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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis and Characterization of Metal Complexes with Unsymmetrical Tetradentate Schiff Base Ligand

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ABSTRACT

A new unsymmetrical tetradentate Schiff base ligand (H_2L) was synthesized using 5-chloro-2-hydroxybenzophenone, *o*-phenylenediamine, and salicylaldehyde. Five metal complexes of this ligand, $[ML]\cdot xH_2O$ ($M = Cu(II), Ni(II), Zn(II), Mn(II)$, and $Co(II)$; $x = 0-3$), have been prepared and characterized by elemental analyses, IR spectra, UV spectra, and molar conductance. Possible structures of these complexes have been proposed.

Key Words: Metal complexes; Schiff base ligand; Macrocycle model; Unsymmetric complex.

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INTRODUCTION

Symmetric tetradentate Schiff base complexes have been used extensively as macrocycle models,[1] while unsymmetric complexes are very important in biological systems and in industrial catalysis.[2,3] Recently, studies of some metal complexes with unsymmetrical Schiff bases derived form acetylacetone, ethylenediamine, and salicylaldehyde have been reported.[4,5] To continue the investigation in this area, a new unsymmetrical Schiff base ligand has been synthesized starting from 5-chloro-2-hydroxybenzophenone, *o*-phenylenediamine, and salicylaldehyde. Since this ligand dose not exist in the literature, this paper deals with the preparation and characterization of the complexes formed from this Schiff base ligand (see Fig. 1) with Cu(II), Ni(II), Zn(II), Mn(II), and Co(II).

EXPERIMENTAL

Reagents

All reagents used in this work were of analytical grade. 5-Chloro-2-hydroxybenzophenone was prepared by the reaction of benzoyl chloride with 4-chlorophenol in the presence of anhydrous aluminum trichloride.[4]

Preparation of Ligand

Mono-Schiff Base (HCBP-DABZ)

o-Phenylenediamine (18.50 g, 171 mmol) dissolved in 150 mL anhydrous ethanol was mixed with piperidine (1.50 g, 17.6 mmol), triethyl orthoformate (25.2 g, 170 mmol), and 5-chloro-2-hydroxybenzophenone (39.80 g, 171 mmol) and refluxed for 6 hr to give an orange–red precipitate. The pre-

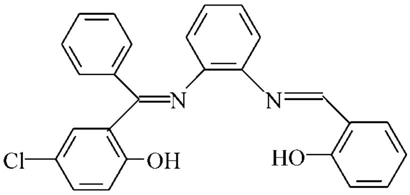

Figure 1. Structure of the ligand.

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cipitate was collected by filtration washed with ethanol and dried in a vacuum. Yield, 36.2 g (65.6%); mp: 193–194 °C.

Unsymmetrical Schiff Base (H_2L)

HCBP-DABZ (4.00 g, 12.4 mmol) dissolved in 150 mL methanol was mixed with salicylaldehyde (1.52 g, 12.4 mmol) and refluxed for 4 hr to give an orange–yellow precipitate. The precipitate was filtered, recrystallized with methanol, and dried in a vacuum. Yield, 4.24 g (80%); mp: 302–303 °C.

Preparation of Complexes

The unsymmetrical Schiff base (1.71 g, 4.0 mmol) dissolved in 60 mL *n*-butyl alcohol was mixed with the metal acetate (4.0 mmol) dissolved in 20 mL methanol and refluxed for 4 hr to give a precipitate. The precipitate was filtered, recrystallized from methanol, and dried in a vacuum. The purity of the complexes was higher than 99%.

