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Unsymmetrical tetradentate Schiff base complexes derived from 2,3-diaminophenol and salicylaldehyde or 5-bromosalicylaldehyde

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Abstract

Salicylaldehyde or 5-bromosalicylaldehyde reacted with 2,3-diaminophenol in absolute EtOH in a 2:1 molar ratio to give new unsymmetrical Schiff bases (H_2L). The bases were used as ligands to coordinate Mn(III), Ni(II) and Cu(II) chlorides leading to $[Mn^{III}ClL] \cdot EtOH$ and $[M^{II}L]$ or $[M^{II}L] \cdot 2H_2O$ (M = Ni or Cu) complexes. Their structures were determined using mass spectroscopy, IR, u.v.–vis and ^{1}H-n.m.r. The cyclic voltammetry in acetonitrile showed irreversible waves for both ligands. Under the same experimental conditions, the complexes exhibited mainly the non-reversible reduction of the Ni(II) or Cu(II) ion to Ni(0) or Cu(0), while the reduction of Mn(III) to Mn(II) was found to be a quite reversible phenomenon.

Introduction

Since the first report of the Schiff reaction [1], the synthesis of symmetrical tetradentate Schiff bases as ligands, and of their complexes, has been widely described. Some of them may be used as catalysts in various chemical processes [2, 3], or as models for a better understanding of some biological systems [4–6]. However, the unsymmetrical tetradentate Schiff base complexes were less studied than the symmetrical ones.

A large number of publications describing the preparation of the half-units of these unsymmetrical ligands, using various derivatives of salicylaldehyde, have been reported [7–22]. Various tridentate and tetradentate Schiff bases and relative metal complexes were obtained. Among these compounds, some were used as catalysts: for instance, the Mn(III) complexes of a new chiral unsymmetrical Schiff-base containing salicylaldehyde and (2-hydroxyphenyl)alkylketone units were found to be good catalysts for the asymmetric epoxidation of unfunctionalised alkenes [20]. Similarly, non-symmetrical tetradentate vanadyl Schiff base complexes derived from 1,2-phenylene diamine and 1,8-naphthalene diamine showed catalytic activity in the oxidation of cyclohexene [22].

Another way was also mentioned to synthesise the analogous complexes *via* the reaction of β-diketones with *o*-aminophenol (OAP) and its derivatives [23, 24] in order to obtain the half-unit condensed Schiff base.

These two latest classes of complexes were not relatively easily obtained.

In the present work, the non-symmetry of the Schiff bases occurs through the diamine moiety *e.g.* 2,3-diaminophenol. The complexes formed with these two new ligands will be precursors for the synthesis of new materials obtained by etherification of the phenolic hydroxyl. They could be used in several applications, such as the modification of monomers (pyrrole, thiophene *etc.*) to form, *via* anodic oxidation, polymers used to build modified electrodes. These new complex species will appear in polymer matrices as pendant functional groups, covalently grafted. The applications of these compounds are very important for electrocatalysis or mainly electroanalysis.

Experimental

Physical measurements

The ^{1}H-n.m.r. spectra of the ligands and the Ni(II) diamagnetic complexes were recorded with a Bruker AC 250 at 25 °C. All chemical shifts ^{1}H are given in ppm using tetramethylsilane (TMS) as internal reference and DMSO-D$_6$ as solvent. The i.r. spectra were recorded on a Perkin-Elmer 1000-FT-IR Spectrometer using KBr discs, while the electronic spectra (u.v.–vis) were obtained on a Unicam UV-300 Spectrophotometer. The melting points were determined with a Kofler bench and were uncorrected. Cyclic voltammograms

were made with a Tacussel PJT potentiostat Galvanostat driven by Pilovit-Num. All measurements were done in a 5 cm^3 Metrohm monocompartment cell equipped with a classical three-electrode. The solvent was acetonitrile with a 10^{-3} mol l^{-1} concentration for the studied species, and the ionic strength was maintained at 0.1 mol l^{-1} with Bu$_4$NClO$_4$ (TBAP). The electrodes were polished with diamond paste and rinsed with large amounts of acetone and finally with acetonitrile. The working electrode was a disc of glassy carbon (diam. 3 mm), the counter electrode a Pt wire, and the reference electrode was a saturated calomel electrode (SCE). The DSC diagrams were obtained with a Shimadzu DSC-60 in the range 20–800 °C. The mass spectra (FAB, electrospray) were recorded on a Jeol JMS 70 spectrometer (Service central d'Analyses Spectroscopiques, Université d'Angers, Pr. P. Richomme).

