Studies of Pendant-arm Macrocyclic Ligands. Part 5.† Synthesis of Two Pyridine-containing Penta-aza Macrocycles with Single Pyrrolidinyl Pendant Arms and Characterisation of their Nickel(II) and Copper(II) Complexes. Crystal Structure of Perchlorato{7-[2′-(1″-pyrrolidinyl)ethyl]-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene}nickel(II) Perchlorate‡

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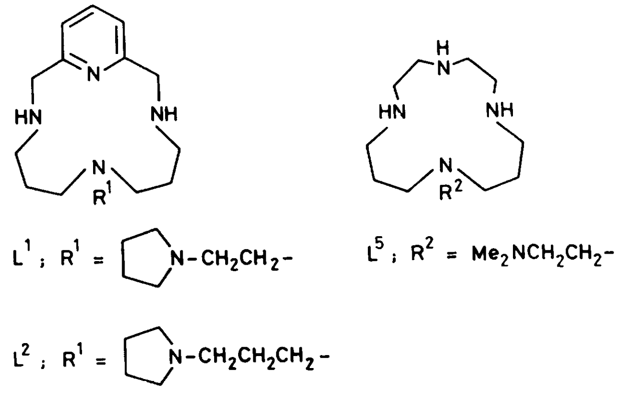
Two new pyridine-containing penta-aza macrocyclic ligands, 7-[2′-(1″-pyrrolidinyl)ethyl]- and 7-[3′-(1″-pyrrolidinyl)propyl]-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1 and L^2 respectively) have been prepared, and their nickel(II) and copper(II) complexes of formulae $[M(L^1)(OClO_3)][ClO_4]$ and $[M(HL)][ClO_4]_3$ (M = Ni or Cu, L = L^1 or L^2) have been isolated and characterised. In the octahedral complex $[Ni(L^1)(OClO_3)][ClO_4]$ the presence of a co-ordinated perchlorate group has been established by *X*-ray crystallography, and the macrocyclic ligand found to co-ordinate close to the corners of a square pyramid with the pendant pyrrolidinyl group at the apical position.

There is considerable current interest in the synthesis and investigation of functionalised macrocyclic ligands and their metal complexes, especially those with pendant co-ordinating arms.[1-12] So far macrocycles with pendant co-ordinating amino, amido, pyridyl, hydroxo, phenolato, and carboxylato arms have been investigated. We report here the isolation of two pyridine-containing macrocycles (L^1 and L^2) which contain pendant arms terminating in pyrrolidinyl groups.

The pendant arms of these new macrocycles were designed to produce five- and six-membered chelate rings, and were obtained for comparison with the related ligands containing $-(CH_2)_nNMe_2$ arms ($n = 2$ or 3) which we reported previously.[9,10] It was expected that the bulkier pyrrolidinyl groups would hinder folding of the macrocycles, and be more likely to produce complexes in which the metal ion is six-co-ordinate, with an axial unidentate ligand (X) occupying a *trans* position to the pendant arm, structure type (**I**), rather than the folded macrocyclic five-co-ordinate structures, type (**II**), found previously.[9]

The nickel(II) and copper(II) complexes of formula $M(L^1)(ClO_4)_2$ have been isolated and characterised, together with complexes of the type $[M(HL)][ClO_4]_3$ (M = Ni or Cu, L = L^1 or L^2) in which the pendant arm is protonated and non-co-ordinating. An *X*-ray structure determination of $[Ni(L^1)(OClO_3)][ClO_4]$ has established the presence of a co-ordinated perchlorate group in a six-co-ordinate complex of type (**I**). The ligands have been characterised by elemental analyses, ^1H and ^{13}C n.m.r. Their complexes were also studied by u.v.–visible spectrophotometry and magnetic susceptibility measurements, and the Ni^{2+} complexes of L^1 by fast atom bombardment (f.a.b.) mass spectrometry.



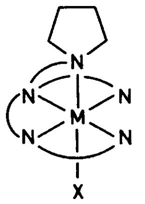
L^1; R^1 = pyrrolidinyl N-CH_2CH_2-

L^5; R^2 = $Me_2NCH_2CH_2$-

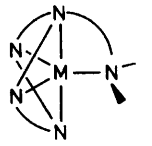
L^2; R^1 = pyrrolidinyl N-$CH_2CH_2CH_2$-

L^3; R^1 = $Me_2NCH_2CH_2$-

L^4; R^1 = $Me_2NCH_2CH_2CH_2$-



(**I**)



(**II**)

Experimental

Materials and Methods.—All chemicals used were of the highest available purity, and were not purified further. Hexakis(dimethyl sulphoxide)-nickel(II) and -copper(II) perchlorates were prepared by a published method.[13] ^1H-Decoupled ^{13}C n.m.r. spectra were recorded at either 45.28 or 100.58 MHz with Bruker WH180 or WH400 Fourier–transform spectrometers, respectively, and ^1H n.m.r. spectra were taken at 220 MHz with a continuous-wave Perkin-Elmer R34 n.m.r. instrument. Chemical shifts are reported on the δ scale relative to internal $SiMe_4$ at δ = 0. U.v.–visible and i.r. spectra were recorded with Shimadzu (model 365) and Perkin-Elmer (model 580B) spectrophotometers, and mass spectra with a Kratos (model MS80) instrument. Magnetic susceptibility measure-

