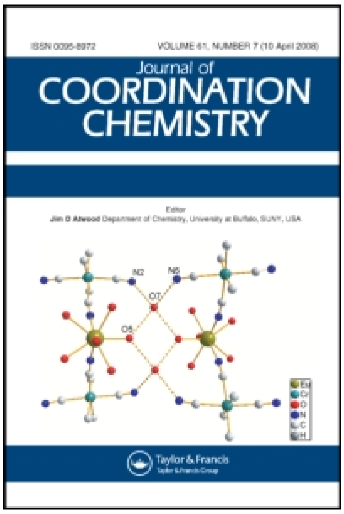

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SYNTHESIS AND COMPLEXATION OF A NEW BRANCHED *vic*-DIOXIME

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SYNTHESIS AND COMPLEXATION OF A NEW BRANCHED *vic*-DIOXIME

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A new *vic*-dioxime; 1,2-*Bis*{[di-*tert*-butyl-4-amino-4-(2-(*tert*-butoxycarbonyl)ethyl)heptanedioate]-N-yl}glyoxime (H_2L) has been prepared from di-*tert*-butyl-4-amino-4-[2-(*tert*-butoxycarbonyl)-ethyl]heptanedioate (1) and cyanogen-di-*N*-oxide. Transition metal complexes with Ni(II), Pd(II), Cu(II), Co(II) and Pt(II) have been synthesized with a metal-ligand ratio of 1:2. All complexes are very soluble in common organic solvents. ^1H and ^{13}C NMR, IR, MS and electronic spectrum data are presented. Electrochemical properties of H_2L and three complexes (Cu, Co and Pt) were investigated by cyclic voltammetry.

Keywords: *vic*-Dioxime; cobalt; nickel; copper; palladium; platinum; dendrimers

INTRODUCTION

The synthesis and spectroscopic features of dendritic macromolecules have been recently reviewed.[1] A first indication of new trends in dendrimer research can be found in a report in 1991 by Newkome *et al.*[2] The first studies on dendritic metal and other complexes demonstrate that dendrimers can be attached to metal centres for the preparation of supramolecular aggregates.[3] The controlled complexation of metal ions at specific binding sites in dendrimer cavities was achieved by Newkome *et al.*,[4] who prepared a dendrimer framework containing triple bonds, which could be complexed by dicobalt hexacarbonyl units. The synthesis of dendrimers is receiving world-wide attention in both academic and industrial laboratories.[5]

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Our primary aim has been the synthesis of new *vic*-dioximes with various functional groups including macrocycles. Owing to their importance as stable MN_4 core-containing coordination compounds, *vic*-dioxime complexes have been much investigated.[6] Vicinal dioximes have received considerable attention as model compounds for molecules such as vitamin B_{12}.[7]

The reaction of amines or thiols with (*E, E*)-dichloroglyoxime or cyanogen-di-*N*-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives.[8–11]

In previous papers we have the synthesis of *vic*-dioximes and their transition metal complexes containing crown ethers,[12,13] monoaza crown ethers,[14,15] cyclopentadienyl groups,[16] tetrathiamacrocycles[17] or N_2O_2 macrocycles.[18] Other types of vicinal dioxime complexes which have been investigated and compared with dimethylglyoximato analogues are transition metal complexes of 5, 6-dihydrocyclopent [f, g] acenaphthylene-1, 2-dione dioxime and acenaphthylene-1, 2-dione dioxime.[19,20]

We herein report the synthesis of a new *vic*-dioxime ligand which can be as a starting material for dendrimers. Only mononuclear complexes (except for Cu^{II}) have been obtained by reaction of H_2L with a variety of transition metals.

