Interaction of Transition and Post-Transition Metal Ions with Oxygen–Nitrogen Donor Macrocycles incorporating Pendant Hydroxyethyl and Carbamoylethyl Groups†

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The interaction of new derivatives of O_2N_2-donor macrocycles incorporating pendant hydroxyethyl or carbamoylethyl arms with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) has been investigated. The thermodynamic stabilities of a range of 1:1 (metal:ligand) complexes of these macrocycles have been determined potentiometrically in 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4 or NMe_4Cl; at 25 °C). Comparison of selected complexes with those of the corresponding parent (non-pendant arm) macrocycles indicates that the former derivatives show more varied co-ordination behaviour than the latter. X-Ray diffraction studies of five nickel(II) complexes have been made. The complexes containing respectively 14-, 15- and 16-membered rings and two pendant alcohol arms have similar distorted-octahedral structures. In each case the nickel ion is situated outside the macrocyclic ring with only the ring nitrogen atoms and the pendant alcohol oxygen atoms co-ordinating; the remaining sites are occupied by the oxygen atoms of a bidentate nitrate ion. In contrast, the structure of the related 15-membered, mono-pendant arm (alcohol) derivative has the nickel in the macrocyclic cavity; the near-octahedral co-ordination sphere consists of two ether oxygens and two nitrogens from the macrocyclic ring in the equatorial plane together with oxygen atoms from the pendant alcohol arm and a water molecule in the axial sites. The structure of a pendant bis(amide) derivative also incorporates the nickel in the macrocyclic cavity with the pendant amide groups co-ordinated in axial sites to yield an overall distorted-octahedral geometry.

Previous work by our group has been concerned with the relationship between mixed-donor macrocycle design and the co-ordination preferences of such compounds towards transition and post-transition metal ions.[1,2] Successful strategies were developed for achieving discrimination between particular ions of the above type and, more importantly, an understanding of the nature of such discrimination has often proved possible. A typical series used for such studies[3,4] is given by L^1–L^4.

Pendant-arm macrocycles (containing donor groups incorporated in the arms) often yield metal-binding behaviour which resembles that of both macrocyclic and open-chain compounds.[5,6] Apart from their promise for yielding interesting co-ordination chemistry, compounds of this type also have potential for attachment to other substrates *via* their appended functional groups to produce, for example, immobilised systems for metal-ion scavenging.[7]

Previously we have reported the metal complexation behaviour of O_2N_2-donor macrocycles incorporating pendant carboxylic acid groups L^5–L^7.[8] The results of these studies suggested that the carboxylic acid groups are involved in complexation and that for some metal ion–ligand combinations there is evidence that macrocyclic ring-size effects influence the overall stability patterns. As an extension of these studies, we now present the results of an investigation of complex formation between cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) and L^8–L^{14}, which incorporate pendant hydroxyethyl and carbamoylethyl groups.

Experimental

The preparation and characterisation of macrocycles L^8–L^{14} from their corresponding precursors are described elsewhere.[9] Positive-ion FAB mass spectra were recorded on a JEOL JMS-DX300 spectrometer (samples in 3-nitrobenzyl alcohol). Other physical measurements were performed as described elsewhere.[10,11]

General Preparation of Selected Nickel(II), *and Copper*(II), *Complexes.*—Macrocycle (2 mmol) in ethanol or methanol was added slowly to a stirred hot solution of nickel(II) nitrate hexahydrate, copper(II) nitrate trihydrate or copper(II) perchlorate hexahydrate (2 mmol) (**CAUTION**: perchlorates may be explosive) in ethanol or methanol. The warm solution was set aside to cool; crystals of product generally formed on cooling or after refrigeration of the solution for 1–3 d. The respective products were filtered off and washed with ethanol or methanol. Yields were greater than 60%. All compounds were dried over phosphorus pentaoxide in a vacuum before analysis. Microanalytical data for the complexes isolated are listed in Table 1.

log K *Determinations.*—The apparatus and conditions (95%

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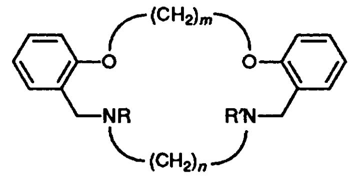
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



	m	n	
L¹	2	2	R, R' = H
L²	2	3	R, R' = H
L³	3	3	R, R' = H
L⁴	4	3	R, R' = H
L⁵	2	3	R, R' = CH_2CO_2H
L⁶	3	3	R, R' = CH_2CO_2H
L⁷	4	3	R, R' = CH_2CO_2H
L⁸	2	2	R, R' = CH_2CH_2OH
L⁹	2	3	R, R' = CH_2CH_2OH
L¹⁰	3	3	R, R' = CH_2CH_2OH
L¹¹	4	3	R, R' = CH_2CH_2OH
L¹²	2	3	R = H, R' = CH_2CH_2OH
L¹³	2	2	R, R' = $CH_2CH_2CONH_2$
L¹⁴	2	3	R, R' = $CH_2CH_2CONH_2$

methanol; I = 0.1 mol dm^{-3}, NEt_4ClO_4 or NMe_4Cl) for the potentiometric determination of ligand protonation constants and corresponding metal stability constants were identical to those used previously.[10,11] Owing to expected competitive chloride binding, only NEt_4ClO_4 was employed for the determinations involving cadmium(II). The potentiometric data were processed using either the program MINIQUAD[12] or SUPERQUAD.[13] Errors represent the average deviation from the mean obtained for between two and five separate experimental determinations (rounded to one significant figure). The stability-constant determinations involved individual solutions containing at least two different metal-to-ligand ratios. In virtually all cases it was not possible to obtain complete titration curves because of either precipitation or competing hydrolysis reactions during the respective runs. The titration data corresponding to the lower portions of the respective titration curves refined satisfactorily assuming 1:1 metal-to-ligand complexation.

Crystal Structure Determinations.—Crystal data. $[NiL^8(NO_3)]NO_3$. Data were collected on a crystal of dimensions 0.45 × 0.22 × 0.10 mm, $C_{22}H_{30}N_4NiO_{10}$, M = 569.19, triclinic, space group $P\bar{1}$(no. 2), a = 14.555(3), b = 10.213(2), c = 8.352(2) Å, α = 97.30(2), β = 95.65(2), γ = 86.31(2)°, U = 1223.8 Å^3, Z = 2, D_c = 1.54 g cm^{-3}, $F(000)$ = 596, μ(Mo-Kα) = 7.96 cm^{-1}.

$[NiL^9(NO_3)]NO_3$. Data were collected on a crystal of dimensions 0.34 × 0.32 × 0.28 mm, $C_{23}H_{32}N_4NiO_{10}$, M = 583.22, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$), a = 15.398(3), b = 20.651(4), c = 8.349(2) Å, β = 103.03(2)°, U = 2586.6 Å^3, Z = 4, D_c = 1.50 g cm^{-3}, $F(000)$ = 1223, μ(Mo-Kα) = 7.03 cm^{-1}.

$[NiL^{10}(NO_3)]NO_3$. Data were collected on a crystal of dimensions 0.40 × 0.29 × 0.24 mm, $C_{24}H_{34}N_4NiO_{10}$, M = 597.24, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$), a = 14.892(3), b = 21.613(2), c = 8.433(2) Å, β = 102.24(7)°, U = 2652.6 Å^3, Z = 4, D_c = 1.75 g cm^{-3}, $F(000)$ = 1256, μ(Mo-Kα) = 7.37 cm^{-1}.

