Complexation Properties of Heteroditopic Cryptands towards Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} in Aqueous Solution: Crystal Structures of $[(H_5L1)(ClO_4)_5]\cdot 4\,H_2O$ and $[(NiL2Cl)Cl]\cdot 5.5\,H_2O\cdot CH_3OH$

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The protonation and metal ion (Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) complexation abilities of three heteroditopic cryptands in solution are described and the relevant equilibrium constants are reported. The two distinct binding subunits of the ligands act cooperatively in the coordination of $M(H_2O)^{2+}$ (M = metal ion) species. The cryptand **L1** binds five protons in very acidic solution and crystallizes as $[(H_5\mathbf{L1})(ClO_4)_5]\cdot 4\,H_2O$ in the monoclinic space group $P2_1/n$ with $a = 14.281(4)$, $b = 14.313(7)$, $c = 24.082(8)$ Å, $\beta = 92.00(2)°$, $Z = 4$, $R = 0.079$, and $wR2 = 0.2010$. The molecule shows an *endo-endo* conformation with a pseudo-threefold symmetry axis passing through the two bridgehead nitrogen atoms. All the cryptands (**L1**–**L3**) readily form inclusion complexes with Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions at the tren end of the cavity. The crystal structure of $[(Ni\mathbf{L2}Cl)Cl]\cdot 5.5\,H_2O\cdot CH_3OH$ is also reported [$C2/c$, $a = 26.671(6)$, $b = 16.784(4)$, $c = 18.591(8)$ Å, $\beta = 101.006(14)°$, $Z = 8$, $R = 0.091$, and $wR2 = 0.1424$]. The Ni^{II} ion resides in a trigonal-bipyramidal coordination environment with the equatorial sites occupied by the three secondary nitrogen atoms of the cryptand and the axial sites occupied by a bridgehead nitrogen atom and a Cl^- ion.

Introduction

Macrocyclic ligands containing various binding functionalities are a topic of considerable current interest due to their ability to show highly selective recognition of different substrates, including both charged (cations, anions) and neutral molecules.[1–9] Among such ligands, macrobicyclic cryptands have attracted great interest since they are characterized by a three-dimensional arrangement of donor atoms and are capable of replacing the first solvation shell of the target species, thereby shielding the complexed species from the external environment.[8–19] However, when the number of cryptand donor atoms is insufficient to complete the coordination environment of the enclosed substrate, the inclusion of partially solvated species is observed. This is the case, for instance, with several transition metal complexes of the macrobicyclic cryptands **L1**–**L3** (Figure 1), where coordinated solvent molecules or anions are drawn into the cavity along with the metal ion.[20–23] Ligands such as **L1**–**L3** display interesting molecular structures composed of two different tripodal binding sites separated by three aromatic rings, which form a highly hydrophobic region. Such ligand structures have proved to be particularly effective in hosting metal ions since they stabilize metal–ligand bonds that are otherwise unstable.[24] The tripodal N_4 moiety represents a well-suited binding site for transition metal ions, although there are insufficient enough donor atoms to saturate the coordination spheres of many metal ions. As a result, the binding properties of the metal ions are directed towards the coordination of further species from the medium, which are constrained to occupy coordination sites located in, or in the proximity of, the hydrophobic region defined by the aromatic rings. Metal ions in such coordination environments, in conjunction with the remaining empty space in the ligand cavity, can be utilized in homogeneous catalytic reactions.[22] As a matter of fact, the secondary species linked to the metal ions display peculiar coordination features in that they are able to interact with both the donor atoms of the empty ligand moiety[21] and the π electron clouds of the benzene rings.[23] Moreover, derivatives of these cryptands have been shown to be well-suited for studying chelation-enhancement of fluorescence[25] and for the construction of ordered structures such as vesicles[26] and Langmuir–Blodgett films.[27] In spite of the large amount of information acquired about these ligands and their complexes, nothing is known regarding the thermodynamics of ligand protonation and metal ion complexation in solution. In order to fill in this gap, we performed the study described herein.

