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Complexes of Nickel(II), Copper(II) and Zinc(II) Metal Ions with a Tetrabasic Octadentate Schiff-Base Derived from 3,3′-Diamino-Benzidine and Salicylaldehyde

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The reaction between 3,3′-diaminobenzidine and salicylaldehyde in 1 : 4 molar ratio affords a novel tetrabasic octadentate Schiff base (H_4L). Its reaction with $Ni(OAc)_2$ or $Zn(OAc)_2$ in 1 : 2 molar ratio leads to the formation of dinuclear complexes of the general formula $[M_2L]$ and the latter, in turn, reacts with the metal halide $M'X_2$ (M′ = Co, Ni, Cu, X = Cl or Br) in 1 : 2 molar ratio to form tetranuclear complexes of the general formula $[M_2LM'_2X_4]$. The coordination of the Schiff base in the dinuclear complexes seems to occur *via* N-azomethine followed by deprotonation of the OH groups, while the further coordination in the tetranuclear complexes seems to take place *via* the lone pair of electrons available on the oxygen atoms. The structural features of the chelates have been confirmed by elemental analytical data, IR, UV-Vis and magnetic measurement.

Key words: Ni(II), Cu(II), Zn(II), Complexes, Schiff base.

INTRODUCTION

A good deal of work has been reported on the synthesis and structural investigation of different types of Schiff bases and their complexes[1]. This is partially due to their capability of acting as multidentate N—N and N—O donors with the formation of mono- or polynuclear complexes[2–4]. In addition to their interesting ligational properties, both Schiff bases and their complexes have important biological and industrial applications[5–8]. Hence, a detailed report on coordination chemistry of Schiff bases with transition and non-transition metal ions has been published recently: their complexes with, *e.g.*, vanadium(IV), titanium(IV), cobalt(II), copper(II), zinc(II), etc.[9–12] and organotin(IV)[13]. Because of the importance of such ligands, we took part in the chemistry of Schiff-bases and their coordination complexes, as they are rather popular ligands, and several articles have been published so far on their mononuclear coordination chemistry with transition and non-transition metals and their biological activity[14–17], and we have reported recently the synthesis of some binuclear Schiff-base complexes[18]

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Only a little work has dealt with Schiff-bases derived from benzidine and their complexes with various metal ions[19–21]. In the present work, we have reported the synthesis of a new type of Schiff-bases derived from 3,3′-diaminobenzidine and salicylaldehyde (Fig. 1), and to study its di- and tetra- nuclear complexes with Ni(II), Co(II) and Zn(II) .