$[NiL^{12}(H_2O)][NO_3]_2$. Data were collected on a crystal of dimensions 0.35 × 0.20 × 0.15 mm, $C_{21}H_{30}N_4NiO_{10}$, M = 557.18, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$), a = 30.897(6), b = 7.604(2), c = 10.057(2) Å, β = 99.09(2)°, U = 2333.1 Å^3, Z = 4, D_c = 1.58 g cm^{-3}, $F(000)$ = 1160, μ(Mo-Kα) = 8.35 cm^{-1}.

$[NiL^{14}][NO_3]_2 \cdot 0.5H_2O \cdot 0.5EtOH$. Data were collected on a crystal of dimensions 0.59 × 0.56 × 0.48 mm, $C_{26}H_{38}N_6NiO_{11}$, M = 669.31, orthorhombic, space group $Pbca$, a = 22.762(3), b = 17.696(2), c = 15.133(2) Å, U = 6095.52 Å^3, Z = 8, D_c = 1.46 g cm^{-3}, $F(000)$ = 2960, μ(Mo-Kα) = 6.8 cm^{-1}.

Data collection and refinement. Data collection for the nickel(II) complexes was carried out using a Philips PW1100 four-circle diffractometer and graphite-monochromated Mo-Kα (λ = 0.710 69 Å) in the range θ 3–25°, with a scan width of 0.80°. No absorption corrections were applied. The method of data collection and calculation of reflection intensities was similar to that described previously.[14] In each case the metal atom was located from a Patterson synthesis.[15] The positions of the remaining non-hydrogen atoms were found from subsequent Fourier and Fourier-difference syntheses with weights $1/\sigma^2(F)$. In the final cycles of full-matrix refinement applied to individual reflections the nickel, oxygen and nitrogen atoms were assigned anisotropic thermal parameters. In each case a final Fourier-difference map showed no regions of significant electron density.

$[NiL^8(NO_3)]NO_3$. The number of unique reflections with $I \geqslant 3\sigma(I)$ was 3211. The final refinement gave R = 0.078, R' = 0.081. Hydrogen atoms were not located directly but included in idealised positions with fixed thermal parameters of 0.08 Å^2.

$[NiL^9(NO_3)]NO_3$. The number of unique reflections with $I \geqslant 3\sigma(I)$ was 2977. Most hydrogen atoms (except four of one aromatic ring) were located using Fourier-difference syntheses on low-angle data (θ < 20°). The hydrogen atoms not located were placed in geometrically idealised positions and constrained to ride on the relevant C atoms with their thermal parameters fixed at 0.08 Å^2. Final R = 0.065 and R' = 0.067.

$[NiL^{10}(NO_3)]NO_3$. The number of unique reflections with $I \geqslant 3\sigma(I)$ was 2579. In this case ten hydrogen atoms (two aromatic and eight aliphatic C-bonded ones) were not located and were placed in idealised positions with fixed thermal parameters of 0.08 Å^2. The final R = 0.091 and R' = 0.092.

$[NiL^{12}(H_2O)][NO_3]_2$. The number of unique reflections with $I \geqslant 3\sigma(I)$ was 2694. Hydrogen atoms were not located directly but were included in idealised positions with fixed thermal parameters of 0.08 Å^2. Final R = 0.098, R' = 0.101.

$[NiL^{14}][NO_3]_2 \cdot 0.5H_2O \cdot 0.5EtOH$. The number of unique reflections with $I \geqslant 3\sigma(I)$ was 3693. Most hydrogen atoms (except one N-bonded of each amide group, four aromatic and two aliphatic ones) were located. Residual electron density was interpreted as due to random occupation of a cavity in the crystal by water or ethanol solvent molecules. The atoms were assigned half occupation. There was also evidence of unresolved disorder of the nitrate counter ions. The hydrogen atoms not found were again fixed in geometrically idealised positions. The hydrogen atoms of the solvating ethanol and water molecules were not included. Final R = 0.067 and R' = 0.074.

The structures of the complexes are illustrated in Fig. 1, fractional coordinates are presented in Table 4, while selected bond lengths and angles are given in Table 3.

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

Results and Discussion

Isolation and Characterisation of Selected Metal Complexes.— In an attempt to obtain suitable crystalline products for X-ray analysis and also to provide a background for the solution studies, nickel(II) and copper(II) complexes of a selection of the present macrocycles have been isolated. Nickel complexes of each of L^8–L^{14} and two copper complexes of L^{13} were prepared by reaction of the respective macrocycles with nickel(II) or copper(II) nitrate [or, in one instance, copper(II) perchlorate] in ethanol or methanol. In each case the corresponding 1 : 1 (metal : ligand) complexes were obtained as microcrystalline or crystalline solids. In all cases where water and/or ethanol were suggested to be present from the microanalytical data, the expected infrared absorptions in the range 3400–3600 cm^{-1} were observed. In one complex, alcohol of crystallisation was postulated to be present; similar association of solvent has been shown to occur in particular nickel complexes of other related macrocyclic ligands.[1,10]

The FAB source mass spectra (positive ion) for the present nickel(II) and copper(II) complexes show strong peaks corresponding to the presence of the $[ML(X)]^+$ ($X = NO_3$ or ClO_4) ion. In most instances, other peaks corresponding to $[MLH_{-1}]^+$ and HL^+ were also identified. The infrared spectra of the nitrate-containing complexes indicated that the nitrate absorptions[16] (in the region 1250–1290 cm^{-1}) were partially masked by the presence of ligand bands and no attempt was made to assign them. The infrared spectrum of $[CuL^{13}][ClO_4]_2{\cdot}H_2O$ gave no firm indication of perchlorate co-ordination;[17] while the broad strong $\nu(ClO_4)$ absorption at 1095 cm^{-1} is not symmetrical, no clear splitting is evident. The infrared spectra of the complexes incorporating pendant amide groups show a lowering of the carbonyl stretch of 9–14 cm^{-1} from the bands of the respective free macrocycles;[9] such shifts suggest that the carbonyl groups in these complexes are involved in co-ordination, in accordance with the situation found by X-ray diffraction for $[NiL^{14}][NO_3]_2{\cdot}0.5H_2O{\cdot}0.5EtOH$.

A range of physical data for the complexes is listed in Table 2. All the nickel(II) complexes have magnetic moments which are typical of this metal in the high-spin state, and their solid-state electronic spectra are consistent with the presence of either octahedral or distorted-octahedral co-ordination. In particular, the electronic spectra of the complexes of L^{12}, L^{13} and L^{14} show three d–d bands corresponding to the transitions ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$, ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ for an octahedral ligand field; the apparent symmetry of these complexes is perhaps surprising when the mixed-donor nature of the ligands is considered. The solid-state spectra for the nickel complexes of the carbamoylethyl pendant-arm ligands, L^{13} and L^{14}, are very similar, suggesting that they have similar geometries. The corresponding solution and solid-state spectra for these two complexes are also similar, consistent with the proposed solid-state structures persisting in solution.

Comparison of the position of the ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ absorption band for the above complexes indicates that the ligand-field strength of the 14-membered ring macrocycle is higher than that of the 15-membered ring system, perhaps reflecting shorter metal-donor distances in the complexes of the smaller ring.[18] A similar decrease in ligand-field strength with increase in ring size has been reported[19] for the corresponding nickel complexes of the parent 14- and 15-membered (O_2N_2-donor) ring systems L^1 and L^2.

The complexes $[CuL^{13}][NO_3]_2{\cdot}3.5H_2O$ and $[CuL^{13}][ClO_4]_2{\cdot}H_2O$ have magnetic moments which are typical of copper(II) with $S = \frac{1}{2}$ (Table 2). The solid-state spectra each shows a broad envelope of bands in the region 500–800 nm. While this pattern is typical, the featureless nature of these spectra results in them being of little value for the assignment of co-ordination geometries.

