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Synthesis, Characterization and Electrochemical Behavior of Co^{II} , Ni^{II} and Cd^{II} Complexes with N_2O_2 Donor Ligands Derived from 4,4'-Diaminobiphenyl and 2-Hydroxybenzaldehyde or 2,4-Dihydroxybenzaldehyde

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Abstract The condensation of 2-hydroxybenzaldehyde or 2,4-dihydroxybenzaldehyde with 4,4'-diaminobiphenyl in absolute EtOH in a molar ratio 2:1 gave, respectively, the Schiff base ligands $\text{H}_2\text{L1}$ or $\text{H}_2\text{L2}$. The bases served as tridentate ligands to coordinate Co^{II} , Ni^{II} and Cd^{II} chlorides, leading to complexes where the metal:ligand ratio is 2:1. All of the compounds were characterized by elemental analysis, infrared, electronic and mass spectroscopy, ^1H -n.m.r. and d.s.c. The cyclic voltammograms of the ligands and their complexes in DMF are discussed.

Keywords Schiff bases · Cobalt(II) complexes · Nickel(II) complexes · Cadmium(II) complexes · Cyclic voltammetry

1 Introduction

Since the first report of their metal complexes, Schiff base compounds have become an important class of ligands that have been extensively studied in coordination chemistry, mainly due to their facile synthesis and easily tunable steric, electronic and catalytic properties [1]. They are also used in constructing supramolecular structures [2–4].

Various transition metal complexes with bi- and tridentate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems and represent interesting models for metallo-enzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen [5, 6]. Furthermore, macrocyclic derivatives of these Schiff bases were

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found to have many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [7–9].

On the other hand, there is a great amount of research interest in the chemistry of the metal complexes of tetradentate N_2O_2 Schiff bases due to their ability to form adducts with dioxygen and thus may catalyze reduction of dioxygen. The transition metal ions in the complexes form adducts with dioxygen via charge transfer. These complexes will thus be expected to show catalytic effects. For instance, complexes of chromium and ruthenium with a wide variety of Schiff bases having donor atoms such as N_2O_2 and N_4 around the metal ion have been used as catalysts for carbonylation, hydrogenation, hydroformylation and epoxydation reactions [10–12]. The cobalt and manganese complexes that coordinate through N_2O_2 donor atoms have been extensively studied as oxygen carriers and also as catalysts for water splitting systems [13, 14].

Macrocyclic ligands also have coordination properties and have attracted much attention [15–17]. Cadmium is an environmental pollutant that inhibits ribonucleic acid (RNA) polymerase activity *in vivo* [18, 19] and reacts readily with proteins and other biological molecules. Consequently, the macrocyclic chemistry of cadmium has recently been developed [20].

Thus, in view of the above preceding research, it was considered worthwhile to prepare some new metal-based macrocyclic skeletons bearing multiple donor sites that could probably be used for the binding of some guest molecules. The present work deals with the synthesis, characterization and cyclic voltammetry of two Schiff-base ligands derived from the condensation of 4,4'-diaminobiphenyl with 2-hydroxybenzaldehyde or 2,4-dihydroxybenzaldehyde and their Co^{2+} , Ni^{2+} and Cd^{2+} complexes.

2 Experimental

2.1 Materials

All materials and solvents were analytical reagent grade and were used without further purification. 2-Hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde and 4,4'-diaminobiphenyl were purchased from Aldrich. All metals were used in the form of their hydrated chlorides and were used as received.