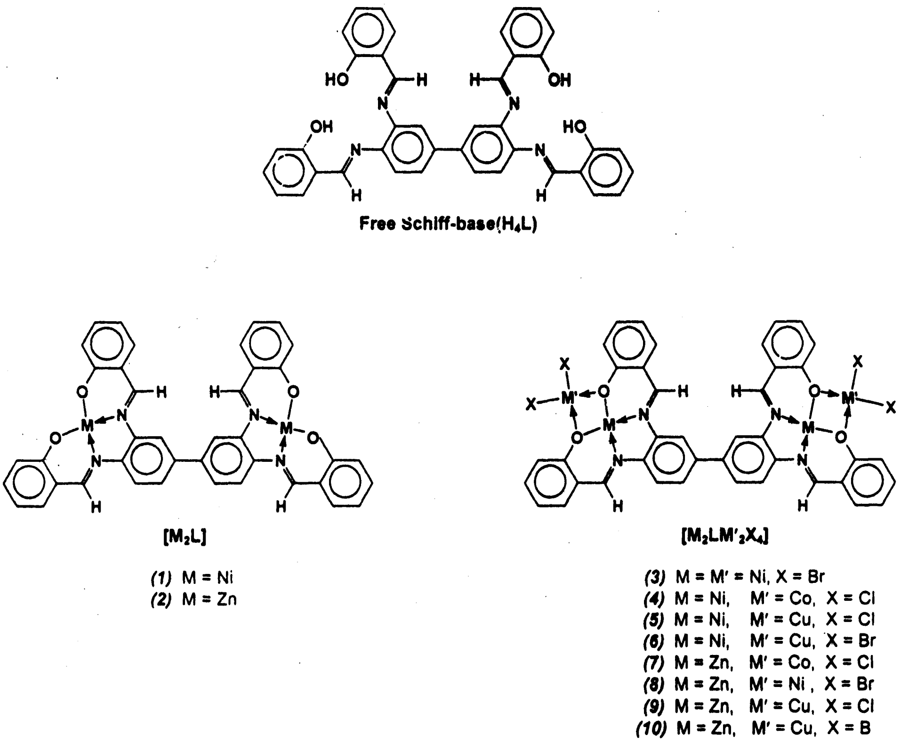

Fig. 1. The proposed structures for the dinuclear (1, 2) and the tetranuclear (3–10) complexes

EXPERIMENTAL

All the chemicals were of AnalaR grade (BDH, Aldrich or Fluka) and used without further purification. Elemental analyses were carried out on CHN analyser, type 1106 (Carlo-Erba). Metal analyses were carried out by standard analytical methods using a Buffer solution of acetic acid and sodium acetate at a pH of 4.5[22, 23]. IR spectra were recorded on a Pye-Unicam SP-2000 spectrophotometer in the 4000–200 cm^{-1} range using CsI discs. Magnetic measurements data were recorded on a Burker BM6 instrument at room temperature using the Faraday method. Electronic spectra were recorded on a Shimadzu UV-Vis spectrophotometer, model 160 Kyoto (Japan) using CH_2Cl_2 as a solvent in the 200–1100 nm range. Conductivity measurements were carried out for 10^{-3} M solutions of the complexes in CH_2Cl_2 at room temperature on a digital conductivity meter, model 4070 (Jenway).

Starting materials: The free Schiff base 3,3′-diaminobenzidine-N-salicylaldimine (Fig. 1) was prepared by dissolving 3,3'-diaminobenzidine (4.28 g, 20 mmol) in EtOH (15 mL) followed by addition of salicylaldehyde (8.4 mL, 80 mmol) and the mixture was refluxed for *ca.* 2 h. This was then cooled to room temperature in which a yellow precipitate started to deposit. The solid was filtered off and recrystallized from hot EtOH. The crystals were washed with Et_2O and dried *in vacuo* for several hours.

Preparation of the complexes

Dinuclear [M_2L] complexes: [Ni_2L] complex (1): The Schiff base (6.30 g, 10 mmol) was dissolved in hot EtOH (30 mL) and a solution of $Ni(OAc)_2{\cdot}4H_2O$ (4.96 g, 20 mmol) in EtOH (20 mL) was added gradually to the hot solution with vigorous stirring. The mixture was refluxed for *ca.* 30 min, then cooled to room temperature. The red crystalline product was filtered off, washed with EtOH and Et_2O and dried *in vacuo* for several hours.

[Zn_2L] complex (2): Since this complex could not be prepared from the direct reaction between the Schiff-base and the metal acetate, a modified *in situ* reaction was then followed: A solution of 3,3′-diaminobenzidine (2.14 g, 10 mmol) in EtOH (15 mL) was added to a solution of salicylaldehyde (4.2 mL, 40 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (4.39 g, 20 mmol) in EtOH (20 mL). The reaction mixture was refluxed for *ca.* 30 min, then cooled to room temperature. The pale yellow precipitate thus formed was filtered off, washed with EtOH and dried *in vacuo* for several hours.

Tetranuclear [$M_2LM'_2X_4$] complexes (3–10)

These were prepared using the following general procedure: the [M_2L]complex (M = Ni or Zn) (2 mmol) was suspended in absolute EtOH (15 mL) and added to the anhydrous metal halide, $M'X_2$ (4 mmol) in MeOH (15 mL). The reaction mixture was heated to a temperature close to the boiling point of the mixture for *ca.* 20 min. The mixture was filtered while it was hot and the filtrate was cooled to room temperature, in which a solid started to deposit (in case the solid was not formed, few drops of petroleum spirit were added until turbidness). The solid was then filtered off, washed with MeOH and dried in air at room temperature.

