76.5	66.08 (66.12)	3.83 (3.82)	14.45 (14.46)	10.12 (10.10)	4.5
ZnL	$C_{32}H_{22}N_6O_2Zn$	Yellow	68.3	65.33 (65.37)	3.78 (3.77)	14.29 (14.30)	11.14 (11.12)	7.8
CoL	$C_{32}H_{22}N_6O_2Co$	Dark brown	65.5	66.06 (66.09)	3.81 (3.81)	14.44 (14.46)	10.14 (10.13)	6.1
MnL	$C_{32}H_{22}N_6O_2Mn$	Yellow	61.4	66.51 (66.55)	3.83 (3.84)	14.53 (14.56)	9.54 (9.51)	8.8
CdL	$C_{32}H_{22}N_6O_2Cd$	Red	60.1	60.65 (60.53)	3.48 (3.49)	13.22 (13.24)	17.75 (17.70)	12.3
H_2L'	$C_{28}H_{24}N_6O_2$	Orange	82.7	70.65 (70.57)	5.11 (5.08)	17.62 (17.64)		
CuL’	$C_{28}H_{22}N_6O_2Cu$	Green	75.3	62.47 (62.50)	4.12 (4.12)	15.61 (15.62)	11.82 (11.81)	5.8
NiL’	$C_{28}H_{22}N_6O_2Ni$	Red	70.4	63.07 (63.07)	4.15 (4.16)	15.75 (15.77)	11.03 (11.01)	4.7
ZnL’	$C_{28}H_{22}N_6O_2Zn$	Yellow	63.2	62.25 (62.29)	4.10 (4.11)	15.53 (15.57)	12.12 (12.11)	11.3
CoL’	$C_{28}H_{22}N_6O_2Co$	Red	67.9	62.98 (63.04)	4.18 (4.16)	15.71 (15.76)	11.07 (11.05)	9.9
MnL’	$C_{28}H_{22}N_6O_2Mn$	Dark brown	59.3	63.37 (63.51)	4.17 (4.19)	15.79 (15.88)	10.41 (10.38)	13.3

Infrared spectra

In general, the ligands exhibited very similar IR features (Table 2). A strong ligand band (for H_2L and H_2L') at about 1280 cm^{-1} has no corresponding bands in the metal chelates, and is assigned to hydrogen-bonded O–H in-plane bending vibration (Figure 1). This assignment is supported by the disappearance of the band when the hydroxy hydrogen is replaced by a metal[7,20,21]. The IR spectra of the ligands also showed a broad and a weak band in the region 2800–2700 cm^{-1}, which confirms the intramolecular hydrogen–bonded OH[7,20,21].

Table 2. IR spectral data of the Schiff bases and their complexes

Compound	$\mathrm{v}_{(C=N)}$		$\mathrm{v}_{(C+C)}$		v(phenolic C-O)	v(M-N)	v(M-O)
H_2L	1605	1587	1497	1460	1281		
CuL	1625	1583	1521	1470	1263	521	439
NiL	1620	1587	1526	1465	1265	542	412
ZnL	1615	1588	1523	1460	1258	505	410
CoL	1610	1580	1523	1468	1261	536	413
MnL	1613	1580	1526	1472	1260	507	411
CdL	1608	1580	1528	1481	1271	509	416
H_2L'	1635	1582	1550	1492	1286		
CuL'	1622	1580	1529	1467	1250	526	445
NiL'	1610	1580	1530	1468	1258	536	419
ZnL'	1631	1581	1531	1466	1256	515	431
CoL'	1601	1580	1530	1445	1256	534	415
MnL'	1615	1575	1528	1443	1260	502	408

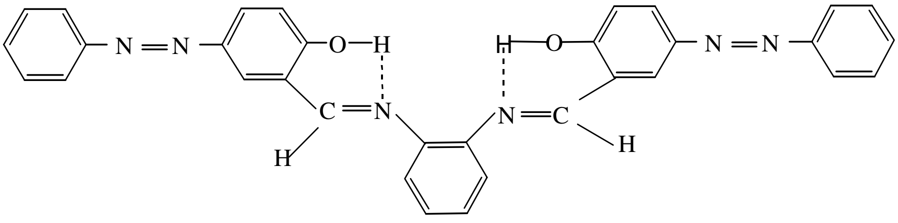


Figure 1. Structural representation of the hydrogen bonding.

The phenolic C–O stretching vibrations appeared at 1281 and 1286 cm^{-1} in the Schiff bases[22,23] under a shift towards lower frequencies (10–36 cm^{-1}) in the complexes (Table 2). This shift confirms the participation of oxygen in the C – O – M bond[24,25]. A strong band appeared at 1605 cm^{-1} in H_2L and 1635 cm^{-1} in H_2L'. This band can be assigned to the C=N stretching vibration[20,24]. In complexes of H_2L, C=N bands are shifted by 3-20 cm^{-1} to higher wave numbers. In complexes of H_2L', C=N bands are shifted by 4-34 cm^{-1} to lower wave numbers. These indicated the possibility of coordination of the imino nitrogen to metal ions. The ring skeletal vibrations (C=C) were consistent in all derivatives and unaffected by complexation.