EXPERIMENTAL

Routine IR spectra were recorded on a Perkin Elmer 983 spectrophotometer in KBr pellets and NaCl cells, electronic spectra were recorded on a Varian DMS 90 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research Centre. Mass spectra were recorded on a VG Zab spec GC-MS spectrometer with electron impact and fast atom bombardment methods. Proton and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Cyclic voltammograms were performed using an EG & G PARC model 273 instrument, controlled by an external computer. A three electrode system with a saturated calomel reference electrode and a platinum wire counter electrode was used. The working electrode was a platinum plate. Triplydistilled water and spectrosel grade DMSO, dried with 4Å molecular sieves, were used in the voltammetric experiments. Tetrabutylammonium perchlorate (0.1 M) was the supporting electrolyte in DMSO. Solutions were purged with nitrogen prior to each voltammetric measurement. Voltammograms were recorded on an X-Y recorder. Di-*tert*-butyl-4-nitro-4-[2-(*tert* butoxycarbonyl) ethyl]heptanedioate, di-*tert*-butyl-4-amino-4-[2-(*tert*-butoxycarbonyl)ethyl]heptanedioate (1) and (*E,E*)-dichloroglyoxime were synthesized according to the published procedures.[21–22]

1, 2-Bis{[di-tert[butyl]4-amino-4-(2-(tert-butoxycarbonyl) ethyl)heptanedioate]-N-yl}glyoxime (H_2L)

Compound **1** (1.04 g, 2.5 mmol) in 50 cm^3 of dichloromethane was stirred at –40°C. A solution of cyanogen di-*N*-oxide[23–25] in dichloromethane (30 cm^3) was added (obtained by treating a suspension of dichloroglyoxime (0.28 g, 1.79 mmol) in dichloromethane with 46 cm^3 of 1 M Na_2CO_3 at –40°C). The solution was stirred at –40°C for 2 h, then allowed to warm to room temperature, dried with Na_2SO_4 and the solvent evaporated to give a yellowish, oily product. Yield: 0.9 g (78.7 %). IR (ν_{max}/cm^{-1}): 3360 (NH), 3220 (OH), 2960 (CH_2), 1720 (C═O), 1620 (C═N), 1460, 1320, 1250, 1140, 1105, 940, 920, 850, 720. MS (EI) *m*/*z*: 916 (100% *M*+1), 885 (53% (*M*+1)—NOH), 842 (85% *M*—OtBu), 770 (54%(*M*+1)—2OtBu), 695 (22% (*M*–1)—3OtBu, 623 (19% *M*—4OtBu), 551 (9% (*M*+1)—5OtBu) and 477 (*M*—6OtBu); λ_{max}/nm ($CHCl_3$) 242(ε/M^{-1} cm^{-1}—13040).

Ni(HL)$_2$

To a solution of 0.366 g (0.4 mmol) of H_2L in 20 cm^3 of methanol, $NiCl_26H_2O$ (0.044 g, 0.2 mmol) in methanol (5 cm^3) was added. A decrease in pH was observed and the mixture was stirred and heated to 55–60°C for 1 h while an equivalent amount of KOH was added dropwise to maintain a pH of 6.5. On cooling to 0°C, a yellowish-orange precipitate was obtained. It was filtered off, washed first with water, then with cold methanol and then dried with cold diethylether. Yield: 0.122 g (32.3 %), m.p. 171–173°C (dec). IR (ν_{max}/cm^{-1}): 3320 (N—H), 2980 (CH_2), 1720 (C═O), 1705 (O—H..O), 1610 (C═N), 1520, 1430, 1360, 1250, 1150, 920 (N—O) 860, 720. MS (FAB) *m*/*z*: 1886 (100% *M*—1); λ_{max}/nm ($CHCl_3$) 242 and 326 (ε/M^{-1} cm^{-1} 10640 and 6820).

Pd(HL)$_2$

To a solution of 0.335 g (0.366 mmol) of H_2L in 20 cm^3 of methanol, Na_2PdCl_4 [prepared by stirring 0.033 g (0.183 mmol) of $PdCl_2$ and 0.021 g (0.366 mmol) of NaCl in methanol (10 cm^3)] was added. The brown mixture was stirred and heated to 55–60°C for 1 h, and the pH was adjusted with KOH to 6.5. On cooling to 0°C, an orange precipitate was obtained. It was filtered off, washed first with water, then with cold methanol and then dried with cold diethylether. Yield: 0.118 g (33.3 %), m.p. 166–168°C (dec.) IR (ν_{max}/cm^{-1}): 3320 (N—H), 2980 (CH_2), 1710 (C═O), 1705 (O—H..O), 1605 (C═N), 1560, 1480, 1380, 1240, 1160, 940 (N—O), 850, 780. MS (FAB) *m*/*z*: 1934 (24% *M*); λ_{max}/nm ($CHCl_3$) 239 and 285 (ε/M^{-1} cm^{-1} 12360 and 10440).

