

Protonation and metal-ion complexation in aqueous solution by pyridine-containing hexaaza macrocycles

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The protonation as well as the metal-binding constants with Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ for the macrocyclic hexadentate ligands L¹ {3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]tetracosal(23),8,10,12(24),19,21-hexaene} and L² {3,7,15,19,25,26-hexaazatricyclo[19.3.1.1^{9,13}]hexacosal(25),9,11,13(26),21,23-hexaene} have been determined at 25 °C in 0.1 mol dm⁻³ KNO₃ or KCl. The heats of protonation and of complexation with Cu²⁺, Cd²⁺ and Pb²⁺ were determined calorimetrically. The value for the fourth protonation step of L¹ showed a medium dependency, being much higher in KNO₃ (aq) than in KCl (aq). The crystal structure of [H₄L¹][NO₃]₄ was determined and consists of discrete centrosymmetric three-ring tetrapositive cations and two crystallographically independent nitrate ions. Hydrogen bonds between the four *endo*-nitrogens of the eighteen-atom ring and the nitrate ions are formed. Mononuclear 1:1 metal-ion complexes were identified with L¹ and L². Electronic spectral data indicate octahedral six-co-ordination for the complexes of Cu²⁺ and Ni²⁺ with L¹ and L². Copper(II) also forms a monoprotonated mononuclear complex and a dinuclear complex with L². The metal-ion affinities of L¹ are compared to those of the fully saturated 1,4,7,10,13,16-hexaazacyclooctadecane L³ using thermodynamic and electronic spectral data. The larger stability of Cu²⁺ with L¹ relative to L³ is entirely due to a more favourable entropy change, indicating that ligand pre-organization is the main reason for the increased stability. The metal-ion affinity of L² is lower than that of L¹ due to the less exothermic heats of complexation.

The metal-ion co-ordination chemistry in aqueous solution of polyazacycloalkane macrocycles has been the subject of numerous investigations and has been extensively reviewed recently.¹ This field is still being explored,²⁻⁸ focusing on polynuclear complexes, anion interactions and the influence of the presence of donor atoms other than the sp³-nitrogen atom. In this connection the replacement of a secondary amino group by a pyridine unit in the macrocyclic structure offers new opportunities to obtain metal-ion complexes with high stability and perhaps good steric efficiency. Indeed, complexes of linear polyamines containing 2- and/or 2,6-substituted pyridyl groups show a higher stability than expected on the basis of the basicity of the pyridine nitrogen in water.⁹ This was attributed to pre-organization and lower ring strain for the formation of the pyridine-containing chelate rings.¹⁰ In addition, π -bonding interactions between the pyridyl group and the metal ion could also contribute to the higher stability, as far as appropriate metal d orbitals are available.⁹ Metal-ion co-ordination in aqueous solution by pyridine-containing polyaza macrocycles has been studied by a large number of workers.¹¹⁻¹⁹ Of particular interest are the studies by Costa and Delgado¹⁹ and by Rothermel *et al.*¹⁸ in which the authors compare, among other things, the co-ordinative properties of macrocyclic polyamines having respectively one and two pyridyl groups in the ring with those of the corresponding tetra- and hexaazacycloalkanes. It was found by Rothermel *et al.*¹⁸ that the hexadentate ligand L¹ [3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]tetracosal(23),8,10,12(24),19,21-hexaene] binds as well as or slightly better than its saturated homologue L³ (1,4,7,10,13,16-hexaazacyclooctadecane, [18]aneN₆) to Zn²⁺, Cd²⁺, Ca²⁺, La³⁺ and Gd³⁺, although the basicity of L¹ is about 3.4 log units lower than that of L³. No other metal ions could be included in the comparison due to the lack of available data. In view of these results it appeared of interest to further

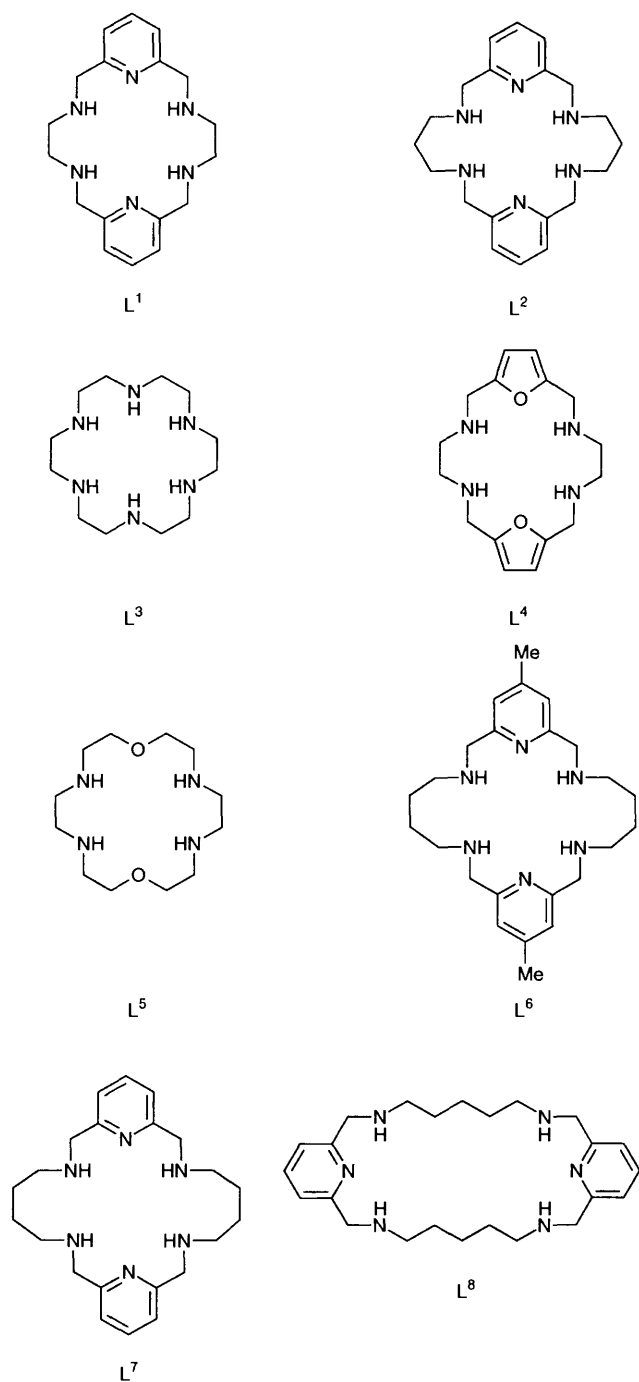
explore the co-ordinative properties of L¹ in aqueous solution and to determine the enthalpic and entropic contributions to the stability of its complexes. The protonation of L¹ was reinvestigated in different electrolyte media. The protonation and the metal-ion complexation of 3,7,15,19,25,26-hexaazatricyclo[19.3.1.1^{9,13}]hexacosal(25),9,11,13(26),21,23-hexaene (L²) was also investigated. This new compound is a larger analogue of L¹ with propylenic chains connecting the secondary amino groups.