Where soluble, the present complexes were either 1 : 1 electrolytes in methanol (expected conductance values: 80–115 S cm^2 mol^{-1})[20] or yielded values that fell between those for 1 : 1 and 2 : 1 electrolytes (Table 2). Hence, under the conditions of measurement, significant complex cation–anion association is present in each case.

Table 1 Analytical data for the complexes

Complex	Colour	Analysis * (%) C	H	N
$[NiL^8(NO_3)]NO_3{\cdot}0.5H_2O$	Blue	45.7 (45.7)	5.5 (5.4)	9.6 (9.7)
$[NiL^9(NO_3)]NO_3{\cdot}0.5H_2O$	Green	46.7 (46.7)	5.9 (5.6)	9.7 (9.5)
$[NiL^{10}(NO_3)]NO_3$	Green	48.2 (48.3)	6.0 (5.7)	9.5 (9.4)
$[NiL^{11}(NO_3)]NO_3$	Green	49.3 (49.1)	6.2 (5.9)	9.1 (9.2)
$[NiL^{12}(H_2O)][NO_3]_2$	Blue	45.6 (45.3)	5.3 (5.4)	10.0 (10.1)
$[NiL^{13}][NO_3]_2{\cdot}4.5H_2O$	Green	41.0 (40.9)	5.4 (5.9)	12.0 (11.9)
$[NiL^{14}][NO_3]_2{\cdot}0.5H_2O{\cdot}0.5EtOH$	Blue-green	46.2 (46.7)	5.7 (5.7)	12.0 (12.6)
$[CuL^{13}][NO_3]_2{\cdot}3.5H_2O$	Blue	41.8 (41.8)	5.6 (5.7)	12.1 (12.2)
$[CuL^{13}][ClO_4]_2{\cdot}H_2O$	Blue	40.3 (40.0)	4.4 (4.7)	7.7 (7.8)

* Calculated values in parentheses.

Table 2 Physical data for the nickel(II) and copper(II) complexes of selected pendant-arm ligands

Complex	Λ^a/S cm^2 mol^{-1}	μ^b/μ_B	Visible reflectance spectrum (nm)	m/z^c
$[NiL^8(NO_3)]NO_3{\cdot}0.5H_2O$	106	3.11	365, 600, 945, 1160(sh)	506
$[NiL^9(NO_3)]NO_3{\cdot}0.5H_2O$	134	3.30	378, 625, 990, 1200(sh)	520
$[NiL^{10}(NO_3)]NO_3$	111	3.25	375, 620, 1010, 1220(sh)	534
$[NiL^{11}(NO_3)]NO_3$	*d*	3.27	380, 630, 1110, 1220(sh)	548
$[NiL^{12}(H_2O)][NO_3]_2$	127	3.07	365, 585, 1090	476
$[NiL^{13}][NO_3]_2{\cdot}4.5H_2O$	128	3.25	375, 620, 1010[e]	560
$[NiL^{14}][NO_3]_2{\cdot}0.5H_2O{\cdot}0.5EtOH$	152	3.27	370, 610, 1055	574
$[CuL^{13}][NO_3]_2{\cdot}3.5H_2O$	139	1.84	693(br)[f]	565
$[CuL^{13}][ClO_4]_2{\cdot}H_2O$	146	1.94	675(br)[g]	602

[a] In methanol at 22 °C. [b] At 22 °C; $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}. [c] Positive-ion FAB mass spectral peak for $[ML(NO_3)]^+$ or $[ML(ClO_4)]^+$. [d] Insoluble. [e] The corresponding solution spectrum in methanol contained peaks at 379(22), 595(15) and 996 nm (ε 15 dm^3 mol^{-1} cm^{-1}). [f] The corresponding solution spectrum in methanol gave a broad peak with a λ_{max} of 680 nm (ε 206 dm^3 mol^{-1} cm^{-1}). [g] The corresponding solution spectrum in methanol gave a broad peak with a λ_{max} of 685 nm (ε 195 dm^3 mol^{-1} cm^{-1}).

Crystal Structures.—The crystal structures of $[NiL^8(NO_3)]NO_3$, $[NiL^9(NO_3)]NO_3$, $[NiL^{10}(NO_3)]NO_3$, $[NiL^{12}(H_2O)][NO_3]_2$ and $[NiL^{14}][NO_3]_2\cdot 0.5H_2O\cdot 0.5EtOH$ have been determined (Fig. 1). The co-ordination geometry of the nickel in $[NiL^8(NO_3)]NO_3$ is distorted octahedral involving both nitrogen donors of the macrocyclic ring and two oxygen atoms of the pendant alcohol groups, with the fifth and sixth positions being occupied by oxygen atoms from a bidentate nitrate ion. The ether oxygens are not bound to the nickel. The main distortion from octahedral symmetry is associated with the small bite of the co-ordinated nitrate ion.