$Cu_2(HL)_2CL_2$

To a solution of 0.155 g (0.17 mmol) of H_2L in 10 cm^3 of methanol, $CuCl_2\,2H_2O$ (0.015 g, 0.085 mmol) in methanol (5 cm^3) was added. The mixture was stirred and heated to 55–60 °C for 1 h, and an equivalent amount of KOH was added to adjust the pH to 6.5. The solvent was evaporated and the green, oily product was dissolved in $CHCl_3$ (20 cm^3), washed with water, and the organic layer dried over Na_2SO_4. The solvent was evaporated to obtain an oily, green complex. Yield: 0.052 g (30.2 %).IR (ν_{max}/cm^{-1}) 3360 (N—H), 3240 (O—H), 2980 (CH_2), 1720 (C=O), 1610 (C=N), 1480, 1420, 1330, 1240, 1140, 980, 910, (N—O) 820, 740. MS (FAB) *m*/*z*: 2024.2 (100%*M*), λ_{max}/nm ($CHCl_3$) 238 and 264 ($\epsilon/M^{-1}\,cm^{-1}$ 9840 and 9520).

$Co(HL)_2$

This was prepared by the same method as $Ni(HL)_2$, 0.155 g (0.17 mmol) of H_2L and $CoCl_2\,6H_2O$ (0.021 g, 0.085 mmol) were used. A brown oily complex was obtained. Yield: 0.063 g (39.3 %). IR (ν_{max}/cm^{-1}): 3360 (N—H), 2980 (CH_2), 1720 (C=O), 1705 (O—H..O), 1640 (C=N), 1560, 1380, 1240, 1160, 980, 900 (N—O), 820. MS (FAB) *m*/*z*: 1887.2 (57% *M*); λ_{max}/nm ($CHCl_3$) 240 and 260 ($\epsilon/\,M^{-1}\,cm^{-1}$ 7640 and 7800).

$Pt(HL)_2$

This was prepared in the same way as $Ni(HL)_2$; 0.335 g (0.366 mmol) of H_2L and K_2PtCl_4 (0.076 g, 0.183 mmol) dissolved in a mixture of methanol-water (1:2.5) were used. A yellowish-orange complex was obtained. Yield: 0.098 g (26.5%), m.p. 172–174 °C (dec.) (ν_{max}/cm^{-1}): 3360 (N—H), 2990 (CH_2), 1720 (C=O), 1705 (O—H..O), 1620 (C=N), 1530, 1480, 1420, 1360, 1280, 1160, 1040, 940 (N—O), 830. MS (FAB) *m*/*z*: 2024 (100% *M*+1); λ_{max}/nm ($CHCl_3$) 239, 253, 317 and 341 ($\epsilon/M^{-1}\,cm^{-1}$ 10600, 10240, 11060 and 12140).

RESULT AND DISCUSSION

1, 2-*Bis*{[di-*tert*-butyl-4-amino-4-(2-(*tert*-butoxycarbonyl)ethyl)heptanedioate]-*N*-yl}glyoxime (H_2L) was prepared by the reaction of di-*tert*-butyl-4-amino-4-[2-(*tert*-butoxycarbonyl)ethyl]-heptanedioate (1) with cyanogen-di-*N*-oxide (Scheme). Elemental analyses of H_2L and its transition metal derivatives given in Table I are agreement with the proposed structures. This ligand (H_2L) and the metal complexes are soluble in common organic solvents such as methanol, chloroform, dichloromethane, *n*-hexane, *etc*.