The results of a study of the complexes of Mg²⁺, Ca²⁺, Sr²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ with L¹ were published by Bryant *et al.*²⁰ during the drawing up of this paper.

Results and Discussion

Crystal structure of [H₄L¹][NO₃]₄

The crystal structure of [H₄L¹][NO₃]₄ consists of discrete centrosymmetric three-ring tetrapositive [H₄L¹]⁴⁺ cations and two crystallographically independent nitrate ions. An ORTEP²¹ drawing of the [H₄L¹]⁴⁺ cation is shown in Fig. 1. The carbon atom C(6) is 0.019 Å below the pyridine group plane. The dihedral angle between the four non-pyridine nitrogen atoms and the pyridine group is 163.8°. The four sp³-nitrogens are in *endo* position with the N-C-N torsion of the *gauche* type. The N-O distances of the anion (1.224–1.267 Å, Table 1) are very similar to those in the literature.²²⁻²⁴ There is direct and rather strong intermolecular hydrogen-bond contact between the NH₂⁺ groups and the nitrate groups, with H...O separations varying from 1.87 to 2.29 Å and subtended N-H...O angles varying from 125 to 167°. The nitrate ions have their shortest H...O contact with one ammonium group and a longer contact distance with the ammonium group at the other side of the pyridine ring. The overall conformation of the



macrocyclic is slightly chair-shaped, and similar to that of $[\text{H}_4\text{L}^6][\text{ClO}_4]_4$.²⁵ Ligand L^6 has *N*-methylated tertiary amino groups instead of the pyridine groups in L^1 .

Protonation of L^1

The protonation constants of L^1 at 25 °C have previously been determined by Rothermel *et al.*,¹⁸ under different experimental conditions of ionic strength and glass-electrode calibration. Their values are given in footnote *a* of Table 2. In neutral solution the diprotonated form $[\text{H}_2\text{L}^1]^{2+}$ is the dominant species with the two hydrogen ions attached to secondary amino groups in positions diametrically opposed to each other. In the tetraprotonated form $[\text{H}_4\text{L}^1]^{4+}$ the two pyridine nitrogens remain unprotonated, as indicated by a ¹H NMR titration down to pH 4.¹⁸ In our study the titration of a concentrated solution of $[\text{H}_4\text{L}^1]^{4+}$ [$5.0 \times 10^{-2} \text{ mol dm}^{-3}$ in $1.0 \text{ mol dm}^{-3} \text{ KNO}_3(\text{aq})$] down to pH 1.0 could not reveal further protonation of $[\text{H}_4\text{L}^1]^{4+}$.²⁶ This is not surprising since the log

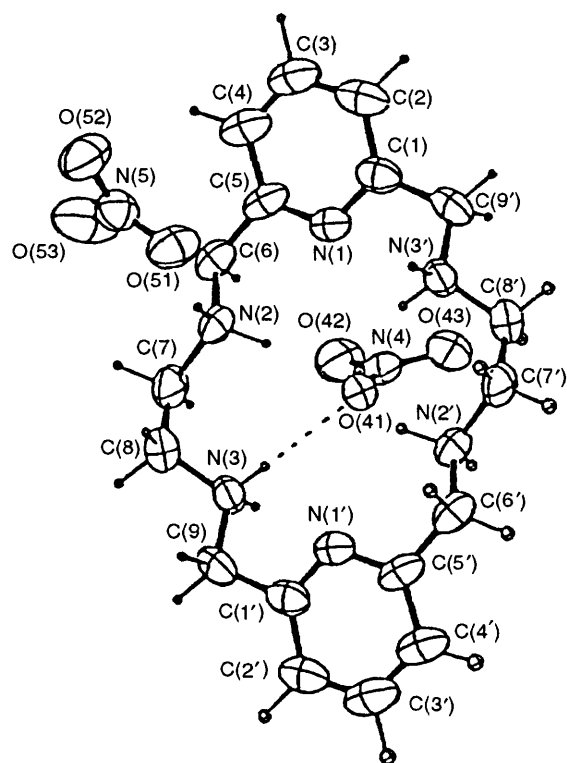


Fig. 1 An ORTEP view of the $[\text{H}_4\text{L}^1]^{4+}$ cation showing the atom numbering and thermal motion ellipsoids (30%)

Table 1 Bond distances (Å) and angles (°) in $[\text{H}_4\text{L}^1][\text{NO}_3]_4$ with estimated standard deviations in the last digit in parentheses

C(1)–N(1)	1.314(4)	C(1)–C(2)	1.416(5)
C(1)–C(9')	1.498(4)	C(2)–C(3)	1.379(5)
C(3)–C(4)	1.350(5)	C(4)–C(5)	1.374(5)
C(5)–C(6)	1.493(5)	C(5)–N(1)	1.347(4)
C(6)–N(2)	1.482(4)	C(7)–N(2)	1.504(4)
C(7)–C(8)	1.489(5)	C(8)–N(3)	1.479(4)
C(9)–N(3)	1.502(4)	N(4)–O(41)	1.267(3)
N(4)–O(42)	1.237(3)	N(4)–O(43)	1.224(3)
N(5)–O(51)	1.237(3)	N(5)–O(52)	1.241(3)
N(5)–O(53)	1.226(3)		
C(2)–C(1)–N(1)	122.4(3)	C(9')–C(1)–N(1)	114.8(3)
C(9')–C(1)–C(2)	122.8(3)	C(3)–C(2)–C(1)	116.4(3)
C(4)–C(3)–C(2)	121.6(3)	C(5)–C(4)–C(3)	118.2(4)
C(4)–C(5)–N(1)	122.5(4)	C(6)–C(5)–N(1)	116.0(3)
C(6)–C(5)–C(4)	121.6(3)	N(2)–C(6)–C(5)	109.5(3)
C(8)–C(7)–N(2)	113.6(3)	N(3)–C(7)–C(1')	109.3(2)
C(5)–N(1)–C(1)	118.9(3)	C(7)–N(2)–C(6)	111.6(2)
O(42)–N(4)–O(41)	119.2(3)	O(43)–N(4)–O(41)	119.4(3)
O(43)–N(4)–O(42)	121.4(3)	O(52)–N(5)–O(51)	121.4(3)
O(53)–N(5)–O(51)	119.9(3)	O(53)–N(5)–O(52)	118.7(3)

K values for pyridine protonation in 2-(aminomethyl)pyridine and in 2-(2-methylaminoethyl)pyridine are 2.00 and 1.91, respectively.²⁷ The tendency for the pyridine group to become protonated in $[\text{H}_4\text{L}^1]^{4+}$ will be even lower due to the high electrostatic repulsion experienced by the two ammonium groups at both sides of the pyridine group.

