Interaction of Transition- and Post-transition-metal Ions with O_2N_2-Donor Macrocycles incorporating Pendant Pyridylmethyl Groups†

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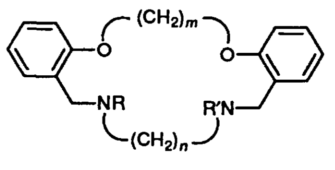
The interaction of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) with pyridylmethyl pendant-arm derivatives of O_2N_2-donor macrocycles incorporating from 14- to 17-membered rings has been investigated. Thermodynamic stabilities of the 1 : 1 (metal : ligand) complexes have been determined in 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4; 25 °C). The data indicate that the pyridyl nitrogens participate in co-ordination to the respective metals in each complex in solution. The crystal structures of the nickel(II) and copper(II) complexes of the 15-membered O_2N_2-donor macrocycle containing two pendant 2-pyridylmethyl groups have also been determined. For the nickel complex only the nitrogens of the macrocyclic ring and the pendant pyridyl nitrogens are co-ordinated; overall, the co-ordination geometry is distorted octahedral, with the fifth and sixth positions being occupied by a bidentate nitrate group. In contrast, in the copper complex the four nitrogens and at least one of the two ring ether oxygens are co-ordinated (there is a long contact with the second); these two oxygens may be considered to displace those of the nitrate chelate found in the nickel complex. In the nickel complex, Ni–N are 2.119(6), 2.113(4) (aliphatic), 2.061(4), 2.032(5) (aromatic) and Ni–O 2.137(5), 2.230(4) Å. In the copper complex, Cu–N are 2.06(1), 2.02(1) (aliphatic), 1.97(1), 2.04(1) (aromatic) and Cu–O 2.319(9), 2.92(1) Å. The N(aliphatic)–M–N(aromatic) angles, *trans* within the ligand, are 111.4(2), 177.2(2) (M = Ni) and 127.6(4), 179.1(5)° (M = Cu).

Our previous studies have been concerned with an investigation of the metal-ion chemistry of a range of mixed oxygen–nitrogen donor macrocycles[1,2] of which L^1–L^4 are typical.[3–5] Structurally these macrocycles fall between the crown polyethers and the range of well studied rings containing only nitrogen donors. In a number of instances such systems have been shown to give rise to significant metal-ion discrimination.[2–6] As an extension of these studies, the synthesis and metal-ion chemistry of pendant-arm derivatives of L^1–L^4, incorporating hydroxyethyl,[7] carbamoylethyl[7] and acetate[8] arms attached to ring nitrogen atoms, have been investigated.

In this paper we report a new investigation of this type involving the interaction of the related pyridylmethyl arm derivatives L^5–L^9 with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II). In other studies, macrocyclic systems incorporating 2-pyridylmethyl arms have been documented to exhibit a wide range of interesting co-ordination chemistry towards metals such as those mentioned above.[9,10]



	m	n	
L^1	2	2	R, R′ = H
L^2	2	3	R, R′ = H
L^3	3	3	R, R′ = H
L^4	4	3	R, R′ = H
L^5	2	2	R, R′ = $CH_2C_5H_4N$
L^6	2	3	R, R′ = $CH_2C_5H_4N$
L^7	3	3	R, R′ = $CH_2C_5H_4N$
L^8	4	3	R, R′ = $CH_2C_5H_4N$
L^9	2	3	R = H, R′ = $CH_2C_5H_4N$

Experimental

Physical Measurements.—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.[11,12]

The apparatus and conditions used for the potentiometric (pH titration) determinations (95% methanol; I = 0.1 mol dm^{-3}, NEt_4ClO_4; 25 °C) were identical to those used previously for analogous studies involving complexes of the precursors L^1–L^4.[3–5] The log K data were processed using local versions of MINIQUAD[13] and SUPERQUAD.[14] All values are the mean of between two and five individual determinations at varying metal : ligand ratios.

Macrocycle Synthesis.—The preparation and characterisation of L^5–L^9 are described elsewhere.[15]

Synthesis of the Metal Complexes.—Three general procedures were employed.

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

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

(*i*) Macrocycle (2×10^{-3} mol) in ethanol or methanol was added slowly to a stirred, hot solution of nickel(II) nitrate hexahydrate (2×10^{-3} mol) in ethanol or methanol. The solution was allowed to cool to room temperature and the crystalline product formed on standing (either at room temperature or on refrigeration of the solution for 1–3 d). The respective products were filtered off and washed with ethanol or methanol.

(*ii*) By a similar procedure to that in (*i*) the required macrocycle in hot methanol was added to a solution of copper(II) perchlorate or nitrate in hot methanol. (**CAUTION**: perchlorates are potentially explosive.) Each of the reaction solutions was stored under refrigeration and the respective products which formed were then filtered off and washed with methanol or ethanol.

(*iii*) For the complexes of cobalt(II), nickel(II), zinc(II) and cadmium(II) perchlorate, a related procedure was again employed. The macrocycle in hot methanol was added to a solution of the corresponding metal nitrate or chloride in the presence of lithium perchlorate in hot methanol. The solution was cooled and was stored under refrigeration whereupon the respective products crystallised; they were filtered off and washed with methanol or ethanol.