Preparation of the ligands and the complexes

All chemicals were analytical grade and were used as received without further purification. The metal salts were acetate derivatives.

Preparation of the ligands

To a solution of absolute EtOH (5 cm^3) containing 1 mmol of 2,3-diaminophenol was added 2 mmol (EtOH, 15 cm^3) of salicylaldehyde or of its derivative. The mixture was stirred under an argon atmosphere and heated at 50 °C for 1 h. It was kept overnight at *ca.* 4 °C. The ligand was recovered by filtration and its purity was verified using TLC with a mixture of CH$_2$Cl$_2$/MeOH (9.5/0.5, v/v) as solvent (Figure 1).

Preparation of the complexes

The complexes were prepared as previously described [25–27]. To a solution of the ligand H$_2$L1 or H$_2$L2 absolute EtOH (0.5 mmol, 10 cm^3) was added slowly the metal acetate (0.475 mmol, 5 cm^3 EtOH). The mixture was heated for several hours under a N$_2$ atmosphere and finally kept overnight at 4 °C. The complex which precipitated was removed by filtration. It was washed several times with a MeOH/H$_2$O mixture (1:1,v/v) previously bubbled with Ar for 15 min mainly in the case of the manganese(III) complexes.

The manganese complexes were obtained under an air atmosphere in order to oxidise Mn(II) to Mn(III) (yield: 70%). In this way, the mixture was heated at 50 °C for 1 h under an air atmosphere. The acetate group was further exchanged with chloride ions using LiCl (10 times more concentrated than the complex solution) under stirring at 50 °C for 1 h.

Results and discussion

The main analytical data for the complexes is given in Table 1.

Molecular formulae

The elemental analysis (Table 1) indicated several molecular formulae: the two Mn(III) complexes showed
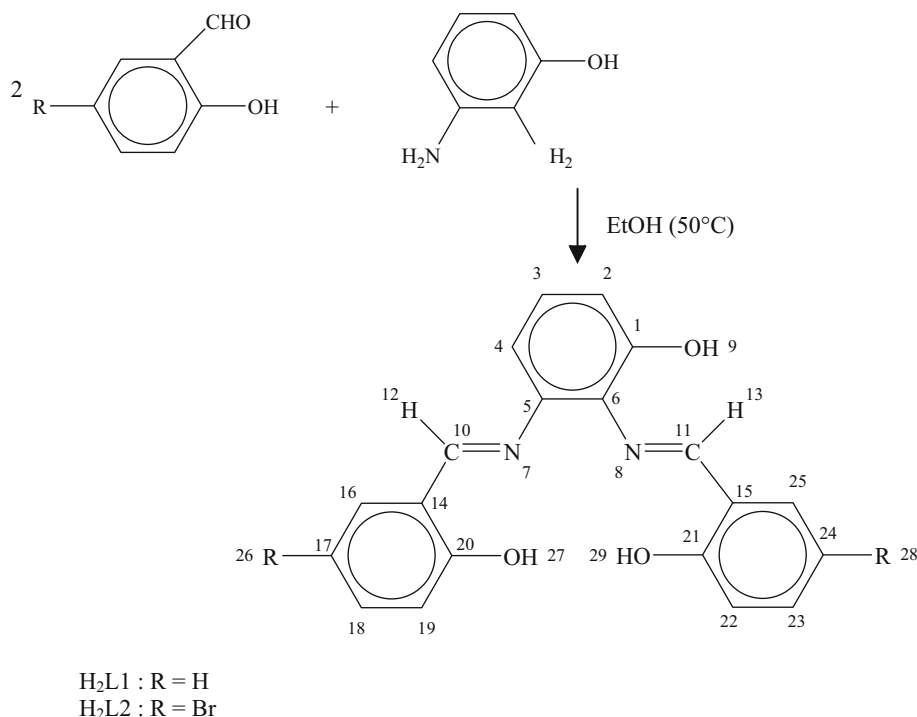

H$_2$L1 : R = H
H$_2$L2 : R = Br

Fig. 1. Synthesis pathway for ligands synthesis.

