Mono- and Poly-nuclear Cryptate Complexes of Cage-like Azamacrocyclic Compounds: a Thermodynamic and Electrochemical Approach*

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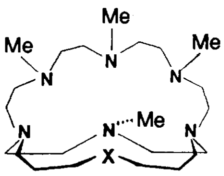
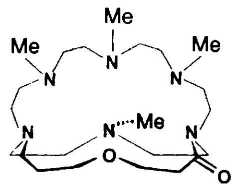
The compounds 4,7,10,17,23-pentamethyl-1,4,7,10,13,17,23-heptaazabicyclo[11.7.5]pentacosane (L^1) and 4,7,10,23-tetramethyl-17-oxa-1,4,7,10,13,23-hexaazabicyclo[11.7.5]pentacosane (L^2), respectively comprised of a tetraaza and a monooxatriaza macrocycle overstructured by a triazabridge, formed mononuclear complexes with Cu^{II}, Zn^{II} and Cd^{II} in aqueous solutions. The co-ordination of these metal ions by L^2 has been studied by means of potentiometric and NMR techniques. Thermodynamic and NMR data indicate that the metal ion is accommodated in the N$_4$ and in the N$_3$O fourteen-membered cyclic moiety in the cases of L^1 and L^2, respectively, while the triaza bridge does not participate in the co-ordination. The complexation of Cu^I by these macrocycles has been studied by means of electrochemical measurements (cyclic voltammetry); both compounds stabilize the low-valent copper complexes. This behaviour can be ascribed to the presence of only tertiary nitrogen donors, which leads to a hydrophobic macrocyclic cavity in which the metal ion is encapsulated. Both compounds also form binuclear complexes with Cu^{II} in methanol solution. In the case of L^1, binuclear assemblies are formed in aqueous solution, allowing for the determination of their stability constants. Mono- and di-hydroxo complexes of the type [M$_2$L^1(OH)]$^+$ and [M$_2$L^1(OH)$_2$] are formed in aqueous media. The macrobicycle 4,7,10,23-tetramethyl-14-oxo-17-oxa-1,4,7,10,13,23-hexaazabicyclo[11.7.5]pentacosane (L^3) has been isolated as its cadmium(II) complex [Cd(HL^3)Cl$_2$]ClO$_4$·H$_2$O the crystal structure of which was determined.

Macrocyclic molecular receptors capable of forming bi- and poly-nuclear transition-metal-ion complexes have attracted considerable attention as potential candidates in supramolecular binding and catalysis.[1] In particular, aza or oxaaza macrobicyclic compounds containing several discrete metal-binding subunits allow for the assembly of several metal cations and eventually bridging species, forming polynuclear cryptate complexes the geometry of which is determined by the receptor's topology.[2-5] In this context, the understanding of the energetic and geometric factors which control the assembly of polymolecular species is one of the main goals in the design and synthesis of polytopic ligands.

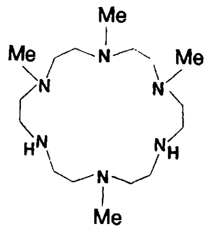
The receptors 4,7,10,17,23-pentamethyl-1,4,7,10,13,17,23-heptaazabicyclo[11.7.5]pentacosane (L^1) and 4,7,10,23-tetramethyl-17-oxa-1,4,7,10,13,23-hexaazabicyclo[11.7.5]pentacosane (L^2) respectively are composed of a tetraaza and a monooxatriaza macrocycle overstructured by a triaza bridge. In a recent communication we described the ability of L^2 to assembly inside its three-dimensional cavity the [Zn$_2$(μ-OH)$_2$]$^{2+}$ cluster inducing selective reactions with substrate molecules in methanolic solution.[6] The monooxatriaza cyclic subunit and the triaza bridge encapsulate the two zinc(II) ions in the [Zn$_2$(μ-OH)$_2$L^2]$^{2+}$ complex. A particular interest is metal complexes containing this cluster as model compounds for mimicking the active centres of a variety of enzymes.[7] On the other hand, the mononuclear zinc complexes of L^1 have the metal ion lodged inside the fourteen-membered tetraaza moiety, while the triaza bridge does not participate in the co-ordination.[8]



L^1 X = NMe
L^2 X = O



L^3



L^4

Aiming to shed further light on the structural and thermodynamic parameters which determine the metal-ion binding features of these receptors, we have studied the co-ordination behaviour of the macrobicycle L^2 toward Cu^{II} and Cd^{II} both in aqueous and methanolic solutions. The present

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

paper deals with the formation of mononuclear complexes by L^1 and L^2 and tries to locate the principal co-ordination site within the macrobicyclic ligands and to establish to what extent the first co-ordinated metal ion co-operates in determining the binding site of the second one.

Furthermore, both in L^1 and L^2 all the amino groups are tertiary ones. Recent studies have pointed out that N-methylation of macrocyclic or linear tetraamines increases the hydrophobic nature of the metal lodging and stabilizes the low-valent complexes of Cu^I.[9,10] With the aim of extending this study to cryptate complexes, we have analysed the electrochemical reduction of the mononuclear copper(II) complexes of the macrobicycles L^1 and L^2, and of the macrocycle L^4. The latter compound is characterized by a monocyclic structure and two secondary amino groups. Consequently, a different electrochemical behaviour of its copper(II) complexes is expected.

Results and Discussion

Mononuclear Complexes.—The co-ordination characteristics of L^2 toward Zn^{2+}, Cu^{2+} and Cd^{2+} have been studied in 0.15 mol dm^{-3} $NaClO_4$ aqueous solutions at 298.1 K and the stability constants of their mononuclear complexes are reported in Table 1, together with those formed by L^1 and L^4. The latter compound, the synthetic precursor of both L^1 and L^2, presents a monocyclic framework, and, as a consequence, a less-rigid and hindered structure.

As far as the $[ML^1]^{2+}$ and $[ML^2]^{2+}$ ($M = Cu^{2+}, Zn^{2+}$ or Cd^{2+}) complexes is concerned, it is of interest that their stability is markedly lower than that of the analogous complexes with L^4, in which the involvement of all the nitrogen donors in the co-ordination has been proposed.[8] In particular, the stability of all the L^1 or L^2 complexes studied here is by far lower than the complexes of azamacromonocyclic ligands containing five and six nitrogen atoms.[11] Moreover, both $[ML^1]^{2+}$ and $[ML^2]^{2+}$ show a greater tendency to bear protonation with respect to the analogous $[ML^4]^{2+}$ complexes (see Table 1). The rather high values of the equilibrium constants for the protonation of $[ML^1]^{2+}$ and $[ML^2]^{2+}$ can reasonably be ascribed to protonation of nitrogen atoms not bound to the metal cation.