All products were dried over phosphorus pentaoxide *in vacuo* before analysis; yields were greater than 60% in each case. Satisfactory elemental analyses for carbon, hydrogen and nitrogen were obtained for each complex (see Table 1); where solvent molecules (water or alcohol) are formulated, their presence was verified by the presence of O–H stretching bands (near 3300 cm^{-1}) in the infrared spectrum.

Crystal Structure Determinations of [NiL^6(NO$_3$)]NO$_3$·H$_2$O *and* [CuL^6][ClO$_4$]$_2$.—Data collection for the nickel(II) and copper(II) complexes of L^6 was carried out using an Enraf-Nonius CAD-4 machine at ≈295 K. Unique data sets were measured to $2\theta_{max} = 50°$ in conventional 2θ–θ scan mode (monochromatic Mo-Kα radiation, $\lambda = 0.710\,73$ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being used in the large-block least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Residuals quoted at convergence are conventional R, R' on $|F|$; statistical reflection weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used. Neutral-atom complex scattering factors were employed;[16] computation used the XTAL 2.4 program system[17] implemented by S. R. Hall. Details of the structures are given in Fig. 1; fractional atomic coordinates and selected bond lengths and angles for each complex are given in Tables 5 and 4, respectively.

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

Crystal and refinement data. [NiL^6(NO$_3$)]NO$_3$·H$_2$O, C$_{31}$H$_{36}$N$_6$NiO$_9$, $M = 695.1$, crystal dimensions $0.18 \times 0.30 \times 0.18$ mm, monoclinic, space group $P2_1/c$, (C^5_{2h}, no. 14), $a = 16.054(7)$, $b = 13.713(2)$, $c = 15.812(9)$ Å, $\beta = 115.03(3)°$, $U = 3154$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 1456$, μ(Mo-Kα) = 6.2 cm^{-1}. $N = 5076$, $N_o = 2834$, $R = 0.051$, $R' = 0.050$.

Abnormal features/variations in procedure. A difference-map artefact was modelled as a water molecule oxygen, assigned unit site occupancy after a trial refinement; associated hydrogen atoms were positioned from difference-map consideration.

[CuL^6][ClO$_4$]$_2$, C$_{31}$H$_{34}$Cl$_2$CuN$_4$O$_{10}$, $M = 757.1$, crystal dimensions $0.11 \times 0.24 \times 0.41$ mm, orthorhombic, space group $Pbnb$ (D^{10}_{2h}, no. 56, variant), $a = 29.144(7)$, $b = 18.646(10)$, $c = 12.641(3)$ Å, $U = 6869$ Å^3, $Z = 8$, $D_c = 1.46$ g cm^{-3}, $F(000) = 3128$, μ(Mo-Kα) 7.9 cm^{-1}. $N = 5354$, $N_o = 3128$, $R = 0.074$, $R' = 0.086$.

Abnormal features/variations in procedure. Atom C(11) of the macrocycle was modelled as disordered over two sites with site occupancies set at 0.5 after initial refinement, and associated hydrogen atoms appropriately disposed. This and very high perchlorate thermal motion, unresolvable into disordered components, are considered responsible for the high residuals.

Results and Discussion

Syntheses and Characterisation of Metal Complexes.—Cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes of L^5–L^8 have been isolated. Thus, these macrocycles react with the required metal nitrate or perchlorate salt (or in some cases metal nitrate in the presence of lithium perchlorate) in ethanol or methanol to yield the corresponding 1:1 (metal:ligand) complexes. The microanalytical data (see Table 1) are consistent with the complexes being of the types [ML(NO$_3$)]NO$_3$·xH$_2$O, [ML][ClO$_4$]$_2$·xH$_2$O or [ML(NO$_3$)]ClO$_4$·xH$_2$O.

Table 1 Analytical data for the metal complexes of the pendant-arm derivatives L^5–L^8