Table 2 lists our thermodynamic data on the protonation of L^1 in aqueous KNO_3 and KCl media. One can see that the values for $\log K^{\text{H}_1}$ and $\log K^{\text{H}_2}$ in both media are almost identical within experimental error, whereas the values for $\log K^{\text{H}_4}$ are clearly influenced by the type of electrolyte salt present. As to the ΔH° values, only ΔH°_4 in KNO_3 is markedly different from the other ΔH°_n values ($n = 1-3$ in KNO_3 and $n = 1-4$ in KCl) which can be averaged to $39 \pm 1 \text{ kJ mol}^{-1}$. This is a 'normal' value for the protonation heat of a secondary amine, taking into account the negative inductive effect of the pyridine

Table 2 Thermodynamic data for the successive protonation of L¹ and of L² at 25 °C in aqueous KNO₃ or KCl media (*I* = 0.100 mol dm⁻³)^a

	<i>n</i> ^b	KNO ₃ (aq)			KCl (aq)		
		log <i>K</i> ^{H_n}	-Δ <i>H</i> ^o _{<i>n</i>} /kJ mol ⁻¹	<i>T</i> Δ <i>S</i> ^o _{<i>n</i>} /kJ mol ⁻¹	log <i>K</i> ^{H_n}	-Δ <i>H</i> ^o _{<i>n</i>} /kJ mol ⁻¹	<i>T</i> Δ <i>S</i> ^o _{<i>n</i>} /kJ mol ⁻¹
L ¹	1	8.99	38.4	12.8	9.00	38.9	12.4
	2	8.16	40.7	5.8	8.13	39.7	6.6
	3	5.97	40.1	-6.1	5.86	38.6	-5.2
	4	5.20	55.1	-25.5	4.87	39.3	-11.5
L ²	1	9.35	38.9	14.4	9.39	38.9	14.6
	2	8.73	42.9	6.9	8.69	43.0	6.5
	3	7.36	47.5	-5.5	7.35	46.0	-4.1
	4	6.59	41.3	-3.7	6.52	41.3	-4.1

^a log *K*^{H_n} ± 0.01, Δ*H*^o ± 0.8 kJ mol⁻¹, *T*Δ*S*^o ± 0.9 kJ mol⁻¹. Values for L¹ measured at 25 °C in 0.2 mol dm⁻³ KCl: log *K*^{H₁} = 9.13, log *K*^{H₂} = 8.32, log *K*^{H₃} = 6.12, log *K*^{H₄} = 5.24, ref. 18. ^b *n*th Protonation step.

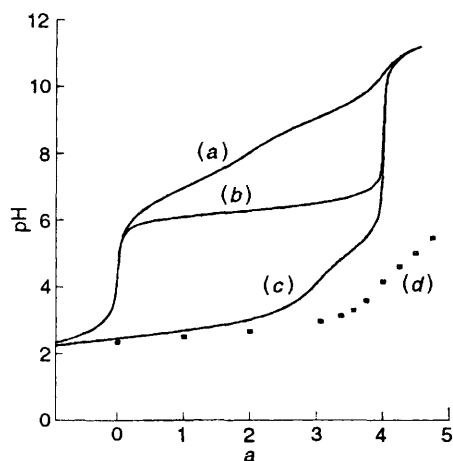


Fig. 2 Potentiometric titration curves of L² for equilibria with H⁺ (a), Pb²⁺ (b) and Cu²⁺ (c) at a 1:1 molar ratio of metal to L². The dotted curve (d) is from an out-of-cell titration at a 2:1 molar ratio of Cu²⁺ to L²; (*a* = mol of 0.250 mol dm⁻³ KOH added per mol of L²), *I* = 0.100 mol dm⁻³ KNO₃, 25 °C

groups.^{1,27} The Δ*H*^o₄ value in KNO₃ is thus clearly out of range and too exothermic. In addition, the *T*Δ*S*^o₄ value is much more negative than expected. These experimental data point to an interaction between the tetraprotonated form of L¹ and the nitrate ions in solution. A similar effect has been observed with the tetraprotonated form of L³ and a variety of anions.^{22,28} The 'normal' values for the protonation of L¹ in KCl can be supported by comparison with literature data on the protonation of L⁴¹⁸ and L⁵²⁹ given in Table 3. The differences in basicity between the first and the second, and between the third and the fourth, protonation step for the three polyamines are also given. First, the log *K*^H sequence at each protonation step reflects the magnitude of the negative inductive effect of the non-amine donor in these compounds: ether oxygen < pyridine N < furan oxygen. Secondly, the Δ log *K*^H_{3,4} values, which should be most susceptible to anion interactions, are identical for the three compounds, data for L⁵ obtained in NaNO₃ included. Moreover, the Δ log *K*^H_{3,4} values compare very well with the Δ log *K*^H_{1,2} values. As strong anion interaction is unlikely to occur with the mono- or di-protonated polyamine species, one may conclude that for the three polyamines under the given experimental conditions, in particular in KCl for L¹, anion binding effects can be neglected. The different values of Δ*H*^o₄ and *T*Δ*S*^o₄ for L¹ in KNO₃ most probably relate to the strong hydrogen-bonding ability of the nitrate ion and to specific conformations of the macrocyclic [H₄L¹]⁴⁺ ion. A similar observation was made for L⁶ where the fourth protonation step was also highly exothermic and entropically very unfavourable (-Δ*H*^o₄ = 51.5 kJ mol⁻¹, *T*Δ*S*^o₄ = -29.7

kJ mol⁻¹ at 25 °C in 0.15 mol dm⁻³ NaClO₄).²⁵ This was ascribed to the ligand conformation and in particular to the *endo* conformation of the four ammonium groups in the [H₄L⁶]⁴⁺ cation, allowing the formation of hydrogen bonds with the solvent, stabilizing the protonated species and producing a strong solvent electrostriction.²⁵ It is evident that this explanation also holds in the case of [H₄L¹]⁴⁺, but the fact that the Δ*H*^o₄ and *T*Δ*S*^o₄ values for L¹ in KCl are 'normal' demonstrates that the type of anion present in solution is of critical importance. The picture that arises from the overall results for L¹ and L⁶ is that only anions with strong hydrogen-bonding abilities such as perchlorate and nitrate co-operate with the polycations to produce the solvent electrostriction in the solvation sphere of the cations. The chloride ion which forms only weak hydrogen bonds is apparently not capable of stabilizing a strongly bound solvent network around the polycations.

