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Synthesis, Spectroscopic, and Electrochemical Characterization of a Schiff Base: 4,4'-bis[(4diethylaminosalicylaldehyde)diphenyl methane]diimine and Its Complexes With Copper(II), Cobalt(II), and Cadmium(II)

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Synthesis, Spectroscopic, and Electrochemical Characterization of a Schiff Base: 4,4'-bis [(4- diethylaminosalicylaldehyde)diphenyl methane] diimine and Its Complexes With Copper(II), Cobalt(II), and Cadmium(II)

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The synthesis of a new ligand tetradentate Schiff base: 4,4'bis[(4-diethyl aminosalicylaldehyde) diphenyl methane] diimine (H₂L), obtained by condensation of 4,4'-diaminodiphenyl methane with 4-diethylaminosalicylaldehyde, and its complexes with copper(II), cobalt(II) and cadmium(II), is described. The metal complexes were characterized by elemental analysis, by UV-visible, infrared, and EPR spectroscopy, by cyclic voltammetry, and by thermal analysis (DTA-TG). The coordination of the metal ions to the ligand occurs through the N₂O₂ system. Thermal studies indicate that the ligand is more stable than the metal complexes (up to 310° C).

Keywords cyclic voltammetry, metal complexes, Schiff base, tetradentate

INTRODUCTION

Over the past two decades, considerable attention has been paid to the chemistry of Schiff bases containing nitrogen and other electron donors and their metal complexes.^[1–6] This can be attributed to their stability^[7] and their potential applications in many fields such as oxidation catalysis^[1] and electrochemistry.^[2] They also find applications in medicine as antibacterial or anticancer agents, in the preventive treatment against corrosion, nuclear wastes, and water treatment.^[8–11] Therefore, symmetrical as well as non-symmetrical Schiff bases have also been extensively employed as ligands for complexation of metal ions.^[12] Recently, some symmetrical Schiff bases with carbonyl functional groups have been described by Anthonysamy et al.^[13] In the corresponding nickel(II) complexes, the coordination occurs through the nitrogen and oxygen atoms of the ligand. Cyclic voltammetry measurements show for each complex two quasireversible one-electron waves. Ramachandraiah et al.^[14] described the synthesis of tetradentate ligands from 4,4'-bis(salicylideneimino)diphenyl methane (sal-dadpmX, with X=H, Me, OMe and Cl). These ligands led to [M₂(sal-dadpm X)₂] complexes, where M is Co(II), Ni(II), Cu(II), or dioxouranium (IV). The copper complexes are pseudotetrahedral binuclear species, whereas other complexes in this series are polynuclear octahedral species. In this article, we describe the synthesis of a new tetradentate Schiff base: 4,4'bis[(4-diethyl aminosalicylaldehyde)diphenyl methane]diimine (H₂L, Figure 1). This compound was reacted with Cu(II) and Co(II) chlorides and Cd(II) perchlorates in order to prepare the corresponding metal complexes. The structures of the products are discussed on the basis of IR spectra and thermal analysis. In addition, the electrochemical behavior of these complexes in dimethylformamide (DMF) is described. Our results will be compared to those obtained by Yoshida et al.^[15] and Kruger et al.,^[16] who studied ligands and their metal complexes identical to ours, but that did not bear the N(Et)₂ function, and Averseng's et al.,^[17] who investigated compounds bearing the N(Et)₂ function with a different internal molecular structure.

EXPERIMENTAL

General

All chemicals used, 4,4'-diaminodiphényl methane, 4diethyl aminosalicylaldehyde, tetrabutylammonium perchlorate (TBAP), spectral-grade organic solvents—ethanol, methanol, dimethylformamide (DMF), dimethylsulfoxyde (DMSO), toluene, chloroform(CDCl₃)), metal salts (CuCl₂.2H₂O,

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FIG. 1. Chemical structure of the ligand.

 $CoCl_2.6H_2O$ and $Cd(ClO_4)_2.6H_2O$)—were purchased from Prolabo[©] and were used without further purification.