Table 1. Analytical data for the complexes

Compound	Colour	Yield (%)	M$^+$	C (%)	H (%)	N (%)
Mn(III)ClL1 · EtOH	Brown	70		56.0 (56.7)	4.2 (4.3)	5.6 (6.0)
Ni(II)L1	Yellow	68	389.0	61.6 (61.7)	3.7 (3.6)	6.9 (7.2)
Cu(II)L1	Green	50	394.0	57.1 (55.9)	3.7 (3.7)	7.8 (6.5)
Mn(III)ClL2 · EtOH	Brown	65		42.9 (42.3)	2.7 (2.9)	4.6 (4.5)
Ni(II)L2 · 2H$_2$O	Yellow	80	546.9	40.1 (41.2)	2.4 (2.7)	5.6 (4.8)
Cu(II)L2 · 2H$_2$O	Green	73	551.9	37.8 (40.8)	3.0 (2.7)	4.7 (4.8)

an EtOH molecule while Ni(II) and Cu(II) exhibited 2 water molecules in the case of H$_2$L2 only. All compounds were obtained with the ligand dianion corresponding to the ionisation of the two phenolic groups. The Ni(II) and Cu(II) complexes are neutral species while Mn(III) complexes appear to be cationic species with chloride anion as counter ion. The molecular masses obtained by mass spectroscopy (Table 1) are in good agreement with the proposed formulae and with the literature [28].

Infrared spectra

The broad absorption which was systematically observed at the 3300–3800 cm^{-1} range either in the ligands (intra-molecular hydrogen bonding) or in the complexes (water lattice), is assigned to the hydroxyl groups of phenol. In the case of the complexes, this broad band expresses the presence of H$_2$O or EtOH molecules, according to the DSC results, the observation of releasing vapour (loss of H$_2$O or EtOH) during the melting point measurements and the elemental analysis [29]. The comparison of the spectra of the free ligands with those of their complexes within the range 1650–1178 cm^{-1} indicates that the ligands coordinate through N and O-atoms.

The stretching vibrations v(C=N), v(C=C) and v(C–O) show very strong bands in the 1615–1602, 1460–1440 and 1330–1178 cm^{-1} ranges, respectively. In this case, the band corresponding to the C=N stretching vibration for the azomethine group –N=CH– [30–34] is shifted to lower wavenumbers (2–12 cm^{-1}), while its intensity decreases. In the meantime the v(C–O) vibration shifts to higher wavenumbers. These two facts are due to coordination of the metal ion

through the oxygen atoms of ionised hydroxyl groups and nitrogen atoms from imino groups [35, 36].

Electronic spectra

In the electronic spectra (Table 2), we note a bathochromic shift in the case of H$_2$L1 when passing from the ligand to the manganese(III) complex Mn(III)ClL1. This bathochromic effect is observed again with all other complexes in this series. As regards the ligands H$_2$L1 and H$_2$L2, a bathochromic effect is also noted due to bromide in H$_2$L1. The molar extinction coefficient ε maxima is higher for H$_2$L2 because of the extension of the electronic conjugation reaching the d-electrons of bromine atoms electronic shell.

^{1}H-n.m.r. spectroscopy

The ^{1}H-n.m.r. spectra of ligand H$_2$L1 and its nickel complex NiL1 were recorded in DMSO-D$_6$. These ^{1}H-n.m.r. results are presented in Table 3 (see Figure 1 for the numbering scheme).

The aromatic protons give a multiplet centred at 7.2 ppm for H$_2$L1 and 7.11 ppm for its nickel complex NiL1. Herein we will attempt to propose some attributions based on the literature [37, 38]. It has been reported that the chemical shift of the hydroxyl proton of 2-hydroxyacetophenone or salicylaldehyde, where the carbonyl group is attached in the *o*-position from the hydroxyl group, resonates at 12.05 ppm [37, 39], shifted more downfield than the phenol proton ($\delta = 7.54$ ppm). This deshielding shift was attributed to the formation of intramolecular hydrogen bonding. Taking account of these considerations [40] for H$_2$L1, we could assign the signal at 9.94 ppm to H(9) and the

Table 2. Spectroscopic data

Compound	Infrared (cm^{-1})			u.v.–vis					
	v (O–H)	v C=N	v (C–O)	λ (nm)	ε (M cm^{-1})	λ (nm)	ε (M cm^{-1})	λ (nm)	ε (M cm^{-1})
H$_2$L1	3398	1610	1210	260	137100	332	116400		
Mn(III)ClL1 · EtOH	3249	1602	1301	336	288500	434	144200		
Ni(II)L1	3475	1608	1153	350	135800	472	77100		
Cu(II)L1	3413	1605	1228	350	168400	334	159400	420	12490
H$_2$L2	3414	1615	1270	266	166900	350	144500		
Mn(III)ClL2 · EtOH	3412	1603	1201	224	101400	338	48700		
Ni(II)L2 · 2H$_2$O	3375	1603	1288	350	199700	458	106600		
Cu(II)L2 · 2H$_2$O	3412	1605	1244	350	80800	460	53000		

