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SYNTHESIS, SPECTRAL AND ELECTROCHEMICAL PROPERTIES OF DIVALENT METAL COMPLEXES CONTAINING THIOHYDRAZONE AND THIOSEMICARBAZONE LIGANDS

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Abstract—The L^1H_4 and L^2H_6 complexes of metal halides MX_2 (M = Cu, Ni, Co, Zn, Cd or Hg, X = Cl, Br or I) have been prepared. The complexes were characterized on the bases of ^1H NMR, IR, electronic and mass spectra, magnetic studies, conductance and analytical data. The stoichiometry and the spectroscopic data indicate that the complexes **1**–**8**, **11**, **12** and **15** the metal ions are coordinated by ligand anions and the complexes **9**, **10**, **13**, **14** and **16** contain the neutral ligand. Electrochemical behaviour of nickel and cobalt complexes was determined by cyclic voltammetry. The reduction of complexes are related to metal-centred reductions. In addition, complexes **3**, **11** and **12** show irreversible waves associated to Ni(II)/Ni(III) process. The reduction/oxidation potentials depend on the unsaturation grade present in the complexes.

Thiosemicarbazone, thiocarbazone and their metal complexes have been intensively studied due to their range of potential biological uses.[1] Schiff base macroligands containing thiosemicarbazone moieties have an additional interest, because these also contain the N=C—C=N structural unit, which forms a strong chelate ring giving a possible electron delocalization associated with extended conjugation that may also affect the nature of the complexes formed.[2] Few electrochemical results have been reported to date for either thiosemicarbazones or their metal complexes, although their biological activity may be related to their redox properties. For example, antifungal activity and electrochemical properties of some copper (II) complexes have been studied and showed a lower reduction potential which seems to be related to an increased biological activity.[1] Recent growing interest in the reductive and oxidative chemistry of nickel(II) and cobalt(II) macrocyclic complexes derives from recognition of the biological importance of the less common oxidation states of nickel and it involves the elucidation of factors that stabilize metal-centred reduced-oxidized species over

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ligand-based reduction oxidation.[3] The redox process can include oxidation and reduction of the central metal ion, various oxidation and reduction reactions of the ligand and processes which involve both the central atom and the ligand.[4] The redox potentials of the M(III)–M(II) and M(II)–M(I) couples have been shown to be markedly affected by the nature of the solvent, background electrolyte and by the structure of the chelating ligand and of the complex as a whole.[5]

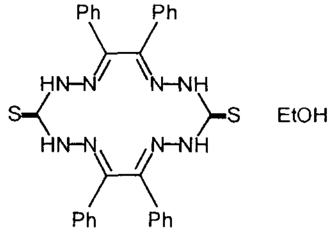
Complexes of neutral tetraaza macrocycles have dominated earlier studies of the first kind of process. For a large number of such ligands it has been possible to identify electrode processes that are attributable to the same ion couple. The influences of various structural features have been gauged, including ring size, degree and arrangement of unsaturation and alkyl substitution.[6]

In previous investigations we synthesized and characterized a number of macrocyclic and open chain ligands containing thiosemicarbazone moieties, and their metal complexes. As part of our work involving the preparation of free imino macroligands in the absence of the template metal ion effect,[7–9] we became interested in the synthesis of mono- and polynuclear metal complexes, which showed a high level of unsaturation yielding unusual coordination geometries.[10,11] The present work stems from our continued interest in the synthesis and reactivity of Schiff base metal complexes. Herein, we report the reactions of two derivatives from thiocarbazide and thiosemicarbazide, 3,4,10,11-tetraphenyl-1,2,5,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4,9,11-tetraene, L^1H_4, and benzilbisthiosemicarbazone, L^2H_6, with copper, nickel, cobalt, zinc, cadmium and mercury salts. Given the potential relationship between biological activities and redox properties of thiocarbazone complexes, these properties of nickel and cobalt complexes are explored.

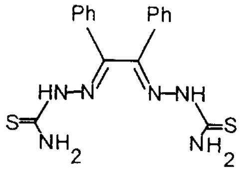
The complexes were characterized on the bases of ^1H NMR, IR, electronic and mass spectra, magnetic studies, conductance an analytical data. The electrochemical properties of nickel and cobalt complexes have been studied by cyclic voltammetry.