Protonation of L²

In the polyamine L² the secondary amino groups are linked pairwise by a propylenic instead of an ethylenic chain as in L¹. The potentiometric titration curve for the protonation of L² in 0.100 mol dm⁻³ KNO₃ solution is shown in Fig. 2, and corresponds to the addition of 4 mol of H⁺ per mol of L² in one buffer region between pH 10.1 and 6.2. A slight change in slope of the titration curve is visible at the point where two hydrogen ions are added to L². Table 2 lists the thermodynamic data obtained for the protonation of L² in 0.100 mol dm⁻³ KNO₃ (aq) and KCl (aq). The two additional methylene groups increase the basicity of L² at the first and the second protonation steps through their positive inductive effect, while the larger ring size considerably reduces the build-up of electrostatic repulsion at the third and the fourth protonation steps. The log *K*^H, -Δ*H*^o and *T*Δ*S*^o values at the third and the fourth protonation steps show a slight dependency on the type of inert salt present in solution. However, one must be cautious in interpreting these differences, particularly as the Δ*H*^o_{*n*} values show a rather unexpected sequence: -Δ*H*^o₁ < -Δ*H*^o₂ < -Δ*H*^o₃ > -Δ*H*^o₄. For tetraaza macrocycles, -Δ*H*^o₃ is usually lower than -Δ*H*^o₂¹ as is the case for L¹. A possible explanation for the higher value of -Δ*H*^o₃ in the case of L² might be internal hydrogen-bond formation between an ammonium group and the remaining free amino group linked by the propylenic chain (see I). Restricted flexibility imposed by the two pyridine groups and further ring stiffening caused by the presence of three ammonium groups combine to produce enough rigidity in the ring structure of [H₃L²]³⁺ to allow for the formation of an internal N-H...N hydrogen bond of more than usual strength. Many examples of analogous internal hydrogen-bond formation can be found in the literature.³⁰⁻³⁴ This hydrogen bond is then broken up on addition of the fourth proton to form the [H₄L²]⁴⁺ species.

Table 3 Comparison of literature data for the successive protonation of L^{4a} and L^{5b} with those for L¹

Compound	log K ^H _n				Δ log K ^H _{n,n+1} ^c	
	n = 1	2	3	4	n, n + 1 = 1, 2	3, 4
L ⁴	8.84	7.73	5.20	4.21	1.11	1.01
L ⁵	9.36	8.40	6.27	5.23	0.96	1.01
L ^{1d}	9.00	8.13	5.86	4.87	0.87	0.99

^a At 0.1 mol dm⁻³ KCl, 25 °C, ref. 18. ^b At 0.1 mol dm⁻³ NaNO₃, 25 °C, ref. 29. ^c Difference between log K^H values at protonation step *n* and step (*n* + 1). ^d At 0.10 mol dm⁻³ KCl, 25 °C, this work.

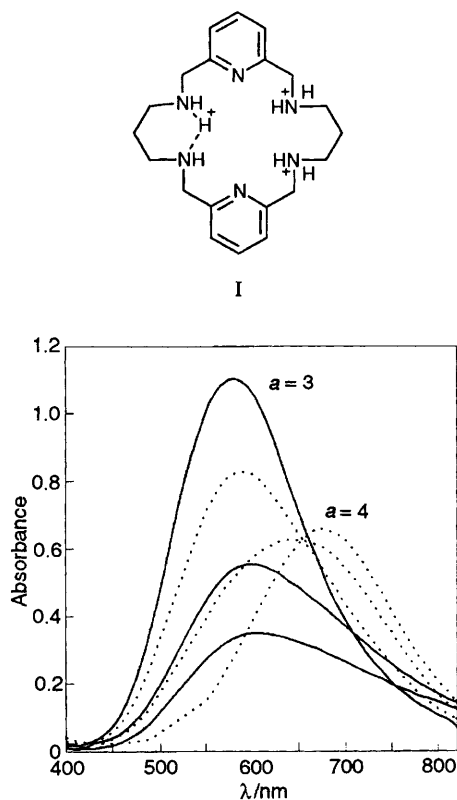


Fig. 3 Selected electronic spectra from a 1:1 molar ratio Cu²⁺ to L² titration as a function of the extent of neutralization of [H₄L²]⁴⁺ upon addition of standard KOH solution (*I* = 0.100 mol dm⁻³ KNO₃, 25 °C, path length = 1.000 cm). The solid-line spectra show the formation of the [Cu(HL²)³]³⁺ complex up to *a* = 3, the dotted-line spectra the deprotonation of [Cu(HL²)³]³⁺ to [CuL²]²⁺

Binding of Cu²⁺ to L¹ and L²

The electronic spectrophotometric titration data for the Cu²⁺–L¹ system were found to be consistent with the formation of only a [CuL¹]²⁺ complex with a log β₁₁₀ value (see Table 4) in good agreement with the literature value previously estimated.¹⁸ The stability of [CuL¹]²⁺ is 1.5 log units larger than for [CuL³]²⁺. This is entirely due to a more positive entropy change upon complexation. The literature data for [CuL³]²⁺ are given in Table 4. This observation definitely supports a pre-organizational benefit in L¹ due to the presence of the two 2,6-bis(aminomethyl)pyridine moieties which hold the donor nitrogen atoms in a more suitable position for co-ordination to Cu²⁺.³⁶ The values of –Δ*H*^o and of *v*_{d-d} are nearly identical for [CuL¹]²⁺ and [CuL³]²⁺ and indicate that replacing two secondary amino groups by pyridyl groups does not enhance covalent binding in [CuL¹]²⁺ relative to [CuL³]²⁺ and that π-bonding interactions between the pyridyl π* orbitals and metal non-bonding t_{2g}(3d) orbitals can be excluded. The small difference in *v*_{d-d} values probably reflects subtle changes in distortion of the octahedral co-ordination sphere around the Cu²⁺ ion.