2.2 Measurements

The 1H -n.m.r. spectra of the ligands and the diamagnetic complexes were recorded on a Jeol GSX WB spectrometer at 270 MHz in $DMSO-D_6$; the chemical shifts are given in p.p.m., using tetramethylsilane (TMS) as the internal reference. The IR spectra were recorded with a Perkin-Elmer 1000 series FT-IR spectrophotometer using KBr disks. The UV-vis spectra were obtained in DMF with a UNICAM UV-300 spectrophotometer. The electron impact mass spectra (ESI) were recorded on a Bruker Daltonics Data Analysis 3.1 spectrometer. The melting points were determined with a Kofler bench and are uncorrected. Differential scanning calorimetry (d.s.c.) diagrams were recorded in the 25–400 °C range with a Mettler DSC 822° unit, with the help of Mettler Toledo STAR° SW 8.10 System software. The heating rate was 10 °C per minute, and all measurements were made in 40 mm³ closed aluminum crucibles.

The elemental analyses were carried out with an EL III-ELEMENTAR. All of these measurements were performed in France. Electrochemical measurements were recorded on

a Radiometer VOLTALAB 32 (DEA 332 type): the working electrode was a 2 mm diameter Pt rotating disk and the auxiliary electrode was a Pt wire. A saturated calomel electrode (SCE) was used as the reference electrode and measurements were carried out at 27 °C. DMF was used as the solvent, and the ionic strength was maintained at 0.1 mol·L⁻¹ with Bu₄NClO₄ (TBAP) as supporting electrolyte. The concentrations of individual chemical species were in the 2.5 × 10⁻³ to 5 × 10⁻³ mol·L⁻¹ range. The sweep speed was 100 mV·s⁻¹ unless otherwise indicated.

2.3 Preparation of the Ligands

The ligands were prepared by condensation of 4,4'-diaminobiphenyl with 2-hydroxybenzaldehyde for H₂L1, and with 2,4-dihydroxybenzaldehyde for H₂L2. The reactions were carried out in EtOH (1:2 molar ratio) [21, 22]. To a solution of 4,4'-diaminobiphenyl (0.43 mol·L⁻¹) in absolute EtOH was added a solution of 2-hydroxybenzaldehyde or 2,4-dihydroxybenzaldehyde (0.87 mol·L⁻¹). The mixture was stirred under a nitrogen atmosphere and refluxed for 3 h. The ligand was recovered by filtration, washed twice with EtOH (10 mL) and dried under vacuum.

2.4 Preparation of the Complexes

All of the complexes were prepared using a synthetic pathway described in the literature [23–26], by mixing appropriate amounts of ligand H₂L1 or H₂L2 (0.1 mol·L⁻¹) and a hydrated metal chloride in 1:2 molar ratio in absolute EtOH. After standing under reflux conditions for 8 h, the mixture was then kept overnight at room temperature. The complex that precipitated was removed by filtration, washed several times with EtOH and dried under vacuum. Their purity was verified using thin layer chromatography (t.l.c.) with CH₂Cl₂/EtOH (7:3 v/v) as eluent.

3 Results and Discussion

3.1 Synthesis and Characterization

The Schiff base ligands H₂L1 and H₂L2 were synthesized according to Fig. 1 and serve as tetradentate ligands in all six complexes reported in this account. The ligands employ two