EXPERIMENTAL

The ligands 3,4,10,11-tetraphenyl-1,2,5,8,9,12,13-octaazacyclotetradeca-7,14-dithione-2,4,9,11-tetraene (L^1H_4) and benzilbisthiosemicarbazone (L^2H_6) were prepared following the method previously reported.[7] $CuBr_2$, $NiCl_2 \cdot 6H_2O$, $NiBr_2$, $Ni(OAc)_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $ZnBr_2$, ZnI_2, $CdCl_2$, $CdBr_2 \cdot 4H_2O$, CdI_2, $HgCl_2$, $HgBr_2$ and HgI_2 were commercial products of highest chemical grade (Fluka). Solvents were purified according to standard procedures.



L^1H_4



L^2H_6

Fig. 1. Structures proposed for L^1H_4 and L^2H_6.

Microanalyses were carried out using a Perkin–Elmer 2400 CHN Elemental Analyser. IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets on a Bomen spectrophotometer. UV–vis spectra of dimethylformamide (DMF) solutions and solid reflectance spectra were run on a Pye-Unicam SP-8-100 spectrophotometer. Conductivity data were measured using freshly prepared DMF solutions (*ca* 10^{-3} M) at 25°C with a Metrohm Herisau model E-518 instrument. ^1H NMR spectra were recorded on a Bruker WH-200 spectrometer with Me_4Si as the internal standard. Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix. Electrochemical measurements were performed with a BAS CV 27 voltammograph and a BAS A-4 XY register using a platinum disk superficie as working electrode, a platinum wire as auxiliary electrode and Ag–AgCl as reference electrode. Cyclic voltammetric studies of ligands and complexes were carried out on 0.01 M solutions in dimethylformamide (DMF) containing 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte. All solutions were purged with nitrogen stream for five minutes. Magnetic susceptibility measurements were carried out using the Faraday method with a Magnet 13-4 Brucker balance at different temperatures (77–295 K).

Preparation of the complexes

Complexes **1**, **2**, **4**, **5**, **7** and **8** were prepared by dropwise addition a solution of $CuBr_2$, NiX_2

(X = Cl and acetate), $CoCl_2 \cdot 6H_2O$, ZnI_2 and CdX_2 (X = Cl, Br and I) (0.1 mmol) in methanol (20 cm^3) to a boiling methanol suspension (20 cm^3) of L^1H_4 (0.1 mmol). Refluxing was continued for an additional 3 h. The precipitate so formed was filtered off, washed with methanol and dried *in vacuo*.

Complex **6**, obtained by the interaction of L^1H_4 with Zn(II) chloride or bromide, complex **9** from HgX_2 (X = Cl, Br and I) and complexes **10**, **11**, **13**–**16** were prepared from L^2H_6 and $CuBr_2$, MCl_2 (M = Ni, Co, Zn, Cd and Hg) and nickel acetate following the method described above but ethanol was used as solvent.

The complex **3** was obtained by interaction of L^1H_4 (0.1 mmol) and nickel bromide (0.1 mmol) in chloroform (30 cm^3) at room temperature. The solution formed was concentrated until a solid was obtained, which was filtered off, washed with diethylether and dried *in vacuo*.

L^2H_6 complex from nickel chloride or bromide **12** was prepared mixing ethanolic solutions of L^2H_6 (0.1 mmol) and nickel halide in a 1 : 1 molar ratio at room temperature. The mixture were stirred for 8 hours and then the solid formed was filtered off, washed with diethylether and dried *in vacuo*.

RESULTS AND DISCUSSION

All complexes obtained are stable to air and moisture. The analyses of the complexes are consistent with the stoichiometry proposed and are summarized in Table 1. The formula for several complexes do not depend on the halide used in the reaction. For example, complex **8** was obtained using chloride, bromide, or iodine as cadmium salt. The analytical data for complexes **1**–**8** and nickel and cadmium **11**, **12** and **15** are consistent when the ligand is deprotonated and coordinated to the metal by its anionic form. On the other hand, the complexes **9**, **10**, **13**, **14** and **16** contain the ligand neutral form.

The conductivity data (Table 1) indicate that the complexes are non-electrolytes compounds, but complex **3** is 1 : 2 electrolyte, suggesting that two bromides are outside the metal coordinated sphere.

The mass spectra of the complexes **11**, **12**, **13** and **15** (Table 2) show the molecular ion peak, and in addition for **12**, **13** and **15** exhibit some daughter peaks. The spectrum of **16** only shows secondary peaks. The spectrum of **12** suggests that one ligand is deprotonaed like complex **11**, and the other acts in the neutral form.