The complexation model for the Cu²⁺–L² system is more complicated. The pH-titration profile for a 1:1 molar ratio of Cu²⁺ to L² (see Fig. 2) shows an inflection point at *a* = 3, corresponding to the formation of a [Cu(HL²)³]³⁺ complex, and an end-point at *a* = 4 corresponding to the formation of [CuL²]²⁺. This profile parallels the pattern of consecutive electronic spectra taken during the 1:1 titration (see Fig. 3), as the absorbance steadily rises up to *a* = 3 with λ_{max} at 580 nm, and then drops to *a* = 4 with λ_{max} at 673 nm and an isosbestic point at 654 nm. However a complexation model consisting only of [Cu(HL²)³]³⁺ and [CuL²]²⁺ did not produce an acceptable fit between experimental and calculated potentiometric data. A satisfactory fit could only be obtained when a [Cu₂L²]⁴⁺ complex was included in the model. Evidence for the formation of a dinuclear complex was supported by the results of an out-of-cell titration of a 2:1 molar ratio mixture of Cu²⁺ and [H₄L²]⁴⁺ with KOH (aq). The pH values in the 2:1 titration are appreciably lower than in the 1:1 titration in the neutralization region between *a* = 3 and 4, and the final electronic spectrum at *a* = 4 in the 2:1 titration shows a maximum at a different wavelength (636 nm) from that in the 1:1 titration (673 nm). For 4 < *a* < 5 there is another buffer region around pH 5 for the 2:1 solution which is disturbed however by a precipitate. From the potentiometric data of the 2:1 out-of-cell titration only an estimate of 26.2 ± 0.5 could be made for log β₂₁₀ of [Cu₂L²]⁴⁺. A species distribution diagram calculated for the 1:1 Cu²⁺–L² system including the species [CuL²]²⁺, [Cu(HL²)³]³⁺ and [Cu₂L²]⁴⁺ is presented in Fig. 4. Table 4 summarizes the complexation data for Cu²⁺ with L². One can see that [CuL²]²⁺ is appreciably less stable than [CuL¹]²⁺ with lower values for –Δ*H*^o and *TΔS*^o, whereas the values of *v*_{d-d} and ε for both complexes are remarkably identical. This indicates that [CuL¹]²⁺ and [CuL²]²⁺ are both six-co-ordinated with comparable ligand-field strength, but the greater distance between the secondary nitrogen atoms due to the propylene linkage in L² makes the process of complex formation less exothermic. From the data given in Tables 2 and 5 one can calculate for the equilibrium Cu²⁺ + [HL²]⁺ ⇌ [Cu(HL²)³]³⁺: log *K* = 17.0, –Δ*H*^o = 81.4 kJ mol⁻¹ and *TΔS*^o = 15.5 kJ mol⁻¹. The complex formation of Cu²⁺ with [HL²]⁺ is thus weaker than with the fully deprotonated L², as expected, but this is entirely due to a much less favourable entropy change, as the corresponding value for –Δ*H*^o is larger for [Cu(HL²)³]³⁺ than for [CuL²]²⁺. Also the *v*_{d-d} value for [Cu(HL²)³]³⁺ is 2300 cm⁻¹ higher than for [CuL²]²⁺.

If the values for –Δ*H*^o and *v*_{d-d} for [CuL¹]²⁺, [CuL²]²⁺, [Cu(HL²)³]³⁺ and [CuL³]²⁺ are positioned relative to the correlation line previously established for tetragonal copper(II) complexes with open-chain polyamines (see Fig. 5),³⁷ it is immediately clear that [Cu(HL²)³]³⁺ is very close to the correlation line, indicating a tetragonal co-ordination geometry around Cu²⁺ with the nitrogen atoms in the equatorial plane and water molecules axial. On the other hand, [CuL¹]²⁺, [CuL²]²⁺ and [CuL³]²⁺ are far to the left of the correlation line, indicating additional nitrogen-donor interaction of axial positions in the co-ordination sphere, producing a weakening of

Table 4 Thermodynamic and electronic spectral data for metal-ion complexation by L¹ at 25 °C in 0.100 mol dm⁻³ KNO₃

Metal ion	log β _{pqr} ^a	-ΔH°/kJ mol ⁻¹	TΔS°/kJ mol ⁻¹	$\tilde{\nu}_{d-d}/\text{cm}^{-1}$
Ni ²⁺	23.8(2) ^b			^c
Cu ²⁺	25.9(1) ^d	100.2(6)	47(1)	14 900(90) ^e
Zn ²⁺	20.73(8) ^f			
Cd ²⁺	17.93(5)	58.5(6)	43.7(9)	
Pb ²⁺	13.84(6)	52.5(6)	26.4(9)	

Data for [CuL³]²⁺ from ref. 35 at 25 °C and in 0.15 mol dm⁻³ NaClO₄: log β₁₁₀ = 24.4, -ΔH° = 100.0 kJ mol⁻¹, TΔS° = 39.1 kJ mol⁻¹ and $\tilde{\nu}_{d-d}$ = 15 200 cm⁻¹ (85 dm³ mol⁻¹ cm⁻¹). ^a β_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r, p = q = 1, r = 0. ^b Standard deviation in parentheses. Value obtained using UV/VIS-pH-metry, 1.3 < pH < 2.8, 10 titration points in duplicate, out-of-cell, 2 weeks storage. ^c ν₁ 12 220 cm⁻¹ (30), ν₂ 18 660 cm⁻¹ (11 dm³ mol⁻¹ cm⁻¹). ^d Value obtained using UV/VIS measurements at pH 1.37, 10 titration points in duplicate. ^e Molar absorptivity coefficient in dm³ mol⁻¹ cm⁻¹ in parentheses. ^f Ten titration points in duplicate, out-of-cell, 1 week storage.

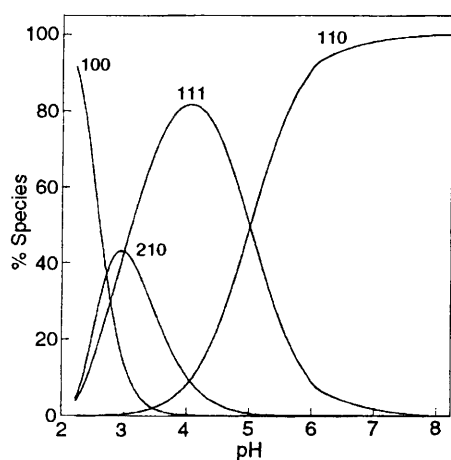


Fig. 4 Species distribution diagram calculated for the 1:1 Cu²⁺-L² system as a function of pH (total ligand concentration 5.00 × 10⁻³ mol dm⁻³). Only copper-containing Cu_pL_qH_r species are shown, indicated by their pqr notation