Both the low stability and the high proton affinity of the $[ML^1]^{2+}$ and $[ML^2]^{2+}$ species can be rationalized by assuming that only a low number of donor atoms is involved in the formation of the L^1 or L^2 complexes in aqueous solution. Furthermore, both receptors form very stable hydroxo-complexes with Cu^{2+}, Zn^{2+} and Cd^{2+}. The equilibrium constants for the addition of OH^- to $[ML^1]^{2+}$ and $[ML^2]^{2+}$ (see Table 1) are significantly high, suggesting again that a low number of nitrogen atoms is involved in the co-ordination. In other words, although both macrobicycles contain enough nitrogen atoms to saturate the first co-ordination sphere of the metal ions, only few of them are involved in the co-ordination and hydroxylation can easily occur at the binding sites occupied by water molecules. This thermodynamic observation of the low overall interaction of both L^1 and L^2 with the studied metal ions is consistent with the co-ordination environment exhibited by Zn^{2+} in the crystal structure of the complex $[ZnL^1{\cdot}H_2O][BPh_4]_2$.[8] In the $[ZnL^1{\cdot}H_2O]^{2+}$ cation Zn^{2+} is co-ordinated by the four nitrogens of the 14-membered tetraazamacrocyclic moiety of L^1, while the bridging triaza moiety does not participate in the co-ordination. Moreover, the Zn^{2+} is bound by a water molecule, which further interacts, *via* hydrogen bonds, with the nitrogens of the triaza bridge. Most likely, such a cyclic N_4 set of donor atoms is the preferred lodging within L^1 for Cu^{2+}, Zn^{2+} and Cd^{2+}

It is also of interest that the L^2 complexes are characterized by a lower thermodynamic stability with respect to those of L^1. This feature is particularly marked in the case of Cu^{2+} and Cd^{2+}. If the fourteen-membered cyclic framework is the binding site for these metal cations, in the $[ML^1]^{2+}$ complexes the metal cation is co-ordinated by an N_4 set of donors, while in the $[ML^2]^{2+}$ complex an N_3O set is available for metal binding. The presence of a weaker M–O interaction in the $[ML^2]^{2+}$ complexes, with respect to M–N in the $[ML^1]^{2+}$ complexes, can explain the lower formation constants of the L^2 metal complexes.

The ^{13}C NMR spectra of $[ML^1]^{2+}$ and $[ML^2]^{2+}$ ($M = Zn^{2+}$ or Cd^{2+}) further confirm these thermodynamic and structural data. The spectrum of a methanolic solution of L^2 exhibits one peak at δ 68.4 (C^{11}), three signals in the range δ 44–42 (roughly integrating 1:2:1 and assigned to the methyl groups), one at δ 28.1 (C^{10}) and seven in the range δ 58–52, due to C^9 and to the carbons of the ethylenic chains. These spectral features are indicative of a C_{2v} symmetry, averaged on the NMR time-scale (Fig. 1).

Table 1 Logarithms of the formation constants of metal complexes of L^4, L^1 and L^2, determined by means of potentiometric measurements in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298.1 ± 0.1 K

Reaction	$L^{4\,a}$	$L^{1\,a}$	L^2
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	20.49	16.02	13.96(2)[b]
$[CuL]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}$	2.97	7.77	6.59(1)
$[Cu(HL)]^{3+} + H^+ \rightleftharpoons [Cu(H_2L)]^{4+}$	2.90		4.21(2)
$[CuL]^{2+} + OH^- \rightleftharpoons [CuL(OH)]^+$		5.20	3.40(2)
$Zn^{2+} + L \rightleftharpoons [ZnL]^{2+}$	13.29	9.36	9.13(3)
$ZnL^{2+} + H^+ \rightleftharpoons [Zn(HL)]^{3+}$			7.76(3)
$[Zn(HL)]^{3+} + H^+ \rightleftharpoons Zn(H_2L)]^{4+}$			6.87(3)
$[ZnL]^{2+} + OH^- \rightleftharpoons [ZnL(OH)]^+$		5.50	5.78(3)
$[ZnL]^{2+} + 2OH^- \rightleftharpoons [ZnL(OH)_2]$			8.76(4)
$Cd^{2+} + L \rightleftharpoons [CdL]^{2+}$	16.75	14.22	11.95(2)
$[CdL]^{2+} + H^+ \rightleftharpoons [Cd(HL)]^{3+}$		6.50	5.36(2)
$[Cd(HL)]^{3+} + H^+ \rightleftharpoons [Cd(H_2L)]^{4+}$			6.46(3)
$[CdL]^{2+} + OH^- \rightleftharpoons [CdL(OH)]^+$		5.90	5.73(3)
$[CdL]^{2+} + 2OH^- \rightleftharpoons [CdL(OH)_2]$			8.53(6)

[a] Values taken from ref. 8. [b] Values in parentheses are standard deviations on the last significant figure.

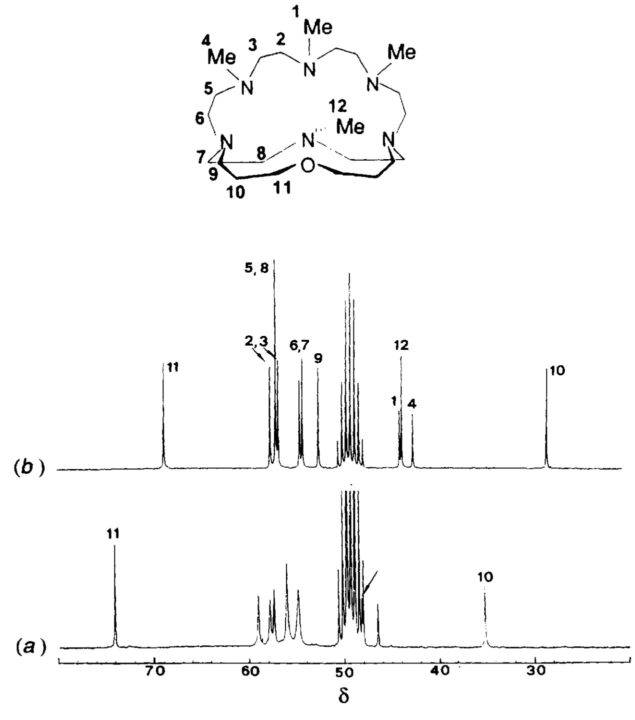

Fig. 1 The ^{13}C NMR spectrum of the Cd^{2+} complex of L^2 (*a*) and of free L^2 (*b*)