Table 3. ¹H-n.m.r. data of ligands and their nickel complexes in DMSO-D$_6$ (Chemical shifts in ppm *vs* TMS)

Compound	Hydrogen atoms					
	a*	9	29	27	13	12
H$_2$L1	7.26	9.94	12.74	13.16	8.90	8.88
H$_2$L2	7.39	10.10	12.70	13.30	8.94	8.90
Ni(II)L1	7.11	11.32	–	–	9.53	8.79
Ni(II)L2	7.33	10.30	–	–	9.90	9.27

*a, aromatic protons; the numbering scheme is given in Figure 1.

signal at 12.74 ppm to H(29) seeing that both interact with the same nitrogen atom of the azomethine group. In the meantime, the peak at 13.16 is assigned to H(27) which interacts exclusively with the nitrogen atom of the second azomethine group. In this ligand (H$_2$L1), we have also observed a very weak difference between the azomethine protons H(12) and H(13) which appear at 8.8 and 8.9 ppm respectively, for the same reasons than those previously indicated for the hydroxyl proton of 2-hydroxyacetophenone [40]. This difference becomes more important in the corresponding nickel complex NiL1 where the signals of the azomethine protons arise at 9.53 for H(13) and at 8.79 for H(12). This fact is supported by a higher structure rigidity, leading to the co-planarity of the different sp^2 systems constituting the complex according to the square planar generally observed for nickel complexes [41]. Reciprocally, this deshielding shift at 9.94 ppm for H(9) in H$_2$L1, and at 11.32 ppm for NiL1, probably, due to the intramolecular hydrogen bonding between the phenol proton H(9) and the nitrogen atom of the azomethine group. These results are in good agreement with those previously reported in the literature [21, 22, 37–39, 41].

DSC diagrams

The DSC diagrams show significant differences between ligands and complexes. For all species, decomposition occurs at temperatures higher than 300 °C. Some exothermic processes occur previously in the 200–240 °C range; according to the nature of the complex. It must also be indicated that these compounds lose their H$_2$O

or solvent molecules giving an endothermic peak under an air flux around 200 °C in the case of the complexes. This is in good agreement with values given in literature [28].

Mass spectrometry

Positive ions corresponding to the different complexes [M$^+$] were identified by the FAB$^+$ method (Fast atom bombardment). The spectra of these complexes also show peaks attributed to [M$^+$ + 1H$^+$] and [M$^+$ + 2H$^+$], respectively. These results agree with the expected structures and the data reported in literature [29].

Electrochemical characteristics of the ligands and the complexes

The cyclic voltammetric data of the ligands and the complexes are summarised in Table 4 and some representative curves are given in Figure 2.

Ligands

In the −2.200 to +2.200 V range, the ligand H$_2$L1 shows, two irreversible waves on the anodic side, with Ep_{a1} = +1.060 and Ep_{a2} = +1.520 V respectively, without any cathodic peaks. These two irreversible waves are attributed to the *para* and *ortho* oxidations of the phenol moieties and of the phenol groups themselves [42]. The same phenomenon is observed for H$_2$L2 but these two oxidation waves are located at +1.440 and +1.840 V. This ligand presents an improved resistance towards oxidation reactions due to *para*-bromine atoms leading to higher oxidation potential values because the *para* and *ortho* positions of the phenol moieties presents a lower electronic density. These results are very close to those reported in the literature for similar compounds [42–45].

Complexes

The Mn(III) complexes show only one reduction wave located at −0.360 V for H$_2$L1 and at −0.040 V in the case of H$_2$L2. The reoxidation of these species occurs at −0.240 and +0.080 V, respectively. So the Mn(III)

Table 4. Voltamperometric results at 25 °C in MeCN, ionic strength 0.1 mol l^{-1} (TBAP), results in V *vs* SCE, sweep speed: 50 mV s^{-1}, E_a: anodic; E_c: cathodic