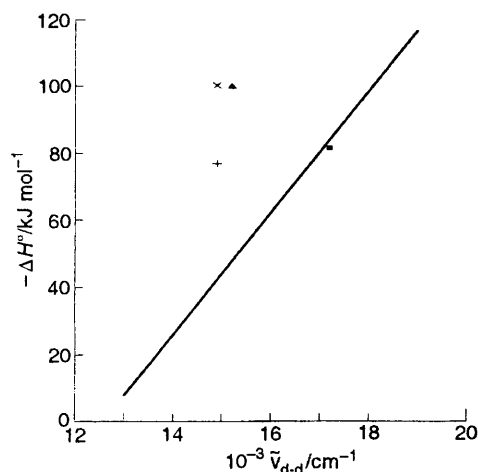


Fig. 5 Positions of [CuL¹]²⁺ (×), [CuL²]²⁺ (+), [Cu(HL²)]³⁺ (■) and [CuL³]²⁺ (▲) relative to the correlation line established³⁷ for tetragonal copper(II) complexes with open-chain polyamines

the in-plane ligand field by a synergic effect.³⁸ This confirms the octahedral co-ordination of Cu²⁺ by the six nitrogen donors in L¹, L² and L³. The situation is comparable with that of the copper(II) complexes with tris(2-aminoethyl)amine or 3,6,9-triazaundecane-1,11-diamine which have a nitrogen donor co-ordinated axially, and also occur to the left of the correlation line.³⁷

It is likely that in the [Cu(HL²)]³⁺ complex one 2,6-bis(aminomethyl)pyridine moiety and an additional secondary amino group are co-ordinated in the equatorial plane, leaving the second pyridyl group and the protonated amino group

unco-ordinated. The -ΔH° value of 81.4 kJ mol⁻¹ for Cu²⁺ + [HL²]⁺ ⇌ [Cu(HL²)]³⁺ compares very well with values for the equilibrium Cu²⁺ + L ⇌ [CuL]²⁺ where L is a large tetraaza macrocycle, such as 1,4,7,10-tetraazacyclotetradecane (80.3 kJ mol⁻¹)³⁹ or 1,5,9,13-tetraazacyclohexadecane (83.7 kJ mol⁻¹).⁴⁰ The hydration of the ammonium group in [Cu(HL²)]³⁺ explains the less favourable entropy change for its formation relative to the formation of [CuL]²⁺. The formation of the [Cu₂L²]⁴⁺ is surprising, as no dinuclear complex was found with the fully saturated hexadentate L³.³⁵ Unlike L³, dinuclear [Cu₂L]⁴⁺ species were found with the hexadentate L⁷ and L⁸,^{12,41} which contain 22 and 24 ring atoms, respectively. To our knowledge, L² is thus the smallest hexadentate macrocyclic polyamine which is able to co-ordinate two Cu²⁺ ions in aqueous solution. Dinuclear copper complexes of the tetraamine precursor of L² were reported in the solid state and in acetonitrile solution with NCS⁻, N₃⁻ or OH⁻ as bridging ligands.⁴² The ease with which the second copper ion is bound by the mononuclear [CuL]²⁺ complex decreases along L⁸ > L⁷ > L²: log K for the equilibrium [CuL]²⁺ + Cu²⁺ ⇌ [Cu₂L]⁴⁺ is 9.68⁴¹ for L⁸, 5.73¹² for L⁷ and 4.9 for L². This sequence parallels the number of ring atoms in these compounds and reflects increasing electrostatic repulsion between the two copper ions with decreasing ring size. It is likely that in the [Cu₂L²]⁴⁺ complex each Cu²⁺ ion is co-ordinated by one 2,6-bis(aminomethyl)pyridine moiety. The following co-ordination geometries for the copper(II) with L² can then be proposed: tetragonal by three nitrogens in the equatorial plane for [Cu₂L²]⁴⁺, tetragonal by four nitrogens for [Cu(HL²)]³⁺ and octahedral by six nitrogens for [CuL²]²⁺.

The 2:1 pH titration profile in Fig. 2 shows an additional buffer region beyond a = 4, indicating a strong hydrolytic tendency of the [Cu₂L²]⁴⁺ complex. No attempts have been made to calculate an equilibrium constant for a [Cu₂L²(OH)]³⁺ species as there was disturbance by a precipitate in this pH region.

Other metal ion binding to L¹ and L²

The ions Ni²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ all form only [ML]²⁺ complexes with L¹ and L². Neither protonated nor dinuclear complexes had to be included in the complexation models to obtain a good fit between the calculated and experimental pH profiles. So, in all these complexes the metal ion is six-co-ordinated. The complexation data are given in Tables 4 and 5. The values obtained for the equilibrium constants for the [ML]²⁺ complexes of Zn²⁺ and Cd²⁺ are in good agreement with those obtained by Rothermel *et al.*,¹⁸ taking into account the difference in ionic medium and ionic strength. The [ZnL¹]²⁺ complex is more stable than [ZnL³]²⁺ (log K for [ZnL³]²⁺ is 18.7 at I = 0.15 mol dm⁻³ and 25 °C). This confirms the six-co-ordination in [ZnL¹]²⁺, which was also observed in the solid state,⁴³ whereas only five of the six secondary amino groups are involved in the co-ordination in

Table 5 Thermodynamic and electronic spectral data for metal-ion complexation by L² at 25 °C in 0.100 mol dm⁻³ KNO₃

Metal ion	pqr	log β _{pqr}	-ΔH°/kJ mol ⁻¹	TΔS°/kJ mol ⁻¹	$\tilde{\nu}_{d-d}/\text{cm}^{-1}$
Ni ²⁺	110	21.0(4) ^a			b
Cu ²⁺	110	21.30(3)	76.8(6)	44.8(8)	14 900(80) ^c
	111	26.31(2)	120.2(6)	29.9(8)	17 200(130)
	210	26.2(5) ^d			15 700(180)
	21 - 1	e			
Zn ²⁺	110	15.83(2) ^f			
Cd ²⁺	110	14.18(2)	38.6(5)	42.0(6)	
Pb ²⁺	110	9.57(2)	36.8(6)	17.7(8)	

^a Value obtained using UV/VIS-pH-metry, 2.2 < pH < 4.2, 10 titration points in duplicate, out-of-cell, 2 weeks storage. ^b ν_1 11 360 cm⁻¹ (36), ν_2 17 860 cm⁻¹ (12 dm³ mol⁻¹ cm⁻¹). ^c Molar absorption coefficient in dm³ mol⁻¹ cm⁻¹ in parentheses. ^d Value obtained using out-of-cell pH-metry, 2:1 metal to macrocycle ratio, 10 solutions, 1 d storage. ^e Not calculated due to precipitation. ^f Ten titration points in duplicate, out-of-cell, 1 week storage.