The complexes $[NiL^9(NO_3)]NO_3$ and $[NiL^{10}(NO_3)]NO_3$

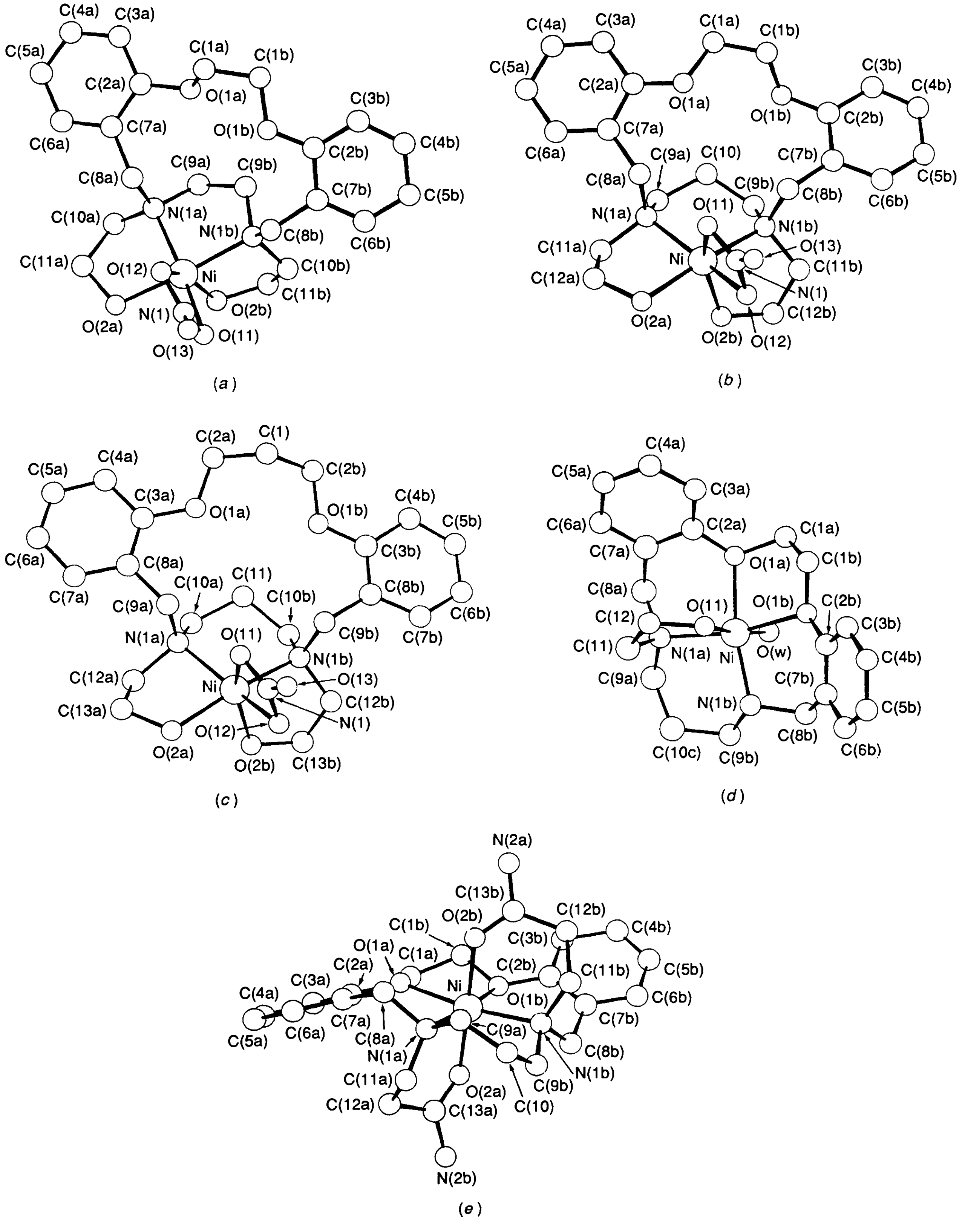


Fig. 1 Crystal structures of the complex cations in (*a*) $[NiL^8(NO_3)]NO_3$, (*b*) $[NiL^9(NO_3)]NO_3$, (*c*) $[NiL^{10}(NO_3)]NO_3$, (*d*) $[NiL^{12}(H_2O)][NO_3]_2$ and (*e*) $[NiL^{14}][NO_3]_2\cdot 0.5H_2O\cdot 0.5EtOH$

Table 3 Selected bond lengths (Å) and angles (°)

(*a*) $[\mathrm{NiL}^8(\mathrm{NO}_3)]\mathrm{NO}_3$							
Ni–N(1a)	2.083(5)	Ni–N(1b)	2.052(5)	N(1)–O(11)	1.275(7)	N(1)–O(12)	1.258(7)
Ni–O(2a)	2.074(4)	Ni–O(2b)	2.056(5)	N(1)–O(13)	1.200(7)		
Ni–O(11)	2.111(5)	Ni–O(12)	2.095(4)				
N(1b)–Ni–N(1a)	86.7(2)	O(2a)–Ni–N(1a)	82.3(2)	O(12)–Ni–N(1a)	98.2(2)	O(12)–Ni–N(1b)	102.3(2)
O(2a)–Ni–N(1b)	98.9(2)	O(2b)–Ni–N(1a)	166.1(2)	O(12)–Ni–O(2a)	158.8(2)	O(12)–Ni–O(2b)	94.4(2)
O(2b)–Ni–N(1b)	84.8(2)	O(2b)–Ni–O(2a)	88.1(2)	O(12)–Ni–O(11)	61.0(2)	O(12)–N(1)–O(11)	114.9(5)
O(11)–Ni–N(1a)	95.6(2)	O(11)–Ni–N(1b)	163.3(2)	O(13)–N(1)–O(11)	121.7(5)	O(13)–N(1)–O(12)	123.3(5)
O(11)–Ni–O(2a)	97.8(2)	O(11)–Ni–O(2b)	95.6(2)	N(1)–O(11)–Ni	91.3(3)	N(1)–O(12)–Ni	92.5(3)
(*b*) $[\mathrm{NiL}^9(\mathrm{NO}_3)]\mathrm{NO}_3$							
Ni–N(1a)	2.102(5)	Ni–N(1b)	2.091(5)	N(1)–O(11)	1.277(7)	N(1)–O(12)	1.258(8)
Ni–O(2a)	2.038(5)	Ni–O(2b)	2.075(5)	N(1)–O(13)	1.221(7)		
Ni–O(11)	2.141(5)	Ni–O(12)	2.135(4)				
N(1b)–Ni–N(1a)	97.4(2)	O(2a)–Ni–N(1a)	80.9(2)	O(12)–Ni–N(1a)	95.0(2)	O(12)–Ni–N(1b)	158.0(2)
O(2a)–Ni–N(1b)	108.8(2)	O(2b)–Ni–N(1a)	171.7(2)	O(12)–Ni–O(2a)	91.1(2)	O(12)–Ni–O(2b)	87.5(2)
O(2b)–Ni–N(1b)	82.9(2)	O(2b)–Ni–O(2a)	91.1(2)	O(12)–Ni–O(11)	60.2(2)	O(12)–N(1)–O(11)	115.7(5)
O(11)–Ni–N(1a)	99.6(2)	O(11)–Ni–N(1b)	99.6(2)	O(13)–N(1)–O(11)	121.3(6)	O(13)–N(1)–O(12)	123.0(5)
O(11)–Ni–O(2a)	151.3(2)	O(11)–Ni–O(2b)	88.5(2)	N(1)–O(11)–Ni	91.6(4)	N(1)–O(12)–Ni	92.4(3)
(*c*) $[\mathrm{NiL}^{10}(\mathrm{NO}_3)]\mathrm{NO}_3$							
Ni–N(1a)	2.101(11)	Ni–N(1b)	2.107(9)	N(1)–O(11)	1.220(17)	N(1)–O(12)	1.238(14)
Ni–O(2a)	2.030(9)	Ni–O(2b)	2.068(9)	N(1)–O(13)	1.263(14)		
Ni–O(11)	2.167(10)	Ni–O(12)	2.107(9)				
N(1b)–Ni–N(1a)	98.5(4)	O(2a)–Ni–N(1a)	81.4(4)	O(12)–Ni–N(1a)	98.7(4)	O(12)–Ni–N(1b)	97.8(4)
O(2a)–Ni–N(1b)	109.3(4)	O(2b)–Ni–N(1a)	169.2(4)	O(12)–Ni–O(2a)	152.7(3)	O(12)–Ni–O(2b)	91.7(4)
O(2b)–Ni–N(1b)	82.7(4)	O(2b)–Ni–O(2a)	88.1(4)	O(12)–Ni–O(11)	59.2(4)	O(12)–N(1)–O(11)	118.3(1)
O(11)–Ni–N(1a)	93.8(4)	O(11)–Ni–N(1b)	155.4(4)	O(13)–N(1)–O(11)	121.3(1)	O(13)–N(1)–O(12)	120.4(1)
O(11)–Ni–O(2a)	93.5(4)	O(11)–Ni–O(2b)	89.2(4)	N(1)–O(11)–Ni	90.1(7)	N(1)–O(12)–Ni	92.5(8)
(*d*) $[\mathrm{NiL}^{12}(\mathrm{H}_2\mathrm{O})][\mathrm{NO}_3]_2$							
Ni–O(1a)	2.104(6)	Ni–O(1b)	2.076(6)	Ni–O(11)	2.076(6)	Ni–O(w)	2.068(6)
Ni–N(1a)	2.049(8)	Ni–N(1b)	2.009(7)	N(1b)–H(N1b)	1.005(7)	O(11)–H(O11)	1.173(6)
N(1a)–Ni–O(1a)	91.0(3)	N(1b)–Ni–O(1b)	92.2(3)	O(w)–Ni–N(1a)	99.3(3)	N(1b)–Ni–O(w)	89.3(3)
N(1a)–Ni–N(1b)	98.4(3)	O(1b)–Ni–O(1a)	79.5(2)	O(w)–Ni–O(1a)	83.3(2)	O(1b)–Ni–O(w)	90.0(2)
O(11)–Ni–N(1a)	83.4(3)	O(11)–Ni–N(1b)	95.5(3)	O(1b)–Ni–N(1a)	165.9(2)	N(1b)–Ni–O(1a)	168.8(3)
O(11)–Ni–O(1a)	91.5(2)	O(1b)–Ni–O(11)	86.5(2)	O(w)–Ni–O(11)	174.2(2)		
(*e*) $[\mathrm{NiL}^{14}][\mathrm{NO}_3]_2\cdot0.5\mathrm{H}_2\mathrm{O}\cdot0.5\mathrm{EtOH}$							
Ni–O(1a)	2.152(4)	Ni–O(1b)	2.171(4)	O(2a)–C(13a)	1.249(7)	O(2b)–C(13b)	1.247(8)
Ni–N(1a)	2.084(5)	Ni–N(1b)	2.070(5)	N(2a)–C(13a)	1.494(10)	N(2b)–C(13b)	1.292(9)
Ni–O(2a)	2.032(4)	Ni–O(2b)	2.016(4)				
O(1b)–Ni–O(1a)	79.1(2)	N(1a)–Ni–O(1a)	90.9(2)	O(2b)–Ni–O(1a)	84.7(2)	O(2b)–Ni–O(1b)	88.7(2)
N(1a)–Ni–O(1b)	169.6(2)	N(1b)–Ni–O(1a)	168.4(2)	O(2b)–Ni–N(1a)	93.3(2)	O(2b)–Ni–N(1b)	90.2(2)
N(1b)–Ni–O(1b)	90.5(2)	N(1b)–Ni–N(1a)	99.7(2)	O(2b)–Ni–O(2a)	172.3(2)	C(13b)–O(2b)–Ni	129.3(4)
O(2a)–Ni–O(1a)	90.0(2)	O(2a)–Ni–O(1b)	84.8(2)	C(13a)–O(2a)–Ni	128.4(4)	N(2b)–C(13b)–O(2b)	120.2(6)
O(2a)–Ni–N(1a)	92.4(2)	O(2a)–Ni–N(1b)	93.9(2)	N(2a)–C(13a)–O(2a)	121.3(6)		