^1H *NMR spectra*

As reference, ^1H NMR spectral data in chloroform for the ligands are included. For L^1H_4: 10.9 s (NH), 10.7 s (NH), 9.9 s (NH), 8.0–7.1 m (CH(Ph)), 4.5 s (OH), 3.6 c (CH_2), 1.2 t (CH_3) ppm. For L^2H_6: 8.4 s (NH), 7.9–7.2 m (CH(Ph)), 6.1 s, 5.0 s (NH_2) ppm.

The ^1H NMR spectra data of the diamagnetic complexes are summarized in Table 3. The disappearance of the NH/NH_2 signals in the nickel

Table 1. Analytical data and some physical properties of complexes

Complex	Colour	Found (calcd) %				m.p.
		C	H	N	Λ_M^a	(°C)
1 $[(L^1H_3)CuBr]EtOH$	dark brown	50.9(51.3)	3.8(3.9)	14.6(14.9)	23.9	250
2 $[(L^1H_3)_2Ni]$	brown	60.9(61.0)	4.1(3.9)	19.0(19.0)	1.8	240
3 $[(L^1H_2)Ni_2]2BrEtOH$	granat	42.8(43.4)	3.5(3.2)	12.8(12.7)	125	266
4 $[(L^1H_3)_2Ni]EtOH$	brown	61.5(61.7)	4.4(4.2)	18.3(18.3)	1.9	200
5 $[(L^1H_3)_2Co(H_2O)_2]$	brown	59.5(59.3)	4.2(4.1)	18.5(18.5)	7.8	214
6 $[(L^1H_2)Zn]EtOH$	red	57.5(57.3)	4.3(4.2)	16.5(16.7)	25.1	250
7 $[(L^1H_2)Zn]$	red	58.2(57.7)	3.8(3.5)	17.6(17.9)	5.5	230
8 $[(L^1H_2)Cd]$	orange	53.9(53.6)	3.7(3.3)	16.2(16.7)	9.8	220
9 $[(L^1H_4)HgX_2]EtOH$	orange	—	—	—	15.3	190–210
10 $[(L^2H_6)_2CuBr_2]$	reddish-brown	41.4(41.0)	3.4(3.4)	17.1(16.9)	3.9	200
11 $[(L^2H_4)Ni]$	reddish-brown	46.3(46.4)	3.4(3.4)	20.2(20.3)	3.1	250
12 $[(L^2H_5)_2Ni]$	brown	50.2(50.0)	3.9(3.9)	22.0(21.9)	2.9	240
13 $[(L^2H_6)Co(H_2O)_2Cl_2]$	dark brown	36.8(36.8)	4.1(3.8)	16.0(16.1)	9.0	250
14 $[(L^2H_6)(ZnCl_2)_3]$	yellow	25.4(25.2)	2.2(2.1)	10.2(10.0)	3.0	250
15 $[(L^2H_3)Cd_2Cl]$	yellow	31.1(31.3)	2.5(2.1)	13.4(13.7)	4.0	250
16 $[(L^2H_6)HgCl_2]$	cream	—	—	—	7.0	(d)

[a] 10^{-3} M DMF solutions and units, $\Omega^{-1}\ cm^2\ mol^{-1}$.

(d) = decompose.

Table 2. Mass spectra of L^2H_6 complexes in THF solutions

Compound	$[M^+]$	$[L^2H_6MCl]^+$	$[L^2H_6M]^+$	$[L^2H_4Ni]^+$	$[C_8H_8S]^+$
11	412.9				
12	768.5			413	178
13	520				178
15	613.2	504.9	468.9		
16		593.1	557.1		178

Table 3. ^1H NMR spectra of diamagnetic complexes (ppm)

Compound	NH/NH_2	Ph	CH_2	CH_3
3	10.7(s)	8.2–7.3(m)	3.5–3.4(q)	1.3–1.2(t)
6	10.7(s)	7.6–7.2(m)	3.7–3.6(q)	1.2–1.1(t)
7	10.7(s)	8.0–7.3(m)	—	—
8	10.8(s)	8.0–7.2(m)	—	—
9	12.4(s),12.2(s)	7.7–7.2(m)	3.5–3.4(q)	1.1–1.0(t)
11	7.7(s)	7.2–6.9(m)	—	—
14	10.1(s), 9.4(s), 8.6(s), 8.5(s), 8.2(s), 8.1(s)	7.8–7.1(m)	—	—
15	11.0(s), 9.5(s), 8.6(s), 8.5(s)	7.8–7.3(m)	—	—
16	9.9(s,br), 8.5(s), 8.2(br)	7.7–7.1(m)	—	—