When 0.5 equivalent of $CdCl_2$ is added to solutions of the macrocycles a different set of signals appears in the NMR spectra, together with the resonances of the receptor, indicating the presence in solution of a cadmium complex. On addition of further Cd^{2+} the signals of this species are enhanced, while the resonances of uncomplexed L^2 considerably decrease in intensity. When the L^2: Cd^{2+} ratio of 1 : 1 is reached, the ^{13}C subspectrum of L^2 disappears and the recorded ^{13}C NMR spectrum can be attributed reasonably to a unique mononuclear cadmium complex. It is noteworthy that this complex and the receptor slowly exchange on the NMR time-scale. This can be explained by considering that the metal ion is deeply embedded in the macrobicyclic cavity.[12] The signal assigned to C^{11}, in α position with respect to the ether oxygen, exhibits a downfield shift (*ca.* 6 ppm). The signal of C^{10}, β with respect to the bridgehead nitrogens and the oxygen donor, shifts downfield remarkably (*ca.* 7 ppm) upon complexation, indicating the involvement of the oxygen and the bridgehead nitrogen donors in co-ordination to the metal ion. Further addition of Cd^{2+} does not affect the ^{13}C NMR spectrum. These features can be explained by the formation of a mononuclear cadmium complex, with the metal ion co-ordinated by the fourteen-membered N_3O moiety of the ligand. Both $[ZnL^1]^{2+}$ and $[ZnL^2]^{2+}$ complexes give rise to similar NMR spectral features when the metal : ligand ratio ranges between 0.1 and 1 : 1. These data indicate that the fourteen-membered cyclic N_4 or N_3O moieties are the metal lodgings for L^1 and L^2, respectively.

Copper(II)*-Copper*(I) *Equilibria*.—Both L^1 and L^2 form less thermodynamically stable complexes than those of L^4 with Cu^{2+}, Zn^{2+} and Cd^{2+}. On the other hand, it has been reported that macrocyclic or linear tertiary tetraamines, *e.g.*, permethylated tetraamines, stabilize low-valent copper(I) complexes in aqueous solution.[9,10] This effect has been attributed to the poor σ-donating properties of tertiary amino groups. Indeed, the absence of hydrogen bonding to the solvent, *via* $M{-}N{-}H \cdots OH_2$, decreases the σ-donating ability of the nitrogen donors as the hydrogen bonds, which clearly contribute energetically more in the divalent complexes, increase the electron density on the nitrogen atoms, thus making them better σ-donors. Furthermore, the absence of the hydrogen bonds reduces the charge transfer from the metal ion to the solvent, thus destabilizing the copper(II) complexes. Moreover, N-methylation increases the hydrophobic nature of the co-ordination site of the metal ion. As solvation stabilizes highly charged complexes, complexation by such hydrophobic ligands leads to a stabilization of the lower-valent complexes.[9]

Both L^1 and L^2 present all tertiary amino-groups and a macrobicyclic 'cage-like' framework. These structural features form a hydrophobic cavity in which the metal ion is lodged. On the contrary, L^4 has a monocyclic backbone and two secondary amino groups. In order to investigate the effects of these different molecular topologies on the stability of the copper(I) complexes, cyclic voltammograms of the copper complexes of L^1, L^2 and L^4 have been recorded at various pH values.

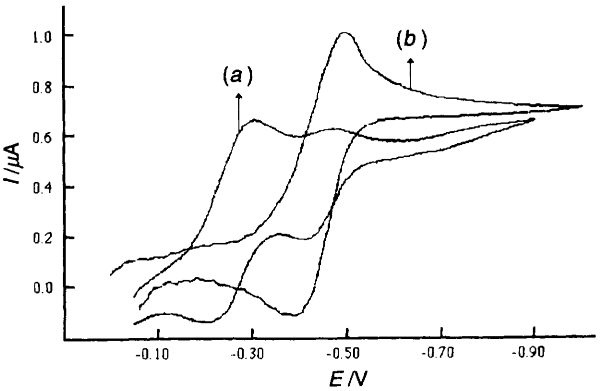

Fig. 2 Cyclic voltammograms (hanging mercury-drop electrode *vs.* Ag–AgCl) of the $[CuL^2]^{2+}$ (*a*) and $[CuL^4]^{2+}$ (*b*) complexes in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution. Rate 20 mV s^{-1} $[Cu^{2+}]$ = 0.001 mol dm^{-3}, $[L^2]$ = 0.002 mol dm^{-3} (*a*), $[L^4]$ = 0.002 mol dm^{-3} (*b*)

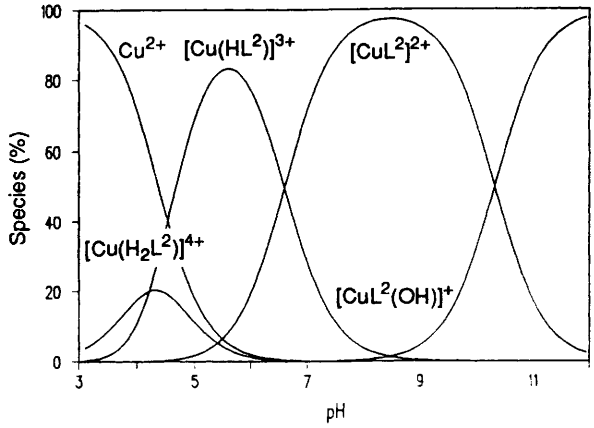

Fig. 3 Distribution diagram of the species formed as a function of pH in the system Cu^{2+}–L^2 in 0.15 mol dm^{-3} $NaClO_4$ solution at 298.1 K. $[Cu^{2+}]$ = 0.001 mol dm^{-3}, $[L^2]$ = 0.002 mol dm^{-3}

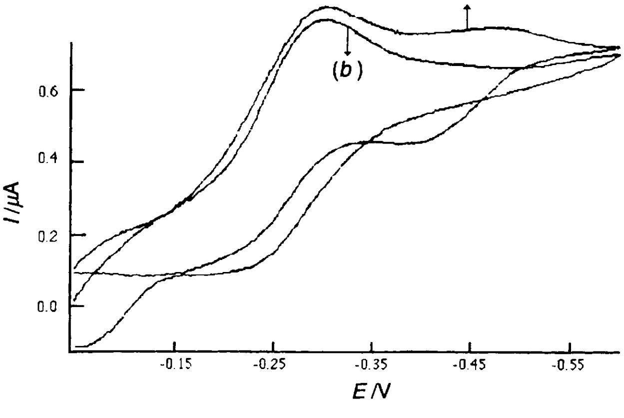

Fig. 4 Cyclic voltammograms (hanging mercury-drop electrode *vs.* Ag–AgCl) of the $[CuL^2]^{2+}$ (*a*) and $[CuL^1]^{2+}$ (*b*) complexes in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution. Rate 20 mV s^{-1}, $[Cu^{2+}]$ = 0.001 mol dm^{-3}, $[L^2]$ = 0.002 mol dm^{-3} (*a*), $[L^1]$ = 0.002 mol dm^{-3} (*b*)