Complex	E_{pa1}	E_{pa2}	E_{pa3}	E_{pc1}	E_{pc2}	i_{pa}/i_{pc}	ΔE [a]	$E_{1/2}$ [b]
Mn(III)ClL1 · EtOH	−0.240			−0.360		0.780	−0.120	−0.300
Ni(II)L1	−0.960	+1.16		−0.880	−1.660	0.260	−0.700	
Cu(II)L1	+0.840	+0.960	+1.420	−0.880	−1.600	0.367	−0.760	
Mn(III)ClL2 · EtOH	+0.080			−0.040		0.833	−0.120	+0.020
Ni(II)L2 · 2H$_2$O	−0.840	+1.150	+1.760	−0.780	−1.400	0.620	−0.560	
Cu(II)L2 · 2H$_2$O	−0.50	+1.360	+1.740		−1.300	0.727	−0.540	

[a] $\Delta E = E_{pc} - E_{pa}$.
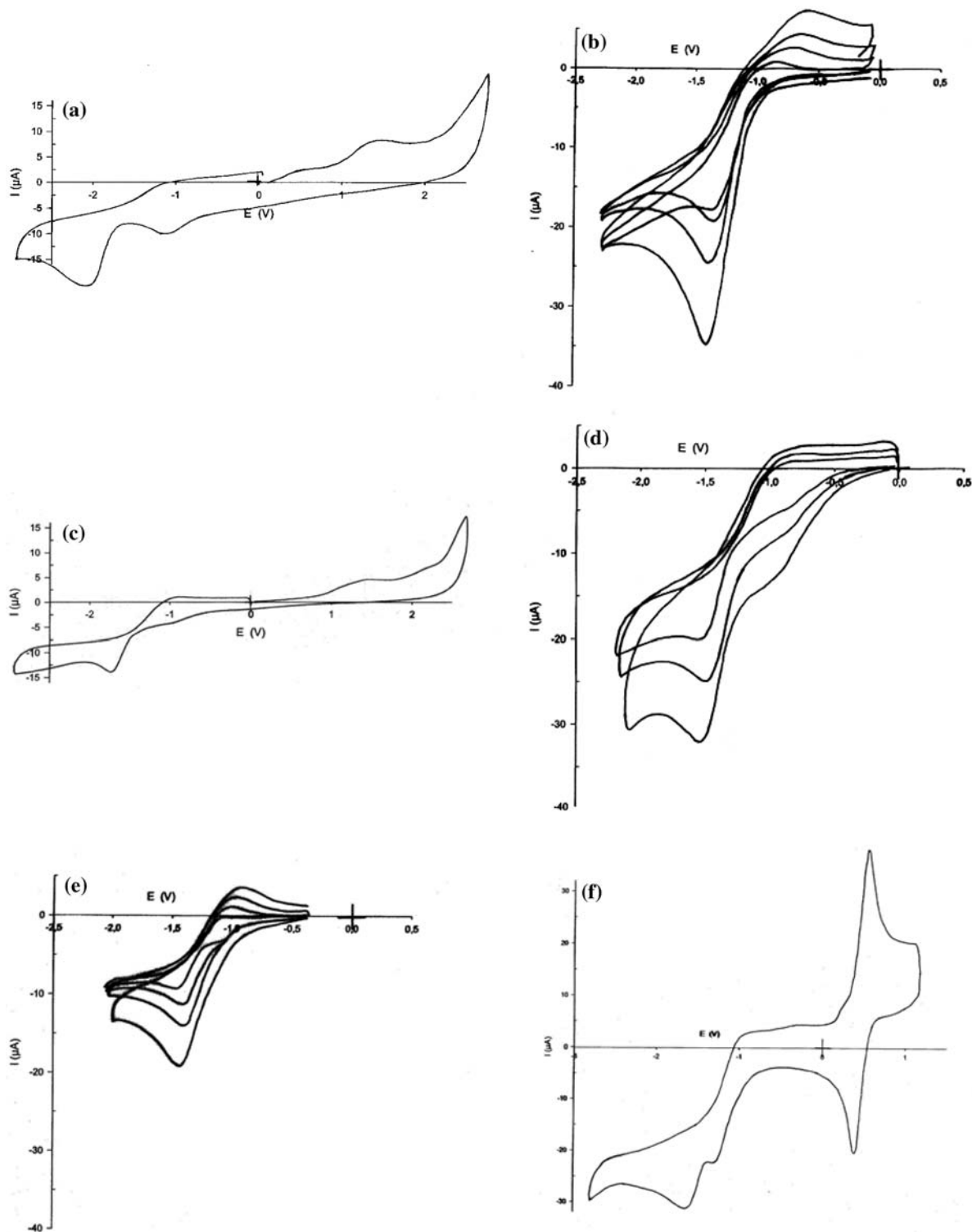[b] $E^{1/2} = 0.5\Delta E + E_{pa}$.