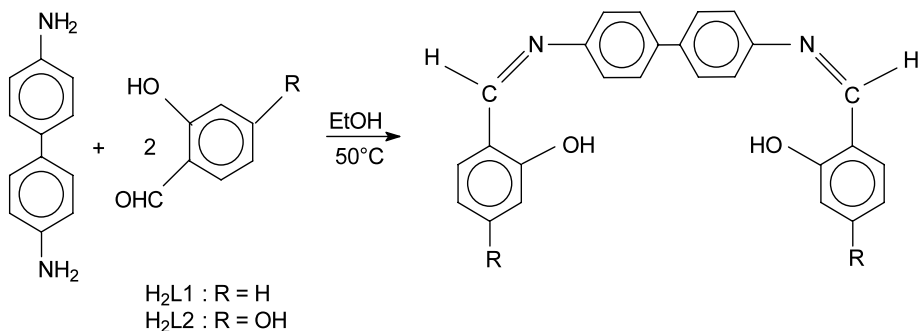


Fig. 1 Synthesis pathway for the Schiff base ligands

Table 1 Main analytical data for the ligands and their complexes

Compound	Color	Yield (%)	$M^+ / g \cdot mol^{-1}$	Elemental analysis, found (Calcd.) (%)		
				C	H	N
H ₂ L1	Yellow	73	392.0	79.36 (79.51)	5.30 (5.10)	6.76 (7.13)
(CoCl ₂) ₂ L1	Yellow	60	650.0	47.91 (47.99)	3.05 (2.77)	4.42 (4.31)
[(NiCl ₂) ₂ L1]·2H ₂ O	Yellow	57	–	45.11 (45.52)	3.32 (3.20)	4.23 (4.08)
(CdCl ₂) ₂ L1	Orange	45	757.0	41.50 (41.22)	2.55 (2.37)	3.85 (3.69)
H ₂ L2	Tan	51	424.0	73.40 (73.51)	5.02 (4.71)	6.34 (6.59)
(CoCl ₂) ₂ L2	Brown	60	–	46.05 (45.76)	2.96 (2.64)	3.91 (4.10)
(NiCl ₂) ₂ L2	Green	46	681.6	46.01 (45.78)	2.81 (2.64)	4.25 (4.10)
(CdCl ₂) ₂ L2	Brown	50	–	39.37 (39.55)	2.50 (2.28)	3.84 (3.55)

imine nitrogens and two phenoxo oxygens to bind the metals. All complexes were synthesized in good yield by the reaction of the hydrated metal chlorides of Co^{II}, Ni^{II} and Cd^{II} with H₂L1 or H₂L2 in a molar ratio of 2:1, using ethanol as solvent at 50 °C. Analytically pure compounds were obtained in all cases as indicated by elemental analysis, with melting points higher than 260 °C, and are consistent with the proposed molecular formulae that show the ratio of metal to ligand to be 2:1 in all cases. The main analytical data for the ligands and their complexes are given in Table 1.

3.2 Mass Spectrometry

The molecular weights of all prepared compounds were determined from their spectra using electron impact (EI) conditions. Parent ion peaks M^+ corresponding to the ligands and some of the complexes were present. The spectra also showed peaks attributed to ($M^+ + 1H$) and ($M^+ + 2H$), together with prominent breakdown peaks that corresponded to a loss of chlorine atoms in the cases of the nickel(II) and cobalt(II) complexes. These results agree with the expected structures and are mentioned in Table 1.

3.3 Infrared Spectra

In the IR spectra of the ligands, the broad bands in the 3232–3625 cm⁻¹ range are attributed to the $\nu(O-H)$ stretching vibration of the phenolic groups [27]. In the case of the nickel(II) complex with ligand H₂L1, this broad band results from the presence of water molecules according to the d.s.c. results. The bands in the 1282, 1284, 1620, and 1631 cm⁻¹ regions are assigned to the stretching vibrations $\nu(C-O)$ and $\nu(C=N)$ of H₂L1 and H₂L2, respectively (Table 2). The $\nu(C=N)$ band of the ligands undergoes small shifts to lower frequencies in the spectra of the complexes (1600–1572 cm⁻¹), indicating coordination of the imine nitrogen [28–31]. Additional evidence for coordination of the nitrogen is the presence of a $\nu(M-N)$ band in the 437–497 cm⁻¹ region.

Coordination through the oxygen atom is inferred from the shifts to lower wavenumbers of the $\nu(C-O)$ band as compared to their position in the ligands [32], and the appearance of a new band in the 528–586 cm⁻¹ region assigned to $\nu(M-O)$, in agreement with earlier reported results [33–36].