The cyclic voltammograms of the copper complexes of L^2 and L^4, recorded at pH 8.5, are compared in Fig. 2. The copper(II) complex of L^4 does not give rise to hydroxo-species even at alkaline pH and, at pH 8.5, $[CuL^4]^{2+}$ is the only species present in solution.[7] At this pH, also in the Cu^{II}–L^2 system, the $[CuL^2]^{2+}$ complex is the predominant species in solution, as shown by the distribution diagram in Fig. 3. Considering the $[CuL^2]^{2+}$ complex, two single-electron reduction processes occur at −0.253 and −0.440 V *vs.* Ag–AgCl, while the $[CuL^4]^{2+}$ complex is reduced by a single two-electron process at −0.436 V. A different behaviour is shown by the Cu^{2+}–L^1 system. The cyclic voltammogram recorded at pH 8.5, where $[CuL^1]^{2+}$ is the prevalent species in solution exhibits a single-electron process at −0.25 ± 0.01 V (Fig. 4), due to the Cu^{II}–Cu^{I} reduction (see below). When the same system is studied at pH 6, where the $[Cu(HL^1)]^{3+}$ protonated complex is predominant in solution, the first reductive process is followed by a second broad not reversible wave at −0.5 V.

By using the formation constants of the copper(II) complexes and these electrochemical data, the complexation constants of Cu^I with L^1, L^2 and L^4 can be estimated as follows: $Cu^+ + L^1 \rightleftharpoons [CuL^1]^+, \log K_1 = 12.9(1)$; $Cu^+ + L^2 \rightleftharpoons [CuL^2]^+$, $\log K_1 = 10.7(1)$; and $Cu^+ + L^4 \rightleftharpoons [CuL^4]^+$, $\log K_1 < 12$.

When the electrochemical reduction of a copper(II) complex takes place *via* two consecutive single-electron processes it is possible to perform the conproportionation process according to equation (1) ($L = L^1$ or L^2).* Indeed, when a copper plate is

$$[CuL]^{2+} + Cu + L \rightleftharpoons 2[CuL]^+ \qquad (1)$$

added to deareated solutions of the copper(II) complex of L^1 or L^2, in the presence of an excess of macrocycle at different pH values, reaction (1) occurs within a few hours. If the resulting colourless solution is exposed to dioxygen, a blue colour, due to the formation of the copper(II) complexes, appears. The electronic spectra of these solutions indicate that the process caused a doubling of the concentration of the copper(II) complexes, according to equation (2).

$$2[CuL]^+ + 0.5O_2 \longrightarrow 2[CuL]^{2+} \qquad (2)$$

As reported above, in the case of the L^1 complexes at slightly alkaline pH, only a single-electron reduction is observed. In order to verify that this process is due to the Cu^{II}–Cu^{I} reduction, the copper(I) complex was prepared by using reaction (1) and then electrochemically oxidized. The oxidation occurs at the same potential as that of the reduction of the copper(II) complex.

These results demonstrate the stabilization of the copper(I) complexes with both L^1 and L^2. This effect can be mainly attributed to the presence of only tertiary nitrogen donors and the consequent hydrophobic nature of the cavity in which the metal ion is lodged.

The electrochemical behaviour of the Cu^{II}–L^4 system confirms this hypothesis. The compound L^4 does not effect a stabilization of its copper(I) complex. The reduction of the $[CuL^4]^{2+}$ complex leads to Cu^0 *via* a two-electron single-step process. The ratio between the equilibrium constants for the formation of the copper-(II) and -(I) complexes of L^4 is remarkably higher than those found for L^1 and L^2. Such a different behaviour can be attributed to the presence of two secondary unmethylated amino-groups in the L^4 framework, which are characterized, as reported above, by a better σ-donating ability in comparison with tertiary nitrogen donors and enables a charge distribution from the metal ion to the solvent, thus stabilizing the higher-valent complex.

It is also of interest that the redox potential of the first process observed in the reduction of the copper complexes of L^1 and L^2 has almost the same value. This finding indicates that the replacement of a tertiary amino-group by an ether oxygen atom does not change significantly the hydrophobic nature of the ligand. Furthermore, the ratios between the complexation constants of Cu^{II} and Cu^{I} for L^1 and L^2 are very similar. It seems likely that the loss in solvation energy by the metal ion upon complexation by these hydrophobic macrobicycles is similar. On the other hand, as already found for the copper(II) complexes, L^1 gives rise to a more stable copper(I) complex with respect to L^2. Again, this effect can be explained by taking into account the presence, in the L^2 framework, of an oxygen which replaces a nitrogen donor of L^1.

The absence of the second reduction wave for the copper(II) complex of L^1, at least in slightly alkaline solutions, is noteworthy. Kinetic considerations could explain such a behaviour. The formation of the copper(II) complexes of L^1, as well as their dissociation, is characterized by kinetic inertness; this behaviour has been ascribed to the rigid macrobicyclic framework presented by L^1.[8] On the other hand, the corresponding complexes of L^2 do not exhibit such kinetic inertness. Most likely, this difference can be attributed to the higher flexibility of a $-CH_2CH_2CH_2XCH_2CH_2CH_2-$ chain when $X = O$ with respect to the case of $X = NMe$. It is reasonable that also the copper(I) complex with L^1 will show a similar kinetic inertness to dissociation, hindering the Cu^I–Cu^0 reduction.

However, at pH 6, when the $[Cu(HL^1)]^{3+}$ species is prevalent in solution, a second not reversible process is observed. The formation at acidic pH of protonated species of the copper(I) complex and the consequent electrostatic repulsion between positive charges facilitate the reduction of Cu^I and loss of Cu^0 from the macrobicyclic cage.