TABLE I Analytical data for H_2L and its complexes Analysis[a]

Compound	*Formula*	*C*	*H*	*N*	*M*
H_2L	$C_{46}H_{82}N_4O_{14}$	(60.37)	(9.03)	(6.12)	
		59.98	8.85	5.81	
$Ni(HL)_2$	$C_{92}H_{162}N_8NiO_{28}$	(58.55)	(8.65)	(5.94)	(3.11)
		58.22	8.43	5.71	2.98
$Pd(HL)_2$	$C_{92}H_{162}N_8O_{28}Pd$	(57.11)	(8.44)	(5.79)	(5.50)
		56.96	8.27	5.50	5.36
$Cu_2(HL)_2Cl_2$	$C_{92}H_{162}Cl_2Cu_2N_8O_{28}$	(54.54)	(8.00)	(5.53)	(6.27)
		54.87	8.12	5.32	6.08
$Co(HL)_2$	$C_{92}H_{162}CoN_8O_{28}$	(58.55)	(8.65)	(5.94)	(3.12)
		58.37	8.41	5.82	2.97
$Pt(HL)_2$	$C_{92}H_{162}N_8O_{28}Pt$	(54.61)	(8.07)	(5.53)	(9.64)
		54.32	7.87	5.40	9.32

[a]Required values are given in parentheses(%).

In the IR spectrum of H_2L an OH stretch is observed at 3220 cm^{-1}. N—H, C=O, C=N and N—O are at 3360, 1720, 1620 and 920 cm^{-1}, respectively. These values are in harmony with the previously reported derivatives.[12,18]

In the ^1H NMR spectrum of H_2L (DMSO-d_6), the OH and NH proton resonances appear as two singlets at $\delta = 8.93$ and 3.5, respectively (Table II). These singlets disappear on deuterium exchange. A single chemical shift for the OH proton indicates that the oxime groups are in the *anti* form.[12–14, 17] The ^1H NMR spectrum exhibits signals for methyl protons at 1.39 ppm and methylene protons at 1.57 – 2.43 ppm. These data are in agreement with previously reported dendrimeric molecules.[21] ^{13}C NMR data are given in Table III. In the ^{13}C NMR spectrum of H_2L, methyl carbons were observed at 27.6 ppm. Other methylene carbons appeared at 29.14 and 34.12 ppm. Quaternary carbons (C—NH_2) and (C—CH_3) were observed at 53.12 and 79.32 ppm, respectively. The carbon resonance of the amidoxime was found at 147.69 ppm.[23] The molecular ion peak at *m/z* 916 in the mass spectrum of H_2L also confirms the proposed structure.

TABLE II Proton NMR spectral data for H_2L (in DMSO-d_6) and its complexes (in $CDCl_3$)

Compound	*CH_3*	*CH_2*	*NH*	*OH*	*O—H...O*
H_2L	1.39 (s, 54H)	1.57–2.23 (m, 24 H)	3.5 (br, s, 2H)	8.93 (s, 2H)	
$Ni(HL)_2$	1.43 (s, 108H)	1.92–2.25 (m, 48H)	4.39 (s, 4H)		15.62 (s, 2H)
$Pd(HL)_2$	1.43 (s, 108H)	1.74–2.28 (m, 48H)	4.43 (s, 4H)		17.65 (s, 2H)
$Pt(HL)_2$	1.43 (s, 108H)	1.94–2.29 (m, 48H)	4.40 (s, 4H)		16.59 (s, 2H)

TABLE III Carbon-13 NMR spectral data for H_2L (in DMSO-d_6) and its complexes (in $CDCl_3$)

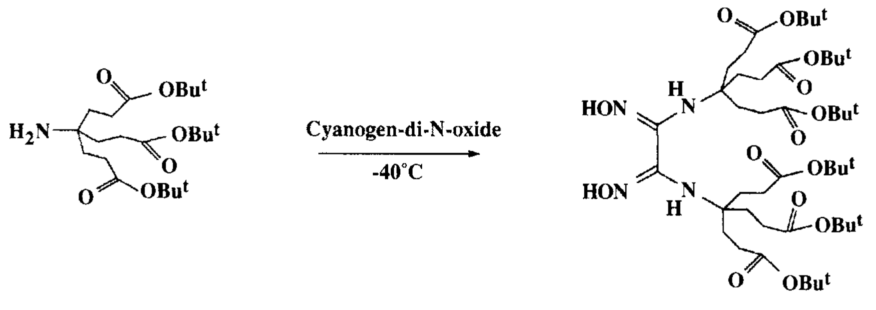
Compound	*CH_3*	*CH_2CO*	*CCH_2*	*CNH_2*	*CCH_3*	*C=NOH*	*C=N–O*	*C=O*
H_2L	27.6	29.14	34.2	53.12	79.32	147.69		171.88
$Ni(HL)_2$	28.13	30.16	32.44	61.12	80.36		146.12	172.47
$Pd(HL)_2$	28.13	30.14	32.34	61.03	80.37		144.44	172.37
$Pt(HL)_2$	28.09	30.09	32.33	61.11	80.37		145.85	172.34