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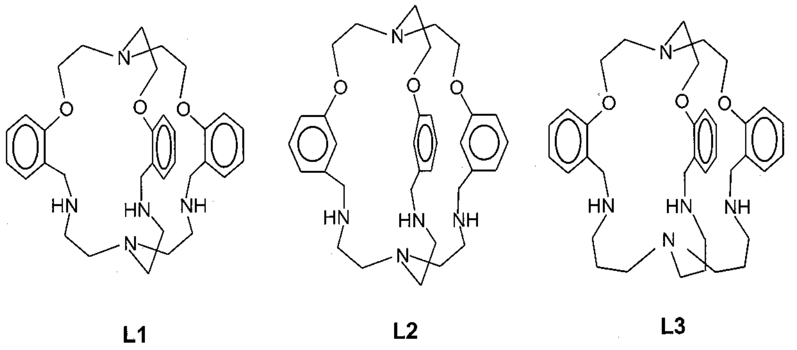

L1 L2 L3

Figure 1. Ligand drawings

Results and Discussion

Ligand Protonation

The protonation constants of cryptands **L1**−**L3**, determined in 0.10 mol dm^{-3} Me_4NNO_3 at 298.1 K, are listed in Table 1. In the case of **L3**, it was not possible to determine the first protonation constant due to precipitation occurring in the pH region where the H**L3**$^+$ species should be formed.

Table 1. Logarithms of ligand protonation constants determined in 0.10 mol dm^{-3} Me_4NNO_3 at 298.1 K

	L1 log *K*[a]	**L2**	**L3**
$L + H^+ = LH^+$	10.45(7)	9.74(6)	
$HL^+ + H^+ = LH_2^{2+}$	10.44(2)	8.68(6)	8.9(1)
$H_2L^{2+} + H^+ = LH_3^{3+}$	5.56(6)	7.47(8)	8.8(1)
$H_3L^{3+} + H^+ = LH_4^{4+}$	3.46(6)	5.6(1)	4.6(1)
$H_4L^{4+} + H^+ = LH_5^{5+}$		2.4(1)	2.9(1)

[a] Values in parentheses are standard deviations in the last significant figure.

The three molecules display rather different protonation properties. Firstly, it can be noted that while in very acidic solutions **L1** is able to form the fully protonated species, as demonstrated by the crystal structure of [(H_5**L1**)$(ClO_4)_5$] 4 H_2O, in the pH range 2.5−10.5 used to determine the protonation constants it behaves, at most, as a tetraprotic base (H_4**L1**$^{4+}$). In the same pH range, **L2** and **L3** are able to form the fully protonated species (H_5**L2**$^{5+}$, H_5**L3**$^{5+}$), indicating higher overall basicities. The first two protonation constants of **L1**, however, are considerably higher than the corresponding values for **L2** and **L3**, while the third and fourth values are significantly lower. Furthermore, the first two protonation constants of **L1** are surprisingly similar within experimental error. It is a common characteristic of cryptand polyamines to display peculiar protonation behavior. This can often be attributed to the presence of solvent molecules in the cavity, which contribute to the stabilities of the protonated species through hydrogen bonding.[23,28,30] As a matter of fact, as shown by recent crystal structures, H_2**L1**$^{2+}$ and H_2**L2**$^{2+}$ are able to bind one[30] and two[23] water molecules, respectively, forming significant hydrogen-bond networks within the cavity involving the ammonium groups. In [(H_2**L1**)$\subset H_2O$]$^{2+}$, the water molecule seems to be bound more strongly than in the H_2**L2**$^{2+}$ cryptate due to the direct participation of both the binding moieties in the former. This is, in turn, a consequence of the different connectivity of the tripodal binding moieties to the benzene rings, the *ortho*-substituted cryptand allowing closer approach of the bridgehead nitrogen atoms than the *meta*-substituted one. Hence, it seems likely that efficient cooperativity of the two opposite binding subunits, as mediated by a cryptate water molecule, is responsible for the higher basicity of **L1** in the first two protonation steps. In **L3**, the benzene rings are *ortho*-substituted but, unlike **L1**, it is more flexible as the tren [tris(2-aminoethyl)amine] unit is replaced by trpn [tris(3-aminopropyl)amine] (Figure 1).