All elemental analysis were carried out at the Service d'Analyse d'analyses du C.N.R.S., I.C.S.N. at Gif-sur-Yvette, France. The melting points were determined with a Köfler bench. FTIR spectra were recorded as pressed KBr discs, using a Perkin-Elmer FTIR 1000 series spectrophotometer in the range 4000–400 cm⁻¹. The UV-visible spectra were recorded in DMSO solutions with a Unicam UV300 spectrophotometer. The ¹H NMR spectra were recorded in CDCl₃ with TMS as internal reference on a JEOL GSX WB spectrometers at 270 MHz. Electrochemical measurements were carried out at 25°C on a Voltalab 32 (DEA 332 type): the working electrode (2 mm diameter) and the auxiliary electrode were Pt. The reference was a saturated calomel electrode. DMF was used as solvent and the ionic strength was maintained at 0.1 M, with TBAP as supporting electrolyte. The concentration of all species was 2.5×10^{-3} M. Thermal analyses were performed on TA instrument DTA/TG 2960. Samples were heated at a programmed rate of 5°C.min⁻¹ in a dynamic He atmosphere. The EPR spectra of the complexes were recorded with a Bruker Elexys 580-FT, using continuous wave in the X-band at room temperature and at 110 K.

Synthesis of the Ligand (H₂L)

The results of all elemental analyses are summarized in Table 1.

The ligand 4,4'-bis[(4-diethylaminosalicylaldehyde)diphenyl methane]diimine was prepared by reacting 4,4'-diaminodiphenyl methane and 4-diethylaminosalicylaldehyde in MeOH (molar ratio 1:2) as previously described. ^[18–20] The mixture was refluxed for 3 h. The yellow product obtained was filtered, washed twice with hot MeOH, and finally recrystallized from toluene and dried under vacuum.

 H_2L (1): (C_{35}H_{40}N_4O_2). Yield: 84.5%, color: yellow, m.p: 205°C. Elemental analysis, found (calculated%): C, 76.93

(76.61); H, 7.42 (7.35); N, 10.34 (10.21). ¹H NMR: (CDCl₃ as solvent, δ in ppm): 8.38 (s, CH=N, 2H), 6.16–7.39 (m, Ar-H, 14H), 13.87 (s, Ar-OH-o, 2H), 1.189 (t, CH/CH₃, 12H), 3.39 (q, CH/CH₂, 8H), 3.97 (s, CH/CH₂, 2H). UV-visible: λ_{max} nm; (ε_{max} M⁻¹.cm⁻¹, DMSO as solvent): 382 (176.8 10³), 270 (44.1 10³). FT-IR: (KBr, cm⁻¹): 3454 ν (Ar-OH), 1629 ν (C=N), 1422 ν (Ar-C=C), 3022 ν (Ar-CH), 2969 ν (Alph-CH), 1246 ν (C-O), 1196 ν (C-N).

Synthesis of the Complexes

All metal complexes were prepared by mixing equimolar amounts of ligand H_2L (0.21 g, 10 mL) in toluene and hydrated chlorides and perchlorates (15 mL) in EtOH. The mixture was refluxed for 8 h. The complex was filtered, washed several times with hot EtOH and dried under vacuum.

- Copper complex (2): Yield: 54.7%, color: brown, m.p.: >260°C. Elemental analysis, found (calculated [the basis of the calculated values will be discussed below]: C, 55.94 (53.84); H, 4.93 (5.42); N, 7.44 (7.18). UV-visible: λ_{max} nm (ε_{max} M⁻¹.cm⁻¹, DMSO as solvent): 390 (170.10³), 274 (52.10³). FT-IR: (KBr, cm⁻¹): 3478 v(H2O), 1613 v(C=N), 1506 v (Ar-C=C), 2974 v (Alph-CH), 1244 v(C-O), 1193 v (C-N), 614v(Cu-O), 530 v(Cu-N).
- Cobalt complex (**3**): Yield: 88%, color: green, m.p.: >260°C. Elemental analysis, found (calculated): C, 60.83 (60.35); H, 5.74 (6.08); N, 8.13 (8.04). UV-visible λ_{max} nm $(\varepsilon_{max} M^{-1}.cm^{-1}, DMSO$ as solvent): 389 (251.10³), 274 (39.5 10³). FT-IR: (KBr, cm⁻¹): 3476 ν (Ar-OH), 1604 ν (C=N), 1506 ν (Ar-C=C), 2976 ν (Alph-CH), 1245 ν (C-O), 1196 ν (C-N), 540 ν (Co-O), 479 ν (Co-N).
- Cadmium complex (4): Yield: 71.45%, color: yellow. m.p.: >260°C. Elemental analysis, found (calculated): C, 62.97 (62.08); H, 5.89 (5.95); N, 8.26 (8.27). UV-visible: λ_{max} nm (ε_{max} M⁻¹.cm⁻¹ DMSO as solvent): 385