The branched *vic*-dioxime derivative forms mononuclear complexes with Ni(II), Pd(II), Co(II) and Pt(II) with a metal-ligand ratio of 1:2 (Figure 1). The most fascinating feature of all these complexes is their solubility in various organic solvents because of the alkyl chains. In all cases only the mononuclear complexes are formed even in the presence of excess metal ions (except for Cu).

The nickel(II) complex of H_2L has a metal:ligand ratio of 1:2 and the ligand is coordinated only by the *N*, *N*' atoms of the *vic*-dioxime. It shows the characteristic features of *vic*-dioxime complexes. The reddish colour of $Ni(HL)_2$ is in accord with that of previously reported *vic*-dioximato complexes.[26] In the IR spectra, the O—H...O bridge is characterized by a broad absorption for the bending vibrations around 1705–1720 cm^{-1}. C=N bands due to oxime groups are observed at 1605–1620 cm^{-1}.

Proton NMR spectral data confirm the hydrogen-bridged structure with a chemical shift at lower field (δ 15.6–17.6) for the deuterium exchangable O–H protons.[12–14] Also, an N-H proton has been observed at $\delta = 4.39$ ppm (Table II).

Comparison of the ^{13}C NMR data for H_2L and its nickel(II) complex reveal a small chemical shift for the carbon atom of the oxime moiety upon complexation. The diamagnetic nature of the palladium(II) and platinum(II) complexes is confirmed by their ^1H NMR spectra which show comparable shifts to those of $Ni(HL)_2$. Consequently we might conclude that both of these d^8 metal ions are coordinated wih dioximate donor sites with square-planar geometry.[14]



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Scheme

H_2L

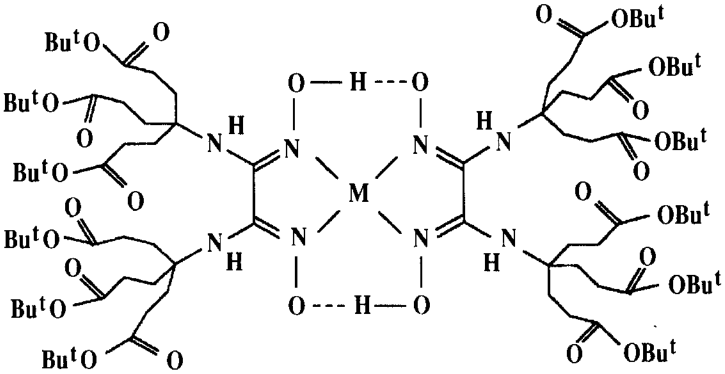

FIGURE 1 The structure of $[M (HL)_2]$, M = Ni(II), Pd(II), Co(II) or Pt(II).

In the ^{13}CNMR spectra, all peaks are approximately identical for the complexes of palladium(II) and platinum(II). Attempts to prepare an octahedral cobalt(III) complex by using pyridine or triphenylphosphine as axial ligands were not successful. All complexes show an intense charge transfer absorption at *ca* 300–340 nm and no weak d-d transitions can be observed. In the case of the copper(II) complex of H_2L a new unusual feature was observed. As shown in Figure 2 the two copper atoms are linked by chloride bridges. This structure is also confirmed by the mass spectrum of $Cu_2(HL)_2Cl_2$ which gives a molecular ion peak at *m/z* 2024 using the FAB technique. In the IR spectrum of $Cu_2(HL)_2Cl_2$ the OH and NH stretching bands are observed at 3240 and 3360 cm^{-1} respectively. Consequently, we propose an *N, O* coordinated structure in which the two molecules are bridged by two chlorine ions as encountered in some camphorquinone dioxime ligands.[27] Because of the pale green colour of this copper complex we were not able to observe a distinct absorption band in the electronic spectrum.