An alternative explanation of such behavior may be found in the abilities of similar cryptand molecules to promote the coordination of anionic species.[19] Inclusion of a negatively charged substrate would lead to stabilization of the positively charged receptor through charge neutralization and, depending on the nature of the anion, through the formation of intramolecular hydrogen bonds. Accordingly, the marked loss of basicity observed in the third and fourth protonation steps of **L1** might stem from disruption of the internal structure as a result of the guest species interacting with the final protonation sites. Indeed, the crystal structure of the compound [(H_5**L1**)$(ClO_4)_5$] · 4 H_2O shows an empty H_5**L1**$^{5+}$ cation (Figure 2) that displays evident stress stemming from the electrostatic repulsion between positive charges.

The crystal structure of [(H_5**L1**)$(ClO_4)_5$] · 4 H_2O reveals the presence of discrete H_5**L1**$^{5+}$ cations, perchlorate anions, and solvating water molecules. The H_5**L1**$^{5+}$ cation interacts with three external perchlorate anions and a water molecule through strong hydrogen bonds (Figure 2, Table 2). The N···N and O···O interatomic distances (Table 2) are consistent with the presence of a pseudo-threefold symmetry axis passing through the two bridgehead nitrogen atoms of H_5**L1**$^{5+}$. As a result of electrostatic repulsion, the cavity of H_5**L1**$^{5+}$ is expanded, albeit only slightly, with respect to that of the free **L1** cryptand.[21] This expansion is mainly manifested in a lengthening of the distances between the secondary nitrogen atoms of the tetraamine moiety, the O···O distances within the opposite tripodal subunit being less affected by protonation (Table 2). The distance between the bridgehead nitrogen atoms in **L1** [6.249(5) Å][21] is maintained in H_5**L1**$^{5+}$ [6.25(2) Å]. As a consequence of the aforementioned expansion, H_5**L1**$^{5+}$ displays some molecular strain. This is evident from the bond angles in the ligand

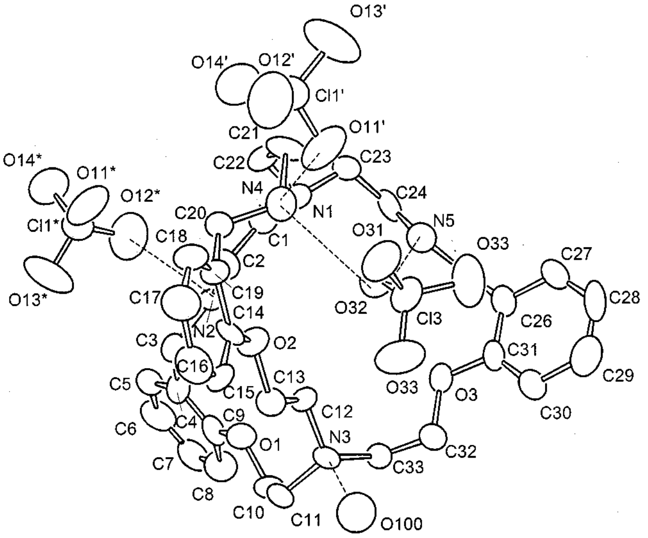

Figure 2. A perspective view of **1** showing the atom numbering scheme

Table 2. Selected intramolecular distances [Å], bond angles [°], and hydrogen-bond lengths [Å] for **1** and **2**