TABLE 1
Analytical data for the ligand and the complexes

Compound				Elemental analysis found (calculated)		
	color	yield%	m.p. (°C)	C (%)	H (%)	N (%)
Ligand $H_2L(1)$	yellow	84.5	205	76.93 (76.61)	7.42 (7.35)	10.34 (10.21)
Copper complex (2)	brown	54.7	>260	55.94 (53.84)	4.93 (5.42)	7.44 (7.18)
Cobalt complex (3)	green	88.0	>260	60.83 (60.35)	5.74 (6.08)	8.13 (8.04)
Cadmium complex (4)	yellow	71.45	>260	62.97 (62.08)	5.89 (5.95)	8.26 (8.27)

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Compound	ν(O-H)	ν (C=N)	v(C-O)	ν(M-O)	ν(M-N)
Ligand $H_2L(1)$	3454 (br)	1629 (sh)	1246 (m)		
Copper complex (2)	3478 (br)	1613 (sh)	1244 (m)	614 (w)	530 (w)
Cobalt complex (3)	3476 (br)	1604 (sh)	1245 (m)	540 (w)	479 (w)
Cadmium complex (4)	3444 (br)	1606 (s)	1238 (m)	622 (w)	494 (w)

TABLE 2 IR spectral assignments for the ligand and its complexes (all wavenumbers in cm^{-1})

br: broad; sh: sharp; m: medium; s: strong; w: weak.

(192.2 10³), 277 (33.10³). FT-IR: (KBr, cm⁻¹): 3444 ν (H₂O), 1606 ν (C=N), 1516 ν (Ar-C=C), 2978 ν (Alph-CH), 1238 ν (C-O), 1192 ν (C-N), 622 ν (Cd-O), 494 ν (Cd-N).

RESULTS

The analytical and spectral data of the Schiff base ligand and its complexes of Cu(II), Co(II), and Cd(II) are summarized in Tables 1, 2, and 3. The isolated solids are stable in air and are insoluble in common organic solvents, but fairly soluble in CDCl₃, DMF, and DMSO.

¹H NMR Spectra

The ligand is symmetrical. Therefore, the hydrogen atoms in the two benzene rings are equivalent. The azomethine group is shown at $\delta = 8.38$ ppm as a singlet, whereas the phenolic proton is observed at $\delta = 13.87$ ppm as a singlet.^[21] The ligand shows singlet signals for CH₃, CH₂ as singlet, and aromatic protons in the ranges of 1.20 ppm, 3.97 ppm, and 6.17–7.39 ppm, respectively. No correct NMR spectra of the complexes could be obtained; as it will be seen subsequently this can be explained by their paramagnetic nature.

Infrared Spectra

In the spectrum of the ligand, the ν (CH=N) vibration of the azomethine group occurs at 1629 cm⁻¹. In the complexes, this vibration is shifted to the lower regions by 16–25 cm⁻¹. This effect can be assigned to the complexation of the metal ion by nitrogen atoms of the azomethine groups (Table 2).^[22]

TABLE 3 Electronic spectral assignments, λ_{max} (nm) for compounds **1–4**

Compound	λ_{max} (nm)	Assignment
$\overline{H_2L(1)}$	270	$\pi - \pi^*$
	382	$n-\pi^*$
Copper complex (2)	274	π - π^*
	390	$n-\pi^*$
Cobalt complex (3)	274	π - π^*
	389	$n-\pi^*$
Cadmium complex (4)	277	π - π^*
• · · ·	385	$n-\pi^*$

The IR spectra of the ligand and its complexes of Cu(II), Co(II), and Cd(II) are characterized by the appearance of a broad band in the 3500–3400 cm⁻¹ region due to the O-H stretching vibrations in the case of the ligand and the complex of Co(II)^[23–25] and to hydration water molecules ν (H₂O)^[26] in the case of the complex of Cu(II) and Cd(II).