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† Part 4, N. W. Alcock, E. H. Curzon, P. Moore, H. A. A. Omar, and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1985, 1361.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1. pp. xvii–xx.
Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. U.v.-visible spectra [λ/nm (ε/dm^3 mol^{-1} cm^{-1})] and magnetic moments ($\mu_{eff.}$) at room temperature in nitromethane solution

Complex	Colour	$\lambda_{max.}(\varepsilon)$	$\mu_{eff.}$
[Ni(L^1)(OClO$_3$)] [ClO$_4$]	Blue	572 (45), 772 (15), 1 368 (17)	2.8
[Ni(HL^1)][ClO$_4$]$_3$	Yellow	468 (148)	0.0
[Cu(L^1)(OClO$_3$)] [ClO$_4$]	Blue	600 (187), 848 (37)	1.7
[Cu(HL^1)][ClO$_4$]$_3$	Purple	554 (122)	1.4*
[Ni(HL^2)][ClO$_4$]$_3$	Yellow	468 (156)	0.0
[Cu(HL^2)][ClO$_4$]$_3$	Purple	550 (156)	1.4*

* Average of two independent measurements with different samples ($\pm$0.05). These unusually low values could indicate some magnetic interaction between two copper(II) ions, possibly through a bridging perchlorate ion. No other evidence for such an interaction was found, and the question was not pursued further.

ments were measured by the method of Evans [14] using a Bruker WH90 n.m.r. spectrometer. The magnetic data and visible spectra are recorded in Table 1.

Preparations.—The synthetic routes are outlined in Schemes 1 and 2.

Preparation of compound (**1**). 1-(2-Aminoethyl)pyrrolidine (24 g, 0.21 mol) was dissolved in acrylonitrile (300 cm^3, 4.56 mol) and glacial ethanoic acid (25.2 g, 0.42 mol) was added. The solution was heated under reflux for 24 h, and excess acrylonitrile was then removed under vacuum. The residue was extracted with dichloromethane (3 × 100 cm^3) and the extract shaken with 0.88 ammonia solution (150 cm^3). The organic phase was separated, washed with water, dried with anhydrous magnesium(II) sulphate, filtered, and then evaporated to give a thick yellow oil. Fractional distillation of the crude product gave a colourless oil (36 g, 0.16 mol, 77%), b.p. 160 °C (0.07 mmHg). ^{1}H N.m.r. (CDCl$_3$): 1.77 (4 H, m), 2.60 (12 H, m), and 2.92 p.p.m. (4 H, t). I.r. (thin film): 2 342 cm^{-1} (CN).

Preparation of compound (**2**). Compound (**1**) (28.6 g, 0.13 mol) was dissolved in dry ethanol (400 cm^3) and stirred under nitrogen during the slow stepwise addition of sodium metal (50 g, 2.17 mol). The resulting solution was heated under reflux for 8 h, and then poured into an equal volume of distilled water. Extraction with dichloromethane (5 × 200 cm^3) followed by drying of the extracts with anhydrous magnesium(II) sulphate, filtration and evaporation gave a crude oil (25 g). Careful fractional distillation gave compound (**2**) (21 g, 0.092 mol, 70%), b.p. 105 °C (0.05 mmHg). ^{1}H N.m.r. (CDCl$_3$): 1.30 (4 H, s), 1.59 (4 H, t), 1.75 (4 H, m), 2.55 (12 H, m), and 2.70 p.p.m. (4 H, t); ^{13}C n.m.r. (CDCl$_3$): 54.49 (1), 54.41 (2), 53.15 (1), 52.30 (2), 40.61 (2), 31.10 (2), and 23.38 p.p.m. (2). I.r. (thin film): 3 350 cm^{-1} (NH).

Preparation of compound (**3**). Pyrrolidine (50 g, 0.7 mol) was dissolved in acrylonitrile (100 cm^3, 1.52 mol) and the mixture heated under reflux at 90 °C for 3 d in a nitrogen atmosphere and with the reaction flask protected from light. The excess acrylonitrile was then removed by vacuum distillation, and the crude product distilled at 0.5 mmHg (b.p. 60 °C). The yield of (**3**) was almost quantitative (84 g, 0.68 mol, 98%). ^{1}H N.m.r. (CDCl$_3$): 1.80 (4 H, m), 2.59 (6 H, m), and 2.80 p.p.m. (2 H, t).

Preparation of compound (**4**). Compound (**3**) (16.12 g, 0.13 mol) was reduced with sodium metal (25 g, 1.09 mol) in ethanol (200 cm^3) in the way described for compound (**2**). Compound (**4**) was extracted with dichloromethane (5 × 200 cm^3) and worked-up as before to give a crude yellow oil (14 g) which distilled at 35 °C (0.5 mmHg), yielding 12 g (0.09 mol, 72%) of pure product. ^{1}H N.m.r. (CDCl$_3$): 1.27 (2 H, s), 1.68 (2 H, t), 1.81 (4 H, m), 2.53 (6 H, m), and 2.80 p.p.m. (2 H, t).