1		2	
N1···N3	6.25(2)[a]	Ni···N(2)	2.243(6)
N5···N4	5.54(2)	Ni···N(12)	2.017(6)
N4···N2	4.59(2)	Ni···N(3)	2.055(6)
O1···O2	4.77(2)	Ni···N(1)	2.151(6)
O1···O3	5.28(1)	Ni···Cl(1)	2.303(2)
O2···O3	5.04(1)		
		N(12)−Ni−N(3)	85.9(2)
		N(12)−Ni−N(1)	85.8(2)
		N(3)−Ni−N(1)	94.5(2)
		N(12)−Ni−N(2)	82.6(2)
		N(3)−Ni−N(2)	97.2(2)
		N(1)−Ni−N(2)	162.7(2)
		N(12)−Ni−Cl(1)	110.86(18)
		N(3)−Ni−Cl(1)	163.15(17)
		N(1)−Ni−Cl(1)	88.88(18)
		N(2)−Ni−Cl(1)	83.42(18)

Hydrogen bond distances for **1**

N5···O32		2.82(2)
N4···O32		2.86(2)
N2···O12	$-x + 1.5, y - 0.5, -z + 1.5$	2.94(2)
N4···O11	$x-1, y, z$	3.01(2)
N3···O100		2.82(2)
O100···O14	$-x + 1.5, y + 0.5, -z + 1.5$	2.99(2)
O200···O11	$x - 1, y, z$	2.88(3)
O200···O500	$x - 1, y, z$	2.38(5)
O400···O500	$-x + 1, -y + 1, -z + 1$	2.15(6)
O500···O33	$x + 1, y, z$	2.77(4)

[a] Values in parentheses are standard deviations in the last significant figure.

chains, which are, on average, significantly larger (mean value 112.4°) than the value expected for sp^3 carbon atoms. The protonated nitrogen atoms N(2), N(4), and N(5) interact with three external perchlorate anions (Figure 2), two of which are symmetry-related (Table 2). The other ClO_4^- anion (Cl3) bridges two ammonium groups (Figure 2). All the anions are strongly bound to the protonated cryptand, as evidenced by the short hydrogen-bond lengths (Table 2). While in the unprotonated **L1** and the diprotonated $[(H_2\mathbf{L1})\subset H_2O]^{2+}$ cryptate the bridgehead nitrogen atoms adopt an *endo-endo* conformation, in $H_5\mathbf{L1}^{5+}$ the acidic proton bound to the bridgehead N(3) points towards the exterior of the molecular cavity, interacting with an external water molecule [N(3)···O(100) distance 2.82(2) Å]. No such hydrogen bonding involving the other bridgehead nitrogen atom can be detected. Consequently, the bridgehead nitrogen atoms assume an *endo-exo* conformation (Figure 2). It thus seems reasonable that the formation of very stable cryptate species is responsible for the high stability of **L1** in the early stages of protonation, while conformational changes, disruption of the cryptate structure, and strong electrostatic repulsions between positive charges combine to produce a rapid loss of stability in the later protonation stages.

Further investigations are in progress aimed at ascertaining the nature of the cryptate species. As a matter of fact, in a recent communication the inclusion, both in solution and in the solid state, of two nitrate anions in the cavity of a similar cryptand has been reported.[19]

Complex Formation

The macrobicyclic ligands **L1**−**L3** are potential heteroditopic receptors for metal ions, being composed of two dissimilar tripodal binding subunits. While the tetraamine moiety has proved to be suitable for the coordination of transition metal ions,[20−23,31] the ethereal moiety can be expected to be effective in the binding of "harder" cations. In order to determine the coordination properties of these ligands in aqueous solution, we have studied the complexation of various metal ions such as Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}, as well as of alkali and alkaline earth cations. From the results of this study, it is clear that the three ligands do not show any tendency to form complexes with alkali or alkaline earth cations, while they are capable of forming stable complexes with the remaining metal ions. Nevertheless, the ethereal moieties of these ligands display a poor propensity to remain vacant; indeed, as shown by crystal structure determinations,[21,23] they are well suited for strong hydrogen-bonding interactions with water molecules inside the ligand cavity, in particular with water molecules linked to metal ions coordinated to the opposite tetraamine site, as is observed in the crystal structures of the Ni^{2+} complex[21] with **L1** and the Cu^{2+} complex[23] with **L2**. Similar features have been observed previously for other cryptand ligands.[28,32]