Electrochemical Measurements

The cyclic voltammogram of H_2L is characterized by two, one-electron reduction waves at –0.53 and –1.13 V respectively (Figure 3). These are *quasi*-reversible at all sweep rates studied.

A typical reduction of the dinuclear Cu(II) complex of H_2L is shown in Figure 4. Three one-electron reduction waves were observed for this complex. These waves show *quasi*-reversible behaviour at all sweep rates studied. The first reduction peak at 0.210 V may be assigned to the Cu(II)/Cu(I) couple. The Cu(II)/Cu(I) redox change in the tetraene occurs at a markedly less negative potential. In order to explain this difference one should consider that the Cu(I), d,^{10} ion can transfer

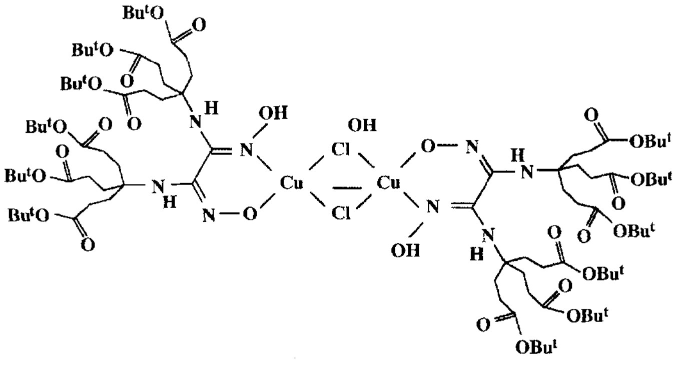

FIGURE 2 The structure of the dinuclear Copper (II) complex.

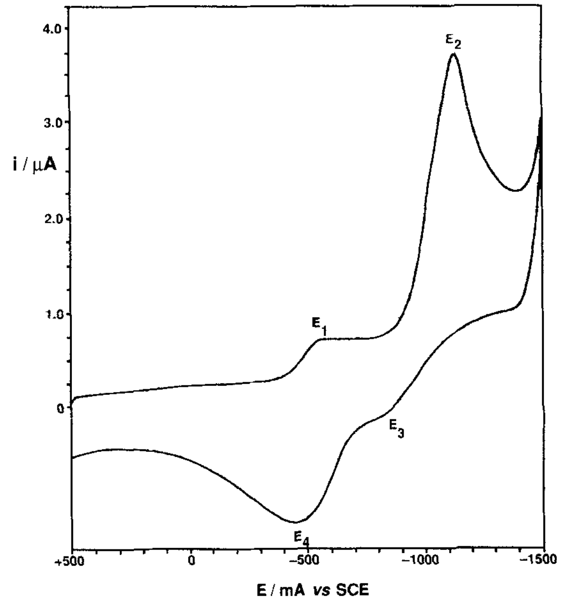

FIGURE 3 Cyclic voltammogram of H_2L .

electronic charge through a back-donation mechanism onto the donor atom system, provided it possesses orbitals of the appropriate type and energy.[28] This situation is probably achieved with the nitrogen atoms of the imine bonds.

The other two reduction waves at −0.585 and −1.150 V correspond to reductions centred in the ligand moiety. Cyclic voltammetry of the copper-containing dinuclear complex clearly shows that the reduction proceeds in two, distinct one-electron steps. After the first one-electron reduction, the redox properties of the second complexed transition metal cation are change.[29]

Diffusion coefficients associated with these waves were calculated using the Randles-Sevcik equation (Table IV). The diffusion coefficients of reduction peaks 2 and 3 appear to be larger than that of oxidation peaks 4 and 5. Thus the larger diffusion coefficients in peaks 2 and 3 means that the molecular size is smaller than that corresponding to peaks 4 and 5.

Cyclic voltammograms of Pt(II) and Co(II) complexes of H_2L are shown in Figure 5 and Figure 6. A one-electron reduction peak at −1.120 V and a one-electron oxidation peak at −0.54 V were observed for the Pt(II) complex. These appeared in the same potential region as the redox waves of the ligand and can be attributed to reactions of the ligand. The waves show *quasi*-reversible behaviour at all sweep rates studied.