Table 2 Main spectroscopic data for the ligands and their complexes

Compound	Infrared (cm^{-1})					UV-vis λ_{max} (nm)	(DMF solution) [$\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$]
	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$		
H ₂ L1	3454	1620	1282	–	–	366	[13600]
(CoCl ₂) ₂ L1	–	1572	1250	572	437	370	[20361]
[(NiCl ₂) ₂ L1]·2H ₂ O	3360	1599	1220	528	493	370	[5388]
(CdCl ₂) ₂ L1	–	1600	1238	574	438	368	[18373]
H ₂ L2	3363	1631	1284	–	–	368	[19204]
(CoCl ₂) ₂ L2	3625	1595	1242	586	497	380	[21936]
(NiCl ₂) ₂ L2	3288	1595	1271	563	489	376	[25744]
(CdCl ₂) ₂ L2	3232	1596	1247	584	491	378	[27412]

3.4 Electronic Spectra

The band maxima (λ_{max}) and molar absorptivities (ϵ) obtained from the electronic spectra of the ligands and complexes were recorded in DMF and the relevant data are presented in Table 2. In general, the UV-visible region of the electronic spectra of these compounds was dominated by intense intra-ligand $\pi-\pi^*$ transitions.

All of the complexes exhibit an absorption band in the 370–380 nm range, which is assigned to a metal-ligand charge transfer band.

In the case of the cobalt(II) complex of ligand H₂L2, two weak bands from d–d transitions, not mentioned in Table 2, were observed at 606 and 654 nm and correspond to a tetrahedral environment around the Co²⁺ ion [37, 38].

3.5 ¹H-n.m.r. Spectra

The observations obtained from the previous analysis were further substantiated by the comparison of ¹H-n.m.r. spectra of the free symmetrical ligands H₂L1 and H₂L2 and their complexes, which were recorded in DMSO-D₆ solutions.

The aromatic protons of the ligands showed multiplets at $\delta = 7.7$ – 6.92 and 7.9 – 7.2 p.p.m., assigned to both phenyl and bipyridyl protons of H₂L1 and H₂L2, respectively. These protons, in each case, could not be distinguished from each other. The spectra also contained absorptions at $\delta = 9.3$ and 8.9 p.p.m. that are ascribed to the protons of the azomethine groups, while the singlets at $\delta = 13.1$ and 13.6 p.p.m. are typical of hydroxyl protons. The remaining –OH absorption of H₂L2 occurred at $\delta = 10.95$ p.p.m. These chemical shifts may be compared with those of literature [39, 40] where the hydroxyl proton of 2-hydroxybenzaldehyde or 2-hydroxyacetophenone is reported to resonate at $\delta = 12.05$ p.p.m. This deshielding, in fact, is due to the formation of intramolecular hydrogen bonding. For H₂L1 and H₂L2 the interaction is exclusively with the nitrogen atoms of the azomethine groups.

This difference becomes more important in the corresponding nickel(II) complexes NiL1 and NiL2, for example, where the aromatic protons in each case gave rise to a multiplet at $\delta = 8$ – 7.25 p.p.m., while the protons of the azomethine groups become deshielded and appeared at $\delta = 10.2$ and 9.1 p.p.m., respectively, for the same reasons as those previously indicated for the hydroxyl protons. This fact is supported by a higher structural rigidity leading to the coplanarity of the different sp² systems constituting the complex, according to the square planar geometry generally observed for nickel complexes [41].

Table 3 Voltammetric results (anodic E_{pa} , cathodic E_{pc}) at room temperature in DMF at the ionic strength $0.1 \text{ mol}\cdot\text{L}^{-1}$ (TBAP) reported in V versus SCE; sweep speed $100 \text{ mV}\cdot\text{s}^{-1}$