		Analysis (%) *		
Complex	Colour	C	H	N
[CoL^6(NO$_3$)]ClO$_4$	Pink	52.4 (52.1)	4.9 (4.8)	9.8 (9.8)
[CoL^7(NO$_3$)]ClO$_4$	Pink	52.4 (52.7)	4.6 (5.0)	9.5 (9.6)
[CoL^8(NO$_3$)]ClO$_4$·0.5H$_2$O	Pink	53.0 (52.7)	5.2 (5.2)	9.3 (9.3)
[NiL^5(NO$_3$)]NO$_3$·2H$_2$O	Purple	51.4 (51.2)	4.9 (5.2)	12.3 (12.0)
[NiL^5(NO$_3$)]ClO$_4$·H$_2$O	Purple	50.5 (50.1)	4.5 (4.8)	9.7 (9.7)
[NiL^6(NO$_3$)]NO$_3$·H$_2$O	Purple	53.6 (53.6)	5.0 (5.2)	11.7 (12.1)
[NiL^7(NO$_3$)]NO$_3$·H$_2$O	Purple	54.3 (54.2)	5.3 (5.4)	11.8 (11.8)
[NiL^8(NO$_3$)]NO$_3$·H$_2$O	Purple	54.6 (54.6)	5.5 (5.5)	11.7 (11.7)
[NiL^8(NO$_3$)]ClO$_4$·0.5H$_2$O	Purple	52.5 (52.7)	4.9 (5.2)	9.3 (9.3)
[CuL^5][ClO$_4$]$_2$·0.5H$_2$O	Blue	47.9 (47.9)	4.2 (4.4)	7.5 (7.5)
[CuL^6][ClO$_4$]$_2$	Blue	48.7 (49.2)	4.7 (4.5)	7.3 (7.4)
[CuL^8][ClO$_4$]$_2$	Blue	50.5 (50.5)	4.9 (4.9)	7.5 (7.1)
[ZnL^6(NO$_3$)]ClO$_4$	Cream	51.3 (51.6)	4.7 (4.8)	9.5 (9.7)
[ZnL^7(NO$_3$)]ClO$_4$·0.5H$_2$O	Cream	51.7 (51.6)	4.7 (5.0)	9.4 (9.4)
[ZnL^8(NO$_3$)]ClO$_4$	White	52.5 (52.9)	4.8 (5.1)	9.3 (9.4)
[CdL^5(NO$_3$)]ClO$_4$	Yellow	47.5 (47.8)	4.1 (4.3)	9.1 (9.3)
[CdL^6(NO$_3$)]ClO$_4$	Yellow	48.2 (48.4)	4.3 (4.5)	9.1 (9.1)
[CdL^7(NO$_3$)]ClO$_4$	Yellow	48.3 (48.1)	4.4 (4.6)	9.0 (9.0)
[CdL^8(NO$_3$)]ClO$_4$	White	48.1 (48.1)	4.8 (5.0)	8.4 (8.5)

* Calculated values in parentheses.

Attempts to isolate pure nickel(II) perchlorate complexes of L^5–L^9 by the addition of macrocycle to a methanol solution of nickel(II) nitrate in the presence of a slight excess of lithium perchlorate were, in general, not successful. Cocrystallisation of the desired nickel complex together with a colourless crystalline solid (which appeared to be the corresponding hydroperchlorate and/or hydronitrate salt of the macrocycle) occurred in all but one case. For the latter, the microanalytical data were consistent with the product being $[NiL^8(NO_3)]ClO_4{\cdot}0.5H_2O$. Protonated ligand salts have been documented previously in the attempted preparation of the nickel(II) complexes of other related mixed-donor macrocycles.[11]

Physical data for the complexes are listed in Table 2. The FAB mass spectra (positive ion) for the metal nitrate complexes all show strong peaks corresponding to the $[ML(NO_3)]^+$ ion, as did the spectra of those complexes incorporating both nitrate and perchlorate anions. Weaker peaks attributable to $[NiL(ClO_4)]^+$ were also present for most of the latter complexes, presumably reflecting ion rearrangement in the vapour phase. In most cases, other peaks corresponding to $[MLH_{-1}]^+$ and/or HL^+ were also identified. For the copper perchlorate complexes the expected $[CuL(ClO_4)]^+$ ion was observed in each case.

The infrared spectra (Fourier transform) of the respective complexes confirmed the presence of perchlorate counter ions (strong, broad stretching modes at approximately 1080 cm^{-1}) where they were suggested to be present by the microanalytical data. In most instances the perchlorate modes were single peaks, consistent with non-co-ordination of this anion.[18] However, the spectrum of $[CuL^8][ClO_4]_2$ contains a split perchlorate band. This may reflect the presence of different environments for the perchlorate anions in this complex arising, for example, from crystal-packing or hydrogen-bonding effects, or it may indicate a lowering of symmetry of the perchlorate group owing to co-ordination to the copper ion. The nitrate absorptions[19] (in the region 1250–1290 cm^{-1}) were partially masked by the presence of ligand bands and no attempt was made to assign these.

Where the complexes were sufficiently soluble, the conductance values in methanol indicate that most of the nitrate-containing species approximate 1 : 1 electrolytes in this solvent.[20] Even for the copper(II) complexes of L^5 and L^6 containing two perchlorate ions the values indicate that some cation–perchlorate association occurs under the conditions of measurement. For compounds containing both nitrate and perchlorate there is much evidence in the literature that nitrate will be favoured over perchlorate co-ordination. Consequently, it appears likely that a nitrate ion occupies one co-ordination position in each of the nitrate-containing complexes in solution and, at least in the case of the nickel(II) nitrate complex of L^6, the X-ray data show that such an arrangement persists in the solid state (see later).

The pale pink cobalt complexes (see Tables 1 and 2) have room-temperature magnetic moments in the range 4.69–4.85 μ_B; such values are typical of high-spin octahedral complexes.[21] The solid-state spectra of these cobalt complexes each show a broad (composite) band with a maximum at 490–495 nm, consistent with the presence of octahedral co-ordination geometries.

In each case the nickel(II) complexes have magnetic moments (3.13–3.25 μ_B) which are typical of high-spin species;[21] their solid-state and solution spectra are broadly similar suggesting that related co-ordination geometries occur in both the solid and solution. The spectra are consistent with the presence of either octahedral or distorted-octahedral co-ordination (Table 2).

The magnetic moments of the copper complexes fall in the range 1.97–2.01 μ_B and hence are typical of copper(II) with $S = \frac{1}{2}$.[21] The solid-state and solution visible electronic spectra of these complexes (Table 2) each shows a broad envelope of bands in the region 500–800 nm. The featureless nature of these spectra results in them being of little value for the assignment of the corresponding co-ordination geometries.