Formation of Binuclear Cryptates.—As reported above, in the mononuclear complexes of Cu^{2+}, Zn^{2+} and Cd^{2+} the fourteen-membered N_4 (L^1) and N_3O (L^2) frameworks seem to be the preferred binding sites, while the bridging triaza moiety does not participate in the co-ordination. On the other hand, in the case of compound L^3, which has almost the same framework as that of L^2, the presence of an amidic bridgehead nitrogen remarkably reduces the binding ability of the cyclic N_3O subunit. Consequently, in its cadmium complex, the metal cation is bound by the bridging triaza moiety, as shown by the crystal structure of the $[Cd(HL^3)Cl_2]^+$ complex cation (Fig. 6). In this case, the presence of an amidic nitrogen [N(1)] and the protonation of N(5) prevent the fourteen-membered cyclic N_3O framework from accommodating the Cd^{2+} cation. Consequently, the metal ion is co-ordinated by the three nitrogens of the bridging chain and completes its co-ordination sphere by binding two chloride anions. In other words, the N_3 bridging subunit can also act as binding site for metal cations. The formation of a binuclear zinc(II) complex by the receptor L^2 in methanolic solutions confirms the binding ability of the N_3 moiety. The crystal structure of the $[Zn_2(\mu\text{-}OH)_2L]^{2+}$ cation shows the $[Zn_2(\mu\text{-}OH)_2]^{2+}$ cluster enclosed in the macrobicyclic cavity of the receptor, with the two Zn^{2+} ions co-ordinated respectively by the triaza bridge and the N_3O cyclic framework.[6,7] Two bridging hydroxo groups complete the co-ordination sphere of the metal cations. However, no binuclear zinc(II) complexes have been observed in aqueous solution.

The formation of binuclear copper(II) complexes with L^1 and L^2 has been studied by using potentiometric titrations (0.15 mol dm^{-3} $NaClO_4$ aqueous solution, 298.1 ± 0.1 K) and recording electronic spectra, at various macrocycle: metal molar ratios. In the system L^1–Cu^{2+}, for $R > 1$, the electronic spectra recorded in methanol solution show a broad band with $\lambda_{max} = 575$ nm. As R decreases from 5 to 1, ε_{max} increases linearly, being 280 dm^3 mol^{-1} cm^{-1} when $R = 1$. This behaviour can be ascribed to the formation of a mononuclear copper(II) complex. As R decreases from 1 to 0.5 a shift of the band toward lower energy is observed, with $\lambda_{max} = 610$ nm and $\varepsilon_{max} = 370$ dm^3 mol^{-1} cm^{-1} when $R = 0.5$. By adding further Cu^{2+} the spectrum does not undergo further changes. These features suggest the formation of a binuclear complex when $R \leqslant 1$. The binuclear species is largely predominant in solution for $R \leqslant 0.5$. Similar results have been obtained for the L^2–Cu^{2+} system in methanolic solutions, with $\lambda_{max} = 620$ nm and $\varepsilon_{max} = 145$ dm^3 mol^{-1} cm^{-1} when $R = 1$ (mononuclear complex) and with

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* The stability constants K_1 for the copper(I) complexes of L^1 and L^2 can be estimated by using the following relations and the experimental reduction potentials: $Cu(aq)^+ + L \rightleftharpoons [CuL]^+$, $K_1 = [CuL^+]/[Cu(aq)^+][L]$; $Cu(aq)^{2+} + L \rightleftharpoons [CuL]^{2+}$, $K_2 = [CuL^{2+}]/[Cu(aq)^{2+}][L]$; $E_1 = E[Cu(aq)^{2+}\text{–}Cu(aq)^+] + 0.059 \log[Cu(aq)^{2+}]/[Cu(aq)^+]$; $E_2 = E[CuL(aq)^{2+}\text{–}CuL(aq)^+] + 0.059 \log[CuL^{2+}]/[CuL^+]$. At equilibrium $E_1 = E_2$ and therefore $K_1/K_2 = [Cu(aq)^{2+}][CuL^+]/[Cu(aq)^+][CuL^{2+}]$, $E[CuL(aq)^{2+}\text{–}CuL(aq)^+] - E[Cu(aq)^{2+}\text{–}Cu(aq)^+] = 0.059 \log(K_1/K_2)$ and $\log K_1 = \log K_2 + \{E[CuL(aq)^{2+}\text{–}CuL(aq)^+] - E[Cu(aq)^{2+}\text{–}Cu(aq)^+]\}/0.059$. The corresponding values for the complex of L^4 can be estimated by using the following relations and the experimental reduction potential: $Cu(aq)^+ + L^4 \rightleftharpoons [CuL^4]^+$, $K_1 = [(CuL^4)^+]/[Cu(aq)^+][L^4]$; $Cu(aq)^{2+} + L^4 \rightleftharpoons [CuL^4]^{2+}$, $K_2 = [(CuL^4)^{2+}]/[Cu(aq)^{2+}][L^4]$; $Cu(aq)^{2+} + Cu^0 \rightleftharpoons 2Cu(aq)^+$, $10^{-6} = [Cu(aq)^+]^2/[Cu(aq)^{2+}]$. $[CuL^4]^{2+} + Cu^0 + L^4 \rightleftharpoons 2[CuL^4]^+, 10^{-6} = [(CuL^4)^+]^2/[(CuL^4)^{2+}][L^4]; K_3 = (K_1[Cu(aq)^+])^2/K_2[Cu(aq)^{2+}]$, $10^{-6}(K_1)^2/K_2$. Since no conproportionation is observed in the solution containing L^4, Cu^{2+} and Cu^0 (plate), clearly $K_3 < 10^{-3}$ dm^3 mol^{-1} and therefore $10^{-6}(K_1)^2/K_2 < 10^{-2}$ and $K_1 < 10^{-2}(K_2)^{\frac{1}{2}}$.

$\lambda_{max} = 665$ nm and $\varepsilon_{max} = 130$ dm^3 mol^{-1} cm^{-1} when $R = 0.5$ (binuclear complex).

Potentiometric measurements carried out in aqueous solution reveal that L^1 forms only mononuclear complexes when $R > 1$ (see Table 1), while also binuclear $[Cu_2L^1(OH)]^{3+}$ and $[Cu_2L^1(OH)_2]^{2+}$ species are observed for $R < 1$. These complexes are characterized by the following formation constants: $2Cu^{2+} + L^1 + H_2O \rightleftharpoons [Cu_2L^1(OH)]^{3+} + H^+$, $\log K = 14.0(1)$; $2Cu^{2+} + L^1 + 2H_2O \rightleftharpoons [Cu_2L^1(OH)_2]^{2+} + 2H^+$, $\log K = 7.9(1)$; and $[Cu_2L^1(OH)]^{3+} + OH^- \rightleftharpoons [Cu_2L^1(OH)_2]^{2+}$, $\log K = 7.6$. For the L^2–Cu^{2+} system, potentiometric measurements carried out at different R values are in accord with the formation of only mononuclear species in aqueous solutions in the pH range investigated, while binuclear complexes are observed in methanol solution. On the other hand, as reported above, the receptor L^1 gives rise to binuclear complexes both in aqueous and methanolic solutions. The ligand L^2 presents a cyclic N_3O binding site, which shows a lower tendency toward copper(II) co-ordination in comparison with the N_4 cyclic framework of L^1. This topological difference reasonably explains the absence of binuclear assemblies in aqueous solution in the L^2–Cu^{2+} system.