RESULTS AND DISCUSSION

The physical properties of the Schiff-base (H_4L), its dinuclear [M_2L] complexes and its tetranuclear [$M_2LM'_2X_4$] complexes are listed in Table-1. Their IR data and magnetic measurements are listed in Table-2. Their electronic spectral data and molar conductivities are listed in Table-3. The elemental composition of the dinuclear complexes correspond to 2 : 1 (metal ion : Schiff base) molar ratio while that of the tetranuclear complexes corresponds to 1 : 2 (M_2L : $M'X_2$) molar ratio (M = Ni or Zn, M′ = Co, Ni or Cu).

TABLE-1
PHYSICAL PROPERTIES AND ANALYSIS OF THE FREE SCHIFF-BASE (H_4L) AND ITS COMPLEXES [M_2L] AND [$M_2LM'_2X_4$]

Seq.	Compound (Colour)	m.p. (°C)	Yield (%)	m.f.	Found (Calcd.) (%)			M or M'
					C	H	N	
	H_4L (yellow)	161	89	$C_{40}H_{30}O_4N_4$	75.3 (76.2)	4.7 (4.8)	8.8 (8.9)	—
(1)	[Ni_2L] (red)	136[a]	63	$C_{40}H_{26}O_4N_4Ni_2$	64.3 (64.6)	3.6 (3.5)	7.6 (7.5)	15.9 (15.8)Ni
(2)	[Zn_2L] (pale yellow)	271	65	$C_{40}H_{26}O_4N_4Zn_2$	63.4 (64.4)	3.5 (3.4)	7.3 (7.4)	17.3 (17.3)Zn
(3)	[$Ni_2LNi_2Br_4$] (red-brown)	126[a]	41	$C_{40}H_{26}O_4N_4Br_4Ni_4$	39.9 (40.7)	2.2 (2.2)	4.6 (4.7)	19.9 (19.9)Ni
(4)	[$Ni_2LCo_2Cl_4$] (brown)	104	39	$C_{40}H_{26}O_4N_4Cl_4Ni_2Co_2$	47.7 (47.9)	2.5 (2.5)	5.4 (5.6)	11.7 (11.7)Co
(5)	[$Ni_2LCu_2Cl_4$] (green)	90[a]	42	$C_{40}H_{26}O_4N_4Cl_4Ni_2Cu_2$	47.3 (47.7)	2.5 (2.6)	5.5 (5.5)	12.6 (12.5)Cu
(6)	[$Ni_2LCu_2Br_4$] (red)	160[a]	41	$C_{40}H_{26}O_4N_4Br_4Ni_2Cu_2$	40.2 (40.3)	2.1 (2.2)	4.8 (4.7)	9.9 (9.8)Ni
(7)	[$Zn_2LCo_2Cl_4$] (brown)	273	34	$C_{40}H_{26}O_4N_4Cl_4Zn_2Co_2$	47.1 (47.2)	2.5 (2.6)	5.6 (5.5)	11.5 (11.6)Co
(8)	[$Zn_2LNi_2Br_4$] (red)	195[a]	47	$C_{40}H_{26}O_4N_4Br_4Zn_2Ni_2$	40.1 (40.2)	2.1 (2.2)	4.7 (4.7)	9.9 (9.8)Ni
(9)	[$Zn_2LCu_2Cl_4$] (green)	149	51	$C_{40}H_{26}O_4N_4Cl_4Zn_2Cu_2$	46.7 (46.9)	2.5 (2.5)	5.3 (5.5)	12.3 (12.4)Cu
(10)	[$Zn_2LCu_2Br_4$] (brown)	269	39	$C_{40}H_{26}O_4N_4Br_4Zn_2Cu_2$	40.1 (39.9)	2.2 (2.2)	4.6 (4.7)	10.6 (10.6)Cu

[a]Complexes melt with decomposition.