In the cyclic voltammogram of the $Co(HL)_2$ complex two, one-electron reduction waves appeared at −0.54 and −1.080 V, respectively. All these peaks are *quasi*-reversible. The peaks are almost in the same potential region as the ligand molecule but peak heights and diffusion coefficients for the Co(II) complex are much higher than of the ligand species. The first peak which is a shoulder in the voltammogram of the ligand, appears a large peak in the case of the Co(II) species. Thus it may be thought that Co(II) could be also reduced in this region.

For H_2L and its complexes studied, the heterogenous electron transfer rate is relatively slow, so that the separation between the cathodic and anodic peaks varies with the sweep rate. The variation of E_p with sweep rate changed from the *quasi*-reversible case to the charge transfer rate-determining case within the sweep rates studied (Table IV). In these complexes the ratio of anodic to cathodic

TABLE IV Current functions and diffusion coefficients for H_2L and its Cu(II), Pt(II) and Co(II) complexes in DMSO and 0.1 M TBAP supporting electrolyte ($v = 0.05\ Vs^{-1}$)

Compound	*Peak No*	*$\delta C^a/V$*	*$E_p\,/\,v$*	*n*	*$\alpha^b n$*	*$I_p/\mu A$*	*$10^{12}\ D/m^2 s^{-1}$*
H_2L	1	0.0410	−0.5300	1	0.7195	0.3750	0.0147
(1×0^{-3} M)	2	0.0965	−1.1300	1	0.3060	3.5250	3.0420
	3	0.0467	−0.7900	1	0.6320	0.7000	0.0590
	4	0.0782	−0.4800	1	0.3770	1.2250	0.2979
$Cu_2(HL)_2Cl_2$	1	0.05892	+0.210	1	0.500	1.875	2.105
(5×10^{-4} M)	2	0.06888	−0.515	1	0.428	8.000	45.35
	3	0.09396	−1.150	1	0.314	19.375	358.42
	4	0.09297	−0.960	1	0.3173	2.750	7.1364
	5	0.03645	−0.160	1	0.8093	5.000	9.2498
	6	0.05209	+0.370	1	0.5663	5.250	14.5746
$Pt(HL)_2$	1	0.06993	−1.120	1	0.4218	1.625	1.877
(5×10^{-4} M)	2	0.08632	−0.540	1	0.3417	2.100	3.87
$Co(HL)_2$	1	0.09820	−1.080	1	0.3004	2.150	4.6075
(5×10^{-4} M)	2	0.09390	−0.500	1	0.3142	0.825	0.6487

[a] $\delta C = E_p/\log V$. [b] $\delta C = 0.0295/\alpha n$; hence α can be obtained.
$I_p = 2.98\times10^5 n\,(\alpha n)^{1/2} D^{1/2} C A v^{1/2}$; hence D can be obtained when αn is known for $v = 0.05\ Vs^{-1}$.

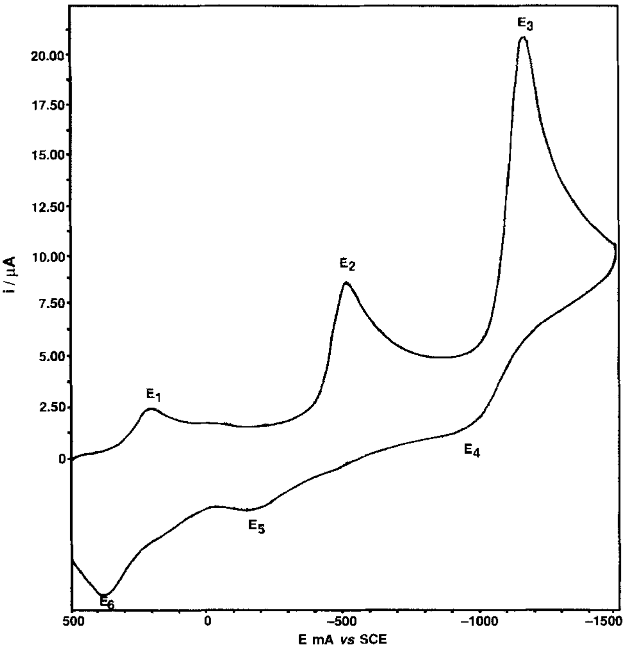

FIGURE 4 Cyclic voltammogram of $Cu_2(HL)_2Cl_2$.

