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Mokhles M. Abd-Elzaher [a]

[a] Inorganic Chemistry Department, National Research Centre, P.O. 12622, Dokki, Cairo, Egypt

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SOME TETRADENTATE SCHIFF BASES AND THEIR NICKEL, COPPER AND ZINC COMPLEXES

Mokhles M. Abd-Elzaher
Inorganic Chemistry Department, National Research Centre, P. O. 12622 Dokki,
Cairo, Egypt
E-mail: mokhlesm20@hotmail.com

ABSTRACT

Three ligands have been formed by the 1:2 molar condensation of *o*-phenylenediamine with salicylaldehyde, 2-hydroxy-1-naphthaldehyde or *o*-hydroxyacetophenone. The potentially tetradentate ligands are N,N-bis-(salicylaldehyde)-*o*-phenylenediamine (SalophH_2), N,N-bis(2-hydroxy-1-naphthaldehyde)-*o*-phenylenediamine (NophH_2) and N,N-bis(*o*-hydroxyacetophenone)-*o*-phenylenediamine (AophH_2), respectively. These ligands form 1:1 complexes with nickel, copper and zinc ions. The complexes have been characterized by IR, ^{1}H NMR, MS, UV/Vis spectra in addition to elemental analyses. The spectral data of the ligands and their complexes are discussed in connection with the structural changes which occur due to complexation.

INTRODUCTION

Tetradentate Schiff bases with a N_2O_2 donor atom set are well known to coordinate with various metal ions and this attracted many authors[1-8]. Complexes of Schiff base ligands have been studied for their dioxygen uptake[9] and oxidative catalysis[10]. Also, complexes of transition metals(II), which involve derivatives of

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salicylaldehyde and a diamine, have received considerable attention. This is because of their potential as catalysts for the insertion of oxygen into organic substrates[11-14].

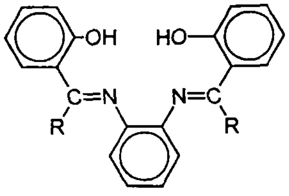
The reactions of tetradentate Schiff bases derived from salicylaldehyde and diamines and their complexes with cobalt, vanadium and antimony were the subject of many authors[1,2,5-7,15-17]. The present study is aimed at investigating the reactions of several tetradentate Schiff bases, derived from the condensation of *o*-phenylenediamine with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, or *o*-hydroxyacetophenone (Fig. 1) with nickel, copper and zinc ions to throw some light on their structure. These complexes were not studied in the literature previously. The prepared ligands and complexes have been characterized by IR, ^1H NMR, MS, UV/Vis spectra as well as elemantal analyses.

EXPERIMENTAL

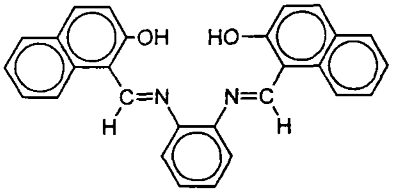
All chemicals and solvents are obtained from Merck except nickel acetate, salicylaldehyde and 2-hydroxy-1-naphthaldehyde which were obtained from Aldrich. The yields refer to analytically pure compounds and were not optimized. ^1H NMR spectra were recorded with a Bruker AC 250 or a Bruker WM 250 spectrometer in DMSO-d_6 as a solvent and are reported relative to TMS as internal standard. IR spectra were recorded on a Perkin Elmer (Spectrum 1000) FT-IR spectrometer, using KBr pellets. Magnetic susceptibility measurements on powdered samples were carried out on a Gouy balance at Cairo University. Mass spectra were determined using a Finnigan MAT 312–EI mass spectrometer. Elemental analyses were determined using a Heraeus CHN-O-RAPID analyzer. Electronic absorptions were recorded on a Shimadzu UV240 automatic spectrophotometer in chloroform.

General Procedure for the Preparation of the Ligands

The ligands were prepared by a modification of the reported methods[15-17]. A typical procedure for the synthesis of Schiff bases is as follows: a solution of 0.01 mole (1.08 g) *o*-phenylenediamine (dissolved in 50 mL ethanol) was slowly added to a solution of 0.2 mole of salicylaldehyde, 2-hydroxy-1-naphaldehyde or *o*-hydroxyacetophenone (in 50 mL ethanol). After stirring the reaction mixture for two hours at 40-50 °C, the resulted precipitate was cooled and collected by filtration. The



R = H: N.N-Bis(salicylaldehyde)-*o*-phenylenediamine (SalophH_2)
R = CH_3: N.N-Bis(*o*-hydroxyacetophenone)-*o*-phenylenediamine (AophH_2)



N,N-Bis(2-hydroxy-1-naphthaldehyde)-*o*-phenylenediamine (NophH_2)

Figure 1. Structural Representation of the Schiff Bases

precipitate was washed several times with distilled water, then ethanol, followed by crystallization in ethanol and drying at 50 °C overnight.