[ZnL³]²⁺,⁴⁴ The [CdL¹]²⁺ complex is less stable than [CdL³]²⁺ for which log K = 18.8, -ΔH° = 64.0 kJ mol⁻¹ and TΔS° = 43.1 kJ mol⁻¹ at 0.15 mol dm⁻³ and 25 °C.¹ Yet, Cd²⁺ is six-co-ordinated as well in [CdL¹]²⁺²⁰ as in [CdL³]²⁺,⁴⁵ and no [Cd(HL)]³⁺ complex is found for both L¹ and L³. The [PbL¹]²⁺ complex is also less stable than [PbL³]²⁺ for which log K = 14.13, -ΔH° = 56 kJ mol⁻¹ and TΔS° = 25 kJ mol⁻¹ at I = 0.15 or 0.20 mol dm⁻³ and 25 °C.^{46,47} From a comparison of the stability constants of a series of [PbL]²⁺ complexes with saturated macrocyclic polyamines and from the presence of a [Pb(HL³)]³⁺ complex, it was concluded that Pb²⁺ was five-co-ordinated in [PbL³]²⁺.⁴⁶ On the other hand, no [Pb(HL¹)]³⁺ species was detected in this work, which indicates that Pb²⁺ is more likely six-co-ordinated in [PbL¹]²⁺. This was recently confirmed by NMR and molecular modelling studies.²⁰

The [ML²]²⁺ complexes of Zn²⁺, Cd²⁺ and Pb²⁺ are considerably less stable than the [ML¹]²⁺ complexes. The formation of the complexes of Cd²⁺ and Pb²⁺ with L² is also less exothermic than with L¹, although the entropy changes do not differ much. The structures of the [ML¹]²⁺ and the [ML²]²⁺ complexes are therefore presumably alike, the propylenic chains being sterically responsible for the lower heat of complex formation. The equilibrium data for Ni²⁺ were obtained by the 'out-of-cell' technique, and therefore should be considered as estimates. The electronic spectra for [NiL¹]²⁺ and [NiL²]²⁺ are typical for an octahedral high-spin six-co-ordination, showing transitions near 12 000 (ν_1) and 18 000 cm⁻¹ (ν_2) with $\epsilon_1 > \epsilon_2$. The exact positions are given in Tables 4 and 5. The third transition ν_3 could not be located precisely due to interference by charge-transfer bands at about 28 000 cm⁻¹. The ligand-field strength in [NiL¹]²⁺ is nearly identical to that in [NiL³]²⁺ (ν_1 at 11 980, ν_2 at 18 850 and ν_3 at 28 980 cm⁻¹),⁴⁸ whereas in [NiL²]²⁺ there is a shift to lower energy for the ν_1 and ν_2 transitions, indicating a weaker ligand field. A peculiar observation is that for both [NiL¹]²⁺ and [NiL²]²⁺ the ν_1 transition features only one band maximum and does not show any asymmetry which could be attributed to tetragonality or to a close approach and subsequent mixing of the ³T_{2g} and the ¹E_g excited states via spin-orbit coupling. As pointed out by Hancock and co-workers,⁴⁹ this phenomenon should be particularly important when the ν_2 transition lies around to 19 000 cm⁻¹. In this case the ν_1 band should show two maxima of equal intensity with their midpoint at 12 000 cm⁻¹. We are unable to rationalize the one-maximum ν_1 band for [NiL¹]²⁺ and [NiL²]²⁺. It is also remarkable that the molar absorption coefficient ϵ_1 of the ν_1 bands of [NiL¹]²⁺ (30 dm³ mol⁻¹ cm⁻¹) and [NiL²]²⁺ (36 dm³ mol⁻¹ cm⁻¹) is appreciably larger than for [NiL³]²⁺ (19 dm³ mol⁻¹ cm⁻¹).⁴⁸ This may be connected with the presence of two pyridine nitrogen donors which introduce some distortion in the [NiL¹]²⁺ and [NiL²]²⁺ complexes, lowering the O_h symmetry in comparison with that

of the [NiL³]²⁺ complex which has six identical secondary amino nitrogen donors.

Experimental

Materials

Compounds L¹ and L² were synthesized as described;⁵⁰ L¹ was obtained in the [H₄L¹][NO₃]₄ and in the [H₄L¹]Cl₄ forms. Crystals of [H₄L¹][NO₃]₄, obtained after recrystallization from water, were suitable for X-ray crystallographic structure determination. Compound L² was obtained only in the [H₄L²]Cl₄ form. All other reagents were of reagent grade. Distilled and deionized water (Milli-Q quality, specific conductance < 0.05 μS cm⁻¹) was used throughout for all solutions. Carbonate-free (< 0.5%) potassium hydroxide solutions (ca. 0.250 mol dm⁻³) were prepared from Titrisol ampoules (Merck) and standardized by titration with potassium hydrogenphthalate (Acros Chimica). Stock solutions of nitric acid were prepared and standardized with the KOH solution. These titrations were also used to check the carbonate content of the KOH titrant solution using the Gran method.⁵¹ Metal-ion stock solutions were prepared from metal nitrates (Merck) and standardized by titration with the disodium salt of ethylenediaminetetraacetate,⁵² using appropriate conditions and electrodes (Radiometer copper, cadmium or lead solid-state electrodes or mercury electrode). All final solutions for the potentiometric, calorimetric and UV/VIS measurements were made up to an ionic strength of 0.100 mol dm⁻³ with potassium nitrate (Merck) or occasionally potassium chloride (Merck).

Potentiometric measurements

The potentiometric measurements were carried out in duplicate at 25 ± 0.05 °C with the equipment and the general procedure previously described.^{30,53} The glass electrode was calibrated for hydrogen-ion concentration measurements. In the case of slow complexation reactions (Ni²⁺ and Zn²⁺ with L¹ and L²), out-of-cell titrations were performed with solutions, each corresponding to a single titration point, which were stored for several days. Attainment of equilibrium was checked by measuring daily the pH and the electronic spectrum, if coloured, of a duplicate test solution corresponding to ca. 75% of complex formation. As the complexation of Cu²⁺ with L¹ was very strong, a combination of pH-metry and visible electronic spectrophotometry was used in acid medium to follow the formation of the complex. Details of the experimental working conditions are given as footnotes in Tables 3, 4 and 5.