Preparation of compound (**5**). Compound (**4**) (11.52 g, 0.09 mol) was reacted with acrylonitrile (128 cm^3, 1.95 mol) in the presence of glacial ethanoic acid (10.8 g, 0.18 mol) as described for compound (**1**). The product was worked-up in the same way, using dichloromethane (200 cm^3) in the extraction, and washing with 0.88 ammonia (100 cm^3). The product was distilled at 180 °C (0.1 mmHg) and obtained in 85% yield (18 g, 0.08 mol). ^{1}H N.m.r. (CDCl$_3$): 1.78 (6 H, m), 2.60 (12 H, m), and 2.95 p.p.m. (4 H, t); ^{13}C n.m.r. (CDCl$_3$): 118.92 (2), 54.44 (2), 54.10 (2), 47.77 (2), 45.04 (1), 29.00 (1), 23.34 (2), and 18.48 p.p.m. (1)

Preparation of compound (**6**). Compound (**5**) (11.72 g, 0.05 mol) was reduced with sodium metal (19.2 g, 0.83 mol) in ethanol (250 cm^3) in the way described for compound (**2**). Compound (**6**) was extracted with dichloromethane (5 × 200 cm^3) and worked-up as before to give a crude orange oil (10 g) which distilled at 140 °C (0.1 mmHg), yielding 7.8 g (0.032 mol, 64%) of pure product. ^{1}H N.m.r. (CDCl$_3$): 1.30 (4 H, br), 1.65 (6 H, m), 1.80 (4 H, m), 2.55 (12 H, m), and 2.83 p.p.m. (4 H, t); ^{13}C n.m.r. (CDCl$_3$): 54.54 (1), 54.17 (2), 52.17 (1), 51.87 (2), 40.66 (2), 31.05 (2), 26.64 (1), and 23.39 p.p.m. (2).

Preparation of L^1. $NiCl_2 \cdot 6H_2O$ (2.35 g, 9.9 mmol) was dissolved in ethanol–water (1:1, 30 cm^3) and compound (**2**) (2.26 g, 9.9 mmol) added to give a blue solution. Pyridine-2,6-dicarbaldehyde (1.34 g, 9.9 mmol) was then added, followed by ethanoic acid (0.8 cm^3), and the resulting brown solution was stirred for 2 h, then heated at 80 °C for 6 h. The solution was then cooled with ice and sodium tetrahydroborate (1.5 g, 39.7 mmol) was added slowly over a period of 30 min. The mixture was stirred at room temperature until effervescence ceased, and then heated at 80 °C for 2 h. The ethanol was then removed by evaporation, and sodium cyanide (4 g, 81.6 mmol) was added. After heating at 80 °C for 1 h, the reaction mixture was cooled and basified with 15% aqueous NaOH to pH 12. The solution was extracted with dichloromethane (8 × 50 cm^3) and the combined extracts were dried with anhydrous magnesium(II) sulphate. Filtration, evaporation, and distillation with a Kugelrohr apparatus gave L^1 (1.26 g, 38 mmol, 38%) as a pale yellow liquid, b.p. 130—132 °C (0.1 mmHg). ^{13}C N.m.r. (CD$_3$NO$_2$): 24.38 (2), 28.76 (2), 47.01 (1), 53.56 (2), 54.25 (2), 55.07 (3), 55.27 (2), 121.10 (2), 137.56 (1), and 161.22 p.p.m. (2); ^{1}H n.m.r. (CDCl$_3$): 1.71 (8 H, m), 2.50 (16 H, m), 3.89 (4 H, s), 7.00 (2 H, d), and 7.55 p.p.m. (1 H, t).

Preparation of [Ni(L^1)(OClO$_3$)][ClO$_4$]. A solution of L^1 (0.166 g, 0.5 mmol) in ethanol (10 cm^3) was added to a solution of [Ni(dmso)$_6$][ClO$_4$]$_2$ (0.364 g, 0.5 mmol; dmso = dimethyl sulphoxide) in ethanol (10 cm^3). The resulting purple precipitate was filtered off, washed with cold ethanol, then diethyl ether, and dried *in vacuo* to give [Ni(L^1)(OClO$_3$)][ClO$_4$] (0.204 g, 0.4 mmol, 81%) (Found: C, 38.3; H, 5.8; N, 11.7. Calc. for $C_{19}H_{33}Cl_2N_5NiO_8$: C, 38.7; H, 5.7; N, 11.9%). The highest mass peaks in the f.a.b. mass spectrum were at *m/z* 488 and 490 as calculated for the [Ni(L^1)(ClO$_4$)]$^+$ ion.