Spectral data and structures: Infrared spectra

From a quick glance to Table-2, it is clear that a downfield shift in the ν(C=N) absorption band by 11–26 cm^{-1} is observed on going from the free Schiff base to its complexes. This is clearly assigned to coordination of the metal to the ligand *via* N-azomethine[24]. The diappearance of ν(O—H) and δ(O—H) absorption bands of the free Schiff base on going to its complexes is unambiguously attributed to the deprotonation of the phenolic OH group, and this in turn leads to the upfield shift of the ν(C—O) band in the complexes compared to the free ligand[25, 26]. On the other hand, the appearance of a new band at 715–734 cm^{-1} in the tetranuclear complexes **(3–10)** is a good indicator that these complexes have been formed through the formation of tricoordinated phenolic oxygen[25, 27]. Some other new bands appearing in the 280–500 cm^{-1} region in the IR spectra of the complexes, which were not present in the spectrum of the ligand, may be attributed to ν(M—O) and ν(M—N) and could not be easily investigated.

TABLE-2
SELECTED IR BANDS OF THE FREE SCHIFF-BASE AND ITS METAL COMPLEXES WITH THE MAGNETIC VALUES

Compound	ν(C=N)(Δ)^b	ν(C—O)(Δ)^b	ν(M—O—M′)	μ_{eff} (B.M.)
H_4L,^{a}	1636	1290		
(1)	1650(–16)	1316(26)		dia^c
(2)	1610(–26)	1300(10)		dia^c
(3)	1615(–21)	1312(22)	732	4.14^d
(4)	1620(–16)	1330(40)	718	4.12^e
(5)	1625(–11)	1326(36)	727	1.91^e
(6)	1624(–12)	1309(19)	728	1.89^e
(7)	1612(–24)	1328(38)	734	3.98^e
(8)	1625(–11)	1300(10)	725	3.28^e
(9)	1610(–26)	1310(20)	715	1.88^e
(10)	1622(–14)	1322(32)	730	1.91^e

[a] For ν(O—H) and δ(O—H) values of the free Schiff-base are 3360 and 1305 cm^{-1}, respectively.
[b] Values for Δ are obtained from $\nu_{complex} - \nu_{Schiff\text{-}base}$.
[c] Complexes have no magnetic properties (diamagnetic).
[d] Value per molecule.
[e] Value per metal ion with MO_2X_2 chromophore.

TABLE-3
ELECTRONIC SPECTRA AND MOLAR CONDUCTIVITY OF THE COMPLEXES IN CH_2Cl_2 ^{a}

Complex	d–d transitions (cm^{-1})	Λ_M (mol^{-1} cm^2 ohm^{-1})
(1)	10580, 13890, 15980, 16990, 20980	4.6
(2)	—	5.6
(3)	10450, 14030, 16080, 17100, 20950	7.2
(4)	10390, 11280, 14100, 15890, 17000, 21380	6.9
(5)	10480, 13060, 15830(br), 22010	5.8
(6)	9580, 10410, 14000, 16010, 17200, 21300, 22430	7.1
(7)	11210, 17050(sh), 24980	7.0
(8)	9450, 10110, 14050, 16700, 19470	6.4
(9)	12120(sh), 15625(br), 22120	7.2
(10)	9620, 23690	3.8

[a] Data obtained for 10^{-3} M solutions of the complexes.