(II) zinc and cadmium complexes **3**, **6**, **7**, **8** and **11** indicates deprotonation of the ligands. In the spectra of **9**, **14** and **15** complexes, the signal due to NH protons shows a downfield shift and split, suggesting coordination by the NH/NH_2 group. The downfield shift of the amine proton in the spectrum of **16** is consistent with this proton being in the deshielding zone of the adjacent thiocarbonyl group and suggests this group is bound to the Hg ion.[12] The spectra of complexes **3**, **6** and **9** show characteristic signals of methyl and methylene groups from the ethanol. Also, the infrared spectroscopy (Table 4) confirms the presence of water or ethanol molecules where it was suggested to be present from the microanalytical data.

Infrared spectra

The most significant IR bands for the complexes are collected in Table 4. The most important bands of the ligands were assigned[7] according to published data.[13] The most significant bands for L^1H_4 in KBr are: 3323, 3267 (NH), 1597 (CN), 1495 (thioamide I), 940 (thioamide IV) cm^{-1}. For L^2H_6 in KBr are: 3420, 3330, 3250, 3150 (NH_2+NH), 1610, 1585 (NH_2+CN), 1465 (thioamide I), 840 (thioamide IV) cm^{-1}.

The infrared spectra of **6**, **7**, **8**, **9** and **11** complexes are in agreement with coordination to the metal atom by the azomethine and the deprotonated amine groups. Moreover, in complex **12**, the coordination polyhedron of the nickel atom is completed by two amine nitrogen provided by another ligand molecule. The spectra of **2** and **4** also agree with two ligands bonded to the metal atom, leading to hexacoordinated nickel with the macrocyclic ligand acting as a tridentate ligand. The same behaviour for the ligand is observed in complex **1**, in addition its infrared spectrum shows a band at 2117 cm^{-1} characteristic for anionic ligand copper complexes.[5,13] The spectra of complexes **5**, **10**, **13** and **14** indicate the ligands act as bidentate and the metal coordination spheres are completed by halide ions in **10**, **13** and **14** and water molecules in **5** and **13**. In the spectrum of **16**, the noticeable difference with the other complexes is the shift in the (C=N) and thioamide (IV) bands, which indicates that both sulfur and nitrogen atoms are involved in coordination. The spectrum of **15** suggests the L^2H_3 is an anionic polydentate ligand. The spectrum of the dinuclear nickel complex **3** shows splitting of the most characteristic bands, which indicate the presence of coordinated and uncoordinated groups and suggest that the two nickel centres are not stereochemically equivalent, which leads to a different arrangement for each nickel atom. Probably, one of them is in a near pseudotetrahedral environment, as it is suggested from the magnetic moment value (1.30 BM).

The planarity of the chelate rings including Ni(II)

Table 4. Relevant IR spectral data and assignment (cm^{-1})

Compound	$\nu(O{-}H)$	$\nu(NH_2/NH)$	$\nu(CN)$	$\nu(C{=}N)$	$\delta(NH_2+H_2O)$	Thioamide I	Thioamide IV
1	3400	3252	2117	1595		1506, 1486	941
2		3269		1600		1500, 1480	950
3	3425	3291, 3174		1602		1540, 1503	898, 747
4	3446	3268		1597		1500, 1481	944
5		3270		1600		1505, 1480	945
6	3468	3269		1597		1483	947
7		3269		1597		1481	943
8		3262		1597		1500, 1483	944
9	3503	3250		1595		1506, 1487	939
10		3420, 3330, 3250, 3150		1590	1610	1465	835
11		3453, 3270, 3103		1626		1441	902
12		3456, 3419, 3279, 3235, 3131		1588, 1602	1610	1474, 1440	869, 823
13	3555–3400	3270, 3247, 3100		1610	1630	1480	890
14		3450, 3420–2165		1620	1615	1533	902
15		3371, 3250, 3149		1619	1606	1537	902
16		3387, 3303, 3270, 3164		1656	1606	1505, 1477	834

in complex **11** is established by ^1H NMR supporting deprotonation of the amide and IR data.