The cryptand **L2** readily forms a mononuclear complex with Ni^{2+}, which has been isolated as $[(Ni\mathbf{L2}Cl)Cl] \cdot 5.5\ H_2O \cdot CH_3OH$. The crystal structure of this complex reveals the presence of $[\mathbf{L2}\subset NiCl]^+$ cations (Figure 3), chloride anions, and methanol and water molecules of crystallization. The Ni^{2+} cation achieves pentacoordination through ligation by the N_4 ligand moiety and a chloride ion, Cl(1), in a trigonal-bipyramidal fashion (Table 2), where the secondary amino nitrogen atoms N(1) and N(2) occupy the axial positions (Figure 3). This coor-

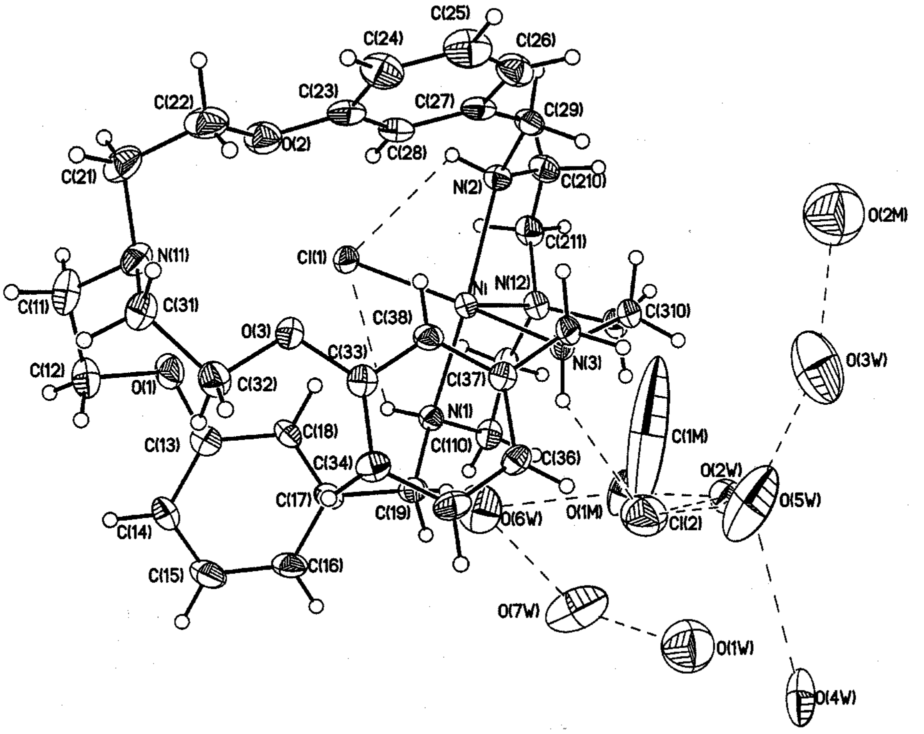

Figure 3. A perspective view of **2** showing the atom numbering scheme

dination geometry is quite similar to that in the pentagonal-bipyramidal cascade complex[20] of the Cu^{2+} ion with the same ligand. Cl(1) also shows hydrogen-bonding interactions with the amine nitrogen atoms N(1) and N(2) [Cl(1)···N(1) 3.121(5) Å; Cl(1)···N(2) 3.025(6) Å]. Seven water and two methanol molecules are also present in the crystal lattice. Both the methanol molecules and three of the water molecules show large thermal displacements and are assigned half-occupancy. All bond lengths and bond angles in the cryptand moiety have typical values within statistical error limits.

It is noteworthy that, although chloride anions and water molecules are similarly drawn into the cryptand cavity by coordinated metal ions, the water cryptate is stabilized by hydrogen bonding to the ethereal oxygen atoms, whereas the chloride ions form hydrogen bonds with the metal-coordinated amine groups.