The analysis of the above spectrophotometric and thermodynamic data leads us to propose a stepwise formation of these binuclear species. In other words, when $R > 1$, only mononuclear copper(II) complexes are present in solution, while for $R < 1$ binuclear complexes are also formed. Most likely, the co-ordination site for the first metal ion is the fourteen-membered N_4 or N_3O cyclic subunit for L^1 or L^2, respectively, while the second cation is bound by the triaza bridge.

In the case of the copper(II) complexes only binuclear hydroxo species are found, at least in the case of L^1. The absence of a $[Cu_2L^1]^{4+}$ species suggests that the formation of binuclear complexes occurs only in the presence of at least one anionic bridging group, such as OH^-, which reduces the electrostatic repulsion between the two metal ions and leads to the assembly of the binuclear complex inside the macrobicyclic structure. A similar behaviour was found in the Cu^{2+} complexes of the macrobicycle 7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane L^5 which has two N_4 binding subunits connected by $[CH_2]_2O[CH_2]_2$ bridges.[4] In aqueous solutions this compound can bind two Cu^{2+} ions bridged by one OH^- group. This binuclear complex shows a high affinity for the hydroxide ion {$\log K = 25.07$ for the equilibrium $2Cu^{2+} + L^5 + H_2O \rightleftharpoons [Cu_2L^5(OH)]^{3+} + H^+$} and, as a consequence, the $[Cu_2L^5]^{4+}$ species is only a minor constituent of this system (less than 5% in aqueous solutions with a 2:1 Cu^{2+}:L^5 ratio).[4b,c,e] The most significant difference from the present case is the absence of dihydroxo complexes, which are found in the Cu–L^1 system. This can be explained by considering the presence of a Cu^{2+} ion co-ordinated by only three nitrogens of the triaza bridge; the metal ion completes its co-ordination environment by binding two OH^- groups. A proposed structure for the $[Cu_2L^1(OH)_2]^{2+}$ cation is shown in Fig. 5.

Finally, considering the cadmium complexes, no binuclear species is observed in aqueous or in methanolic solutions. Most likely, the dimensions of the macrobicyclic cavity do not allow the formation of polynuclear complexes with the larger Cd^{2+} ions.

Crystal Structure of $[Cd(HL^3)Cl_2]ClO_4 \cdot H_2O$.—The molecular structure consists of discrete $[Cd(HL^3)Cl_2]^+$ cations, perchlorate anions and lattice water molecules. Fig. 6 shows an ORTEP[13] drawing of the $[Cd(HL^3)Cl_2]^+$ cation. Selected bond distances and angles for the metal co-ordination sphere are given in Table 2.

The metal atom is five-co-ordinated by the adjacent nitrogen atoms N(2), N(3) and N(4) and by the chloride ions Cl(1) and Cl(2). The Cd–N distances fall in the range 2.388(6)–2.417(6) Å, while the Cd–Cl distances are 2.465(2) and 2.520(3) Å for Cl(2) and Cl(1), respectively. The resultant co-ordination geometry is not regular and can be described as intermediate between a trigonal bipyramid and a square pyramid. Considering the former geometry, the N(3) and Cl(1) atoms occupy the axial positions, while, in the latter, the N(2), N(3), N(4) and Cl(1) atoms describe a rather distorted basal plane [displacement from this mean plane for the nitrogen donors ranges between 0.263(6) Å for N(4) to 0.397(6) Å for N(3)]. The Cd–Cl(2) bond is almost perpendicular to this plane, with a deviation of just 2.2(1)° from the normal and the cadmium ion deviates by 0.4643(5) Å towards the apical position. The irregular disposition of the five donors around the metal ion can be ascribed to the presence of the N(2)–C(3)–C(4)–N(3) and N(3)–C(5)–C(6)–N(4) ethylenic chains [N(2)–Cd–N(3) and N(3)–Cd–N(4) 77.1(2) and 77.9(2)°, respectively, *vs.* 90° required by a regular disposition of the donor atoms in both the considered co-ordination geometries]. Furthermore, the

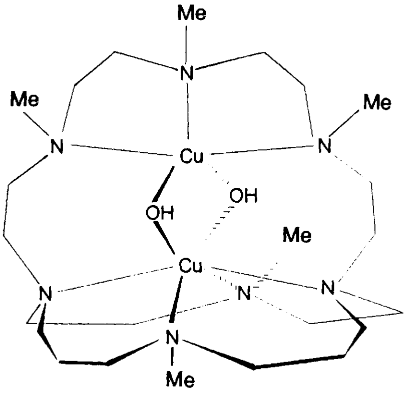

Fig. 5 Proposed stucture for the $[Cu_2L^1(OH)_2]^{2+}$ species

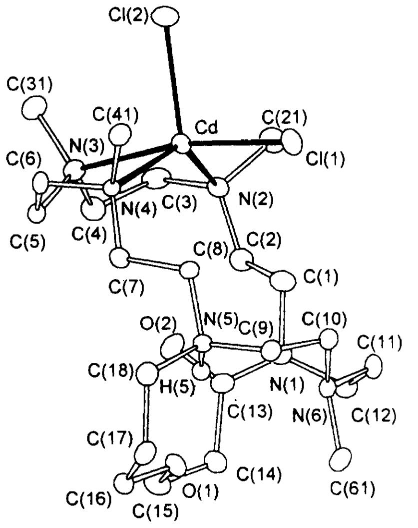

Fig. 6 An ORTEP drawing of the $[Cd(HL^3)Cl_2]^+$ cation (thermal ellipsoids at 20% probability level)

Table 2 Selected bond lengths (Å) and angles (°) for $[Cd(HL^3)Cl_2]ClO_4 \cdot H_2O$

Cd–N(2)	2.388(6)	Cd–Cl(2)	2.465(2)
Cd–N(4)	2.403(6)	Cd–Cl(1)	2.520(3)
Cd–N(3)	2.417(6)		
N(2)–Cd–N(4)	135.5(2)	N(3)–Cd–Cl(2)	93.6(2)
N(2)–Cd–N(3)	77.1(2)	N(2)–Cd–Cl(1)	100.6(2)
N(4)–Cd–N(3)	77.9(2)	N(4)–Cd–Cl(1)	96.7(1)
N(2)–Cd–Cl(2)	108.7(2)	N(3)–Cd–Cl(1)	168.4(2)
N(4)–Cd–Cl(2)	109.0(2)	Cl(2)–Cd–Cl(1)	97.94(8)

N(2)–Cd–N(4) angle [135.5(2)°] is far from both the values required by a trigonal-bipyramidal (120°) and a square-pyramidal environment (180°).