Preparation of [Ni(HL^1)][ClO$_4$]$_3$. [Ni(L^1)(OClO$_3$)][ClO$_4$] (0.118 g, 0.2 mmol) was stirred in ethanol (10 cm^3) and 4 or 5 drops of 70% perchloric acid added slowly causing a complete and rapid colour change from purple to orange-red. The precipitate was filtered off, washed with cold ethanol, then diethyl ether, and dried *in vacuo* to give [Ni(HL^1)][ClO$_4$]$_3$ (0.128 g, 0.18 mmol, 92%) (Found: C, 32.6; H, 5.2; N, 10.1. Calc. for $C_{19}H_{34}Cl_3N_5NiO_{12}$: C, 33.1; H, 5.0; N, 10.2%). Peaks were found in the f.a.b. mass spectrum at *m/z* 590 and 588 as calculated for the [Ni(HL^1)(ClO$_4$)$_2$]$^+$ ion.

Preparation of [Cu(L^1)(OClO$_3$)][ClO$_4$] *and* [Cu(HL^1)]-[ClO$_4$]$_3$. These were obtained in 88 and 93% yields as blue and purple solids respectively, using the same methods described for the nickel(II) analogues (Found for blue solid: C, 37.0; H, 5.5; N,

Table 2. Atomic co-ordinates (× 10^4) for $[Ni(L^1)(OClO_3)][ClO_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	2 328(1)	6 871(1)	6 789(1)	C(3)	2 398(10)	9 526(12)	7 788(8)
Cl(1)	3 674(2)	1 849(4)	5 789(2)	C(4)	1 748(8)	9 730(11)	6 283(7)
Cl(2)	13(2)	7 250(3)	6 790(2)	C(5)	1 456(8)	8 851(14)	5 546(9)
O(11)	2 904(7)	2 568(10)	5 496(9)	C(6)	975(8)	9 235(13)	4 788(8)
O(12)	4 434(7)	2 671(12)	5 857(8)	C(7)	658(8)	8 307(14)	4 173(7)
O(13)	3 697(9)	1 428(15)	6 610(8)	C(8)	806(7)	6 881(15)	4 353(7)
O(14)	3 686(11)	659(12)	5 349(8)	C(9)	1 294(8)	6 521(12)	5 131(7)
O(21)	944(5)	7 022(8)	7 150(5)	C(10)	1 408(8)	5 065(11)	5 426(7)
O(22)	−501(6)	6 488(12)	7 188(7)	C(11)	1 613(8)	3 955(12)	6 775(7)
O(23)	−194(7)	6 999(17)	5 955(7)	C(12)	2 250(9)	3 739(11)	7 605(8)
O(24)	−162(7)	8 617(10)	6 883(9)	C(13)	2 364(9)	4 987(11)	8 200(8)
N(1)	2 828(6)	6 224(9)	7 967(6)	C(14)	3 802(8)	5 916(12)	8 068(7)
N(2)	2 422(7)	9 036(9)	6 980(6)	C(15)	4 008(8)	5 546(12)	7 284(7)
N(3)	1 634(6)	7 462(10)	5 697(5)	C(16)	4 277(8)	7 807(12)	6 765(8)
N(4)	1 981(6)	4 887(9)	6 242(5)	C(17)	5 028(8)	7 431(13)	6 379(9)
N(5)	3 656(6)	6 611(8)	6 643(6)	C(18)	4 661(8)	6 263(13)	5 777(8)
C(1)	2 748(9)	7 286(12)	8 608(8)	C(19)	3 712(8)	6 106(13)	5 815(8)
C(2)	3 049(9)	8 754(13)	8 455(9)				

11.6. Calc. for $C_{19}H_{35}Cl_2CuN_5O_9$: C, 37.3; H, 5.8; N, 11.4%. Found for purple solid: C, 32.8; H, 5.1; N, 10.3%. Calc. for $C_{19}H_{34}Cl_3CuN_5O_{12}$: C, 32.9; H, 4.9; N, 10.1%).