Compound	E_{pa1}	E_{pa2}	E_{pa3}	E_{pc1}	E_{pc2}	E_{pc3}	ΔE	$E_{1/2}$
H ₂ L1		1.05	1.60		0.32		−0.73	0.685
(CoCl ₂) ₂ L1	0.46		0.96			−1.46		
[(NiCl ₂) ₂ L1]·2H ₂ O	0.47	0.68	1.24	1.10		−1.50	−0.14	1.170
(CdCl ₂) ₂ L1	0.45					−1.43		
H ₂ L2	0.56	1.03			0.31		−0.25	0.435
(CoCl ₂) ₂ L2	0.52	0.74	1.20	1.06		−1.50	−0.14	1.130
(NiCl ₂) ₂ L2	0.66	0.81		1.01		−1.68	0.20	0.910
(CdCl ₂) ₂ L2	0.52					−1.50		

In addition to this, the disappearance of the hydroxyl protons at $\delta = 13.1$ and 13.6 p.p.m. in the ¹H-n.m.r. spectra of the complexes obviously indicates that the −OH groups becomes deprotonated during coordination. The absorption that is observed at $\delta = 10.53$ p.p.m. in the NiL2 spectrum is due to the remaining hydroxyl group in position four of the azomethine group.

3.6 Thermal Analysis

The d.s.c. diagrams show significant differences among the ligands H₂L1, H₂L2 and their complexes. The decomposition of all these compounds occurs at temperatures higher than 300 °C and is generally followed by several exothermic peaks due to this decomposition.

The d.s.c. diagram of the nickel(II) complex derived from H₂L1 shows many peaks at the 130–200 °C range that are due to the loss of water molecules.

The cobalt(II) and cadmium(II) complexes of ligand H₂L1 or H₂L2 are very stable thermally and show endothermic peaks in the 360–390 °C range. These results are in good agreement with literature values [42].

3.7 Electrochemical Behavior of the Ligands and the Complexes

The main electrochemical results for the ligands and the complexes in this study are summarized in Table 3 and some representative voltammograms are shown in Fig. 2.

3.8 Ligands

In the −1.8 to +1.8 range, the cyclic voltammogram of the ligand H₂L1 (Fig. 2a) shows two waves on the anodic side, with peak potentials of +1.05 and +1.60 V that can be ascribed to the irreversible oxidations of the phenol moieties, and one cathodic peak at +0.32 V due to the reduction of the oxidized species of the ligand (oxidation of the azomethine moiety) [43].

In the case of H₂L2 (Fig. 2b), the cyclic voltammogram shows two irreversible waves on the anodic side with only one cathodic peak. The potentials of the anodic peaks are at +0.56 and +1.03 V. During the reduction sweep, a broad cathodic peak was obtained at +0.31 V resulting from reduction of the imino group. This ligand seems to have an increased tendency towards oxidation due to the presence of the electron donating groups (OH) in the meta-positions of the phenol moieties, leading to lower oxidation potentials. Electron withdrawing substituents usually yield shifts to more positive potentials [44].