Electronic spectra

The electronic spectra of the complexes in the solid state and in DMF solutions are shown in Table 5. These data for the cobalt (II) complexes **5** and **13** and for the nickel complexes **2**, **4** and **12** are consistent to an octahedral environment for the metal.[14] The *d–d* bands in complexes **3** and **11** agree with a quasi-planar arrangement for the metal. The spectral data for copper complexes confirm the different environment, suggesting a pseudo-tetrahedral geometry for complex **1** and a copper atom hexacoordinate[14] in complex **10**. Electronic spectra of zinc (II) complexes (red colour) **6**, **7** and cadmium and mercury complexes with the macrocyclic ligand, **8** and **9**, display charge transfer bands in the 490–440 and 335–370 nm regions. The band at *ca* 450 nm may be assigned to metal–ligand charge transfer bands. These spectral data suggest cross conjugation between the hydrazone units inside the ligand.

Electrochemical properties

The cyclic voltammetry parameters for nickel(II) and cobalt(II) complexes **2**, **3**, **11**, **12**, **5** and **13** are

Table 5. Electronic spectra of complexes (nm)

Compound	DMF solutions	Solid reflectance
1	610, 510, 330	
2	630, 570, 510, 330	
3	720, 510, 380, 310	560
4	500, 350	670, 580
5	550, 320	
6	450, 340	
7	490, 335	
8	440, 340	
9	470, 360	
10	560, 500	
11	708, 426, 416	695, 580
12	660, 590	708, 642, 916
13	480, 360	550, 500

Table 6. Summary of electrochemical data for nickel complexes[a]

Compound	Oxidation $E_p(A)$	Reduction $E_p(B)$	$E_p(C)$	E	$E_{1/2}$	ipc/ipa	$E_p(D)$
2	—	−650	−825	175	−737	0.8	−1900(i)
2[b]	—		−1025(i)				−2000(i)
3	825	−675	−825	150	−750	0.70[c]	−1900(i)
3[b]			−1000(i)				−1925(i)
11	950	−1100	−1125	25	−1110	0.67[d]	−1700(i)
12	900	−1025	−1075	50	−1060	0.40[c]	

[a] Electrochemical redox potential in mV, measured at 298 K, scan rate 100 mV s^{-1}, q = quasi-reversible, i = irreversible. $E_{1/2} = 1/2/E_p(C)+E_p(B)$.

[b] Cyclovoltammogram registered in the range from 0.0 to −2 V.

[c] The ratio *ipc/ipa* increase when the scan increase.

[d] The ratio *ipc/ipa* is constant for scan in the range 50–600 mV s^{-1}.

given in Tables 6 and 7, respectively. The voltammograms were recorded in the range +1.5 to −2.5 V at room temperature.

The cyclic voltammogram of L^2H_6 only shows poorly resolved waves near the more negative margin. This wave may be attributed to the reduction of the conjugated portion of the thiosemicarbazone ligand.[15]

The cyclic voltammogram of complex **11** (Fig. 2) (Table 6) exhibits an irreversible oxidation wave (peak A) associated to the Ni(II)/Ni(III) process. The peak couple B/C can be assigned to the Ni(II)/Ni(I) process.[16] Analysis of the latter shows the following features: the anodic to cathodic peak current ratio (ip_a/ip_c) remained practically constant when the scan rate was varied between 25 and 1000 mV s^{-1}. Moreover, the difference between the potential of the anodic peak and the cathodic peak (E_p) remains constant. Also, the ratio between the cathodic peak current and the square root of the scan rate ($ipcv^{1/2}$) is practically constant in the range studied. All these data are diagnostic for a simple quasi-reversible one-electron charge transfer controlled by diffussion following the equation:

$$[\mathrm{Ni^{II}L}]+e^- \leftrightarrow [\mathrm{Ni^{I}L}] \quad \text{peaks B/C.}$$

Cyclic voltammogram of complex **12** shows the same pattern above described and its electrochemical data are included in the Table 6.