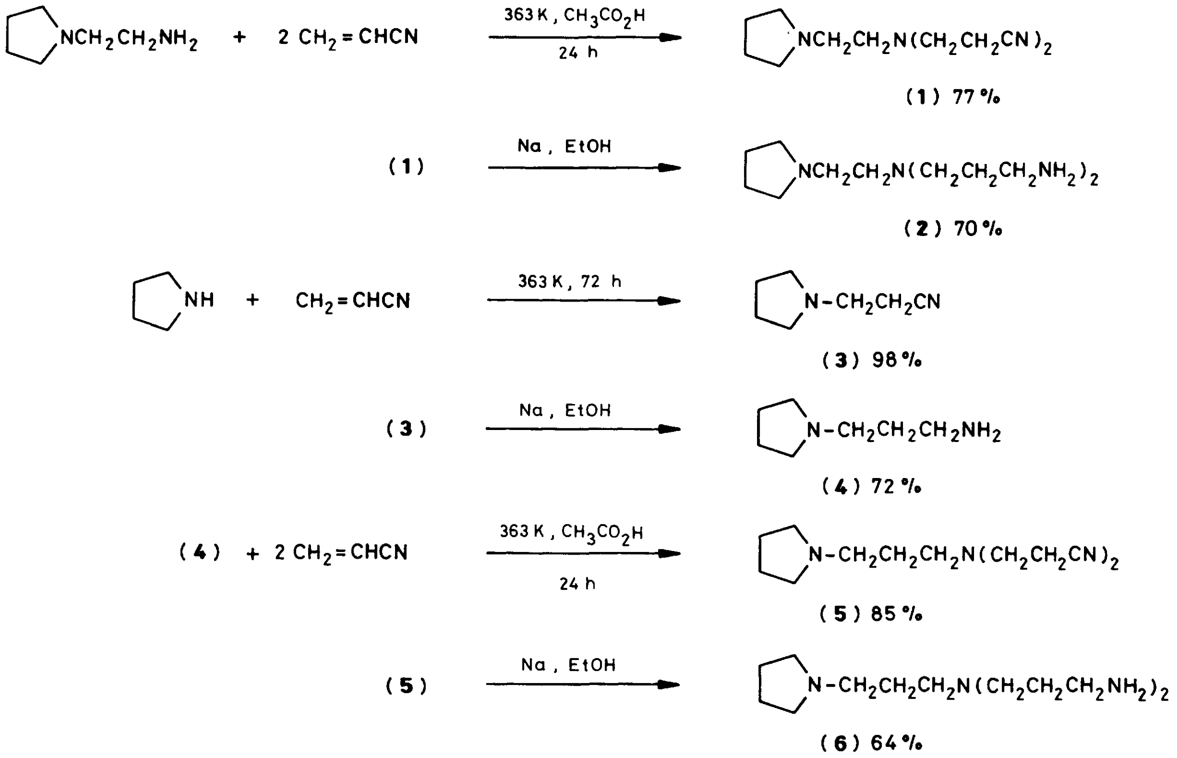
Preparation of L^2. $NiCl_2{\cdot}6H_2O$ (2.35 g, 9.9 mmol) and compound (**6**) (2.40 g, 9.9 mmol) were dissolved in ethanol–water (1:1, 30 cm^3) to give a greenish-blue solution. Pyridine-2,6-dicarbaldehyde (1.34 g, 9.9 mmol) and glacial ethanoic acid (0.8 cm^3) were added and the solution stirred for 2 h. Unlike the preparation of L^1, heating the solution at 80 °C for 6 h did not bring about the expected template reaction, there being no noticeable change in the colour of the solution from blue to brown. However, on continued heating at 80 °C for 4 d, the expected colour change did occur. The solution was then cooled on ice, and treated with sodium tetrahydroborate (1.59 g, 39.7 mmol) as described in the preparation of L^1. The product was worked-up in the way described for L^1 to give L^2 (after Kugelrohr distillation: 0.95 g, 0.28 mmol, 28%), b.p. 120—122 °C (0.05 mmHg). ^{13}C N.m.r. ($CDCl_3$): 159.46 (2), 136.37 (1), 120.49 (2), 54.73 (2), 54.27 (5), 52.04 (2), 46.44 (1), 27.60 (1), and 23.42 p.p.m. (4). There was evidence in the ^{13}C n.m.r. spectrum of a small amount of impurity, but the ligand was used without further purification, since this was found to give pure complexes.

Preparation of nickel(II) *and copper*(II) *complexes of* L^2. These complexes were prepared on a 0.5-mmol scale by the methods described for the analogous complexes of L^1. Mixing solutions of $[Ni(dmso)_6][ClO_4]_2$ (0.364 g) in ethanol (10 cm^3) with L^2 (0.173 g) in ethanol (10 cm^3) gave an orange solution which on cooling on ice gave yellow-orange crystals (0.18 g). The n.m.r. spectra and combustion analysis showed that the diamagnetic protonated ligand complex $[Ni(HL^2)][ClO_4]_3$ had formed (Found: C, 33.8; H, 5.0; N, 9.8. Calc. for $C_{20}H_{36}Cl_3N_5NiO_{12}$: C, 34.1; H, 5.2; N, 9.9%). ^{13}C N.m.r. (CD_3NO_2): 160.04 (2), 143.05 (1), 120.66 (2), 56.94 (2), 56.84 (2), 55.89 (2), 54.44 (1), 51.09 (2), 49.91 (1), 24.20 (2), 24.03 (2), and 18.25 p.p.m. (1). Using the same method with $[Cu(dmso)_6][ClO_4]_2$ (0.365 g) and L^2 (0.173 g) gave a blue solid (0.200 g) which analysed as a mixture of $[Cu(L^2)(OClO_3)][ClO_4]$ and $[Cu(HL^2)][ClO_4]_3$. This mixture was converted to the monoprotonated ligand complex by suspending it in ethanol (10 cm^3) and adding a few drops of 70% $HClO_4$. A purple solid formed which was washed with ethanol and diethyl ether (Found: C, 32.8; H, 5.1; N, 10.3. Calc. for $C_{20}H_{36}Cl_3CuN_5O_{12}$: C, 32.9; H, 4.9; N, 10.1%).