Table 3. Logarithms of complexation constants determined in 0.10 mol dm^{-3} Me_4NNO_3 at 298.1 K

Reaction	**L1**	**L2** log K[a]	**L3**
$Cu^{2+} + L = CuL^{2+}$	15.22(3)	14.36(3)	
$Cu^{2+} + HL^{+} = CuLH^{3+}$		11.2(1)	7.44(3)
$CuL^{2+} + H^{+} = CuLH^{3+}$		6.6(1)	8.70(8)
$CuL^{2+} + OH^{-} = CuLOH^{+}$		5.6(1)	4.38(8)
$Zn^{2+} + L = ZnL^{2+}$	8.83(5)	7.06(6)	
$Zn^{2+} + HL^{+} = ZnLH^{3+}$		5.07(6)	4.8(1)
$ZnL^{2+} + H^{+} = ZnLH^{3+}$		7.76(6)	7.45(2)
$ZnL^{2+} + OH^{-} = ZnLOH^{+}$	3.78(7)		3.66(6)
$Cd^{2+} + L = CdL^{2+}$	11.14(2)	7.35(8)	
$Cd^{2+} + HL^{+} = CdLH^{3+}$		6.94(8)	
$CdL^{2+} + H^{+} = CdLH^{3+}$		7.94(9)	
$CdL^{2+} + OH^{-} = CdLOH^{+}$	3.83(3)		
$Pb^{2+} + L = PbL^{2+}$	13.09(2)	9.52(9)	
$Pb^{2+} + HL^{+} = PbLH^{3+}$	6.95(9)		
$PbL^{2+} + H^{+} = PbLH^{3+}$	7.16(9)		
$PbL^{2+} + OH^{-} = PbLOH^{+}$	3.25(5)	3.8(1)	

[a] Values in parentheses are standard deviations in the last significant figure.

Stability Constants

The stability constants for the Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} complexes with **L1** and **L2**, as well as for the Cu^{2+} and Zn^{2+} complexes with **L3**, are reported in Table 3. As mentioned in the Experimental Section, it was not possible to study the complexation of Cd^{2+} and Pb^{2+} with **L3** due to solubility problems. Stability constants for the Ni^{2+} complexes of the three ligands could not be determined, again due to solubility problems.

L1 forms both $ML1^{2+}$ and hydroxylated $ML1(OH)^{+}$ species with all the metal ions except for Cu^{2+}, while **L2** and **L3** are also able to form the monoprotonated species. In the case of the Zn^{2+} and Cd^{2+} complexes with **L2**, however, formation of a hydroxylated species was not observed due to precipitation occurring in alkaline solution. Although the set of stability constants is incomplete, some interesting conclusions regarding the coordination properties of these ligands can be drawn. Firstly, it can be noted that some dimensional recognition is exhibited by these cryptands. As a matter of fact, considering the metal ions (Zn^{2+}, Cd^{2+},

Pb^{2+}) for which ligand-field stabilization is not possible, complex stability is seen to increase with increasing metal ion size. Such a trend in the coordination ability is evidently connected with the macrobicyclic nature of these ligands, since an opposite trend in stabilities is observed for the Zn^{2+} and Cd^{2+} complexes with the ligand tris(2-aminoethyl)amine, tren {log $K = 14.5$ for $Zn(tren)^{2+}$, log $K = 11.7$ for $Cd(tren)^{2+}$,[33a] log $K = 10.21(1)$ for $[Pb(tren)]^{2+}$ [33b]}, which can be considered as an acyclic analogue of the tetraamine moieties of **L1** and **L2**. Due to their bicyclic structures, cryptands are more rigid than acyclic molecules. Consequently, they show a reduced tendency to modify their arrangements so as to satisfy the coordination requirements of metal ions. The present cryptands are apparently too large to give a good fitting with all the studied metal ions, which accounts for the observed stability increase with increasing cation dimensions.