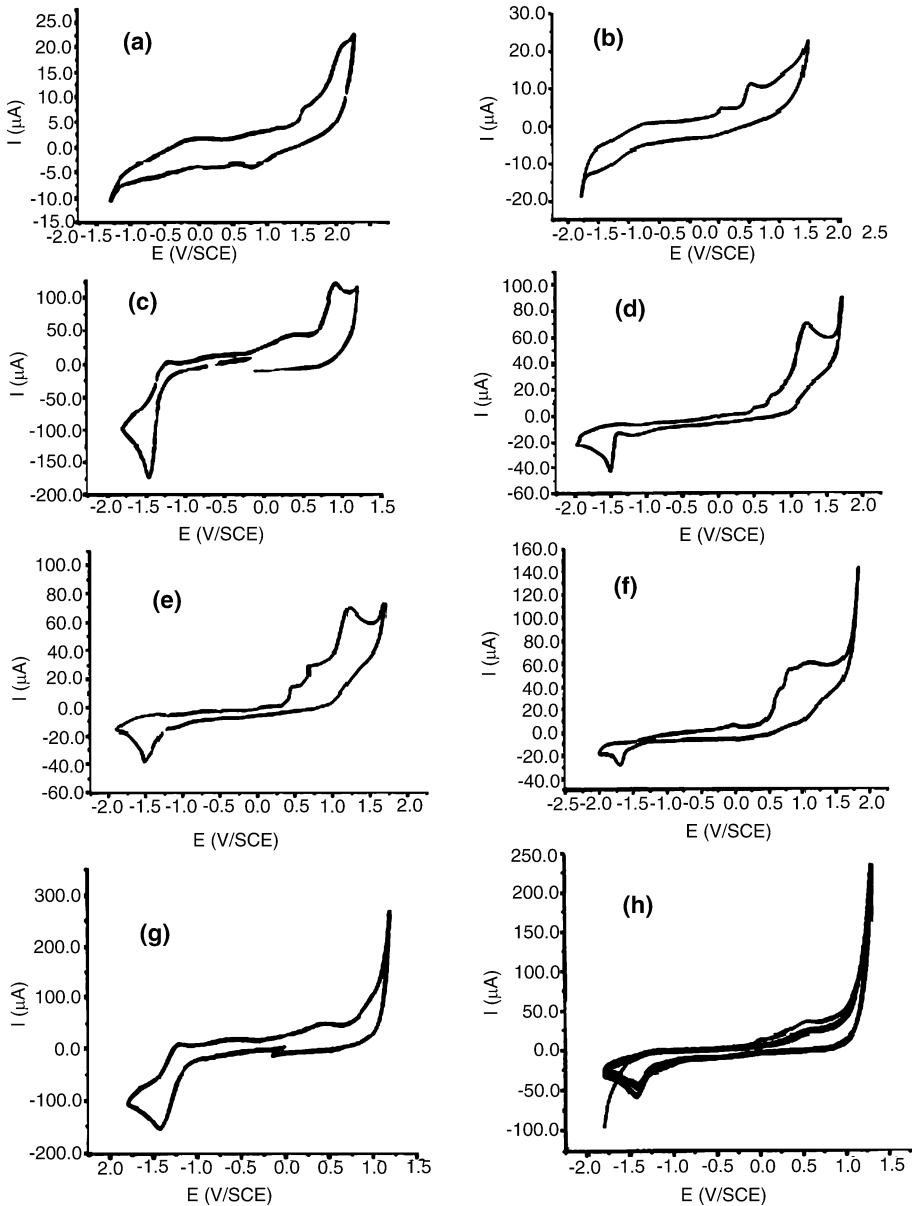


Fig. 2 Representative cyclic voltammograms in DMF (25 °C, ionic strength of 0.1 mol·L⁻¹, Bu₄NClO₄, *i* in μA, *v* = 100 mV·s⁻¹) of: H₂L1 (a), H₂L2 (b), Co^{II}L1 (c), Co^{II}L2 (d), Ni^{II}L1 (e), Ni^{II}L2 (f), Cd^{II}L1 (g), and Cd^{II}L2 (h)

3.9 Complexes

Because the ligands used in this electrochemical examination are not reversibly oxidized or reduced in the applied potential range, the behavior of the complexes showed similar responses that could be considered as the sum of the individual response of the metal center

and of the ligands. For example, there are no E_{pa1} and E_{pc1} peaks for H_2L1 , whereas for its nickel complex there is a new oxidation peak E_{pa1} at +0.47 V and a new reduction peak E_{pc1} at +1.10 V. This clearly indicates that there is an effect from the metal center on the electrochemical properties. The voltammetric responses of the cobalt(II) complexes show cathodic peaks at -1.46 V corresponding to the reduction of complexed Co^{II} to Co^0 for H_2L1 (Fig. 2c) and -1.50 V and +1.06 V for H_2L2 (Fig. 2d). The electrooxidation of Co^0 to Co^{II} in these species, in addition to those of the ligands (observed at nearly the same potential values as the corresponding H_2L1 and H_2L2), occur at +0.46 and +0.52 V. These values agree with those previously published for cobalt complexes in the same solvent [45].