Fig. 2. Voltammograms of NiL1 (a), NiL2 (c) scan rate 5 m V s^{-1}; NiL1 (b), NiL2 (d), and CuL2 (e) with variable scan rate; CuL2 with ferrocene (f) in MeCN ($\mu = 0.1$ mol l^{-1}).

complexes show diffusion controlled quasi-reversible couples: Mn(III)ClL/Mn(II)ClL (L = L1 or L2). The variation of the scan rate ($v = 100$ to 500 V s^{-1}) shows that the curve E_{pc} as a function of log$v$ is a straight line and it does not depend upon the sweep speed. The potential peaks separation is $\Delta E_p = 0.120$ V and the i_{pa}/i_{pc} ratios are close to 1. The acceptor effect of *p*-bromine substituent in Mn(III)ClL1 shifts the half-

wave potential from -0.300 V (in Mn(III)ClL1 5,5′-not substituted) to $+0.020$ V (Mn(III)ClL2, 5,5′-brominated) as previously described [27].

The reduction waves of nickel(II) complexes are located at -1.660 V (ligand H$_2$L1) and -1.400 V (ligand H$_2$L2) [46, 47]. When the speed rate changes, this single reduction wave is sometimes decomposed into two steps and the second peak is often more clear than
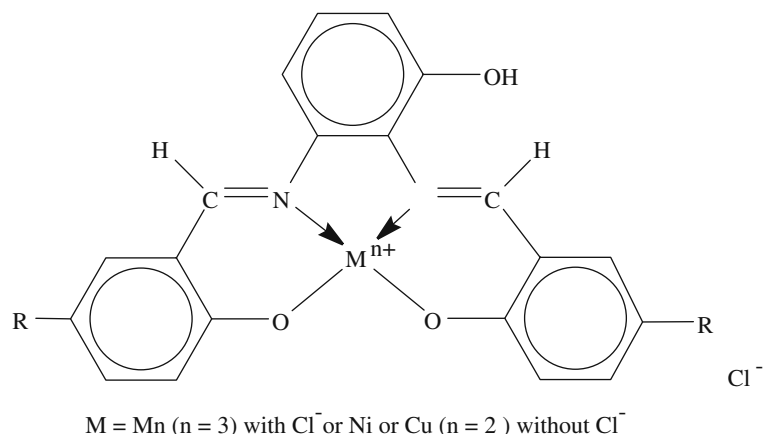
M = Mn (n = 3) with Cl⁻ or Ni or Cu (n = 2) without Cl⁻

Fig. 3. Proposed structures for the complexes: R = H (H₂L1) or Br (H₂L2).

the first. These two successive reduction waves are observed in the CV of Ni(II)L2 at various scan rates (100 to 10 mV s^{-1}) but Ni(II)L1 gives only one wave in any case. A similar behaviour has been found for the corresponding copper complexes.

Two reduction waves are also observed for Cu(II)L1 at all scan rates but, in the case of Cu(II)L2, they appear clearly in the 25 to 5 m V s^{-1} range only. The peaks separation between this anodic wave and the corresponding anodic peak ΔE_p is greater than 0.500 V; this value is higher than those reported for a Nernstian process. Nevertheless, these voltamperograms exhibit a pair of anodic and cathodic peaks showing a chemical reversibility with a chemical reaction associated to the electrochemical processes as indicated by the shape of the curve Ip *vs.* scan rate square root (not shown).

When ferrocene is added, very few changes occur in the CV (i_p or E_p) for Ni(II) complexes. In the case of Mn(III) compounds, the cathodic current intensity was enhanced by 50%. Ferrocene should be used as a good external reference for the electrochemical study of these manganese compounds; it will be also useful for their detection at low concentrations. For Cu(II) complexes, the intensities of the two cathodic waves are 30% higher when ferrocene is added. In the meantime, the E_{pc1} value remains unchanged while the second E_{pc} peak is shifted by 0.180 V on the cathodic side.

Proposed structures

The proposed structures for the complexes are given in Figure 3. The Mn(III) (cationic) and Ni(II) (neutral) complexes are square planar species. In the case of the Mn^{3+} compounds a positive charge remains and the chloride ion is located outside the complex structure. In the copper complexes, the metal ion presents a distorted octahedral geometry with the two ligands in a plane and two H₂O molecules along the z-axis of the complex (ligand H₂L2). In the Cu(II) complex the copper ion presents a square planar geometry.

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TMCH 6334