The spectra of the ligand and its complexes are also dominated by bands at 2978–2969 cm⁻¹ due to ν (Alph-CH) groups.^[27] The band at 1246 cm⁻¹ for the ligand H₂L is assigned to the phenolic C-O stretching vibration that is shifted to lower frequencies by 1–8 cm⁻¹ due to O-metal coordination.^[28] Complementary evidence of the bonding is also shown by the fact that new bands in the IR spectra of the complexes appear at 530–479 and 622–540 cm⁻¹ assigned to ν (M-N)^[29–31] and ν (M-O) stretching vibrations.^[32]

Electronic Spectra

The electronic spectra of the ligand and their complexes were recorded in DMSO. The absorption bands below 300 nm are almost identical and can be assigned to $\pi - \pi^*$ transitions in the benzene ring and azomethine (C=N) groups.^[33] The absorption bands observed in the 382–390 nm range are probably due to the transitions of $n-\pi^*$ of imine groups.^[34] There are changes in the shape of the spectra of the complexes, which results in a bathochromic shift assigned to an intramolecular charge transfer interaction.^[35] MLCT transitions cannot be detected, probably



FIG. 2. DTA-TG analyses curves of ligand (color figure available onlne).

 TABLE 4

 Decomposition temperature of compounds 1–4

Compound	T _d (°C)
Ligand $H_2L(1)$	310
Copper complex (2)	235
Cobalt complex (3)	250
Cadmium complex (4)	220

due to either their low extinction coefficients or the large width of the bands (Table 3).

Thermal Analysis

In order to have more information about their thermal stability, the ligand and its metal complexes were studied by thermogravimetric (DTA-TG) techniques in the temperature range of 25–400°C under a helium atmosphere. The thermogram of the ligand exhibits a single endothermic peak at 205°C, corresponding to its melting point. The ligand is stable up to 310°C, and then decomposes (Figure 2). The TG curve of the copper complex (2) show a loss of weight where the corresponding DTA curve show an exothermic peak at 235°C, which indicates decomposition of the complex backbone. The complex of cobalt (3) and cadmium (4) decomposes in one step at 250°C and 220°C, respectively, therefore showing that the thermal stability of the compounds studied increases in the order H₂L¹ (1) > Co complex (3) > Cu complex (2) > Cd complex (4) (Table 4).

Electrochemical Behavior

The electrochemical profiles of the ligand H_2L and its complexes were studied in DMF by cyclic voltammetry on a platinum working electrode and a saturated calomel reference electrode, using TBAP as the supporting electrolyte. The main electrochemical data are given in Table 5 and some typical voltammograms are presented in Figure 3.

For the ligand, a cyclic sweep in the +0.00 to -2.00 V range shows a cathodic peak at -1.85 V and an anodic peak at -0.84 V (Figure 3a). The peak at -1.85 V is due to the reduction of the imino moiety of the molecule.^[36] When the sweep is performed between 0.00 and +1.80 V, two anodic peaks are obtained at +0.95 and +1.35V, the first one being assigned to the amine moiety and the second one to the phenol group (Figure 3b).^[36]

