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Synthesis and Structural Studies of Bidentate Schiff Bases and Their Complexes with Cu(II), Ni(II), Co(II), Cd(II) and Zn(II)

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Novel Schiff bases prepared by condensation of substituted aniline with aldehydes as [NO] chelating bidentate ligands have been characterized by their elemental analysis, IR and electronic spectra. Their complexes of Cu(II), Ni(II), Co(II), Cd(II) and Zn(II) ions have been synthesized and characterized with the spectroscopic methods, magnetic susceptibility and elemental analysis. The results indicate that metal ions coordinate with azomethine nitrogen atoms and phenolic oxygen atoms of ligands. The mole ratio of ligands and metal ions in the complexes has been determined to be 2:1, according to the results of elemental analysis. All complexes have been considered in four coordinated configurations. While Cu(II) complexes had square-planar configuration, the others possessed tetrahedral geometries. The TG and DTA properties of compounds have been studied.

Key Words: Schiff bases, Salicylaldehydes, Transition metal complexes, Bidentate ligands, Charge transfer.

INTRODUCTION

Metal complexes of Schiff bases play an important role in the growth of coordination chemistry, presenting a large part of literature on synthetic and biochemical studies[1-8]. The synthesis, structure, spectral characterization and the coordination chemistry of Schiff base complexes have been studied extensively[9-14]. Schiff bases derived from salicylaldeydes are well known as polydentate ligands[15,16], coordinating in deprotonated or neutral forms. Schiff bases derived from salicylaldeydes have drawn considerable attention because of their similarity to the biological dioxygen carriers, as well as their potential as catalyst for the insertion of oxygen into organic substrates[17-19].

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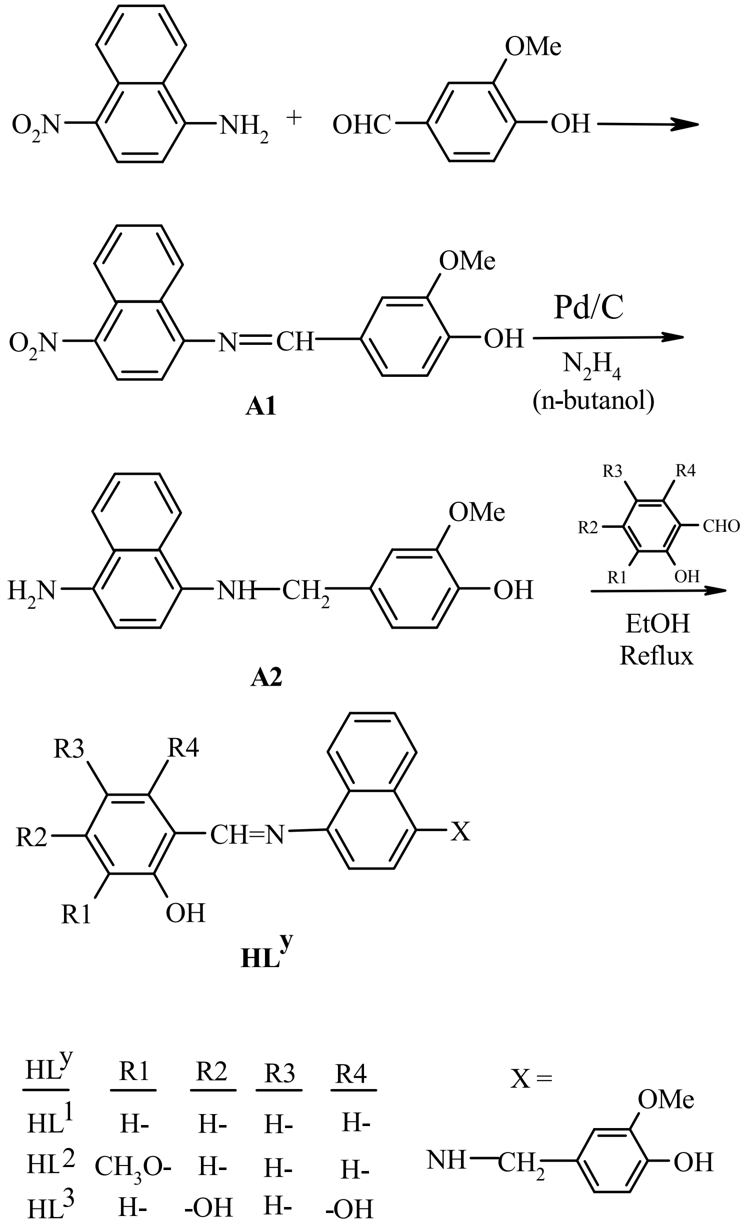
In this study, the syntheses and characterization of some Schiff base ligands condensed from aniline derivative and salicylaldehydes with a 1:1 ratio and their complexes with Cu(II), Ni(II), Co(II), Cd(II) and Zn(II) ions with a 2:1 ratio. The synthetic process for Schiff base ligands are shown in **Scheme-I**.