As far as the conformation of the ligand is concerned, it can be noted that the 14-membered ring is further stiffened by the presence of the carbonyl group and strong intramolecular hydrogen bonds involving the H(5) acidic proton, localized on the N(5) bridgehead nitrogen, and O(1) and N(6) [H(5)···O(1) and H(5)···N(6) 2.00(6) and 2.63(8) Å, respectively]. Moreover, the C(12)–N(1)–C(13)–C(14) torsional angle is only −30(1)°, forcing the atoms C(12) and C(14) into an almost-eclipsed position.

The O(3) oxygen of the lattice water molecule bridges *via* hydrogen bonds the chloride ion Cl(2) and the oxygen O(20) of a symmetry-related perchlorate anion, as shown by the short intermolecular distances O(3)···Cl(2) [3.199(8) Å] and O(3)···O(20′) [2.88(4) Å].

Conclusion

Both L^1 and L^2 form in aqueous solutions mononuclear complexes with Cu^{2+}, Zn^{2+} and Cd^{2+}. In these complexes the metal ions are accommodated in the fourteen-membered N_4 (L^1) or N_3O (L^2) moieties, while the triaza bridge does not participate in the co-ordination. The cations complete their co-ordination environments by binding a water molecule or, at alkaline pH, an OH^- group. These macrocycles give rise to less thermodynamically stable complexes than those formed by their synthetic precursor L^4 which is characterized by a more flexible and less-hindered structure where all the nitrogen donors can be involved in the co-ordination. These structural features explain the higher stability of complexes of L^4 in comparison to those of the former macrobicycles.

On the contrary, both L^1 and L^2 give rise to a stabilization of the low-valent copper(I) complexes, while L^4, which is characterised by two secondary nitrogens in its cyclic framework, does not exhibit this behaviour. This stabilization can be ascribed to the presence of all-tertiary nitrogens in the ligands L^1 and L^2, which leads to an increase of the hydrophobic nature of the cavity and to the absence of hydrogen bonding to the solvent, *via* N–H···OH_2, thus inhibiting the σ-donating ability of the nitrogen donors.

Even if the fourteen-membered N_4 or N_3O frameworks seem the preferred binding subunits in the mononuclear L^1 and L^2 complexes, the N_3 bridging moiety can also accommodate a metal, as confirmed by the crystal structure of the $[Cd(HL^3)]^{3+}$ cation. Consequently, both L^1 and L^2 form binuclear complexes with Cu^{2+} and Zn^{2+}, at least in methanolic solutions. In these complexes the metal ions are each co-ordinated by one binding sub-unit (the N_3 and the N_4 or N_3O moiety for L^1 and L^2, respectively). The presence of hydroxide groups bridging the two metal ions plays a determining role in the stabilization of these complexes. Macrocycle L^1 forms binuclear species of the type $[Cu_2L^1(OH)]^{3+}$ and $[Cu_2L^1(OH)_2]^{2+}$ in aqueous solution. For this compound the formation of binuclear assemblies is also observed in methanolic solutions, while L^2 gives rise to binuclear complexes only in non-aqueous media. This different behaviour can be ascribed to the different set of donors available for the co-ordination. For both mono- and bi-nuclear complexes the presence of seven nitrogen donors in L^1 leads to a stabilization of its cryptates in comparison with the analogous complexes of L^2, which is characterized by a N_6O set of donors and, consequently, by somewhat poorer co-ordinative properties toward the bivalent cations investigated.

Experimental

Synthesis of the Compounds.—The compounds L^1 and L^4 were obtained as described.[14] Compounds L^2 and 4,7,10,23-tetramethyl-14,20-dioxo-17-oxa-1,4,7,10,13,23-hexaazabicyclo[11.7.5]pentacosane L^6 were synthesized as described previously;[6,7] L^3 was obtained by reduction of L^6 with diborane.

4,7,10,23-*Tetramethyl*-14-*oxo*-17-*oxa*-1,4,7,10,13,23-*hexaazabicyclo*[11.7.5]*pentacosane* (L^3). Diborane (0.02 mol) in dry tetrahydrofuran (thf) (50 cm^3) was added dropwise under an inert atmosphere to a cooled solution (20 cm^3) of dry thf containing L^6 (1.95 g, 4.4 mmol) over a period of 30 min. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature before being refluxed for 6 h. It was then cooled to 0 °C, and water (15 cm^3) added. The white solid obtained was filtered off and dissolved in HCl–water–MeOH (2:6:20 cm^3) and refluxed for 4 h. The reaction mixture was treated with water (15 cm^3) and the resulting solution filtered and made strongly alkaline with tetramethylammonium hydroxide. This solution was extracted with chloroform (5 × 20 cm^3), and the combined extracts were dried over sodium sulfate. The solvent was removed under reduced pressure to give a colourless oil, which is a mixture of L^2 and L^3, as shown by ^{13}C NMR spectroscopy ($CDCl_3$): L^2, δ 27.04, 41.93, 43.24, 43.55, 50.69, 52.96, 53.26, 55.67, 55.97, 56.27, 67.05; L^3, δ 26.41, 28.71, 33.70, 40.55, 43.87, 44.07, 44.32, 48.86, 50.96, 52.61, 52.90, 54.23, 54.85, 55.29, 56.09, 56.68, 57.48, 58.27, 68.28, 67.96.

$L^3 \cdot HClO_4 \cdot CdCl_2 \cdot H_2O$. A solution of $CdCl_2 \cdot 2.5H_2O$ (45.6 mg, 0.2 mmol) in methanol (15 cm^3) was slowly added to a hot solution of the above mixture (80 mg) in methanol (15 cm^3). The resulting solution was refluxed for *ca.* 10 min and then butanol (10 cm^3) was added. By slow evaporation a colourless powder was isolated, which was dissolved in methanol and again precipitated by adding butanol. Crystals of the complex $L^3 \cdot HClO_4 \cdot CdCl_2 \cdot H_2O$, suitable for X-ray analysis, were obtained by fractionated crystallization from methanol–butanol (3:2). Yield: 10 mg (7%). (Found: C, 37.7; H, 7.1; N, 12.0. Calc. for $C_{22}H_{49}CdCl_2N_6O_7$: C, 37.80; H, 7.05; N, 12.0%).

$L^3 \cdot 3HClO_4$. This salt can be obtained in almost quantitative yield by treating a solution of its cadmium(II) complex in ethanol with concentrated $HClO_4$. The white solid precipitated was filtered off and washed with ethanol (Found: C, 37.3; H, 6.6; N, 11.7. Calc. for $C_{22}H_{46}Cl_3N_6O_{14}$: C, 37.25; H, 6.55; N, 11.85%).