Stability Constants.—Comparison of the log *K* values for the bis(pyridylmethyl) pendant-arm ligands L^6–L^9 (Table 3) with the corresponding values for the previously studied parent (non-pendant-arm) derivatives show that the former yield complexes for which the respective stabilities are consistently significantly lower than for the latter. Undoubtedly this is a consequence of the participation of the pyridyl group(s) in metal co-ordination; the strong donor capacity of pyridyl nitrogen towards metal ions of the present type has previously been

Table 2 Physical data for selected metal complexes of the pendant-arm ligands L^5–L^9

			Visible spectra[c] (nm)		
Complex	Λ^a/S cm^2 mol^{-1}	μ^b/μ_B	Solid state	MeOH solution	*m/z*[d]
$[CoL^6(NO_3)]ClO_4$	*e*	4.69	490, 610(sh)		615
$[CoL^7(NO_3)]ClO_4$	*e*	4.78	495, 600(sh)		629
$[CoL^8(NO_3)]ClO_4{\cdot}0.5H_2O$	*e*	4.85	495, 570(sh)		643
$[NiL^5(NO_3)]NO_3{\cdot}2H_2O$	87	3.22	555, 975	549(31), 662(sh), 900(22)	602
$[NiL^5(NO_3)]ClO_4{\cdot}H_2O$	114	3.17	555, 810, 945	*e*	602
$[NiL^6(NO_3)]NO_3{\cdot}H_2O$	72	3.20	570, 920	572(35), 652(sh), 920(14)	614
$[NiL^7(NO_3)]NO_3{\cdot}H_2O$	69	3.18	565, 980	572(40), 652(sh), 919(14)	628
$[NiL^8(NO_3)]NO_3{\cdot}H_2O$	66	3.13	565, 960	572(37), 652(sh), 922(12)	642
$[NiL^8(NO_3)]ClO_4{\cdot}0.5H_2O$	84	3.25	570, 940	*e*	642
$[CuL^5][ClO_4]_2{\cdot}0.5H_2O$	125	1.97	615(br)	625(534), 652(529) 642	
$[CuL^6][ClO_4]_2$	132	1.97	680(br)	675(71)	656
$[CuL^8][ClO_4]_2$	*e*	2.01	580(br)	*e*	684
$[ZnL^6(NO_3)]ClO_4$	104				620
$[ZnL^7(NO_3)]ClO_4{\cdot}0.5H_2O$	90				634
$[ZnL^8(NO_3)]ClO_4$	82				648
$[CdL^5(NO_3)]ClO_4$	120				656
$[CdL^6(NO_3)]ClO_4$	126				670
$[CdL^7(NO_3)]ClO_4$	122				684
$[CdL^8(NO_3)]ClO_4$	119				696

[a] Conductance at 20 °C in methanol; expected range for a 1 : 1 electrolyte in methanol is 80–115 S cm^2 mol^{-1} while that for a 2 : 1 electrolyte is 160–220 S cm^2 mol^{-1}, see ref. 10. [b] At 23 °C. [c] All spectra contained an absorption in the ultraviolet region with a 'tail' that extended into the visible region; solid-state spectra recorded on Nujol mulls spread on filter-paper. For the solution spectra, absorption coefficients (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [d] Positive-ion FAB mass spectral peak for $[ML(NO_3)]^+$ or $[ML(ClO_4)]^+$. [e] Insufficiently soluble.

Table 3 Ligand protonation constants and stability constants[a] for the metal complexes of L^6–L^9

	Free L			$\log K_{ML}$ ($M^{2+} + L \rightleftharpoons ML^{2+}$)				
Ligand	$\log K_1^H$	$\log K_2^H$	$\log K_3^H$	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}
L^6	8.27	5.28	≈2.5	7.1	*b*	> 14	7.8	7.8
L^7	8.11	5.31	≈2.0	7.3	*b*	> 14	8.0	7.3
L^8	8.56	5.63	≈1.5	8.5	*b*	*b*	8.5	8.4
L^9	10.20	4.00	≈2.0	*b*	9.3	> 14	*b*	

[a] In 95% methanol ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4) at 25 °C; the values quoted are the mean of at least two and up to five separate determinations; unless otherwise indicated, individual values did not differ by more than 0.1 from the mean. The log *K* values for L^5 could not be determined under the conditions employed, see text. [b] Precipitation and/or competing hydrolysis inhibited $\log K_{ML}$ determination.

Table 4 Selected cation geometries (lengths in Å, angles in °) for the nickel(II) and copper(II) complexes of L^6

(*a*) Metal-atom environment: *r* is the metal–ligand atom distance; other entries in each matrix are the angles subtended at the metal by the relevant atoms at the head of the row and column

(*i*) The nickel complex

Atom	*r*	O(12)	N(2)	N(23)	N(2′)	N(23′)
O(11)	2.137(5)	59.2(2)	157.4(2)	90.5(2)	92.3(2)	90.4(2)
O(12)	2.230(4)		99.2(2)	84.5(2)	96.7(2)	149.5(2)
N(2)	2.119(6)			80.2(2)	97.0(2)	111.4(2)
N(23)	2.061(4)				177.2(2)	99.9(2)
N(2′)	2.113(4)					80.4(2)
N(23′)	2.032(5)					