HL^y	R1	R2	R3	R4
HL^1	H-	H-	H-	H-
HL^2	CH_3O-	H-	H-	H-
HL^3	H-	-OH	H-	-OH

Scheme-I. Synthetic process for Schiff base ligands

EXPERIMENTAL

Metal salts were purchased from E. Merck and were used as received. Nitro naphthalene, hydroxylamine, vanillin, hydrazine hydrate (100 %), Pd/C (10 %), salicylaldehyde, *o*-vanillin and 2,4,6-trihydroxy benzaldehyde were obtained from Fluka. Solvents were of analytical grade and were purified by standard methods. Elemental analyses were performed using a Carlo Erba 1106 elemental analyzer. Infrared spectra were obtained using KBr discs (4000-400 cm^{-1}) on a Schimadzu 8300 FT-IR spectrometer. The electronic spectra in the 200-900 nm range were obtained on a Schimadzu UV-160 A spectrometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the compounds were determined in DMSO (*ca.* 10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter. Thermal analyses were performed on Shimadzu DTA and TG 50 H models using 10 mg samples. In all cases measurements were taken in air, within 25-800 ºC temperature range.

Synthesis of ligands

Synthesis of N-(4-nitro-1-naphthylamine)-1-hydroxy-2-methoxy-4-benzaldimine (A1): A solution of 4-nitro-1-naphthylamine (10 mmol, 1.88 g) in ethanol (50 mL), was added into a solution of vanillin (10 mmol, 1.52 g) in ethanol (50 mL) and heated to 80 ºC. The reaction mixture was stirred for 3 h, then was cooled to room temperature. The dark green precipated product was filtered and washed with hexane.

Synthesis of N-(4-nitro-1-naphthylamine)-1-hydroxy-2-methoxy-4-benzylamine (A2): A saturated solution of the compound **A1** (8 mmol, 2.578 g) in ethanol was prepared at 80 ºC. 1,0 g Pd/C (10 %) was added into solution. Finally, hydrazine hydrate 50 mL, 100 %) was added to the reaction flask dropwise at the same temperature. Reaction mixture was refluxed for 1.5 h, then cooled to room temperature. The mixture was filtered and the filtrate evaporated to eliminate EtOH. The dirty brown residue was extracted with $CHCl_3$. The extract was reduced *in vacuo* and cooled in a refrigerator at -10 ºC. The resulting light brown crystals were filtered off and washed with cold hexane.

Synthesis of Schiff base ligands: The Schiff base ligands HL^1, HL^2 and HL^3 were prepared with the same method as follows: the derivative of benzaldehyde (2 mmol) (salicylaldehyde for HL^1, *o*-vanillin for HL^2 and 2,4,6-trihydroxybenzaldehyde for HL^3) in absolute EtOH (20 mL) was carefully added with stirring, to a solution of freshly prepared A2 (2 mmol, 0.589 g) in absolute EtOH (20 mL), the resultant mixture was boiled under reflux for 3 h, then cooled to room temperature and was kept for 2-3 h. The solvent was evaporated *in vacuo* and the resulting product (brown for HL^1 and HL^2

and dark red for HL^3) was washed with cold ethanol and dried *in vacuo* (Tables 1-3 for yield, spectroscopic and elemental analysis results).