In the low frequency region, the band observed in the complexes in the region 408-445 cm^{-1} was attributed to ν (M-phenolic O) and in the region 502-542 cm^{-1}was attributed to ν (M-N). All the IR data suggest that the metal was bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen[25,26].

^{1}H NMR spectra of the compounds

The ^{1}H NMR spectra of the compounds were obtained in d_6 – DMSO at room temperature using TMS as an internal standard. The ^{1}H NMR data and assignments of the compounds are presented in Table 3.

Table 3. ^{1}H NMR spectra of the Schiff bases and their complexes in d$_6$-DMSO (δ, ppm).

Compound	OH	Arom.H	C(H)=N	CH$_2$-CH$_2$
H_2L	10.2(S,2H)	7.4-8.2(m,2OH)	8.8(S,2H)	
NiL		7.3-8.3(m,2OH)	8.6(S,2H)	
H_2L'	10.7(S,2H)	7.2-8.2(m,2OH)	8.8(S,2H)	3.4(S,4H)
ZnL$'$		7.4-8.1(m,2OH)	8.7(S,2H)	3.4(S,4H)

*s=singlet, m=multiplet

The chemical shift observed for the OH protons in the ligands (10.2 ppm, 10.7 ppm) was not observed in any of the complexes. This confirms the bonding of oxygen to the metal ions (C-O-M). The same result was confirmed by the IR spectra.

The presence of a sharp singlet for the –C(H)=N proton in H_2L and H_2L' (8.8 ppm) clearly indicates that the magnetic environment is equivalent for all such protons, suggesting the presence of a planar ligand in these complexes[4]. The multiplets of aromatic protons appeared within the range 7.2–8.3 ppm and they were not affected by chelation. In ligand H_2L' and its complex, the proton peak of –CH$_2$ at 3.4 ppm was not affected by chelation.

Electronic spectra

The electronic spectra data of the Schiff bases and their complexes are summarized in Table 4. The spectra of the Schiff base H_2L exhibit 3 main peaks: at 258.0, 315.0 and 370.0 nm. The first and second peaks were attributed to benzene $\Pi - \Pi^*$ and imino $\Pi - \Pi^*$ transitions, respectively. The first band of MnL was shifted to a shorter wavelength (36 nm) along with an increase in its intensity. The first band of the other complexes of the Schiff base H_2L was not significantly affected by chelation. The second band of CuL and NiL was not significantly affected by chelation. The second band of ZnL, CoL, MnL and CdL was shifted to a shorter wavelength (12.5–46 nm). The third band in the spectra of H_2L (370 nm) was assigned to $n - \Pi^*$ transition. This band was shifted to a longer wavelength (11–36 nm) along with an increase in its intensity. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base H_2L to the metal ion (N→M)[5].

Table 4. Electronic spectra data of the Schiff bases and their compounds.

	$\lambda\,$max(ε, L/mol cm) in DMF		
H_2L	370.0(33050)	315.0(31000)	258.0(24000)
CuL	394.0(61050)	315.0(31500)	255.0(27500)
NiL	387.5(61050)	317.0(22500)	255.0(22000)
ZnL	404.5(48100)	302.5(30100)	258.0(24000)
CoL	400.5(53750)	279.0(30150)	258.0(25000)
MnL	406.0(65050)	295.0(30350)	222.0(30600)
CdL	446.0(27600)	381.0(37250)	299.0(23300)
			258.0(24500)
H_2L'	364.5(38200)	273.5(24050)	
CuL$'$	394.0(40350)	269.0(22450)	
NiL$'$	400.0(47350)	265.0(29300)	
ZnL$'$	374.5(45450)	266.0(23650)	
CoL$'$	401.5(52250)	266.0(36000)	
MnL$'$	397.0(43100)	268.0(37500)	

The spectra of the Schiff base H_2L' exhibit 2 main peaks: at 273.5 and 364.5 nm. The first peak was attributed to benzene $\Pi - \Pi^*$. This band was not significantly affected by chelation. The second band in the spectra of the Schiff base H_2L' (364.5 nm) was assigned to $n - \Pi^*$ transition. This band was shifted to a shorter wavelength (10–37 nm) along with an increase in its intensity. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base H_2L' to the metal ion (N→M)[5].

On the basis of the physical and spectral data of the Schiff bases and the complexes discussed above, one can assume that the metal ions are bonded to the Schiff bases via the phenolic oxygen and the imino nitrogen as illustrated in Figure 2.

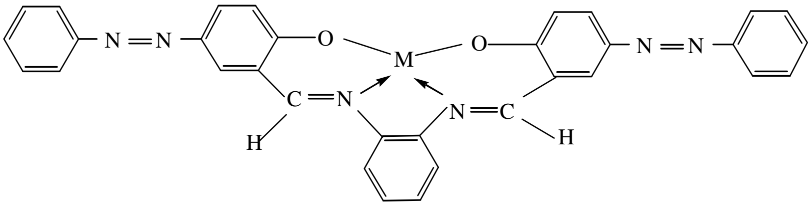


Figure 2. Structural representation of the Schiff base complexes, M=Cu, Ni, Zn, Mn or Cd.

Acknowledgments

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