General Procedure for the Preparation of the Complexes

The various complexes were prepared by the addition of 5 mmole of $Ni(CH_3COO)_2.4H_2O$ (1.24 g), $Cu(CH_3COO)_2.H_2O$ (1.0 g) or $Zn(CH_3COO)_2.2H_2O$ (1.1 g), dissolved in about 20-30 mL of water, into a hot methanolic solution (200 mL) of 5 mmole of the ligand (1:1 molar ratio). The color of the solutions changes within a few minutes. The mixture was then refluxed for 2 h. The precipitated solids were filtered from the ice-cooled reaction mixture, washed with methanol and then with diethyl ether, followed by drying at 50 °C overnight.

RESULTS AND DISCUSSION

Reactions of Ni, Cu and Zn acetate with the dibasic, tetradentate Schiff bases SalophH_2, NophH_2 and AophH_2 in 1:1 molar ratio in methanol may be represented as follows:

$$M(CH_3COO)_2 + SB\text{-}H_2 \xrightarrow{\text{Methanol}} MSB + 2CH_3COOH$$

where SB-H_2 represents the Schiff bases of Fig. 1.

The tetradentate N_2O_2 donor-sites of the ligands (SalophH_2, NophH_2 and AophH_2) are capable of complexing various transition metal ions. In this article, the synthesis and characterization of Ni(II), Cu(II), and Zn(II) complexes of the mentioned ligands are reported. All of the complexes were prepared from equimolar amounts of the ligands and the corresponding metal acetates in methanol. The elemental analysis data of the Schiff bases and their complexes are given in Table I and are consistent with the calculated results from the empirical formula of each compound.

IR Spectra

In general, the ligands exhibited very similar IR features (Table II). A strong ligand band (for SalophH_2, NophH_2 and AophH_2) at about 1276 cm^{-1}, has no corresponding band in the metal chelates and is assigned to the hydrogen-bonded O-H in-plane bending vibration, (Fig. 2). This assignment is supported by the disappearance of this band when the hydroxy hydrogen is replaced by a metal. An additional band of strong intensity at 909 cm^{-1} is assigned to the hydrogen bonded out-of-plane O-H bending vibration[17-19]. The IR spectra of the ligands showed also a broad and a weak band in the region 2800-2700 cm^{-1} which confirms the intramolecular hydrogen-bonded OH[17-19].

The phenolic C-O streching vibrations that appeared at 1298 cm^{-1} in the Schiff bases[20-21] undergo a shift towards higher frequencies (20-40 cm^{-1}) in the complexes (Table II). This shift confirms the participation of the oxygen in the C-O-M bond[22,23]. Also, a strong band appeared at about 1613 cm^{-1} in the free ligands as well as their complexes. This band is attributed to the C=N streching vibration[18,22]. 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 410-438 cm^{-1} is attributed to ν(M-Ophenolic) and in the region 505-516 cm^{-1} to ν(M-

Table I. Analytical Data and some Physical Properties of the Schiff Bases and their Complexes

	Formula (F. w.)	Color (M. p.)	Yield (%)	%C found (calc.)	%H found (calc.)	%N found (calc.)
SalophH$_2$	$C_{20}H_{16}N_2O_2$ (316.4)	Orange (158)	81.3	75.82 (75.93)	5.26 (5.10)	9.10 (8.85)
Ni(Saloph)	$C_{20}H_{14}N_2O_2Ni$ (373.0)	Brownish-red (>280)	76.8	64.22 (64.40)	3.70 (3.78)	7.33 (7.51)
Cu(Saloph)	$C_{20}H_{14}N_2O_2Cu$ (377.9)	Dark brown (228)	65.4	63.29 (63.57)	3.49 (3.73)	7.29 (7.41)
Zn(Saloph)	$C_{20}H_{14}N_2O_2Zn$ (379.7)	Yellow (221)	62.6	63.01 (63.26)	3.54 (3.72)	7.24 (7.38)
NophH$_2$	$C_{28}H_{20}N_2O_2$ (416.5)	Yellow orange (215)	79.4	80.64 (80.75)	4.73 (4.84)	6.92 (6.73)
Ni(Noph)	$C_{28}H_{18}N_2O_2Ni$ (473.2)	Red (>280)	74.3	71.19 (71.08)	3.74 (3.83)	5.71 (5.92)
Cu(Noph)	$C_{28}H_{18}N_2O_2Cu$ (478.0)	Dark brown (264)	66.8	70.43 (70.36)	3.70 (3.80)	5.72 (5.86)
Zn(Noph)	$C_{28}H_{18}N_2O_2Zn$ (479.9)	Lemon yellow (256)	67.4	69.89 (70.09)	3.76 (3.78)	5.70 (5.84)
AophH$_2$	$C_{22}H_{20}N_2O_2$ (344.4)	Orange (150)	77.4	76.44 (76.72)	5.59 (5.85)	8.00 (8.13)
Ni(Aoph)	$C_{22}H_{18}N_2O_2Ni$ (401.1)	Brownish-red (212)	70.3	65.63 (65.88)	4.43 (4.52)	6.76 (6.98)
Cu(Aoph)	$C_{22}H_{18}N_2O_2Cu$ (406.0)	Dark brown (218)	65.6	65.00 (65.09)	4.22 (4.47)	6.66 (6.90)
Zn(Aoph)	$C_{20}H_{18}N_2O_2Zn$ (407.8)	Lemon yellow (194)	68.3	64.58 (64.80)	4.32 (4.45)	6.71 (6.87)