Cyclic voltammogram of **13** (Fig. 3) exhibits one chemically reversible (peak A/B) and one irreversible reduction (Peak C) (Table 7). The first cathodic process can unambiguously be assigned to the reduction of Co(II) to Co(I) as shown in previous electrochemical studies for similar complexes.[5]

The voltammograms of complexes **2** and **3**, derived from the macrocyclic ligand, show a different behaviour as is shown in Table 6. The cyclic voltammogram of **2** exhibits three peaks. The peak couple B/C can be assigned to a quasi-reversible one-electron process Ni(II)/Ni(I). When the range measured is restricted to 0.0 to −2.0 V the electrochemical response changes giving an irreversible wave at more negative potential.

The cyclic voltammogram of complex **3** shows the same reduction pattern of complex **2**, but in addition, it exhibits an irreversible oxidation wave (peak A) associated to a Ni(II)/Ni(III) process. The voltammogram of cobalt (II) complex **5** agrees with an irreversible reduction process (peak B).

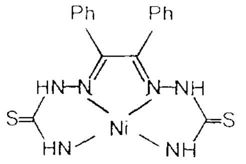
In all nickel(II) complexes, metal-centred reductions were observed. The reduction potentials of complexes **11** and **12** show similar values,

Table 7. Summary of electrochemical data for cobalt(II) complexes[a]

Compound	$E_p(A)$	$E_p(B)$	E	$E_{1/2}$	ipc/ipa	$E_p(C)$
5		−900(i)				−2000(i)
13	−900	−950	50	−925	1[b]	−2200(i)

[a] Electrochemical redox potential (mV), measured at 298 K, scan rate 100 mV s^{-1}, i = irreversible, r = reversible.

[b] The ratio *ipc/ipa* is constant for scan rates in the range 50–600 mV s^{-1}.



11

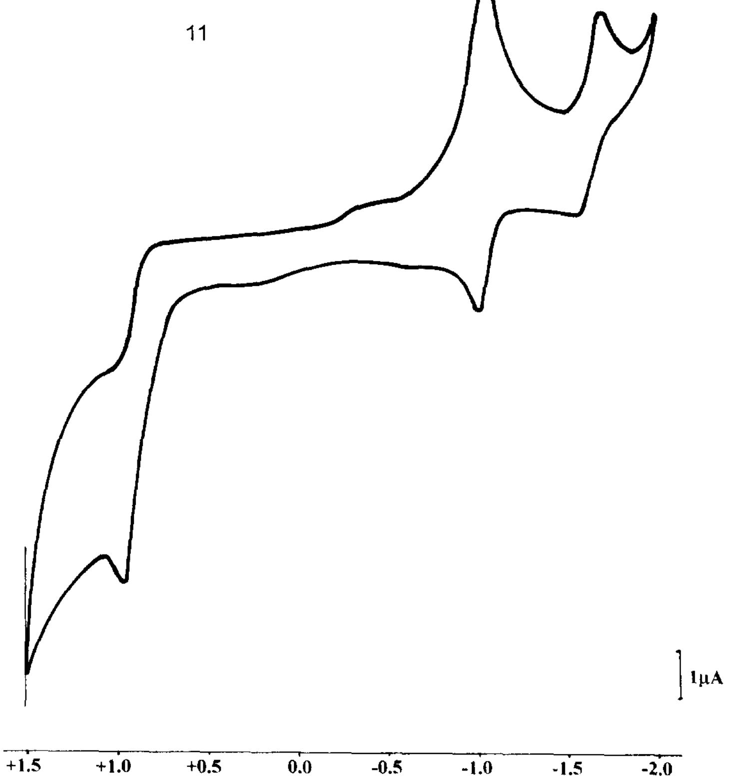


Fig. 2. Cyclic voltammogram of [(L^{2}H$_4$)Ni], **11**, v = 0.1 V s^{-1}.

although slightly more positive for the latter complex. The octahedral geometry in **12** can be invoked to contribute to the more positive $E_{1/2}$ found for this complex as it can more easily accommodate the size increase expected with the addition of an antibonding *d* electron.