Calorimetric measurements

The calorimetric measurements were carried out in duplicate

Table 6 Final positional parameters for non-hydrogen atoms in $[\text{H}_4\text{L}^1][\text{NO}_3]_4$ with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
N(1)	1.1302(2)	0.4146(3)	0.6333(2)
C(1)	1.1843(2)	0.5046(3)	0.6608(2)
C(2)	1.2157(2)	0.5014(4)	0.7425(3)
C(3)	1.1870(3)	0.3995(5)	0.7923(2)
C(4)	1.1310(3)	0.3089(4)	0.7646(2)
C(5)	1.1038(2)	0.3191(3)	0.6844(2)
C(6)	1.0432(2)	0.2215(3)	0.6487(2)
N(2)	0.9770(2)	0.2944(2)	0.6031(1)
C(7)	0.9178(2)	0.2001(3)	0.5608(2)
C(8)	0.8445(2)	0.2677(4)	0.5223(2)
N(3)	1.1342(1)	0.6550(2)	0.5526(2)
C(9)	1.2099(2)	0.6083(3)	0.5992(2)
N(4)	0.6208(2)	0.1459(3)	0.5498(1)
O(41)	0.5544(1)	0.0781(2)	0.5408(1)
O(42)	0.6193(2)	0.2671(3)	0.5352(1)
O(43)	0.6854(2)	0.0896(3)	0.5707(2)
N(5)	0.4075(2)	0.3783(3)	0.7029(2)
O(51)	0.4198(2)	0.4555(2)	0.7613(2)
O(52)	0.3907(2)	0.4205(3)	0.6328(2)
O(53)	0.4101(2)	0.2573(3)	0.7142(2)

with a Tronac model 1250 isoperibol calorimeter as described.^{30,53} The protonation heats of L^1 and L^2 were determined by titrating a solution (25.00 cm^3) containing the compound in its basic form (ca. 0.05 mmol) with a standardized solution of HNO_3 or HCl (ca. 0.1 mol dm^{-3}); KNO_3 or KCl was then used as indifferent electrolyte, respectively. The complexation heats of L^1 and L^2 with Cu^{2+} , Cd^{2+} or Pb^{2+} were determined by titrating a solution (25.00 cm^3) containing the compound in its basic form (ca. 0.05 mmol) with the appropriate metal nitrate solution (ca. 0.1 mol dm^{-3}). Dilution experiments were also done. The exact concentration of the components in each solution was determined by separate potentiometric titrations.

Spectrophotometric measurements

The electronic absorption spectra were recorded at 25 °C on a Hewlett-Packard 8451 A diode-array spectrophotometer in the wavelength region between 300 and 820 nm. A Cary 14 spectrophotometer was used for the nickel(II) complexes in the region between 800 and 1300 nm. Aqueous solutions of Ni^{2+} and macrocycle in 0.1 mol dm^{-3} KNO_3 were prepared with a $c_{\text{L}}:c_{\text{Ni}}$ ratio of ca. 1.10 to 1.0:1 and c_{Ni} ca. 1.0×10^{-2} mol dm^{-3} . A calculated volume of a standardized KOH solution was then added to obtain maximum complexation of the metal ion. The solutions of the nickel(II) complexes were stored in sealed vials and their spectra recorded periodically until no further change was observed. The complexation of Cu^{2+} with L^1 and L^2 was also monitored spectrophotometrically by titrations started in acid medium and by adding standardized KOH solution, taking a spectrum at various extents of neutralization of the macrocycle.

Calculations

The equilibrium constants for ligand protonation and for metal-ion complexation were calculated with the computer program SUPERQUAD.⁵⁴ At least 100 points from different normal titrations were used. About 20 points were selected from out-of-cell titrations. The statistical parameters σ and χ^2 , as calculated by this program, were used to judge the goodness of fit and were respectively lower than 3 (error of 0.2 mV on electromotive force readings and of 0.2 cm^3 on burette volume delivered) and about 12.5 in the case of normal titrations. The statistics were less good for the out-of-cell titrations and these results should therefore only be considered as good estimates. The overall protonation and complexation enthalpies were

calculated with the program CALO.⁵³ Literature values for the dissociation equilibrium constant and for the dissociation enthalpy of water at 25 °C and $I = 0.1$ mol dm^{-3} were used: $\text{p}K_w = 13.78$ and $\Delta H_w^\circ = 56.6$ kJ mol^{-1} .^{27,53,55} The computer program SQUAD⁵⁶ was used to calculate the complexation constants of Cu^{2+} and Ni^{2+} with L^1 and of Ni^{2+} with L^2 from the spectrophotometric titrations. The results were verified using formation curves.⁵⁷ Distribution curves for the complexes were calculated with the program EQUIL.⁵⁸

The errors quoted as the standard deviations of the stepwise $\log K$, ΔH° and $T\Delta S^\circ$ values were calculated by normal propagation of errors from the overall values calculated by the programs. They should be considered as lower limits.

Crystallography

Crystal data. $\text{C}_{18}\text{H}_{30}\text{N}_{10}\text{O}_{12}$, $M = 578.5$, orthorhombic, space group $Pbca$, $a = 15.980(1)$, $b = 10.015(1)$, $c = 16.204(2)$ Å, $U = 2593.3(1)$ Å³ (by least-squares refinement of diffractometer angles of 25 carefully centred reflections in the range θ 9–14°, $\lambda = 0.71069$ Å), $Z = 4$, $D_c = 1.48$ ($D_m = 1.49$ by flotation) g cm^{-3} , $F(000) = 1216$. Prismatic colourless crystal, approximate dimensions 0.3 × 0.3 × 0.2 mm, $\mu(\text{Mo-K}\alpha) = 0.8$ cm^{-1} .

Data collection and processing. Enraf-Nonius CAD4 X-ray diffractometer. The intensity data were collected at room temperature with the ω - 2θ scan technique, with ω scan width = $1.0^\circ + 0.35 \tan \theta$, ω -scan speed 1.6–5.5° min^{-1} , graphite-monochromatized Mo-K α radiation; 5473 reflections measured ($2.5 < \theta < 26^\circ$, $\pm h$, $\pm k$, $\pm l$), 1215 observed [merging $R = 0.014$ with $I > 3.0\sigma(I)$]. Two standard reflections monitored: no loss of intensity observed. All data were corrected for Lorentz polarization effects, and an empirical absorption correction, based on the ψ scan, was applied⁵⁹ (maximum, minimum transmission factors = 0.99, 0.97).

Structural analysis and refinement. Direct methods, refined by full-matrix least-squares calculations, with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. All non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms, located by ΔF maps, were refined isotropically with fixed thermal parameters 1 Å² greater than those of the attached carbon or nitrogen atoms. Convergence was reached at $R = 0.040$ and $R' = 0.049$ where $w = 1.6/[\sigma^2(|F_o| + 10^{-4}|F_o|^2)]$. The residual electron density in the final Fourier-difference map was 0.21, -0.18 e Å⁻³.

Complex neutral-atom scattering factors⁶⁰ were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76⁶¹ program package and the ORTEP²¹ plotting program. Final fractional coordinates for non-hydrogen atoms are given in Table 6.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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