The cyclic voltammogram for the electro-oxidation of the Cu(II) complex (2) in region from 0.00 to +1.80 V, shows three anodic peaks at +0.60, +0.97, and +1.32V and one cathodic peak observed at +0.20 V (Figure 3c). The quasireversible oxidation peak at +0.60V is due to the oxidation of the complexed Cu(II) to Cu(III) and the return peak at +0.20V corresponds to the reduction of Cu(III) to Cu(II).^[37,38] The peaks at +0.97 and +1.32V are nearly at the same potential values as the corresponding ligand. When sweeping from -1.50 to 1.00 V (Figure 3d) three cathodic peaks occur at +0.20, -0.75, and -1.48V and two anodic peaks at -0.32 and +0.60 V. The first, second and third reduction waves correspond to $Cu(III) \rightarrow Cu(II)$, Cu(II) \rightarrow Cu(I) and Cu(I) \rightarrow Cu(0), respectively.^[39,40] Finally Cu(0) is oxidized back to coordinated Cu(II) (anodic peak at -0.32 V) because this peak disappears when the sweep is limited to -1.00V. When performing successive sweeps, the potential of the peak at -0.32V is shifted to -0.16V. This displacement is probably due to the deposition of copper.

The reduction voltammogram of the Co(II) complex, recorded between 0.00 and -1.40 V vs. SCE (Figure 3e), displays two cathodic peaks located at -0.41 and -1.05 V vs. SCE. They correspond to the reduction of Co(II) \rightarrow Co(I) and Co(I) \rightarrow Co(0), respectively. Additionally, there is one reoxidation peak located at -0.18 V vs. SCE. This latter peak corresponds to the reoxidation to Co(II) of the Co(0) deposited at -1.05 V vs. SCE.^[41,42]

The electrochemical oxidation of the Co(II) shows three anodic peaks when sweeping from -1.80 to +1.80 V (Figure 3f). The first, quasireversible, one (Figure 3g) located at +0.52 V vs. SCE corresponds to a one-electron transfer couple [Co(II) \rightarrow Co(III)], the second and third irreversible peaks, located at +0.88 V and +1.30 V vs. SCE are assigned to the oxidation of the amine and phenol groups.

Cyclic voltaininetry						
			Oxidation		Reduction	
Compound	sweep	E range (V)	E _a (V)	$E_{c}(V)$	$\overline{E_a(V)}$	E _c (V)
Ligand $H_2L(1)$	1	0.00/-2.00 0.00/+1.80	+0.95 +1.35		-0.84	-1.85
Copper complex (2)	1 3	0.00/+1.80 -1.50/+1.00	+0.60+0.97+1.32 +0.60	+0.20 +0.20	-0.32	-0.75 -1.48
Cobalt complex (3)	1 3	0.00/-1.40 -1.80/+1.80	+0.52 +0.88 +1.30	+0.16	-0.18 -0.18	-0.41 -1.05 -0.93 -1.18 -1.70
Cadmium complex (4)	1	-1.80/+1.80	+1.15 + 1.43		-0.57	-1.45

TABLE 5 Cyclic voltammetry

DMF, 25°C, TBAP 0.1 M, V vs. SCE; Ea: anodic; Ec: cathodic.



FIG. 3. Cyclic voltammetry (DMF, 25°C, ionic strength: 0.1 mol.L⁻¹, TBAP 0.1 M, V vs. SCE, $v = 100 \text{ mV s}^{-1}$, I in $\mu \mu A$). (3a): ligand (1) (0.00 to -2.00 V), (3b): ligand (1) (0.00 to +1.80 V), (3c): Cu(II) complex (2) (0.00 to +1.80 V), (3d): Cu(II) complex(2) (-1.50 to +1.00V), (3e): Co(II) complex (3) (0.00 to -1.40 V), (3f): Co(II) complex (3) (-1.80 to +1.80 V), (3g): Cd(II) complex (4) (-1.80 to +1.80 V) (color figure available onlne).



FIG. 4. EPR spectra of (a) $\{Cu\}$ (2), (b) $\{Co\}$ (3) and (c) $\{Cd\}$ (4) at 110 K in the solid state.

For the Cd(II) compound (4), when sweeping from -1.80 to +1.80 V, one cathodic wave at -1.45 V and three anodic waves at -0.57, +1.15, and +1.43 V are obtained (Figure 3g). In this case, it can be noted that the oxidation of the phenolic part of the Schiff base occurs at higher potential values than for the other compounds (+1.43 V instead of +1.38 V). The peak at -1.45 V correspond to the reduction of Cd(II) complex.