have similar distorted-octahedral structures to that above. Once again the ether oxygen atoms of the respective rings do not co-ordinate. Comparison of corresponding bond lengths and angles in each structure confirms that they are generally quite similar (see Table 3). The Ni–N bond lengths in all three complexes vary from 2.052(5) to 2.107(9) Å and hence fall within the literature range (2.04–2.33 Å) which is typical of nickel to sp^3-nitrogen bonds.[21] The remaining Ni–O bond lengths are also unremarkable. Thus, the nickel to alcohol oxygen bond lengths are in the range 2.030–2.075 Å which compares favourably with those of similar bonds in the nickel(II) complex of *N*,*N*′,*N*″,*N*‴-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane reported previously.[22]

In contrast to the structure described above, $[\mathrm{NiL}^{12}(\mathrm{H}_2\mathrm{O})][\mathrm{NO}_3]_2$ has its metal ion situated in the macrocyclic cavity such that the overall geometry is near octahedral (see Fig. 1). The co-ordination sphere of the nickel consists of two ether oxygen atoms and two nitrogen atoms from the macrocyclic ring (co-ordinated in a plane) together with oxygen atoms from the single pendant alcohol arm and a water molecule occupying the axial sites. Only one of the ionic nitrate groups shows evidence of disorder.

In $[\mathrm{NiL}^{14}][\mathrm{NO}_3]_2\cdot0.5\mathrm{H}_2\mathrm{O}\cdot0.5\mathrm{EtOH}$ the nickel atom is six-co-ordinate with the complex displaying near-octahedral geometry; the $\mathrm{O}_2\mathrm{N}_2$-donor set of the macrocyclic ring is co-ordinated in the equatorial plane with the carbonyl oxygen atoms of the pendant amide groups co-ordinated in the axial sites. Unlike the complexes of the bis(hydroxyethyl) derivatives L^8–L^{10} discussed above, neither of the nitrate groups is involved in co-ordination.

The crystal structure of the nickel complex of *N*,*N*′,*N*″,*N*‴-tetrakis(2-carbamoylethyl)-1,4,8,11-tetraazacyclotetradecane shows that two carbonyl atoms (from two of the 2-carbamoylethyl arms) are co-ordinated in axial positions [Ni–O 2.058(3)