Table II. IR Spectral Data of the Schiff Bases and their Complexes (cm^{-1})

	ν(C=N)	ν(C=C)	ν(C-O phenolic)	ν(M-N)	ν(M-O)
SalophH$_2$	1613 s	1585 m, 1561 m, 1480 m	1298 m		
Ni(Saloph)	1605 s	1576 m, 1521 s, 1491 m	1340 m	506 w	410 m
Cu(Saloph)	1608 s	1577 m, 1522 s, 1488 m	1335 m	505 m	438 w
Zn(Saloph)	1615 s	1586 m, 1530 m, 1462 s	1325 m	515 m	410 w
NophH$_2$	1624 s	1580 m, 1530 m, 1480 m	1300 m		
Ni(Noph)	1621 s	1580 m, 1532 m, 1481 m	1315 m	508 w	408 m
Cu(Noph)	1622 s	1580 m, 1532 m, 1482 m	1318 m	507 m	414 m
Zn(Noph)	1624 s	1582 m, 1530 m, 1482 m	1321 m	512 m	421 w
AophH$_2$	1628 s	1581 m, 1530 m, 1481 s	1303 m		
Ni(Aoph)	1630 s	1581 m, 1530 m, 1481 s	1331 m	507 w	409 m
Cu(Aoph)	1632 s	1581 m, 1532 m, 1482 m	1333 m	514 m	418 m
Zn(Aoph)	1633 s	1581 m, 1532 m, 1481 m	1328 m	516 m	423 w

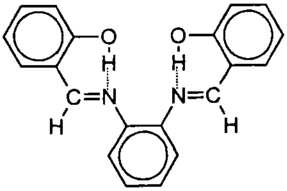


Figure 2. Structural Representation of Hydrogen Bonding in the Ligands

N). All the IR data suggest that the metal is bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen[24].

^{1}H NMR Spectra

The ^{1}H NMR spectra of the compounds were carried out in DMSO-d_6 solution at room temperature using TMS as an internal standard. The spectra of the Schiff base

Table III. ^1H NMR Spectra of the Schiff Bases and their Complexes[a] in DMSO-d_6 (δ, ppm)

	OH	Arom. H	C(H)=N	CH_3
SalophH_2	13.1 (s, 2H)	6.9-7.7 (m, 12H)	8.5 (s, 2H)	
Ni(Saloph)		6.8-7.8 (m, 12H)	8.3 (s, 2H)	
Zn(Saloph)		6.8-7.7 (m, 12H)	8.3 (s, 2H)	
NophH_2	13.2 (s, 2H)	6.8-7.7 (m, 16H)	8.6 (s, 2H)	
Ni(Noph)		6.9-7.7 (m, 16H)	8.3 (s, 2H)	
Zn(Noph)		6.9-7.7 (m, 16H)	8.3 (s. 2H)	
AophH_2	13.1 (s, 2H)	6.9-7.7 (m, 12H)		2.1 (s, 6H)
Ni(Aoph)		6.9-7.7 (m, 12H)		2.0 (s, 6H)
Zn(Aoph)		6.9-7.7 (m, 12H)		2.0 (s, 6H)

[a] s = singlet, m = multiplet

AophH_2, containing a methyl group, and its complexes were found more useful from the structural point of view because of the presence of distinguishing methyl protons. Also the spectra of the Cu(II) complexes were not simple as that of Ni(II) or Zn(II). This is may be due to the paramagnetism of the Cu(II) compounds.

The signal observed for the OH protons of the ligands (13.1 ppm) was not observed in any of the complexes (Table III), which 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 SalophH_2 and NophH_2 (8.6 ppm) clearly indicates that the environment is equivalent for all such protons, suggesting the presence of a planar ligand in these complexes[3].