(*ii*) The copper complex

Atom	*r*	O(10)	N(2)	N(23)	N(2′)	N(23′)
O(10′)	2.319(9)	60.3(3)	137.7(4)	89.4(4)	89.7(4)	94.6(4)
O(10)	2.917(10)		77.3(3)	79.3(3)	100.4(3)	154.6(3)
N(2)	2.06(1)			83.5(4)	97.4(5)	127.6(4)
N(23)	1.97(1)				179.1(5)	97.2(4)
N(2′)	2.02(1)					82.6(5)
N(23′)	2.04(1)					

(*b*) Macrocycle torsion angles

Atom sequences		Nickel complex		Copper complex	
(a)	(b)	(a)	(b)	(a)	(b)
C(1′)–C(0)–C(1)–N(2)	C(1)–C(0)–C(1′)–N(2′)	70.0(6)	−76.0(7)	41(2)	34(2)
C(0)–C(1)–N(2)–M	C(0)–C(1′)–N(2′)–M	−48.9(6)	56.5(6)	−72(1)	−59(1)
C(1)–N(2)–M–N(2′)	C(1′)–N(2′)–M–N(2)	30.2(4)	−33.1(4)	38(1)	20(1)
C(0)–C(1)–N(2)–C(21)	C(0)–C(1′)–N(2′)–C(21′)	−165.4(5)	167.7(5)	178(1)	59(1)
C(0)–C(1)–N(2)–C(3)	C(0)–C(1′)–N(2′)–C(3′)	71.4(6)	−68.7(6)	61(1)	179(1)
C(1)–N(2)–C(3)–C(4)	C(1′)–N(2′)–C(3′)–C(4′)	55.5(6)	−39.1(7)	168(1)	175(1)
M–N(2)–C(3)–C(4)	M–N(2′)–C(3′)–C(4′)	—	—	−67(1)	53(1)
N(2)–C(3)–C(4)–C(9)	N(2′)–C(3′)–C(4′)–C(9′)	−101.5(7)	109.7(7)	77(1)	−73(1)
C(3)–C(4)–C(9)–O(10)	C(3′)–C(4′)–C(9′)–O(10′)	7.9(10)	2.7(10)	−1(2)	6(2)
C(4)–C(9)–O(10)–M	C(4′)–C(9′)–O(10′)–M	—	—	−51(1)	51(1)
C(4)–C(9)–O(10)–C(11)	C(4′)–C(9′)–O(10′)–C(11′)	−124.2(8)	−164.4(7)	−162(1), 159(2)*	−105(1)
M–O(10)–C(11)–C(11′)	M–O(10′)–C(11′)–C(11)	—	—	50(1), −45(3)*	35(2), −25(2)*
C(9)–O(10)–C(11)–C(11′)	C(9′)–O(10′)–C(11′)–C(11)	175.3(8)	170.3(7)	165(1), 105(3)*	−174(1), 126(2)*
O(10)–C(11)–C(11′)–O(10′)	O(10′)–C(11′)–C(11)–O(10)	−61.8(9)	—	−57(2), 49(3)*	—
M–N(2)–C(21)–C(22)	M–N(2′)–C(21′)–C(22′)	43.9(5)	43.5(6)	40(1)	−31(1)
C(1)–N(2)–C(21)–C(22)	C(1′)–N(2′)–C(21′)–C(22′)	167.8(5)	−74.4(6)	153(1)	−152(1)
C(3)–N(2)–C(21)–C(22)	C(3′)–N(2′)–C(21′)–C(22′)	−68.6(6)	161.6(5)	−90(1)	92(1)
N(2)–C(21)–C(22)–N(23)	N(2′)–C(21′)–C(22′)–N(23′)	−38.1(6)	−27.9(9)	−33(1)	17(2)
C(21)–C(22)–N(23)–M	C(21′)–C(22′)–N(23′)–M	10.6(6)	−5.1(9)	6(1)	6(1)

* Corresponding to alternate site occupancies of C(11).

documented in log *K* studies involving open-chain analogues of L^5–L^8.[22] For each ligand the individual values are in accord with the expected Irving–Williams stability order.[23]

The log *K* values for the 14-membered derivative L^5 could not be determined under the conditions employed; in each case only the lower portions of the respective titration curves were obtained (and these corresponded to complete complex formation) before precipitation of the individual complexes occurred at higher pH values. Nevertheless, from the curves it appears likely that the stabilities of the respective complexes of L^5 are higher than those for the analogous complexes of the larger-ring derivatives L^6–L^8. Such an enhancement may be rationalised, at least in part, by the formation of more stable five-membered chelate rings (between the metal ion and the nitrogen atoms of the macrocyclic ring) in the complexes of L^5.

As is usually the case with simple amine ligands the stability constants for the respective zinc(II) and cadmium(II) complexes do not differ greatly.