Table 4 Refined atomic positional parameters

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[\mathrm{NiL}^{8}(\mathrm{NO}_3)]\mathrm{NO}_3$							
Ni	0.268 31(6)	0.095 67(7)	0.358 66(10)	C(3a)	0.541 4(5)	0.554 0(7)	0.224 9(9)
O(1a)	0.395 8(3)	0.532 2(4)	0.336 8(6)	C(3b)	0.058 7(6)	0.661 8(9)	0.197 4(11)
O(1b)	0.211 9(3)	0.561 6(4)	0.227 1(6)	C(4a)	0.624 0(5)	0.498 7(8)	0.188 0(10)
N(1a)	0.366 7(3)	0.189 0(4)	0.254 8(6)	C(4b)	−0.032 8(6)	0.654 4(9)	0.206 0(11)
N(1b)	0.171 1(3)	0.218 0(5)	0.248 9(6)	C(5a)	0.649 5(5)	0.365 6(7)	0.208 3(9)
O(2a)	0.286 5(3)	−0.047 2(4)	0.162 7(5)	C(5b)	−0.068 5(6)	0.546 1(9)	0.253 0(11)
O(2b)	0.156 8(3)	−0.003 0(4)	0.404 3(6)	C(6a)	0.584 7(4)	0.293 8(7)	0.267 9(8)
N(1)	0.349 4(4)	0.109 7(5)	0.636 7(7)	C(6b)	−0.008 2(5)	0.441 7(8)	0.300 9(10)
O(11)	0.363 1(3)	0.011 5(4)	0.529 8(6)	C(7a)	0.499 7(4)	0.346 7(6)	0.306 2(7)
O(12)	0.287 6(3)	0.193 8(4)	0.594 5(5)	C(7b)	0.086 5(5)	0.447 4(7)	0.296 2(8)
O(13)	0.394 9(4)	0.121 6(5)	0.767 8(6)	C(8a)	0.432 1(4)	0.268 5(6)	0.374 9(7)
N(2)	0.840 8(4)	0.100 2(7)	0.217 8(8)	C(8b)	0.153 0(4)	0.342 1(6)	0.360 8(8)
O(21)	0.837 3(4)	0.147 2(6)	0.084 3(7)	C(9a)	0.314 6(4)	0.277 2(6)	0.143 6(8)
O(22)	0.858 2(5)	0.169 5(7)	0.345 3(8)	C(9b)	0.214 1(4)	0.242 9(6)	0.102 9(8)
O(23)	0.830 9(6)	−0.014 9(7)	0.222 9(9)	C(10a)	0.419 7(4)	0.077 8(6)	0.166 5(8)
C(1a)	0.357 4(5)	0.653 9(7)	0.285 5(10)	C(10b)	0.088 2(5)	0.138 3(7)	0.210 8(9)
C(1b)	0.259 6(5)	0.666 9(7)	0.323 8(9)	C(11a)	0.357 5(4)	−0.017 6(7)	0.066 9(8)
C(2a)	0.477 6(4)	0.483 2(6)	0.287 1(8)	C(11b)	0.072 8(5)	0.067 6(7)	0.354 1(9)
C(2b)	0.120 1(5)	0.558 1(7)	0.241 6(9)				
(*b*) $[\mathrm{NiL}^{9}(\mathrm{NO}_3)]\mathrm{NO}_3$							
Ni	0.236 37(5)	0.0382 1(3)	0.249 83(11)	C(3a)	−0.038 6(5)	0.270 3(4)	0.380 4(11)
N(1a)	0.141 4(3)	0.085 6(2)	0.353 5(7)	C(3b)	0.415 5(5)	0.324 9(4)	0.311 6(11)
N(1b)	0.344 9(3)	0.097 7(2)	0.350 1(7)	C(4a)	−0.119 6(5)	0.234 8(4)	0.364 0(11)
O(1a)	0.114 7(3)	0.258 0(2)	0.363 5(8)	C(4b)	0.502 9(6)	0.319 9(4)	0.325 4(11)
O(1b)	0.271 4(4)	0.270 7(2)	0.250 2(8)	C(5a)	−0.316 9(5)	0.181 8(4)	0.305 5(11)
O(2a)	0.222 8(3)	−0.029 5(2)	0.420 0(6)	C(5b)	0.545 6(6)	0.262 4(4)	0.317 4(12)
O(2b)	0.333 5(3)	−0.017 0(2)	0.177 5(6)	C(6a)	−0.068 8(5)	0.146 8(3)	0.264 9(10)
N(1)	0.146 0(3)	0.031 4(3)	−0.042 1(8)	C(6b)	0.492 2(5)	0.206 6(4)	0.287 7(10)
O(11)	0.201 5(3)	0.077 2(2)	0.006 1(6)	C(7a)	0.016 3(4)	0.171 0(3)	0.281 3(9)
O(12)	0.140 5(3)	−0.010 5(2)	0.064 5(6)	C(7b)	0.401 5(4)	0.209 2(3)	0.272 8(9)
O(13)	0.101 9(3)	0.029 1(2)	−0.183 2(6)	C(8a)	0.088 0(4)	0.132 0(3)	0.231 3(9)
N(2)	0.356 2(4)	−0.063 4(3)	0.801 8(11)	C(8b)	0.342 6(4)	0.150 1(3)	0.222 9(9)
O(21)	0.356 9(4)	−0.070 1(3)	0.654 3(9)	C(9a)	0.179 0(4)	0.117 2(3)	0.516 0(9)
O(22)	0.292 1(4)	−0.039 6(4)	0.083 94(9)	C(9b)	0.343 8(4)	0.123 6(3)	0.513 9(9)
O(23)	0.418 2(4)	−0.081 7(3)	0.911 5(8)	C(10)	0.260 0(4)	0.158 7(3)	0.521 0(10)
C(1a)	0.131 4(6)	0.311 6(4)	0.269 1(12)	C(11a)	0.084 9(4)	0.030 8(3)	0.382 7(9)
C(1b)	0.224 3(6)	0.325 8(4)	0.292 1(12)	C(11b)	0.424 0(4)	0.053 6(3)	0.364 6(9)
C(2a)	0.030 3(5)	0.234 3(3)	0.337 5(10)	C(12a)	0.140 2(4)	−0.024 3(3)	0.474 8(9)
C(2b)	0.361 3(5)	0.269 5(5)	0.281 9(10)	C(12b)	0.418 8(4)	0.013 3(3)	0.215 4(10)
(*c*) $[\mathrm{NiL}^{10}(\mathrm{NO}_3)]\mathrm{NO}_3$							
Ni	0.265 80(11)	0.547 67(7)	0.271 64(20)	C(6a)	0.659 6(10)	0.6700(7)	0.199 4(18)
O(1a)	0.412 3(6)	0.754 7(4)	0.228 6(13)	C(6b)	−0.071 5(10)	0.740 3(6)	0.230 5(18)
O(1b)	0.198 2(6)	0.774 8(4)	0.237 2(13)	C(7a)	0.589 2(10)	0.638 3(6)	0.249 8(18)
N(1a)	0.371 1(6)	0.589 2(5)	0.177 9(13)	C(7b)	−0.010 1(10)	0.691 9(6)	0.260 2(18)
N(1b)	0.158 3(6)	0.608 9(4)	0.173 1(12)	C(8a)	0.504 0(8)	0.666 4(5)	0.251 4(15)
O(2a)	0.277 7(6)	0.482 7(4)	0.103 6(11)	C(8b)	0.081 7(9)	0.704 6(5)	0.256 6(16)
O(2b)	0.159 4(6)	0.496 1(4)	0.326 2(12)	C(9a)	0.428 7(8)	0.630 3(5)	0.307 5(15)
N(1)	0.351 1(8)	0.541 8(6)	0.558 9(15)	C(9b)	0.153 0(9)	0.654 0(6)	0.297 2(16)
O(11)	0.360 2(6)	0.500 6(5)	0.464 9(13)	C(10a)	0.337 7(9)	0.621 3(6)	0.018 8(16)
O(12)	0.298 6(6)	0.585 0(4)	0.507 6(11)	C(10b)	0.167 3(5)	0.636 7(6)	0.015 7(16)
O(13)	0.397 5(7)	0.541 3(6)	0.703 0(11)	C(11)	0.259 8(9)	0.669 8(6)	0.232 9(16)
C(1)	0.330 0(10)	0.841 1(7)	0.301 2(19)	C(12a)	0.423 3(8)	0.535 2(5)	0.143 3(15)
C(2a)	0.401 7(11)	0.821 1(7)	0.211 2(19)	C(12b)	0.076 9(9)	0.563 1(6)	0.132 3(18)
C(2b)	0.228 6(12)	0.837 9(7)	0.221 4(22)	C(13a)	0.361 6(9)	0.487 3(6)	0.041 6(17)
C(3a)	0.491 6(9)	0.727 4(6)	0.214 0(16)	C(13b)	0.069 5(11)	0.524 9(7)	0.277 2(19)
C(3b)	0.105 2(9)	0.763 0(6)	0.225 3(17)	N(2)	0.158 6(9)	0.459 7(7)	0.720 2(18)
C(4a)	0.563 2(9)	0.762 1(6)	0.157 5(17)	O(21)	0.152 9(7)	0.439 8(6)	0.852 3(13)
C(4b)	0.038 6(10)	0.817 7(7)	0.189 6(19)	O(22)	0.135 9(10)	0.434 2(6)	0.599 1(15)
C(5a)	0.644 2(10)	0.730 4(7)	0.153 6(18)	O(23)	0.173 1(12)	0.517 0(8)	0.711 9(19)
C(5b)	−0.050 9(11)	0.796 5(7)	0.195 1(19)				
(*d*) $[\mathrm{NiL}^{12}(\mathrm{H_2O})][\mathrm{NO}_3]_2$							
Ni	0.381 08(4)	0.225 85(13)	0.649 80(11)	C(4a)	0.456 9(3)	−0.213 0(14)	1.013 2(10)
O(1a)	0.440 8(2)	0.118 3(8)	0.744 4(6)	C(5a)	0.440 2(4)	−0.120 1(16)	1.110 6(11)
N(1a)	0.367 1(2)	0.313 7(9)	0.830 9(7)	C(6a)	0.424 7(3)	0.049 8(14)	1.089 8(11)
O(11)	0.346 9(2)	0.004 4(7)	0.694 8(6)	C(7a)	0.425 1(3)	0.129 6(13)	0.962 3(10)
O(w)	0.420 7(2)	0.430 0(8)	0.605 5(6)	C(8a)	0.407 6(3)	0.311 3(12)	0.933 5(9)
O(1b)	0.399 5(2)	0.075 4(7)	0.487 5(6)	C(9a)	0.352 3(3)	0.502 1(12)	0.819 0(10)
N(2)	0.254 6(3)	0.503 6(10)	−0.014 7(8)	C(11)	0.331 1(3)	0.199 4(13)	0.871 4(10)