The multiplets of the aromatic protons appeared within the range of 6.8 to 7.8 ppm (Table III), whereas the methyl protons of AophH_2 appeared in the range 2.0-2.1 ppm and were not affected by chelation.

Mass Spectra

The mass spectra of the Schiff base SalophH_2 and its complexes with copper and zinc are given in Table IV as representative examples. The molecular ion peaks

Table IV. Mass Spectra Data of the Schiff Base SalophH$_2$ and its Complexes with Copper and Zinc

Compound	M/e	Relative intensity (%)	Fragment
SalophH$_2$	316	100	M$^+$($C_{20}H_{16}N_2O_2$)
	223	26.3	$C_{14}H_{12}N_2O$
	210	63	$C_{13}H_{11}N_2O$
	196	42.7	$C_{13}H_{11}NO$
	120	10.5	C_7H_7NO
	77	19.3	C_6H_5
Cu(Saloph)	378	100	M$^+$($C_{20}H_{14}N_2O_2Cu$)
	286	17.5	$C_{14}H_{10}N_2OCu$
	259	44.2	$C_{13}H_9NOCu$
	183	21.5	$C_{13}H_9NOCu$
	169	49	C_7H_5Ocu
	64	87	Cu
Zn(Saloph)	380	100	M$^+$($C_{20}H_{14}N_2O_2Zn$)
	288	9.5	$C_{14}H_{10}N_2OZn$
	261	11.8	$C_{13}H_9NOZn$
	171	41.3	C_7H_5Ozn
	66	16	Zn

are in good agreement with their empirical formula as indicated from elemental analyses. The other peaks represent fragments of the molecular ion.

Electronic Spectra

The electronic spectra of the Schiff bases and their complexes are summarized in Table V. The spectra of the ligands exhibit three main peaks, at about 270, 333 and 372 nm. The first and the second peaks are attributed to the benzene π-π^* and imino π-π^* transitions, respectively. These bands were not significantly affected by

Table V. Electronic Spectral Data[a] of the Schiff Bases and their Complexes (nm)

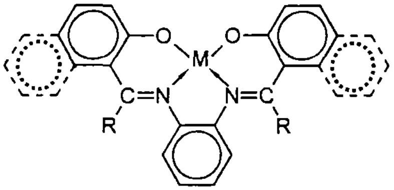
	λ_{max}, (ε, L mol^{-1} cm^{-1}) in $CHCl_3$				
SalophH$_2$	372 (7600)	333 (8400)	270 (9800)		
Ni(Saloph)	535 (78)	482 (8300)	410 (8000)	366 (24000)	
Cu(Saloph)	570 (350)	427 (8000)	395 (6600)	325 (9800)	307 (17800)
Zn(Saloph)	460 (sh)	392 (48)	341 (sh)	295 (800)	
NophH$_2$	376 (8000)	339 (9200)	271 (10100)		
Ni(Noph)	538 (74)	488 (6950)	418 (7600)	360 (12400)	
Cu(Noph)	572 (370)	429 (8000)	400 (6800)	328 (9700)	309 (16500)
Zn(Noph)	458 (sh)	389 (42)	340 (sh)	293 (840)	
AophH$_2$	374 (7900)	336 (9180)	269 (9800)		
Ni(Aoph)	540 (68)	480 (7900)	412 (8200)	362 (22600)	
Cu(Aoph)	569 (373)	426 (6900)	390 (6800)	324 (10000)	306 (17200)
Zn(Aoph)	463 (sh)	395 (46)	343 (sh)	298 (860)	

[a] sh = shoulder

chelation. The third band in the spectra of the ligand (372 nm) is assigned to the n-π^* transition. This band is shifted to longer wave length (28 nm) with an increase in intensity. This shift may be attributed to the donation of the lone pair of electrons of the nitrogen atoms of the Schiff base to the metal ion[25].

The spectra of the nickel(II) complexes consist of two bands at about 535 and 488 nm. These complexes have diamagnetic properties as determined on a Gouy balance. The brownish-red color of these complexes, their diamagnetism and the position of the electronic absorption bands of medium intensity are characteristic of low-spin square-planar Ni(II) complexes[5,26].

The spectra of the Cu(II) complexes show two bands in the visible region at about 570 and 428 nm and assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions, respectively. The observed magnetic moment of these complexes range from 1.82 to 1.88 B.M. The electronic bands and paramagnetism values suggest also a square-planar geometry around the copper(II) ion[27].



M = Ni, Cu or Zn; R = H, CH_3

Figure 3. Structural Representation of the Schiff Base Complexes,

On the basis of the physical and spectral data of 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 Fig. 3.

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Referee I: S. R. Berryhill
Referee II: E. S. Gould