In the case of nickel(II) complexes, the cyclic voltammograms on the negative scan show four reduction peaks at -1.50 and +1.10 V for $Ni(II)L1$ (Fig. 2e), and -1.68 and +1.01 V for $Ni(II)L2$ (Fig. 2f). The cathodic waves at -1.50 V and -1.68 V correspond to the reductions of complexed Ni^{II} to Ni^0 whereas, on the reverse sweep, up to three oxidation peaks occur in each case. The peaks that are absent in the cyclic voltammograms of the free ligands are located at +0.47 V (ligand H_2L1) and +0.66 V (ligand H_2L2). These peaks can be associated to the irreversible oxidation of Ni^0 to Ni^{II} . The electrochemical responses of the $Ni(II)$ compounds are essentially the same with minor shifts in the potential values (Table 3), and agree with those previously described for nickel complexes in the same solvent [46].

In addition, a linear dependence was observed between i_p and $v^{1/2}$ and E_p and i_p as the voltage scan rate (v) was increased (i.e., at 100, 200, 300, and 500 $mV \cdot s^{-1}$), indicating a diffusion controlled electron exchange reaction. The plot of i_{pa} for the oxidation peak potential of $Ni(II)L1$ and that of $Ni(II)L2$, each as a function of the square root of the scan rate (not shown), gave a straight line parallel to the horizontal axis ($\log_{10} v$) indicating a quasi-reversible electrode exchange reaction [42]. Furthermore, the ratio i_{pc}/i_{pa} was independent of scan rate and equal to unity for scan rates varying from 100 $mV \cdot s^{-1}$ to 1 $V \cdot s^{-1}$.

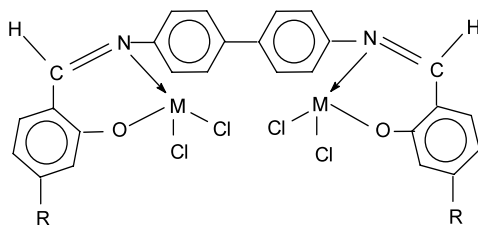
Finally, the cadmium(II) complexes also undergo reduction processes located at -1.43 V for $Cd(II)L1$ (Fig. 2g) and -1.50 V for $Cd(II)L2$ (Fig. 2h). These peak values correspond to the reduction of Cd^{II} to Cd^0 . The reoxidations at +0.45 V for $Cd(II)L1$ and +0.52 V for $Cd(II)L2$ are due to the oxidation of Cd^0 back to coordinated Cd^{II} .

When the scan rate changes, this last single reduction peak (at -1.50 V) sometimes is decomposed into two waves and the second peak is often more distinct than the first. These two successive reduction peaks are observed in the cyclic voltammogram of $Cd(II)L2$ at various scan rates (100 to 10 $mV \cdot s^{-1}$), but $Cd(II)L1$ gives only one peak in each case. A similar behavior has been observed for other symmetric Schiff bases [45, 47].

3.10 Proposed Structures

The proposed structures are given in Fig. 3. The cobalt(II), cadmium(II) and nickel(II) compounds exhibit the same structure. These species are binuclear complexes and the coor-

Fig. 3 The proposed structures for the complexes $R = H$ (H_2L1) or OH (H_2L2)



$M = Co, Cd$ or Ni (with $2 \cdot H_2O$ in case of ligand H_2L1)

dination of the metal ions is through nitrogen and oxygen atoms. The cobalt(II) and the cadmium(II) compounds present a distorted tetrahedral geometry while the nickel(II) complexes exhibit a typical square planar structure [48]. In addition, two water molecules are present in the case of the nickel(II) complex (ligand H₂L1) as indicated by infrared spectroscopy and thermal analysis.

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