The complexation ability has been found to be highly dependent on the ligand structure. While the lower tendency of **L3** to form complexes with the present metal ions was expected, due to the formation of six-membered chelate rings rather than the more stable five-membered ones formed by **L1** and **L2**, the difference in stability between the complexes of **L1** and **L2** is rather surprising. All complexes formed by **L1** are considerably more stable than those with **L2**, this difference in stability amounting to more than three orders of magnitude in the case of the Cd^{2+} and Pb^{2+} complexes. It is worth noting that, on the basis of X-ray crystallographic studies[20,22] on free **L1** and **L2** and their metal complexes, the cavity in **L2** has been shown to be much more rigid compared to that in **L1**. Consequently, the entering metal ion cannot adjust the coordination geometry to its liking in the former.

Conclusion

Cryptand ligands are characterized by rigid structures and consequently simple ligand modifications can lead to significant changes in their binding properties. This has clearly been shown to occur with **L1**−**L3**. In particular, the presence of *ortho*-substituted aromatic spacers in **L1** gives rise to an evident enhancement in basicity and metal ion coordination properties with respect to **L2**, which contains *meta*-substituted spacers. These cryptands show a particular tendency to form inclusion complexes in which multiple species are enclosed in the ligand cavity. In spite of this tendency and of the presence of two separate binding subunits in the ligands, **L1**−**L3** are not able to form binuclear metal complexes in aqueous solution. Nevertheless, in accordance with their structures, these ligands display heteroditopic properties in metal ion coordination since the two distinct binding subunits act cooperatively in the binding of $M(H_2O)^{2+}$ (M = metal ion) species. Furthermore, the abilities of these cryptands to promote inclusive coordination make these compounds promising candidates for the binding and recognition of anionic substrates, both in the presence and absence of coordinated metal ions.

Experimental Section

General Procedures and Materials: Cryptands **L1**−**L3** were synthesized as described previously[20,23,34] and were used in the form of free amines. − Crystals of $[(H_5\mathbf{L1})(ClO_4)_5]\cdot 4\,H_2O$ (**1**) suitable for single-crystal X-ray analysis were obtained by slow evaporation of the solvents at room temperature from a solution containing **L1** and an excess of $HClO_4$ in ethanol/H_2O (80:20, v/v). − $C_{33}H_{58}Cl_5N_5O_{27}$ (1134.1): calcd. C 34.95, H 5.16, N 6.18; found C 35.0, H 5.2, N 6.2. − ***Caution!*** *Care must be taken when treating organic compounds with perchloric acid as potentially explosive mixtures may be formed.* − $[(Ni\mathbf{L2}Cl)Cl]\cdot 5.5\,H_2O\cdot CH_3OH$ (**2**) was prepared by adding a solution of $NiCl_2\cdot 6\,H_2O$ (0.24 g, 0.1 mmol) in MeOH (5 mL) to **L2** (0.056 g, 0.1 mmol) in MeOH (5 mL). A bluish-green solid separated immediately, which was collected by filtration, washed with MeOH, and dried in air. Recrystallization from MeCN afforded X-ray quality single crystals as green rectangular parallelepipeds. − $C_{34}H_{60}Cl_2N_5NiO_{9.5}$ (820.5): calcd. C 49.77, H 7.37, N 8.54; found C 49.7, H 7.4, N 8.5.