Physical Measurement

Elemental analyses were carried out with a model 2400 Perkin–Elmer analyzer. The metal content was determined gravimetrically. The ultraviolet spectra were recorded on a Shimadzu UV-3000 spectrophotometer in DMSO. The molar conductance was measured with a Shanghai DDS-11A conductivity meter. Infrared spectra of the ligand and complexes were recorded in KBr pellets using a Bio-Rad FTS 165 spectrophotometer. Thermogravimetric measurements were made using a Perkin–Elmer TGA7 instrument. The heating rate was programmed to be $10\,^{\circ}\mathrm{C\,min^{-1}}$ with a protecting stream of N_2 flowing at a rate of $40\,\mathrm{mL\,min^{-1}}$. The mass spectrogram of the ligand was recorded on a Finnegan MAT-212 mass spectrometer.

RESULTS AND DISCUSSION

The synthesis reactions of the ligand are shown in Fig. 2.

The synthesis reaction of the complexes may be represented as shown below.

$$M(OAc)_2 \cdot nH_2O + H_2L \longrightarrow ML \cdot xH_2O + 2HOAc + (n - x)H_2O$$

The results of the elemental analyses and molar conductance data are shown in Table 1. The molar conductance values of the complexes measured

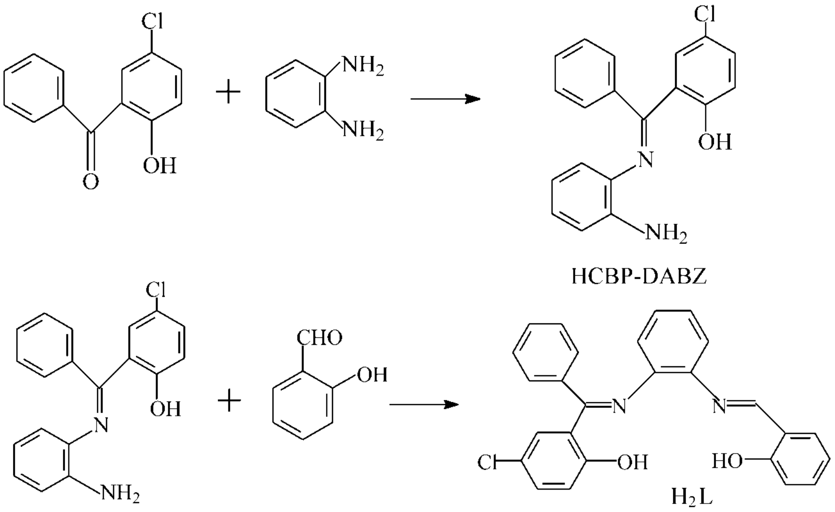

Figure 2. Preparation of the ligand.

in DMSO in $10^{-3}\,\mathrm{mol\,L^{-1}}$ solution fall in the range $8.29-18.6\,\mathrm{S\,cm^{2}\,mol^{-1}}$ indicating their non-electrolytic nature.[6] The complexes are stable in air and soluble in DMF and DMSO; however, they are insoluble in benzene, acetone, diethyl ether, and water.

Mass Spectra

The mass spectra of HCBE-DABZ and H_2L are shown in Fig. 3. The data of the molecular weights indicate that the reaction product (HCBE-DABZ) of 5-chloro-2-hydroxybenzophenone with 1,2-diaminobenzene is a mono-Schiff base and H_2L prepared from HCBE-DABZ and salicylaldehyde is an unsymmetrical di-Schiff base.

IR Spectra

The infrared spectra of the ligand and its complexes are shown in Table 2. The shift of $\nu(\mathrm{C{=}N})$ from $1630.4\,\mathrm{cm^{-1}}$ in the ligand to very strong absorption bands in the region $1602.7-1611.1\,\mathrm{cm^{-1}}$ in the complexes, suggests the formation of a C=N–M band system. The vibration $\nu(\mathrm{C{-}O})$ of H_2L occurs at $1209.1\,\mathrm{cm^{-1}}$. The shift to lower frequency by about $20\,\mathrm{cm^{-1}}$ in the metal