Electromotive Force Measurements.—All the potentiometric measurements were carried out in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K, in the range pH 2.5–10, by using equipment described previously.[15] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalence point by Gran's method[16] which allows one to determine the standard potential E° and the ionic product of water ($pK_w = 13.73$ in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K). At least three measurements were performed for each system (100 data points per each set of measurements). For the determination of the stability constants, the metal to macrocycle molar ratio was varied from 0.5 to 2:1 to verify the formation of polynuclear complexes. The computer program SUPERQUAD[17] was used to calculate both protonation and stability constants from emf data. The titration curves for each system were treated either as a single set or as separate entities without significant variations in the values of the stability constants. Finally all the data for both protonation and complexation were merged and the equilibrium constants for protonated and complexed species simultaneously refined to give the final values. All the macrocycles used in the potentiometric titrations ($L^1 \cdot 4HClO_4$ and $L^2 \cdot 3HClO_4$) had satisfactory elemental analysis.

NMR Spectroscopy.—The 200.0 MHz ^1H and 50.32 MHz ^{13}C NMR spectra in MeOD solutions were recorded at 318 K on a Bruker AC-200 spectrometer. Peak positions are reported

Table 3 Atomic coordinates ($\times 10^4$) for $[Cd(HL^3)Cl_2]ClO_4 \cdot H_2O$

Atom	*x*	*y*	*z*
Cd	2112(1)	4260(1)	2844(1)
Cl(1)	2474(2)	4528(1)	4504(1)
Cl(2)	2909(3)	3206(1)	3078(2)
Cl(3)	4761(2)	6314(1)	420(1)
N(1)	−861(6)	5900(3)	2797(4)
N(2)	−493(6)	4285(3)	2255(4)
N(3)	1676(6)	4218(3)	1199(4)
N(4)	4083(6)	4857(2)	2651(3)
N(5)	3805(6)	6418(2)	3600(4)
N(6)	1172(6)	6631(3)	4212(4)
O(1)	1864(5)	7149(2)	2330(3)
O(2)	597(6)	5846(3)	1896(4)
O(10)	3474(7)	6235(4)	684(4)
O(20)	5160(45)	6942(12)	497(25)
O(30)	4772(39)	6765(14)	−114(23)
O(40)	4498(18)	6202(17)	−521(11)
O(50)	4762(34)	5767(10)	−12(25)
O(60)	5780(26)	6352(19)	1241(18)
O(70)	6035(28)	5998(17)	898(22)
O(3)	2645(7)	2651(3)	4956(4)
C(1)	−558(9)	5268(3)	3015(5)
C(2)	−1245(8)	4874(3)	2196(5)
C(21)	−1044(9)	3879(4)	2833(6)
C(3)	−779(8)	4035(3)	1308(5)
C(31)	2046(9)	3635(4)	866(5)
C(4)	112(8)	4346(4)	787(5)
C(41)	5402(8)	4616(4)	3347(5)
C(5)	2607(8)	4697(3)	1014(4)
C(6)	4121(7)	4676(3)	1706(4)
C(61)	1017(9)	7280(4)	4254(5)
C(7)	4070(8)	5516(3)	2679(4)
C(8)	4092(7)	5765(3)	3611(4)
C(9)	3872(8)	6633(3)	4559(4)
C(10)	2578(8)	6426(3)	4840(4)
C(11)	−60(8)	6322(4)	4367(5)
C(12)	−1325(8)	6239(4)	3471(5)
C(13)	−205(8)	6143(3)	2220(5)
C(14)	−563(8)	6786(4)	1901(5)
C(15)	586(8)	7067(4)	1552(5)
C(16)	3063(8)	7417(3)	2096(5)
C(17)	4372(9)	7406(3)	2938(5)
C(18)	4882(8)	6773(3)	3252(5)
H(5)	2968(74)	6526(31)	3214(44)

relative to $SiMe_4$. The NMR titrations were performed by adding a 5×10^{-3} mol dm^{-3} methanolic solution of $CdCl_2 \cdot 2.5H_2O$ to 5×10^{-3} mol dm^{-3} solutions of L^1 or L^2 in MeOD.

Electronic Spectroscopy.—The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with 1 cm cell thermostatted at 298 K. Spectrophotometric titrations were performed by adding a 1×10^{-3} mol dm^{-3} methanolic solution of $Cu(ClO_4)_2 \cdot 6H_2O$ to 1×10^{-3} mol dm^{-3} solutions of L^1 or L^2 in MeOH.

Electrochemical Measurements.—All solutions were prepared from A. R. grade chemicals, by using distilled water further purified by passing through a Milli Q Millipore set-up (final resistivity < 10 MΩ cm^{-1}). The cyclic voltammograms were recorded on an EG&G model 263 potentiostat/galvanostat. The working electrode was EG&G model 303A static mercury drop electrode and EG&G model 270/250 Research Electrochemistry 4.00 software was employed. The pH was measured with a Corning 220 pH-meter.

Crystallography.—*Crystal data.* $C_{22}H_{49}CdCl_3N_6O_7$, $M = 728.42$, monoclinic, space group $P2_1/c$, $a = 9.593(5)$, $b = 22.315(4)$, $c = 15.24(1)$ Å, $\beta = 107.53(5)°$, $U = 3111(3)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1512$. Prismatic, colourless crystals, dimensions $0.2 \times 0.3 \times 0.5$ mm, μ(Mo-Kα) = 1.008 mm^{-1}.

Data collection and processing.[18] CAD4 diffractometer, θ–2θ scan mode with θ scan width = $0.8 + 0.35\tan\theta$, θ scan speed = 4.1° min^{-1}, graphite-monochromated Mo-Kα radiation, ambient temperature. 3264 Reflections measured ($2.8 \leqslant \theta \leqslant 24.95°$), Lorentz and polarization corrections applied. No intensity decay observed.

Structure analysis and refinement. Patterson method (Cd atom) followed by normal full-matrix least-squares refinement. Absorption correction applied after structure solution (DIFABS). All non-hydrogen atoms anisotropic, methylene and methyl hydrogen atoms in calculated positions with one, overall, fixed $U_{iso} = 0.051$ Å^2. An acidic proton H(5) was found in the final ΔF and isotropically refined. Two different models (population parameter 0.5) were applied for the oxygen atoms of the perchlorate anion, except O(10). The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 2.56P]$ with $P = [\max(F_o^2, 0) + 2F_c^2]/3$; 388 refined parameters. Final $R = 0.045$ for 3144 unique reflections with $I > 2.0\sigma(I)$; $wR_2 = 0.102$. Table 3 lists the final positional parameters. Programs, source of scattering factors and anomalous dispersion corrections are given in ref. 18.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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