Table 4 (*continued*)

Atom	x	y	z
(*d*) $[NiL^{12}(H_2O)][NO_3]_2$			
O(21)	0.286 4(2)	0.466 5(9)	0.066 4(8)
O(22)	0.224 7(2)	0.396 2(9)	−0.043 4(8)
O(23)	0.250 4(2)	0.655 3(8)	−0.068 0(7)
N(3)	0.526 3(3)	−0.447 2(11)	0.670 1(8)
O(31)	0.503 2(3)	−0.508 6(11)	0.747 2(7)
O(32)	0.512 3(3)	−0.322 9(11)	0.597 9(9)
O(33)	0.560 8(3)	−0.503 0(13)	0.651 6(10)
N(1b)	0.330 4(2)	0.336 3(9)	0.529 1(7)
C(1a)	0.463 6(3)	0.046 2(12)	0.641 3(9)
C(2a)	0.442 1(3)	0.029 8(12)	0.865 4(9)
C(3a)	0.457 2(3)	−0.138 4(14)	0.888 7(10)
C(12)	0.334 6(3)	0.008 7(12)	0.827 1(9)
C(1b)	0.432 3(3)	−0.047 3(13)	0.539 0(9)
C(2b)	0.366 1(3)	0.015 9(11)	0.387 5(9)
C(3b)	0.365 1(3)	−0.153 6(13)	0.337 4(9)
C(4b)	0.332 9(3)	−0.197 8(15)	0.237 0(10)
C(5b)	0.300 1(4)	−0.083 8(15)	0.184 5(11)
C(6b)	0.300 9(3)	0.087 7(13)	0.238 0(10)
C(7b)	0.334 7(3)	0.138 9(12)	0.337 2(9)
C(8b)	0.336 5(3)	0.325 4(12)	0.386 0(9)
C(9b)	0.322 1(3)	0.521 8(12)	0.566 1(9)
C(10)	0.313 3(3)	0.536 0(13)	0.709 5(9)
(*e*) $[NiL^{14}][NO_3]_2{\cdot}0.5H_2O{\cdot}0.5EtOH$			
Ni	0.135 46(3)	0.404 61(4)	0.612 30(5)
O(1a)	0.136 8(2)	0.350 7(2)	0.484 9(3)
O(1b)	0.045 7(2)	0.423 4(2)	0.568 7(3)
N(1a)	0.224 5(2)	0.382 3(3)	0.630 0(3)
N(1b)	0.116 0(2)	0.451 8(3)	0.734 0(3)
O(2a)	0.152 0(2)	0.505 9(2)	0.554 2(3)
O(2b)	0.110 7(2)	0.302 2(2)	0.657 3(3)
N(2a)	0.207 1(2)	0.608 2(3)	0.528 4(4)
N(2b)	0.046 2(3)	0.220 0(3)	0.708 0(4)
N(1)	0.362 6(4)	0.637 6(5)	0.547 8(7)
O(11)	0.327 2(2)	0.651 9(3)	0.487 0(4)
O(12)	0.415 6(3)	0.648 9(6)	0.531 0(7)
O(13)	0.344 1(5)	0.618 5(5)	0.619 5(6)
N(2)	−0.088 8(4)	0.215 4(5)	0.848 3(7)
O(21)	−0.040 5(3)	0.190 0(4)	0.841 4(5)
O(22)	−0.108 5(4)	0.198 8(6)	0.924 7(8)
O(23)	−0.109 2(6)	0.253 2(8)	0.798 5(9)
C(1a)	0.084 9(3)	0.372 2(4)	0.435 6(5)
C(1b)	0.033 2(3)	0.373 5(4)	0.496 5(5)
C(2a)	0.187 1(3)	0.033 50(4)	0.435 8(4)
C(2b)	−0.001 3(3)	0.441 6(4)	0.624 0(4)
C(3a)	0.188 7(3)	0.342 6(4)	0.345 3(5)
C(3b)	−0.057 1(3)	0.413 2(4)	0.609 6(5)
C(4a)	0.242 2(3)	0.326 1(5)	0.301 4(5)
C(4b)	−0.102 0(4)	0.432 6(5)	0.669 1(5)
C(5a)	0.289 1(3)	0.303 8(4)	0.346 7(5)
C(5b)	−0.091 0(3)	0.479 7(4)	0.738 3(5)
C(6a)	0.287 3(3)	0.296 9(4)	0.438 4(5)
C(6b)	−0.034 6(3)	0.506 5(4)	0.752 6(5)
C(7a)	0.235 8(3)	0.313 3(4)	0.484 9(4)
C(7b)	0.011 4(3)	0.487 2(4)	0.696 3(4)
C(8a)	0.235 7(3)	0.303 8(4)	0.584 1(4)
C(8b)	0.072 2(3)	0.515 0(4)	0.716 8(4)
C(9a)	0.232 3(3)	0.368 5(4)	0.727 0(5)
C(9b)	0.170 4(3)	0.490 2(4)	0.765 0(4)
C(10)	0.222 0(3)	0.435 6(4)	0.787 0(5)
C(11a)	0.268 9(3)	0.439 7(4)	0.600 8(4)
C(11b)	0.095 1(3)	0.400 1(4)	0.806 2(4)
C(12a)	0.253 1(3)	0.486 0(3)	0.518 4(4)
C(12b)	0.051 5(3)	0.338 6(4)	0.782 5(4)
C(13a)	0.200 6(3)	0.534 4(3)	0.535 4(4)
C(13b)	0.071 5(3)	0.285 5(4)	0.711 4(4)
C(1g)	0.468 6(19)	0.095 3(24)	−0.062 1(31)
C(2g)	0.438 5(8)	0.105 1(10)	0.027 2(12)
O(1f)	0.411 7(8)	0.039 9(10)	−0.009 8(12)
O(1g)	0.442 8(8)	0.349 4(10)	0.457 0(12)

and 2.084(4) Å, respectively].[23] Comparison with the structure of $[NiL^{14}][NO_3]_2{\cdot}0.5H_2O{\cdot}0.5EtOH$ shows that the nickel to axial carbonyl oxygen bond lengths in the latter complex are only marginally shorter [2.032(4) and 2.016(4) Å].

For the latter complex there is evidence for hydrogen-bond formation between a nitrate counter ion and amide hydrogens on adjacent $[NiL^{14}]^{2+}$ cations. Namely, the structure consists of two $[NiL^{14}]^{2+}$ cations linked by a hydrogen-bonded nitrate group; the respective bond distances are 2.014 Å for H(N2c)···O(11) in symmetry position 1 and 2.301 Å for H(N2e)···O(12) in symmetry position 4.

Stability Constants.—The protonation constants for L^8–L^{12} were obtained by potentiometric titration in 95% methanol (I = 0.1 mol dm^{-3}; NEt_4ClO_4 or NMe_4Cl) at 25 °C (Table 5). The low solubilities for the pendant amide derivatives L^{13} and L^{14} precluded further study on these systems. The stability constants for a range of 1 : 1 (L : M) complexes of L^8–L^{12} with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) were also obtained potentiometrically under the above conditions. In most cases, data for both chloride and perchlorate media were obtained since this provided the means for checking whether the more strongly co-ordinating chloride results in a major log K variation, as might occur if changes in the co-ordination sphere were induced relative to the perchlorate case. However, in general, the variation between both sets of values tended to be relatively minor. For comparison, the log K values determined previously for the corresponding complexes of the parent (non-pendant-arm macrocycles) L^1–L^4 are also listed in Table 5.[3,4]

All systems follow the expected Irving–Williams stability order of $Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$.[24] For the 14-membered cyclic ring system L^8 the presence of the two hydroxyethyl arms on the nitrogen atoms has a significant effect on the stability of corresponding metal complexes relative to those of the parent ring L^1. In general, the log K values for the complexes of L^8 tend to be significantly higher than for the corresponding complexes of the latter (unsubstituted) ring. Since the incorporation of the two hydroxyethyl arms results in enhanced stability, it seems likely that the alcohol functions are involved in binding to the metal ion, as occurs in the solid. This pattern is repeated for the corresponding 15- to 17-membered rings, L^9–L^{11}, and may reflect that all four systems display similar solution behaviour towards particular metal ions. As discussed above, the crystal structures of the nickel complexes of L^8–L^{10} show that similar solid-state co-ordination geometries are adopted in each case.