TABLE-1
IR SPECTRAL (cm^{-1}) BANDS OF SCHIFF BASES AND THEIR METAL COMPLEXES

Compound	ν(OH/H_2O)	ν(C-OH)[a]	ν(N-H)[b]	ν(C=N)	ν(CH_2)	ν(M-N)	ν(M-O)
A1	-	3380 m	-	1630 s	-	-	-
A2	-	3385 m	3035 m	-	2945 s	-	-
HL^1	-	3450 m	3045 m	1632 s	2938 m	-	-
$(L^1)_2Cu$	-	-	3110 s	1615 s	2925 s	473 s	433 s
$(L^1)_2Ni.H_2O$	3430 m	-	3125 s	1630 s	2930 w	485 s	431 s
$(L^1)_2Co$	-	-	3105 s	1621 s	2939 w	469 s	448 s
$(L^1)_2Cd$	-	-	3095 s	1628 s	2943 s	495 s	440 s
$(L^1)_2Zn.H_2O$	3473 m	-	3140 s	1619 s	2937 s	504 s	455 s
HL^2	-	3401 s	3036 w	1639 s	2921 m	-	-
$(L^2)_2Cu$	-	-	3120 w	1627 s	2938 m	481 s	438 s
$(L^2)_2Ni.H_2O$	3452 m	-	3141 m	1618 s	2923 s	462 s	443 s
$(L^2)_2Co.H_2O$	3464 m	-	3134 m	1629 s	2941 s	489 s	451 s
$(L^2)_2Cd$	-	-	3086 m	1613 s	2936 s	473 s	439 s
$(L^2)_2Zn.H_2O$	3442 m	-	3131 m	1623 s	2934 s	496 s	458 s
HL^3	-	3472 s	3051 m	1635 s	2931 m	-	-
$(L^3)_2Cu$	-	-	3108 m	1617 s	2926 s	471 s	434 s
$(L^3)_2Ni.H_2O$	3491 m	-	3133 m	1622 s	2933 w	482 s	445 s
$(L^3)_2Co.H_2O$	3494 m	-	3144 m	1626 s	2944 s	461 s	456 s
$(L^3)_2Cd$	-	-	3116 m	1615 s	2927 s	489 s	453 s
$(L^3)_2Zn.H_2O$	3496 m	-	3124 m	1610 s	2942 s	493 s	447 s

[a]The (C–OH) group at the *para* position; [b]These bands observed for both ligands and complexes because of $–NH–CH_2–$ group.

Synthesis of metal complexes: Solution of corresponding metal salts *i.e.*, (0.05 mmol) [$Cu(CH_3COO)_2{\cdot}H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Cd(CH_3COO)_2{\cdot}2H_2O$ and $Zn(CH_3COO)_2{\cdot}H_2O$] in EtOH (10 mL) was added to the solution of the ligand (0.05 mmol) (0.199 g for HL^1, 0.214 g for HL^2 and 0.215 g for HL^3) in EtOH (40 mL). The reaction mixture was stirred for 2 h at 80 ºC, then cooled to room temperature. The mixture was kept at room temperature for 1 d and the resulting solid was filtered. The complex was washed with cold ethanol and dried in a vacuum dessicator. The analytical and spectroscopic details of the Schiff bases and their metal complexes are presented in Tables 1-3.