The Crystal Structures.—The results of the room-temperature single-crystal structure determinations of the two complexes are consistent with their formulation as 1 : 1 adducts

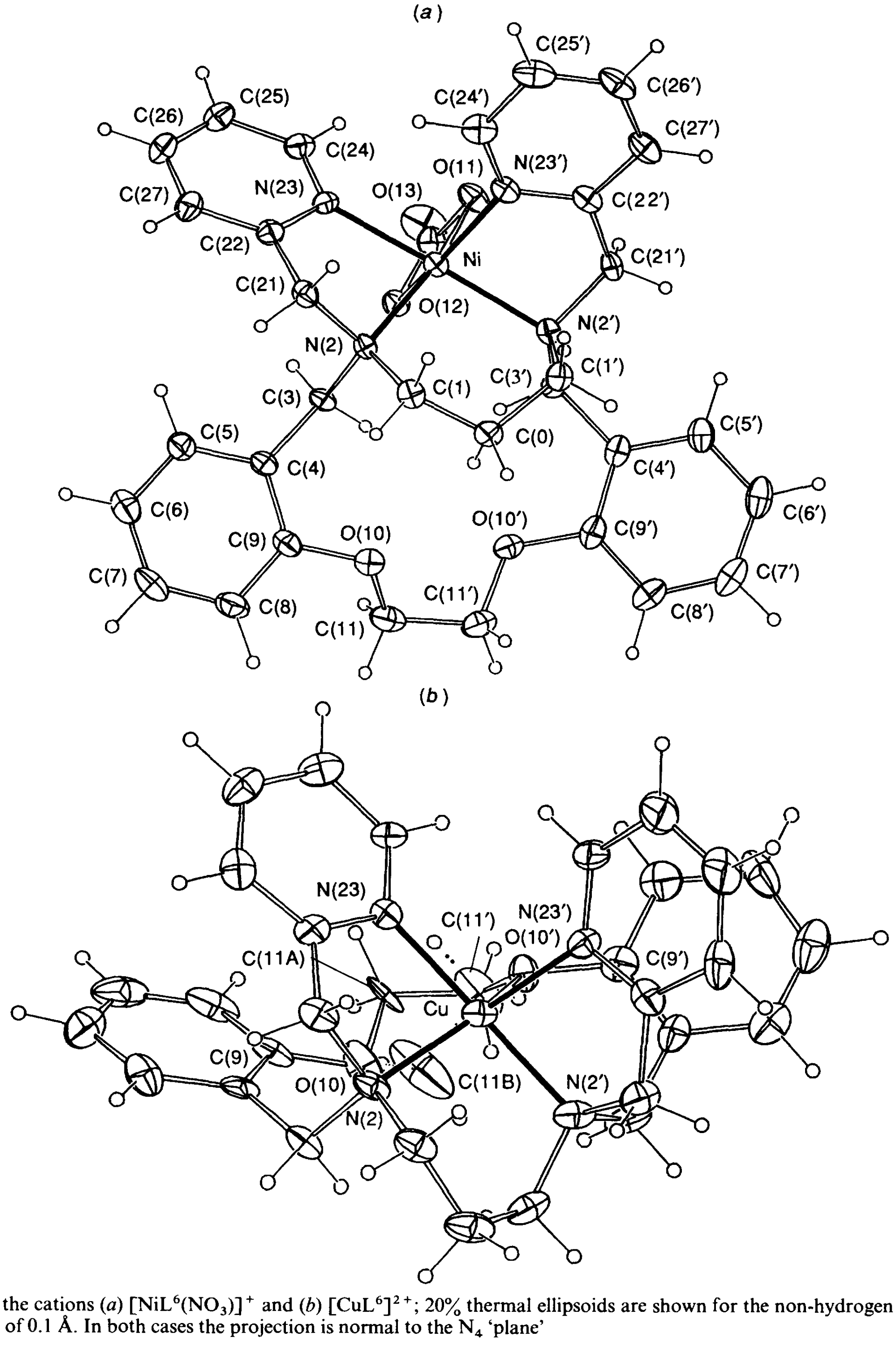

Fig. 1 Projection of the cations (*a*) $[NiL^6(NO_3)]^+$ and (*b*) $[CuL^6]^{2+}$; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogens having arbitrary radii of 0.1 Å. In both cases the projection is normal to the N_4 'plane'

of the metal(II) bis(oxyanion) salt and L^6; the nickel salt is a monohydrate. In both structures the asymmetric unit comprises the formula unit, without any crystallographically imposed symmetry, and the four nitrogen atoms of the ligand occupy four co-ordination sites about the metal. As is evident from Fig. 1 and from the data in Table 4, the ligand conformation about the metal atom in the string supported by the nitrogen atoms is similar in each structure, although some significant differences occur. Within the MN_4 co-ordination environment the metal–aliphatic nitrogen distances are, as expected, significantly longer than the metal–aromatic nitrogen distances, except in the primed section of the copper complex where they are comparable; the distances in the nickel complex are generally longer than those of the copper complex, as is also expected. The N(23)–M–N(2') angle in both complexes approaches linearity; by contrast, N(2)–M–N(23') is greatly diminished but very different in the two complexes [111.4(2) (Ni), 127.6(4)° (Cu)]. The 'bite' angles of the ligand halves are similar within each complex [80.2(2), 80.4(2), (Ni); 83.5(4), 82.6(5)° (Cu)] but differ between the two complexes somewhat, those for copper being slightly larger. The four nitrogen atoms are not coplanar, deviations of N(2), N(2'), N(23), N(23') and the metal from the N_4 'best plane' being 0.434(6), −0.489(6), −0.586(7), 0.739(7), −0.573(1) (Ni) and 0.42(1), −0.57(2), −0.44(1), 0.41(1), −0.49(2) Å (Cu); the dihedral angles between the C_5N pyridyl planes are 86.4(3) (Ni) and 73.2(6)° (Cu), the difference being associated with the change in chirality of the chelate ring, dihedral angle M–N(2)–C(21)–C(22) and its primed counterpart being 43.9(5), 43.5(6) (Ni) and 40(1), −31(1)° (Cu). The six-membered chelate ring linking the two 2-aminomethylpyridyl