From the available evidence it is inappropriate to predict the co-ordination or otherwise of the ether donors in solution for the respective complexes of L^8–L^{11} but, at least for the nickel(II) complexes, the X-ray data indicate that these donors do not co-ordinate in the solid state.

The stability of the copper(II) complex of the 15-membered ring L^{12} (which incorporates one pendant alcohol arm) is comparable to that of the corresponding complex of the analogous dialcohol derivative L^9, but higher than found for

Table 5 Stability constants for the complexes of L^1–L^4 and L^8 and L^{12} in 95% MeOH (I = 0.1 mol dm^{-3}, NEt_4ClO_4 or NMe_4Cl at 25 °C)[a]

		log K_{ML} ($M^{2+} + L \rightleftharpoons ML^{2+}$)					Free L	
Ligand	Medium	M = Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}	log K_1	log K_2
L^1	NEt_4ClO_4	~3	3.4	7.7	<4	<4[b]	9.27	5.14
	NMe_4Cl	<4.5	~3.7	8.2	~3		9.19	5.40
L^2	NEt_4ClO_4	<3.6	4.8	7.3	<4.5	<3[b]	9.85	6.78
	NMe_4Cl	<4.5	5.4	7.2	4.1		9.81	6.82
L^3	NEt_4ClO_4	4.1	5.0	7.1	5.5	*c*	10.03	6.83
	NMe_4Cl	<4.5	5.8	7.7	4.3		10.07	7.09
L^4	NEt_4ClO_4	<4[b]	<4[b]	7.5[b]	<4.5[b]	<4[b]	9.76[b]	8.14[b]
	NMe_4Cl	<4.5	~3.5	7.2	4.1		9.63	8.10
L^8	NEt_4ClO_4	5.2	*c*	>9	5.8	6.5	10.09	3.06
	NMe_4Cl	5.3	7.1	>9	5.0		9.90	3.46
L^9	NEt_4ClO_4	<4	*c*	8.1	<4	<4.5	9.22	6.35
	NMe_4Cl	<4	*c*	7.7	<4		9.22	6.33
L^{10}	NEt_4ClO_4	<4	4.1	8.5	<4.5	<4.5	9.16	6.35
	NMe_4Cl	<4	4.0	8.0	<4.5		9.10	6.27
L^{11}	NEt_4ClO_4	~4	4.4	8.8	~4	<4.5	9.27	6.85
	NMe_4Cl	<4	4.3	8.3	<4.5		9.21	6.89
L^{12}	NEt_4ClO_4	<4	5.7	7.8	<4.5	<4.5	10.27	5.26
	NMe_4Cl	<4	5.8	7.9	<4.5		10.15	5.39

[a] Unless otherwise indicated, data for L^1–L^4 in NEt_4ClO_4 and NMe_4Cl media were taken from refs. 3 and 4. The error is estimated to be ±0.1 for each log K_{ML} value. Low solubilities of L^{13} and L^{14} precluded potentiometric measurements. [b] This work. [c] Precipitation prevented usable data being obtained.

that of the parent ring L^2. This may imply that both the alcohol and ether groups co-ordinate in this case, as occurs in the corresponding solid-state nickel complex.

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References

1 K. R. Adam, S. P. H. Arshad, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, B. J. McCool, M. McPartlin, B. A. Tailor and P. A. Tasker, *Inorg. Chem.*, 1994, **33**, 1194.

2 K. R. Adam, D. S. Baldwin, A. Bashall, L. F. Lindoy, M. McPartlin and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, 1994, 237 and refs. therein.

3 G. Anderegg, A. Ekstrom, L. F. Lindoy and R. J. Smith, *J. Am. Chem. Soc.*, 1980, **102**, 2670; L. F. Lindoy, H. C. Lip, J. H. Rea, R. J. Smith, K. Henrick, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1980, **19**, 3360; K. R. Adam, G. Anderegg, L. F. Lindoy, H. C. Lip, M. McPartlin, J. H. Rea, R. J. Smith and P. A Tasker, *Inorg. Chem.*, 1980, **19**, 2956.

4 K. R. Adam, A. J. Leong, L. F. Lindoy and G. Anderegg, *J. Chem. Soc., Dalton Trans.*, 1988, 1733.

5 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, 1989.

6 T. A. Kaden, *Top. Curr. Chem.*, 1984, **121**, 157; P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **93**, 297; G. W. Gokel, *Chem. Soc. Rev.*, 1992, **21**, 39.

7 V. Dudler, L. F. Lindoy, D. Sallin and C. W. Schlaepfer, *Aust. J. Chem.*, 1987, **40**, 1557; J. S. Bradshaw, R. M. Izatt, J. J. Christensen, K. E. Krakowiak, B. J. Tarbet and R. L. Bruening, *J. Incl. Phenom.*, 1989, **7**, 127; J. H. Cameron, H. B. Harvey and I. Soutar, *J. Chem. Soc., Dalton Trans.*, 1992, 597.

8 K. R. Adam, A. J. Leong, L. F. Lindoy, P. Hendry, S. V. Smith and D. Yellowlees, *J. Coord. Chem.*, 1988, **19**, 189.

9 P. S. K. Chia, A. Ekstrom, I. Liepa, L. F. Lindoy, M. McPartlin, S. V. Smith and P. A. Tasker, *Aust. J. Chem.*, 1991, **44**, 737.

10 K. R. Adam, M. Antolovich, D. S. Baldwin, L. G. Brigden, P. A. Duckworth, L. F. Lindoy, A. Bashall, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1992, 1869.

11 K. R. Adam, K. P. Dancey, A. J. Leong, L. F. Lindoy, B. J. McCool, M. McPartlin and P. A. Tasker, *J. Am. Chem. Soc.*, 1988, **110**, 8471.

12 P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

13 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.

14 M. K. Cooper, P. J. Guerney, H. J. Goodwin and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1982, 757.

15 G. M. Sheldrick, SHELX 76, program for crystal structure determination, University of Cambridge, 1976.

16 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.

17 B. I. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

18 L. Y. Martin, L. J. De Hayes, L. J. Zompa and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 4046; L. Y. Martin, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 2968; Y. Jung, L. Y. Martin, S. C. Jackels, A. M. Tait and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4029.

19 L. G. Armstrong, P. G. Grimsley, L. F. Lindoy, H. C. Lip, V. A. Norris and R. J. Smith, *Inorg. Chem.*, 1978, **17**, 2350.

20 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

21 N. F. Curtis, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979, p. 219.

22 R. W. Hay, M. P. Pujari, W. T. Moodie, S. Craig, D. T. Richens, A. Perotti and P. Ungaretti, *J. Chem. Soc., Dalton Trans.*, 1987, 2605.

23 G. M. Freeman, E. K. Barefield and D. G. Van Derveer, *Inorg. Chem.*, 1980, **23**, 3092.

24 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.

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