Crystal Data for $[Ni(L^1)(OClO_3)][ClO_4]$.—The crystals (pink prisms and plates) of formula $C_{19}H_{33}Cl_2N_5NiO_8$, M = 589.12, are monoclinic, space group $P2_1/c$, with a = 15.583(3), b = 9.656(3), c = 16.835(3) Å, β = 104.95(2)°, U = 2 447.4(10) $Å^3$, Z = 4, D_c = 1.50 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 10.68 cm^{-1}, F(000) = 1 232.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 45°, with scan range ±1.2° (2θ) around $K_{\alpha 1}$–$K_{\alpha 2}$ angles, scan speed 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The crystal was held at ambient temperature. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 high-angle reflections. 1 394 Observed reflections with $I/\sigma(I) > 3.0$ were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last by Gaussian integration; maximum and minimum transmission factors were 0.83 and 0.89. The crystal dimensions were 0.17 × 0.33 × 0.24 mm. Systematic absences $h0l$, $l = 2n$; $0k0$, $k = 2n$, indicated space group $P2_1/c$. The heavy atom was located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.07 $Å^2$, as defined by the molecular geometry, and not refined. Final refinement was by cascaded least-squares methods, with anisotropic thermal parameters for all atoms other than hydrogen. The largest peak on a final difference Fourier synthesis was of height 0.8 e $Å^{-3}$ (in the vicinity of the ClO_4^- ion). A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.0009 was used. This was shown to be satisfactory by a weight analysis. The final R value was 0.059. Computing was with the SHELXTL system[15] on a Data General DG30 computer. Scattering factors were in the analytical form, and anomalous dispersion factors were taken from ref. 16. Final atomic co-ordinates are given in Table 2, and selected bond lengths and angles in Table 3.

Crystal Data for $[Ni(HL^2)][ClO_4]_3$.—The crystals of formula $C_{20}H_{36}Cl_3N_5NiO_{12}$, M = 703.6, are yellow blocks which are apparently monoclinic, space group $P2_1/n$, with a = 18.308(3), b = 7.640(1), c = 20.618(3) Å, α = 90.00(1), β = 90.27(1), γ = 89.97(1)° (values of α and γ of 90° were used in the calculations), U = 2 884.0(9) $Å^3$, Z = 4, D_c = 1.39 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 9.2 cm^{-1}, F(000) = 1 380.



Scheme 1.

Table 3. Selected bond lengths (Å) and angles (°) in $[Ni(L^1)(OClO_3)][ClO_4]$

Ni–N(1)	2.034(9)	Ni–N(4)	2.134(9)
Ni–N(2)	2.114(9)	Ni–N(5)	2.159(10)
Ni–N(3)	1.961(8)	Ni–O	2.393(8)
N(1)–Ni–N(2)	99.3(4)	N(1)–Ni–N(3)	169.5(4)
N(2)–Ni–N(3)	81.7(4)	N(1)–Ni–N(4)	97.8(3)
N(2)–Ni–N(4)	162.4(3)	N(3)–Ni–N(4)	80.8(4)
N(1)–Ni–N(5)	86.4(4)	N(4)–Ni–N(5)	89.4(3)
N(2)–Ni–N(5)	95.8(4)	N(3)–Ni–N(5)	103.9(4)
O–Ni–N(1)	85.1(3)	O–Ni–N(2)	86.2(4)
O–Ni–N(3)	84.5(3)	O–Ni–N(4)	91.1(3)
O–Ni–N(5)	171.5(3)		