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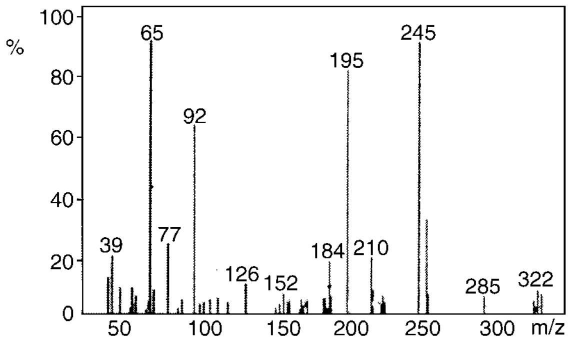
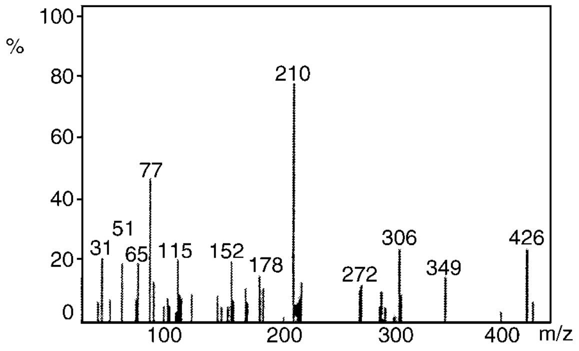
Table 1. Analytical and physical data of the ligand and its complexes.

Compounds	Empirical formula	Formula weight	Yields (%)	Color	D.p.[a] (°C)	Anal. found (calcd.) % C	H	N	M	Molar conductance ($S\,mol^{-1}\,cm^2$)
H_2L	$C_{26}H_{19}ClN_2O_2$	426.9	80	Orange	302[b]	73.27 (73.15)	4.17 (4.49)	6.86 (6.56)		
CuL	$C_{26}H_{17}ClCuN_2O_2$	488.4	76	Yellow	265	63.88 (63.94)	3.48 (3.51)	5.74 (5.74)	13.29 (13.01)	9.84
$[NiL] \cdot H_2O$	$C_{26}H_{19}ClN_2NiO_3$	501.6	72	Brownish red	235	62.08 (62.26)	3.78 (3.82)	5.57 (5.59)	11.68 (11.70)	16.7
$[ZnL] \cdot 3H_2O$	$C_{26}H_{23}ClN_2O_4Zn$	544.2	70	Yellow	240	57.04 (57.38)	4.05 (4.26)	4.93 (5.15)	11.84 (12.02)	18.3
$[MnL] \cdot H_2O$	$C_{26}H_{19}ClMnN_2O_3$	497.8	76	Brown	210	61.33 (62.73)	3.88 (3.85)	5.62 (5.63)	11.04 (11.04)	8.29
$[CoL] \cdot H_2O$	$C_{26}H_{19}ClCoN_2O_3$	501.8	69	Brown	223	62.27 (62.23)	3.79 (3.82)	5.58 (5.58)	11.75 (11.74)	20.6

[a] Decomposition point.
[b] Melting point.



Mass Spectrum of H_2L



Mass Spectrum of HCBP-DABZ

Figure 3. Mass spectra of unsymmetrical Schiff base and mono-Schiff base.

Table 2. Main IR bands of ligand and complexes (cm^{-1}).

Compounds	ν(O–H)	ν(C=N)	ν(C–O)	ν(O–M)	ν(N–M)
H_2L	3116.9 s	1630.4 s	1209.1 m		
CuL		1602.7 s	1180.6 m	420.25 w	539.36 w
$[NiL] \cdot H_2O$	3127.2	1611.1 s	1179.3 m	416.28 w	547.63 w
$[ZnL] \cdot 3H_2O$	3151.3 s	1610.7 s	1187.8 m	413.52 w	527.09 w
$[MnL] \cdot H_2O$	3151.7 s	1607.1 s	1195.4 m	447.46 w	542.52 w
$[CoL] \cdot H_2O$	3117.2 s	1605.6 s	1179.0 m	420.25 w	539.24 w

Table 3. UV spectra for ligand and complexes.