TABLE-2
MAGNETIC MOMENTS, MOLAR CONDUCTANCE AND ELECTRONIC SPECTRA OF THE LIGANDS AND COMPLEXES

Compound	μ_{eff} (BM)	Λ_M (Ω^{-1} cm^2 mol^{-1})	λ (nm) ethanol			
			d-d	π-π* (with Me) d-π*[a]	π-π* (with CH=N) and n-π*[b]	π-π*
A1	-	1.4			390	296,287(sh),209
A2	-	1.1			361	307,284,261(sh)
HL^1	-	1.7			409,321	264,216,207(sh)
$(L^1)_2Cu$	1.89	8.9	631	384	336	241,216
$(L^1)_2Ni.H_2O$	3.08	7.1	685,571	470	314	236,210
$(L^1)_2Co$	3.90	7.8	614	371	336	291,224
$(L^1)_2Cd$	-	6.9		424	314	291,266,221
$(L^1)_2Zn.H_2O$	-	6.4		478	354	272,233,214(sh)
HL^2	-	1.8			428,364	236,218
$(L^2)_2Cu$	1.87	9.5	637	396	303	284,225
$(L^2)_2Ni.H_2O$	3.05	8.6	690,586	370		244,215
$(L^2)_2Co.H_2O$	3.86	8.4	621	383	319	221,208(sh)
$(L^2)_2Cd$	-	6.1		418	319	284,258,205
$(L^2)_2Zn.H_2O$	-	6.0		469	341	269,245,210
HL^3	-	1.9			474,381	286,271(sh),234
$(L^3)_2Cu$	1.83	8.7	644	396	384	281,231(sh)
$(L^3)_2Ni.H_2O$	3.10	7.3	665,581	389	321	266,209
$(L^3)_2Co.H_2O$	3.86	7.9	611	354	332	248,207
$(L^3)_2Cd$	-	6.2		422	367	282,236,208
$(L^3)_2Zn.H_2O$	-	6.3		477	388	294,235,212(sh)

[a] Sifted π-π* transition with Metal(II) and the charge transfer d–π* transition

[b] π-π* absorption with the chromophore –CH=N– group interactions have coincidence the n–π* transitions.

RESULTS AND DISCUSSION

Bidentate Schiff base ligands with NO donor sets were formed by the reactions of benzaldehyde derivatives and N-(4-nitro-1-naphthylamine)-1-hydroxy-2-methoxy-4-benzylamine (**A2**) (**Scheme-I**). Metal(II) complexes were synthesized from the free ligands and metal acetates. The analytical data for the ligands and complexes have been listed in Tables 1-3. Elemental analysis and spectral data show the formation of the bidentate Schiff base ligands. The results of elemental analysis seem to agree with the composition of the proposed complexes and support the fact that the mole ratio of Schiff base to the metal complexes is 2:1 as shown in Fig. 1. The analytical data of C, H and N lead to the postulate $(L)_2M{\cdot}xH_2O$ (x = 0 or 1) for all complexes (Table-3). Although the complexes show different solubility in polar organic solvents, all are soluble in DMF, DMSO, THF and dioxane. The conductivity