The remaining reduction processes included in Tables 6 and 7 for all complexes are less straightforward but they probably correspond to metal centred reductions of M(I) to M(0) reductions.[17]

For macrocyclic ligands a number of factors have already been identified that control the oxidation/reduction site and the redox potentials of their nickel(II) complexes; these include chelate ring size/hole,[6,18] ring ruffling/axial ligation,[19] degree and distribution of unsaturations[6,20] and substitution pattern in the chelate ring.[6,10] The reduction site depends both upon the relative energies of the d_{xy} metal orbital and of the macrocyclic orbital; furthermore the energy of this latter orbital is lowered when the degree of unsaturation of the ligand is increased.[6,20] The reduction potentials of our macrocyclic complexes **2** and **3** show similar values but they are more positive than those in the open chain complexes. This fact may be due to the ability of the macrocyclic ligand to stabilize a wide range of oxidation states of a coordinated metal ion. The effect of the imine function on the reduction of the nickel macrocycle is very pronounced and structures containing this moiety form stable complexes in lower valence states under the influence of a relatively mild potential.[6]

If one stays within the same chelated ligand framework and ring size, a smaller but noticiable effect on the oxidation potential of the Ni(II)/Ni(III) process can be seen from the presence of variable amount of ligand unsaturation. If the unsaturation increases, the stability of the Ni(II) complex relative to the Ni(III) increases. This is probably due to the degree of polarizability of the metal–ligand bond increasing in the more unsaturated derivatives.[6] For the macrocyclic derivatives

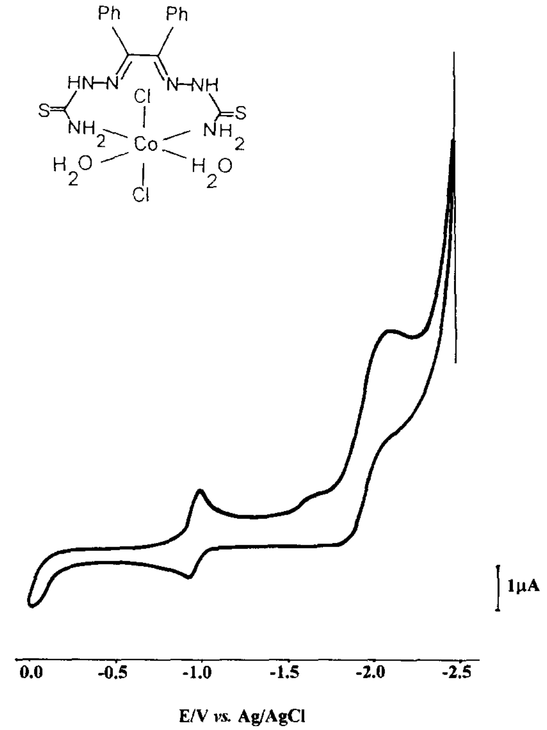


Fig. 3. Cyclic voltammogram of $[(L^2H_6)Co(H_2O)_2Cl_2]$, **13**, $v = 0.1$ V s^{-1}.

2 and **3**, only the voltammogram of complex **3** shows an oxidation wave, this fact may be attributed to the 2 : 1 nickel : ligand ratio. Therefore, the relative unsaturation per nickel atom is the lowest in our complexes (Table 6). No oxidation wave was noted for the most unsaturated complex, **2** (ratio nickel : ligand 1 : 2) in the observable range of our studies. Potential values of the oxidation process of the nickel complexes (Table 6) show that complex **12** is easier to oxidize than complex **11** by 50 mV.

The electrochemical data for cobalt (II) complexes (Table 7) show similar reduction potential values. These data agree with the same structure for both complexes proposed from the spectral data. For the open chain complex **13** the reduction process is reversible but for the macrocyclic derivative **5** its data suggest an irreversible process.

The formation of complex **11**, in dimethylformamide solutions, was studied by cyclic voltammetry. The cyclic voltammograms of $NiCl_2 \cdot 6H_2O$ solutions in DMF, in which L^2H_6 was gradually added until a 1 : 3 molar ratio, were recorded. Changes in the colour and in the electrochemical response were shown from the first addition of ligand (1 : 0.1 molar ratio), especially those related with the intensities and shifts of the reduction/oxidation potential, which increased when the ligand proportions increased. But, the cyclic voltammogram registered for 1 : 1, 1 : 2 and 1 : 3 molar ratio solutions do not reproduce the cyclic voltammogram recorded for **11** and **12** complexes in DMF (Fig. 2). However, if the complex was prepared in the same solvent in 1 : 1 or 1 : 3 molar ratio and then the cyclic voltammogram recorded, the electrochemical response corresponds to the complex previously isolated and dissolved in DMF. These results indicate that the reaction to yield the complex **11** is slow. The donor character of the solvent may be the reason for that, due to the difficult substitution by the L^2H_6, therefore the electrochemical response could correspond to a mixed complex.

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