Table 5 Fractional atomic coordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[NiL^6(NO_3)]NO_3{\cdot}H_2O$							
Ni	0.697 94(5)	0.849 97(6)	0.834 83(5)	N(23′)	0.787 9(3)	0.749 3(4)	0.918 8(4)
C(0)	0.861 0(4)	0.982 7(5)	0.807 2(4)	C(24′)	0.793 5(4)	0.654 8(6)	0.902 4(5)
C(1)	0.818 5(4)	0.905 9(5)	0.734 4(4)	C(25′)	0.851 2(6)	0.592 2(5)	0.970 7(6)
N(2)	0.722 1(3)	0.879 5(3)	0.715 5(3)	C(26′)	0.904 5(5)	0.628 7(7)	1.057 9(6)
C(21)	0.697 6(4)	0.787 5(5)	0.662 3(4)	C(27′)	0.899 7(5)	0.726 3(6)	1.075 4(5)
C(22)	0.610 3(5)	0.747 4(5)	0.659 7(5)	C(3′)	0.759 6(4)	1.041 3(5)	0.930 3(4)
N(23)	0.601 5(3)	0.759 0(3)	0.739 7(3)	C(4′)	0.823 7(4)	1.125 5(5)	0.973 1(4)
C(24)	0.525 5(5)	0.724 8(5)	0.743 8(5)	C(5′)	0.875 7(4)	1.133 3(5)	1.069 0(5)
C(25)	0.456 6(5)	0.678 8(5)	0.671 3(6)	C(6′)	0.933 9(5)	1.212 1(7)	1.108 4(5)
C(26)	0.466 1(6)	0.666 2(6)	0.589 1(5)	C(7′)	0.939 9(5)	1.283 7(6)	1.049 7(7)
C(27)	0.544 3(6)	0.700 9(5)	0.584 1(5)	C(8′)	0.888 9(5)	1.279 4(5)	0.955 6(6)
C(3)	0.655 6(4)	0.959 2(4)	0.664 7(4)	C(9′)	0.830 4(4)	1.201 0(5)	0.917 5(5)
C(4)	0.653 5(4)	0.995 1(5)	0.573 5(4)	O(10′)	0.773 1(3)	1.195 8(3)	0.823 9(3)
C(5)	0.600 7(4)	0.948 9(5)	0.489 7(5)	C(11′)	0.791 3(6)	1.255 6(6)	0.759 7(6)
C(6)	0.592 9(5)	0.987 1(6)	0.405 2(5)	N(1)	0.565 7(4)	0.910 1(4)	0.871 1(4)
C(7)	0.637 1(6)	1.070 2(7)	0.404 0(5)	O(11)	0.624 5(3)	0.847 9(3)	0.920 4(3)
C(8)	0.689 6(5)	1.119 8(5)	0.484 9(5)	O(12)	0.578 9(3)	0.949 4(3)	0.805 2(3)
C(9)	0.695 7(5)	1.080 3(5)	0.569 2(5)	O(13)	0.498 3(3)	0.930 1(4)	0.884 8(4)
O(10)	0.750 0(3)	1.126 7(4)	0.652 1(3)	N(1′)	1.105 5(6)	1.050 6(8)	0.740 6(5)
C(11)	0.730 0(6)	1.223 7(6)	0.663 9(6)	O(11′)	1.148 0(6)	1.117 8(7)	0.768 7(5)
C(1′)	0.882 0(4)	0.950 5(5)	0.906 1(4)	O(12′)	1.031 0(6)	1.050 2(8)	0.734 6(5)
N(2′)	0.800 0(3)	0.944 0(4)	0.927 7(3)	O(13′)	1.131 9(9)	0.982 3(7)	0.719 9(7)
C(21′)	0.829 9(4)	0.891 4(5)	1.017 9(4)	O(0)	0.677 5(4)	1.027 7(5)	1.104 9(4)
C(22′)	0.840 6(4)	0.784 8(5)	1.003 7(5)				
(*b*) $[CuL^6][ClO_4]_2$							
Cu	0.394 54(6)	0.258 58(8)	0.454 9(1)	N(23′)	0.354 9(4)	0.269 6(6)	0.586 6(8)
C(0)	0.420 7(7)	0.424 0(7)	0.365(1)	C(24′)	0.351 9(5)	0.228 6(8)	0.670(1)
C(1)	0.450 3(5)	0.385 8(7)	0.446(1)	C(25′)	0.329 3(6)	0.245(1)	0.762(1)
N(2)	0.456 4(4)	0.307 9(6)	0.422 9(8)	C(26′)	0.308 6(7)	0.309(1)	0.765(1)
C(21)	0.487 2(5)	0.278 8(8)	0.504(1)	C(27′)	0.309 8(6)	0.355(1)	0.681(2)
C(22)	0.477 5(6)	0.199 8(8)	0.521 2(9)	C(3′)	0.313 9(6)	0.309 0(8)	0.338(1)
N(23)	0.434 0(4)	0.180 6(6)	0.508 2(8)	C(4′)	0.285 3(6)	0.254 1(9)	0.391(1)
C(24)	0.421 9(5)	0.112 8(8)	0.528(1)	C(5′)	0.241 2(8)	0.269 3(9)	0.424(1)
C(25)	0.452 1(6)	0.063 9(8)	0.563(1)	C(6′)	0.214 2(7)	0.218(1)	0.468(2)
C(26)	0.497 7(6)	0.083 4(9)	0.576(1)	C(7′)	0.229 9(7)	0.150(1)	0.483(1)
C(27)	0.510 8(5)	0.152(1)	0.553(1)	C(8′)	0.275 5(6)	0.131 3(8)	0.451(1)
C(3)	0.479 4(5)	0.300 2(8)	0.317(1)	C(9′)	0.302 6(6)	0.186 4(9)	0.404(1)
C(4)	0.496 7(7)	0.224 9(7)	0.292(1)	O(10′)	0.347 2(3)	0.173 9(5)	0.376 4(7)
C(5)	0.544 2(7)	0.210(1)	0.299(1)	C(11′)	0.354 1(7)	0.135(1)	0.280(1)
C(6)	0.559 9(8)	0.144(1)	0.277(1)	Cl(1)	0.353 5(2)	−0.070 5(3)	0.457 3(5)
C(7)	0.529(1)	0.091(1)	0.244(2)	O(11)	0.363 2(5)	−0.144 7(7)	0.450(1)
C(8)	0.483 5(8)	0.106(1)	0.238(1)	O(12)	0.389 4(5)	−0.035 3(7)	0.400(1)
C(9)	0.466 6(7)	0.171 7(9)	0.260(1)	O(13)	0.353 8(6)	−0.040(1)	0.557(1)
O(10)	0.422 2(5)	0.191 2(7)	0.256 5(9)	O(14)	0.312 6(5)	−0.058 9(8)	0.409(1)
C(11A)*	0.397(1)	0.118(2)	0.257(2)	Cl(1′)	0.401 0(2)	0.079 5(3)	0.905 5(4)
C(11B)*	0.382(2)	0.168(4)	0.207(3)	O(11′)	0.439 4(6)	0.049(1)	0.946(2)
C(1′)	0.378 7(6)	0.385 1(8)	0.326(1)	O(12′)	0.397 9(6)	0.146(1)	0.949(2)
N(2′)	0.353 4(5)	0.337 3(6)	0.399 9(9)	O(13′)	0.367 8(5)	0.038 9(9)	0.925(2)
C(21′)	0.336 8(5)	0.378 9(8)	0.494(1)	O(14′)	0.409 4(8)	0.093(1)	0.807(1)
C(22′)	0.333 4(5)	0.331 0(9)	0.589(1)				