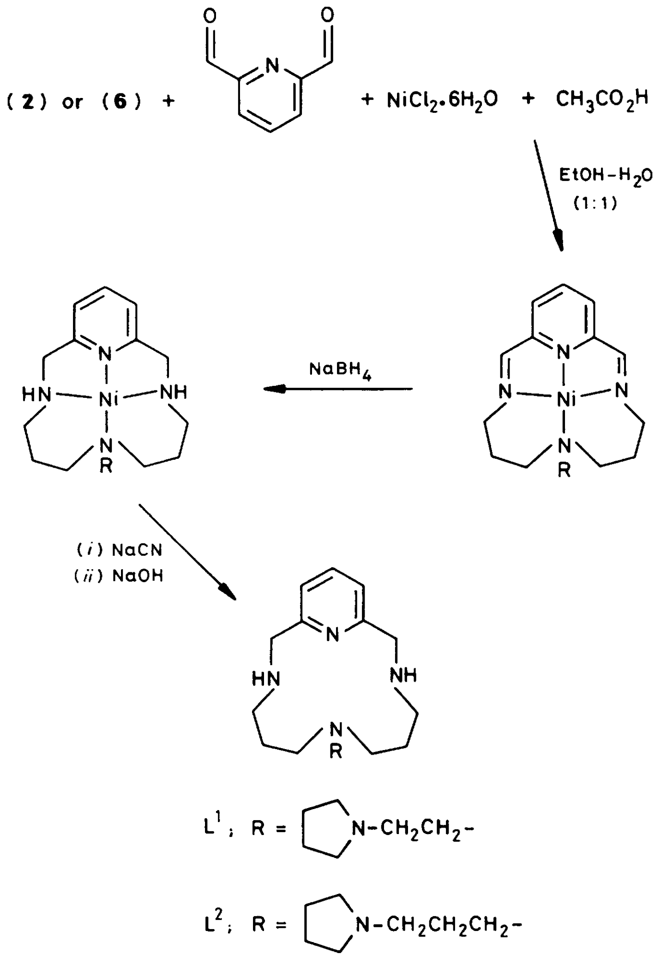
Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range $\pm 0.9(2\theta)$ around the $K_{\alpha 1}$–$K_{\alpha 2}$ angles, scan speed 2.5—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections and showed no significant changes during data collection. Unit-cell dimensions and standard deviations were obtained by a least-squares fit to 15 high-angle reflections. 1 453 Observed reflections with $I/\sigma(I) > 3.0$ were used in the refinement and corrected for Lorentz and polarisation effects. Systematic absences were $h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$. The Ni atom was located by Patterson techniques, and most light atoms were found on successive Fourier syntheses, showing the unco-ordinated pendant arm in an extended configuration as expected, and the presence of the three $[ClO_4]^-$ ions. Refinement proceeded to $R = 0.12$, but several of the ring atoms had large thermal parameters, or could not be located at all. An attempt at refinement in space group Pn produced no improvement. The problem was clearly caused either by severe disorder in the macrocyclic ring, or by undetected twinning (plausible in view of the value of β). The determination did reveal the gross nature of the complex, and the expected protonated pendant arm. It was not felt that re-collection of the data was worthwhile as the structure clearly contained a square-planar Ni^{2+} ion. The determination was therefore terminated at this stage.

Results and Discussion

Ligand Syntheses.—The Michael addition of excess acrylonitrile to 1-(2-aminoethyl)pyrrolidine proceeds smoothly in the presence of ethanoic acid as a catalyst. We have invariably observed that addition of this catalyst gives cleaner products and the reaction time is significantly shortened. The two nitrile groups of (**1**) are readily reduced to the corresponding amino groups [(**2**); Scheme 1] using sodium in ethanol. The amine (**6**) [analogous to (**2**) but containing an extra CH_2 group] required for the synthesis of L^2 was synthesised in a multistep process starting from pyrrolidine as shown in Scheme 1.

The macrocycles were prepared by a standard template method as shown in Scheme 2. Formation of the di-imine macrocyclic complexes took 6—8 h starting with amine (**2**), and several days for the reaction of pyridine-2,6-dicarbaldehyde with (**6**) in the presence of Ni^{2+}. The sluggish nature of these reactions, especially in the latter case, may be due to the formation of 'umbrella-like' complexes well known for the analogous ligand tren (2,2′,2″-triaminotriethylamine), in which the primary amino groups are not favourably disposed for the di-imine formation which requires a planar geometry. Sodium tetrahydroborate was used to reduce the two imine groups, and the free ligands were liberated by treatment with excess sodium cyanide.

Synthesis of Nickel(II) *and Copper*(II) *Complexes of* L^1 *and* L^2.—Reactions of L^1 with $[M(dmso)_6][ClO_4]_2$ (M = Ni or



Scheme 2.

Cu) in ethanolic solution rapidly gives complexes of formula $M(L^1)(ClO_4)_2$ which precipitate soon after mixing and can be recrystallised from nitromethane–ethanol. The blue nickel(II) complex is paramagnetic ($\mu_{eff.} = 2.8$) and six-co-ordinate as shown by the crystal structure (Figure 1). Bonding is of type (**I**) in which the pendant arm is co-ordinated at the apex of a square pyramid, with a perchlorate ion co-ordinated in a *trans* position to the pendant arm and the macrocyclic ring occupying the equatorial plane. The complex remains six-co-ordinate in nitromethane solution as shown by the visible spectrum (Table 1). The copper(II) and nickel(II) complexes of L^1 are isomorphous, and both may be protonated to give four-co-ordinate complexes of formula $[M(HL^1)][ClO_4]_3$ (M = Ni or Cu) in which the pendant arm is protonated and non-co-ordinating. The yellow protonated nickel(II) complex is diamagnetic, and in nitromethane solution the sharp ^{13}C n.m.r. spectrum and visible spectrum confirm the expected square-planar geometry. The n.m.r. data show that only a single symmetric isomer is present. Three isomers are possible as shown schematically in Figure 2; of the two possible symmetric isomers, (**A**) is believed to be more likely based on our previous studies and the crystal structure in Figure 1. The visible spectrum of $[Cu(HL^1)][ClO_4]_3$ indicates that this is also four-co-ordinate. The protonation–deprotonation equilibria are reversible, careful adjustment of the pH to *ca.* 6—7 with a suitable base immediately regenerating the complexes with the pendant arm co-ordinated.