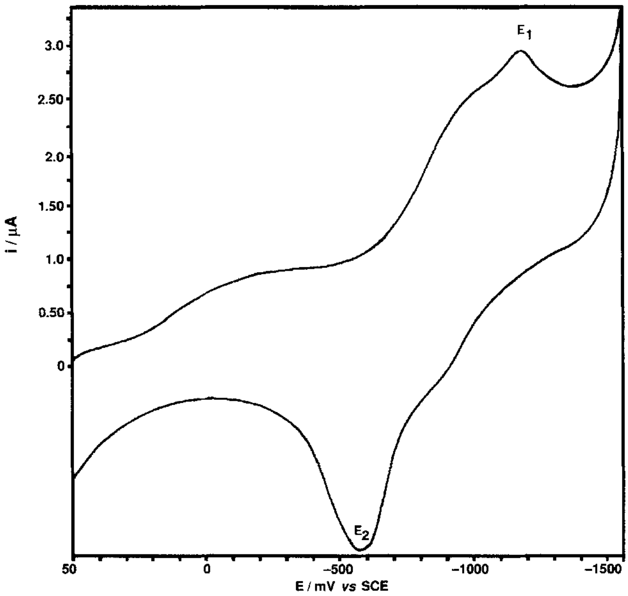

FIGURE 5 Cyclic Voltammogram of Pt $(HL)_2$.

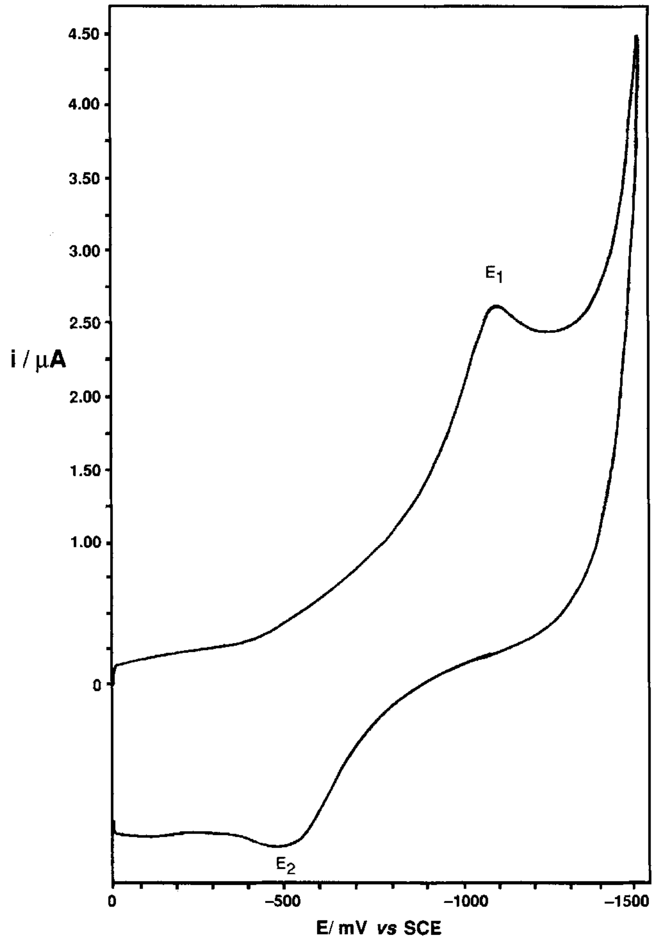

FIGURE 6 Cyclic voltammogram of $Co(HL)_2$.

peak currents differs from unity and depends on the switching potential, demonstrating the presence of coupled chemical reactions. Coulometric measurements were carried out at the constant potentials corresponding to the CV peak potentials of the complexes. The bulk electrolysis of 10^{-3} M H_2L and its 5×10^{-4} M Co(II), Pt(II) and Cu (II) complexes at the platinum electrode corresponding to one-electron reduction waves for all species.

Acknowledgments

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