* Site occupancy factor = 0.5.

entities is nicely chair-like in the nickel complex but adopts a distorted-boat arrangement in the copper complex (see the first three lines of the torsion angles in Table 4).

From the above considerations it is clear that the metal-atom environments in both complexes deviate considerably from octahedral, approaching more closely the requirements of a trigonal-bipyramidal array with the linearly disposed ligand atoms, N(23) and N(2′), in the axial positions. The occupancy of the fifth co-ordination site differs between the two complexes, being associated with differing interactions between counter ions and the O,O′ 'strap' of the ligand. The fifth co-ordination site in the nickel complex is occupied by the symmetrically bidentate nitrate ion [Ni–O 2.137(5), 2.230(4) Å], a ligand of small 'bite'. Associated geometries are given in Table 4. As well, it is of interest that the angles associated with the hypothetically mean N(1) [N(1)–Ni–N(2, 23′) and N(1)–Ni–N(2′, 23) 128.3(2), 85.4(2) and 96.9(2), 120.0(2)°] are indicative of an unsymmetrical disposition *vis-à-vis* the associated components of the trigonal bipyramid. This is presumably a consequence of the coplanarity of the nitrate group with the Ni–N(2, 23′) array, with its unsymmetrical aliphatic–aromatic nitrogen atom combination. As is evident in Fig. 1, O(10, 10′) lie well clear of the metal atom.

Presumably in the copper complex the copper–perchlorate oxygen interactions are uncompetitive with the copper–ether oxygen alternative and, in consequence, the ligand 'strap' is reoriented to permit the latter. The Cu–O lengths are grossly unsymmetrical, with Cu–O(10′,10) 2.319(9), 2.917(10) Å both long, where O(10′) is co-ordinated while any interaction with O(10) must be considered dubious (see Fig. 1), particularly in view of the associated disorder (see above). Again the interaction of O(10′) in the trigonal plane is lopsided [O(10′)–Cu–N(2, 23′) and O(10′)–Cu–N(2′, 23) 137.7(4), 94.6(4) and 89.7(4), 89.4(4)°] although the angles to the axial atoms are closely rectangular. The equatorial 'lopsidedness' is similar in sign and magnitude to that of N(1) in the nickel complex as described above.

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