The reactions of L^2 with nickel(II) and copper(II) are somewhat different to those of L^1, and parallel the differences found in our earlier studies of the related ligands L^3 and L^4.[10] The ligands with three methylene groups in the pendant arms do not readily form complexes in which the pendant arms are co-ordinated, which points to a reduced stability of the six-membered chelate ring compared with the five-membered chelate rings formed by the pendant arms of L^1 and L^3. Steric interactions between the propyl backbones of the macrocyclic ring and the trimethylene pendant arms probably contribute to the lower stability observed. Thus, on mixing ethanolic solutions of L^2 and $[Ni(dmso)_6][ClO_4]_2$ a transient blue colour is observed which rapidly turns to a yellow as the protonated macrocyclic complex forms. The source of the proton is uncertain, although it could arise from traces of water, or from formic acid formed during the synthesis of the dimethyl sulphoxide metal salts. The ^{13}C n.m.r. spectrum of $[Ni(HL^2)]^{3+}$ in nitromethane solution again indicates the presence of a single symmetric isomer, and the visible spectrum confirms the square-planar geometry. The analytical data obtained for the product of the reaction of $[Cu(dmso)_6][ClO_4]_2$ and L^2 indicate that a

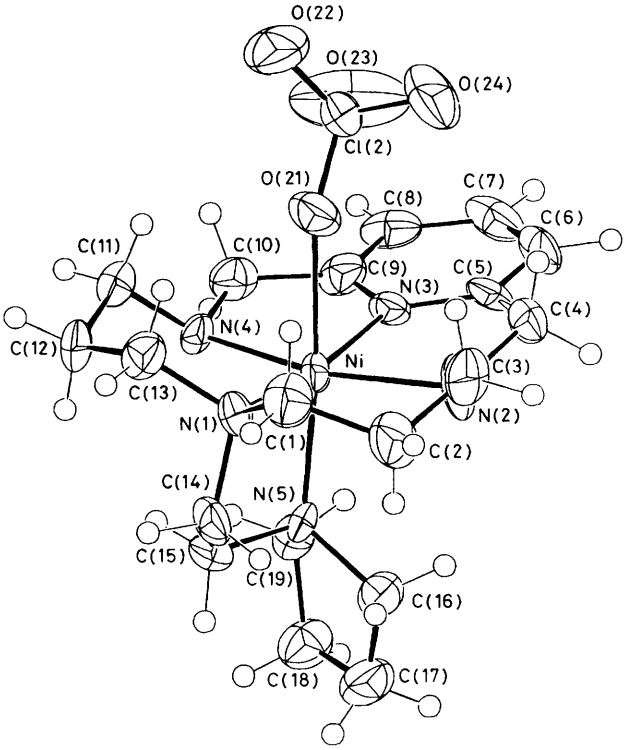


Figure 1. *X*-Ray structure of $[Ni(L^1)(OClO_3)][ClO_4]$ showing the atomic numbering scheme

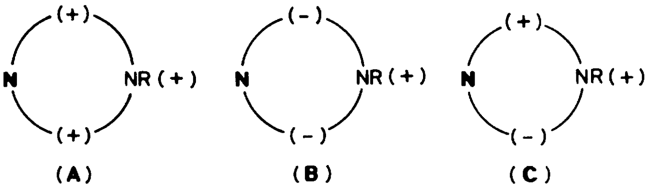


Figure 2. Schematic representation of the three possible isomers of square-planar $[Ni(HL)]^{3+}$ ions (L = L^1 or L^2); (+) and (−) represent the positions of either macrocyclic NH groups or N pendant arm (R), either above (+) or below (−) the macrocyclic ligand plane. The pyridine-N atom is in bold type. (**C**) is enantiomeric

mixture of unprotonated and monoprotonated complexes is formed. Addition of $HClO_4$ gives the pure product, $[Cu(HL^2)][ClO_4]_3$, which has a very similar visible spectrum to the analogous complex of L^1.

Crystal Structures.—The crystal structure of $[Ni(L^1)(OClO_3)][ClO_4]$ (Figure 1) shows that the macrocycle co-ordinates in a square-pyramidal fashion, bonding mode (**I**), in contrast to the trigonal-bipyramidal geometry, bonding mode (**II**), found for the Ni^{2+} complex of the similar pendant-arm ligand L^5.[9] The pyridine group of L^1 probably aids the formation of the square-pyramidal mode of co-ordination, and the bulkier pendant pyrrolidine group will also assist such a geometry for steric reasons. The overall geometry of the complex in Figure 1 is close to octahedral as shown by the bond angles at Ni^{2+} which are in the range 81—104°. The Ni–N bond lengths are all close to 2.1 Å except that to the pyridine-N atom which is significantly shorter (1.96 Å). This behaviour has been observed in several related structures. The Ni–O bond length is somewhat longer at 2.39 Å, as expected.

Although our attempts to refine the crystal structure of $[Ni(HL^2)][ClO_4]_3$ were unsuccessful (Experimental section), nevertheless the data obtained did help to confirm the square-planar geometry, and the presence of an un-co-ordinated pendant arm.

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