TABLE-3
ANALYTICAL AND PHYSICAL DATA OF THE LIGANDS AND COMPLEXES

Compound	m.f.	m.w.	Colour	Yield (%)	m.p. (ºC)	Elemental analysis (%)					
						C		H		N	
						Found	Calcd.	Found	Calcd.	Found	Calcd.
A1	$C_{18}H_{14}N_2O_4$	322.31	Dark green	78	186	67.10	67.07	4.5	4.4	8.66	8.69
A2	$C_{18}H_{18}N_2O_2$	294.34	Light brown	69	182	73.46	73.44	6.4	6.2	9.48	9.52
HL^1	$C_{25}H_{22}N_2O_3$	398.45	Brown	73	193	75.37	75.35	5.7	5.6	7.05	7.03
$(L^1)_2Cu$	$C_{50}H_{42}N_4O_6Cu$	858.43	Black	61	>250	69.97	69.95	4.9	4.9	6.55	6.53
$(L^1)_2Ni.H_2O$	$C_{50}H_{44}N_4O_7Ni$	871.58	Brown	64	>250	68.91	68.88	5.2	5.1	6.47	6.43
$(L^1)_2Co$	$C_{50}H_{42}N_4O_6Co$	853.81	Black	68	>250	70.36	70.33	5.1	5.0	6.58	6.56
$(L^1)_2Cd$	$C_{50}H_{42}N_4O_6Cd$	907.23	Black	63	>250	66.24	66.19	4.8	4.7	6.20	6.18
$(L^1)_2Zn.H_2O$	$C_{50}H_{44}N_4O_7Zn$	878.28	Brown	69	>250	68.39	68.37	5.1	5.0	6.41	6.38
HL^2	$C_{26}H_{24}N_2O_4$	428.47	Dark red	67	198	72.89	72.88	5.7	5.6	6.56	6.54
$(L^2)_2Cu$	$C_{52}H_{46}N_4O_8Cu$	918.48	Brown	58	>250	67.98	67.99	5.1	5.0	6.14	6.10
$(L^2)_2Ni.H_2O$	$C_{52}H_{48}N_4O_9Ni$	931.63	Black	63	>250	67.05	67.03	5.2	5.2	6.05	6.01
$(L^2)_2Co.H_2O$	$C_{52}H_{48}N_4O_9Co$	931.87	Black	64	>250	67.06	67.02	5.3	5.2	6.04	6.01
$(L^2)_2Cd$	$C_{52}H_{46}N_4O_8Cd$	967.33	Brown	62	>250	64.58	64.56	4.9	4.8	5.83	5.79
$(L^2)_2Zn.H_2O$	$C_{52}H_{48}N_4O_9Ni$	938.33	Brown	59	>250	66.59	66.55	5.2	5.2	5.97	5.97
HL^3	$C_{25}H_{22}N_2O_5$	430.45	Brown	69	191	69.78	69.75	5.3	5.2	6.55	6.51
$(L^3)_2Cu$	$C_{50}H_{42}N_4O_{10}Cu$	922.43	Dark brown	61	>250	65.14	65.10	4.6	4.6	6.13	6.08
$(L^3)_2Ni.H_2O$	$C_{50}H_{44}N_4O_{11}Ni$	935.58	Dark brown	66	>250	64.21	64.18	4.6	4.5	6.01	5.99
$(L^3)_2Co.H_2O$	$C_{50}H_{44}N_4O_{11}Co$	935.82	Black	68	>250	64.19	64.17	4.5	4.5	6.03	5.98
$(L^3)_2Cd$	$C_{50}H_{42}N_4O_{10}Cd$	971.28	Black	57	>250	61.84	61.82	4.5	4.4	5.81	5.77
$(L^3)_2Zn.H_2O$	$C_{50}H_{44}N_4O_{11}Zn$	942.28	Brown	65	>250	63.76	63.73	4.6	4.5	5.98	5.95

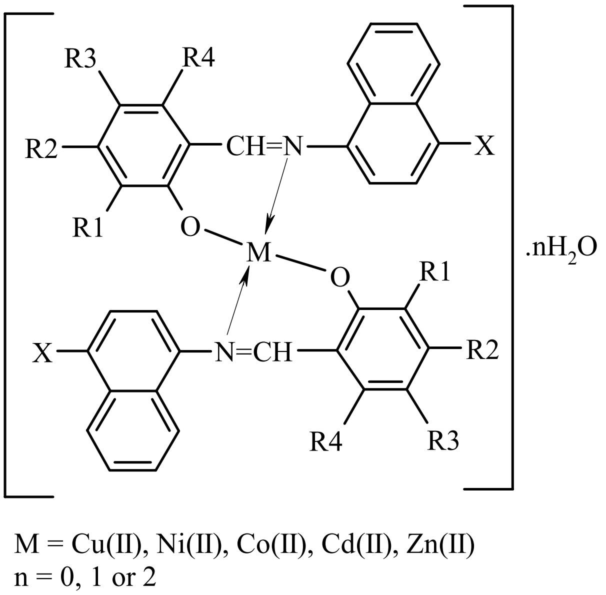


Fig. 1. Suggested structures of the complexes

data in DMSO in the 1.1-9.5 $\Omega^{-1}cm^2 mol^{-1}$ range indicate that all complexes are nonionic[20]. These results show that the ligands coordinate to the metal(II) ions to form neutral coordination compounds, accompanied by the release of the anions.