EPR Spectroscopy

The X-band EPR spectra of the Cu, Co and Cd complexes (2-4) have been recorded as powdered samples at 110 K using DPPH as the g marker (Figure 4). The EPR spectral parameters are presented in Table 6. Although a complete analysis of these complexes has not yet been completed, the spectra show the presence of paramagnetic species, but they differ markedly as a function of the cation involved. The Cd complex shows a narrow signal. Because Cd⁺⁺ is diamagnetic, it must

be assumed that the origin of this signal lies in the formation of organic radical species formed during synthesis. In the case of Cu complex, the EPR line shape is broad and slightly asymmetric. Its g value is relatively close to that of the free electron. There is no evidence of signal around g = 4 or traces of hyperfine splitting. Examples of this are present in related systems studied as powdered samples.^[43] Complexes of cobalt show an extremely broad and asymmetric signal indicating that the magnetic site is strongly distorted. This signal can be analyzed in

TABLE 6EPR parameters of the complexes 2–4

Compound	g (110K)	$\Delta H_{PP}(G)$
Copper complex (2)	2.024	200
Cobalt complex (3)	2.273	_
Cadmium complex (4)	2.009	15

terms of g/(1.52) and $g \perp (2.46)$ contributions that could be attributed to some symmetry of the paramagnetic site.

DISCUSSION

Schiff base ligands similar to the one we have synthesized have already been described in the literature but they either lack the N(Et)₂ moiety,^[15,16] or their central arrangement is different.^[17] Structure and properties of transition metal complexes of these ligands have been reported.

As evidenced by thermal analysis, the presence of metal atoms in our complexes dramatically reduces the stability of the formed moieties, contrary to the observations of Averseng et al.^[20] on similar systems.

The electrochemistry of the pure ligand is irreversible. Electrochemical measurements also show that the complexes are not stable and that they are very sensitive to reduction and oxidation steps. It is even possible that in the case of copper and cobalt, the metal is deposited on the electrode during reductive processes.

From the literature, all the structures clearly indicate that the metallic ion is bound by two nitrogen and two oxygen atoms (N_2O_2) . In some cases, 1:1 complexes are formed, in agreement with the close proximity of the two NO groups.^[17]. On the other hand, complexes of $Zn^{[15]}$ and of Cu and $Co^{[16]}$ have a structure involving two metallic ions and two ligands. In the latter case, the two NO binding sites belong to different ligands.

The chemical formula of the various complexes can be defined by analogy with that of complexes having a similar structure, as described in the literature.^[42,44,45] Thus, it is possible to postulate the following formulas for the various metal complexes $C_{35}H_{42}Cl_2Cu_2N_4O_4$, $C_{35}H_{42}Cl_2CoN_4O_3$, and $C_{35}H_{40}CdN_4O_3$. They are in good agreement with the elemental analysis (calculated values, Table 1). The elemental analysis of complexes of Co and Cd is also in complete agreement with a 2:2 complex,^[16] although it is not possible to differentiate ML from M_2L_2 based only on the composition. The major difference is found in the case of Cu complexes, for which the analysis would point towards a M_2L_1 structure. This is rather surprising since the same ligand was used and the preparation/purification methods were identical in all cases studied.

Finally, the existence of Cu_2L complexes with similar ligands seems unique and is currently under investigation.

CONCLUSION

We have described three new metal complexes obtained with 4,4'-bis[(4-diethylaminosalicylaldehyde)diphenyl methane]diimine (H₂L), which behaves as a N₂O₂ tetradentate ligand toward Co(II) and Cd(II) ions. In every case, the coordination occurs through the N azomethine atoms and the oxygen atoms of the phenolic hydroxyl. The complex of Cu(II) is binuclear but copper ions do not interact. Thermal studies showed that the ligand is more stable than the corresponding complexes.

It is quite striking that the presence of $N(Et)_2$ functions may have such a strong impact on the stability of the complexes. This point obviously necessitates further investigation that is presently in progress.

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