Compounds	λ_{max1} (nm)	$\varepsilon_1 \times 10^{-4}$ (L mol^{-1} cm^{-1})	λ_{max2} (nm)	$\varepsilon_2 \times 10^{-4}$ (L mol^{-1} cm^{-1})
H_2L	258	0.642	342	0.425
CuL	262	2.56	344	1.76
$[NiL] \cdot H_2O$	265	4.26	348	2.96
$[ZnL] \cdot 3H_2O$	263	3.25	346	0.682
$[MnL] \cdot H_2O$	262	0.983	348	0.334
$[CoL] \cdot H_2O$	266	2.55	349	1.66

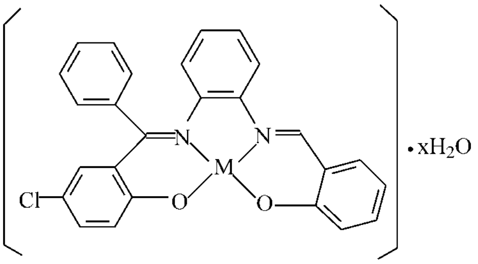
complexes indicates the coordination of oxygen to metal ions. In the spectra of the complexes, the occurrence of bands at 413–448 cm^{-1} (M–O) and 527–548 cm^{-1} (M–N) provides evidence for the bonding of oxygen and nitrogen to the central metal ion.[7] The spectra of the Ni(II), Zn(II), Mn(II), and Co(II) complexes exhibit a broad band at 3117.2–3157.1 cm^{-1}, which is attributed to ν(O–H) of the water molecules of crystallization.[8]

Electronic Spectra

The spectral data are shown in Table 3. The electronic spectra of the complexes in DMSO exhibit the same two spectral bands in the regions at 262–266 and 344–349 nm, which are also observed in the spectrum of the ligand.

Table 4. Thermal analysis data of the complexes.

Complex	Temperature range (°C)	Weight loss (%) by TG Found	Weight loss (%) by TG Calcd.	Assignment	Final products
CuL	265–343	83.38	83.71	–L	CuO
$[NiL] \cdot H_2O$	62–125	3.70	3.59	$-H_2O$	NiO
	235–370	81.41	81.52	–L	
$[ZnL] \cdot 3H_2O$	69–139	9.70	9.93	$-3H_2O$	ZnO
	240–409	75.38	75.11	–L	
$[MnL] \cdot H_2O$	65–128	3.68	3.62	$-H_2O$	MnO
	210–371	82.32	82.13	–L	
$[CoL] \cdot H_2O$	60–120	3.48	3.59	$-H_2O$	CoO
	223–395	81.39	81.48	–L	



M = Cu, x = 0; M = Ni, Mn, Co, x = 1; M = Zn, x = 3)

Figure 4. Suggested structure of the complexes.

Compared with the electronic spectrum of the ligand, there is a shift to lower frequency, which further testifies to the formation of complexes.

Thermal Decomposition Studies

The DTG-TG curves of the complexes were determined in a stream of N_2 at a flow rate of 40 mL min^{-1}. The thermal analysis data of the complexes are shown in Table 4. The Cu(II) complex gave a one-stage decomposition pattern, which corresponds to the loss of the ligand molecule. The other complexes decompose in two steps. The first decomposition step corresponds to the loss of water molecules. The fact that the water molecules were lost at a low temperature suggests that the water is crystal water. The second step corresponds to the loss of ligand molecule. In all cases, the final products are metal oxides. The total weight loss is in agreement with the composition of the complexes.

Finally, the results presented here clearly indicate that Cu(II), Ni(II), Zn(II), Mn(II), and Co(II) can from stable solid complexes with H_2L. The structure proposed for the complexes is shown in Fig. 4.

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