The infrared spectral data of the free ligands and their metal complexes are given in Table-1. The compound **A1** shows a strong ν(OH) band at 3380 cm^{-1}, indicating that there is a hydrogen bonding in the compound. It also shows a typical ν(C=N) band[21] at 1630 cm^{-1}. The compound **A2** prepared from **A1** with reduction shows a ν(N-H) band at 3030 cm^{-1} and a ν(CH_2) band at 2945 cm^{-1}. All free ligands (HL^1, HL^2 and HL^3) have strong, hydrogen-bonded ν(OH) bands at 3450, 3401 and 3472 cm^{-1}, respectively. The strong peaks observed for the free ligands in the 1640-1630 cm^{-1} region assignable to ν(C=N) bands and ν(CH_2) peaks at 2938, 2921 and 2031 cm^{-1}, which originally come from **A2**, indicate that the condensation between **A2** and the derivatives of salicylaldehydes has been successful. It can also be observed that ν(C=N) bands in the complexes are shifted to the lower energy regions about 10-20 cm^{-1} relative to those of the corresponding free ligands. This observation for the ν(C=N) bands in the complexes is indicative of the coordination of the azomethine nitrogens to the metal ions. In the complexes the bands at 504-461 and 458-431 cm^{-1} range can be assigned for the ν(M-N) and ν(M-O) modes[22-24].

The spectral data listed in Table-2 have been obtained in EtOH solutions for all compounds. The UV-Vis spectra of the ligands and the complexes show π-π* absorption bands at the region of 307-205 nm which can be accounted for the benzene rings[25]. π-π* absorption with the chromophore azomethine group interactions[26-28] show coincidence with the interligand π-π* transitions[29] between 474-303 nm. The intense bands at the range of 478-354 nm can be attributed to the shifted π-π* transitions due to metal ions[30] and the charge transfer d-π* transitions (ligand to metal or metal to ligand)[31].

The bands in the 690-570 nm range in all copper(II), nickel(II) and cobalt(II) complexes come from *d-d* transitions of the metal ions.

The *d-d* transition bands for Cu(II) ions with three ligands at 644-631 nm ranges suggest that Cu(II) ions have square-planar geometries[32]. The magnetic moments of the Cu(II) complexes (1.89, 1.87 and 1.83 BM, respectively) indicate the presence of one unpaired electron. This also suggests that Cu(II) ions have square-planar geometries[33].

For all the Ni(II) complexes, the results of *d-d* transitions in the range of 690-571 nm is consistent with distorted geometry from planar to tetrahedral metal configuration[34]. Owing to the magnetic moment values of 3.08, 3.05 and 3.10 BM for nickel(II) complexes, which point to the presence of two unpaired electrons, tetrahedral structures have to be ascribed to the Ni(II) complexes[35].

In the UV-Visible spectra of cobalt(II) complexes, the *d-d* transition bands observed at the range of 621-611 nm suggest that cobalt(II) ions have tetrahedral symmetry[36]. The magnetic moments of Co(II) complexes are 3.9, 3.86 and 3.86 BM, which is the characteristic value for the presence of three unpaired electrons, suggesting that Co(II) ions have tetrahedral geometries. The zinc(II) and cadmium(II) complexes are diamagnetic and tetrahedral.

All Ni(II) and all Zn(II) complexes and Co(II) complexes with L^2 and L^3 indicate the loss of one lattice water molecule for each complex at the range of 30-80 ºC. The results of the thermal analyses confirm the proposed structures of the compounds. Suggested structures of the complexes are shown in Fig. 1.

The present studies can be summarized as: Three Schiff base ligands and their copper(II), zinc(II), cadmium(II), nickel(II) and cobalt(II) complexes were synthesized and characterized by elemental analyses, conductivity and magnetic susceptibility, FT-IR and electronic absorption. In order to evaluate the hydrated water content of the complexes, TG and DTA instruments were employed. It was found that all complexes are monomers with tetrahedral geometries around metal ions except copper(II) complexes which possess square-planar symmetries. Elemental analyses confirmed the proposed structure of the free ligands and the complexes. Molar conductivities of the Schiff base ligands and their complexes were in the 1.1-9.5 Ω^{-1} cm^2 mol^{-1} range, therefore considered to be non-electrolytes.

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