Magnetic measurements and electronic spectra

The dinuclear Ni(II) complex **(1)** is diamagnetic in the solid state, which clearly indicates its square-planar configuration. However, its electronic spectrum in CH_2Cl_2 is not consistent with this and clearly shows some changes on going from solid to solution. The spectrum consists of several bands, some are characteristic of a square-planar Ni(II) (15980 and 20980 cm^{-1}) and others (at 10580 as well as the shoulders at 13890 and 16990 cm^{-1}) are characteristic of a tetrahedral structure. With two Ni(II) ions present in the molecule, it is possible that their configurations are not identical or that in solution both configurations, the square-planar and the tetrahedral, are present. Sacconi *et al.*[28] reported the presence of both the square-planar and the tetrahedral Ni(II) complexes with NiN_2O_2 chromophore in benzene solution while in the solid state the structure of Ni(II) is that of a diamagnetic square-planar complex. The $[Ni_2LNi_2Br_4]$ complex (3) gave a magnetic moment value of 4.14 B.M. per molecule. This is possible if we assume that each neighbouring pair of Ni(II) having mixed-spin dinuclear with no spin interaction between the two ions. A value of a magnetic value of 2.0 B.M. has been reported for a dinuclear Ni(II) complex having a mixed spin state[29, 30]. The electronic spectrum of the tetranuclear Ni(II) complex (3) is well comparable to that of the dinuclear complex (1). The situation here is more complicated with the possibility of the inner Ni(II) complexes which have (as in the solid state) a square-planar arrangement while the outer Ni(II) complexes with NiO_2X_2 chromophore have the tetrahedral arrangement. Another plausible possibility is the square-planar-tetrahedral configuration for the inner complexes with a tetrahedral arrangement for the outer Ni(II) complexes. The paramagnetic outer ions with $M'O_2X_2$ chromophore seem to be well separated since no lowering of the magnetic moments were observed in the tetranuclear $M_2LM'_2X_2$.

Assuming a diamagnetic Ni(II) in the solid state, the magnetic moment value of 4.12 B.M. [Co(II)] found for the $[Ni_2LCo_2Cl_4]$ complex (4) is somewhat higher than the spin only value (3.87 B.M.) which may be due to orbital contribution. Similarly, the magnetic moment values of 1.9 B.M. [per Cu(II)] found for the two complexes $[Ni_2LCu_2Cl_4]$ and $[Ni_2LCu_2Br_4]$ (5 and 6) are also somewhat higher than the spin only value (1.73 B.M.). The electronic spectra of complexes (4, 6) are rather complicated and consist of bands which are difficult to interpret . The $[Zn_2LCo_2Cl_4]$ complex (7) showed a magnetic moment value of 3.98 B.M. [per Co(II)] and electronic spectral bands characteristic of a distorted tetrahedral configuration[30]. The $[Zn_2LNi_2Br_4]$ complex (8) possesses a magnetic value of 3.28 B.M. [per Ni(II)] and its electronic spectrum shows bands at 10100, 14000, 16700 and 19470 cm^{-1} and a shoulder near 9450 cm^{-1}. These facts seem to suggest a distorted tetrahedral structure around both nickel ions[28]. Attempts to isolate the chloride analogue failed and the tarry constituent obtained was difficult to solidfy or to dissolve.

The $[Zn_2LCu_2Cl_4]$ and $[Zn_2LCu_2Br_4]$ complexes (9, 10) both have magnetic moments of *ca.* 1.9 B.M. [per Cu(II)] which are well compared with their Ni(II) analogues, *i.e.*, complexes (5, 6) (Table-2). The electronic spectrum of complex (9) showed a broad band centered at 15625 cm^{-1} characteristic of a square-planar Cu(II) with CuO_2Cl_2 chromophore[31]. On the other hand, the absence of any absorption band between 10000–20000 cm^{-1} from the spectrum of complex (10) might suggest a tetrahedral configuration for this complex[32]. However, comparisons of nickel complexes (4, 5 and 6) with those of zinc analogues (7, 9 and 10) show that both Co(II) and Cu(II) of complexes (4, 6) might have a tetrahedral configuration while that of complex (5) might have a square-planar arrangement around Cu(II).

Conductivity measurements

All the dinuclear and tetranuclear complexes showed conductivity values ranging between 3.8–7.2 mol^{-1} cm^{-2} ohm^{-1} (Table-3) in CH_2Cl_2 at room temperature, indicating non-conductive species[33].

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