Crystal Structure Determination: A summary of X-ray data collection, structure solution, and refinement for both **1** and **2** is presented in Table 4. In each case, the cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 carefully centered reflections. The intensities of two standard reflections were monitored every hour during data collection to check the stability of the diffractometer and of the crystal. Intensity data were corrected for Lorentz and polarization effects and, in the case of **1**, an absorption correction was applied once the structure had been solved by the DIFABS method.[35] In the case of **2**, an analytical absorption correction was applied. Both structures were solved by direct methods[36] and refined by full-matrix least-squares techniques on F^2 using SHELXL-97[37a] and SHELX-93[37b] for **1** and **2**, respectively, which use the analytical approximation for atomic scattering factors and anomalous dispersion corrections for all atoms taken from ref.[38] Anisotropic displacement parameters were used for all non-hydrogen atoms. In each case, hydrogen atoms were introduced in calculated positions. For **1**, an overall unrefined temperature factor was assigned for the hydrogen atoms, while for **2** overall refined thermal parameters were used for aliphatic, amino, and aromatic hydrogen atoms. Crystallographic data

Table 4. Crystal data and structure refinement for $[H_5\mathbf{L1}](ClO_4)_5\cdot 4\,H_2O$ and $[(Ni\mathbf{L2}Cl)Cl]\cdot 5.5\,H_2O\cdot CH_3OH$

Empirical formula	$C_{33}H_{58}Cl_5N_5O_{27}$	$C_{34}H_{60}Cl_2N_5NiO_{9.5}$
Formula mass	1134.09	820.48
Temperature	298 K	293 K
Wavelength	0.71069 Å	0.71069 Å
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions	$a = 14.281(4)$ Å $b = 14.313(7)$ Å $c = 24.082(8)$ Å $\beta = 92.00(2)°$	$a = 26.671(6)$ Å $b = 16.784(4)$ Å $c = 18.591(4)$ Å $\beta = 101.006(14)°$
Volume	4920(3) $Å^3$	8169(3) $Å^3$
Z	4	8
Density (calculated)	1.531 Mg/m^3	1.333 Mg/m^3
Absorption coefficient	0.389 mm^{-1}	0.662 mm^{-1}
Crystal size	0.3 × 0.2 × 0.15 mm	0.35 × 0.34 × 0.27 mm
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0790$ $wR2 = 0.2010$[a]	$R1 = 0.0912$ $wR2 = 0.1424$
R indices (all data)	$R1 = 0.1860$ $wR2 = 0.2906$[a]	$R1 = 0.2077$ $wR2 = 0.3122$

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR^2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

(excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140417 and CCDC-140418 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Potentiometric Measurements: All pH-metric measurements ($pH = -\log [H^+]$) used for the determination of protonation and complex formation constants were performed in 0.10 mol dm^{-3} Me_4NNO_3 solutions at 298.1 ± 0.1 K using equipment and methodologies described in a previous report.[39] The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free Me_4NOH solutions and determining the equivalent point by Gran's method.[40] This allows determination of the standard potential E^o and the ionic product of water [$pK_w = 13.83(1)$ at 298.1 ± 0.1 K in 0.1 mol dm^{-3} Me_4NNO_3]. At least three measurements were performed for each system. In all experiments, the ligand concentration [L] was $5 \cdot 10^{-4}$ mol dm^{-3}, while in the complexation experiments the metal ion concentration was about 0.8 [L]. Test measurements were performed in presence of higher metal ion concentrations in order to confirm that no polynuclear complexes were formed. The pH range investigated was 2.5−10.5 for all measurements, although in some cases the formation of precipitates curtailed the useful range for the determination of equilibrium constants. This was the case at $pH > 8$ in the titrations performed to determine the protonation constants of **L3** and the stability constants of the Zn^{2+} and Cd^{2+} complexes with **L2**. In the case of **L3**, only the complexes with Cu^{2+} and Zn^{2+} were sufficiently soluble for adequate study. Complexation reactions with these ligands were found to be rather slow. For this reason, equilibration times of 5−15 min were necessary after each addition of titrant. Conventional potentiometric titrations were performed to determine the stability constants in the system Pb^{2+}/tren ([tren] = $1 \cdot 10^{-3}$ mol dm^{-3}, [Pb^{2+}] = 0.8 [tren]) under the same experimental conditions (0.1 mol dm^{-3} Me_4NNO_3, 298.1 ± 0.1 K). The computer program HYPERQUAD[41] was used to calculate both protonation and complexation constants from the e.m.f. data.

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