Studies of Pendant-arm Macrocyclic Ligands. Part 1. Synthesis of Two New Penta-aza Ligands, and Observation of pH-Dependent Reversible Equilibria between Trigonal-bipyramidal and Square-planar Forms of their Nickel(II) and Copper(II) Complexes. Crystal Structure of a Trigonal-bipyramidal Nickel(II) Complex †

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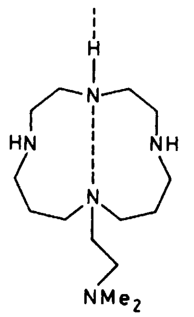
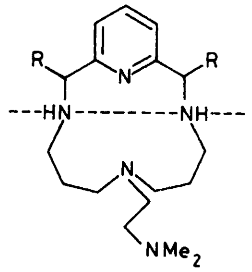
Two new pendant-arm quinquedentate aza-macrocyclic ligands have been prepared, and their nickel(II) and copper(II) complexes found to undergo reversible rearrangements between approximately trigonal-bipyramidal structures at neutral pH, and protonated square-planar structures at low pH in which the pendant arms are protonated and non-co-ordinating. The crystal structure of $[NiL^1][ClO_4]_2$ [L^1 = 11-(2-dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane] establishes an approximately trigonal-bipyramidal geometry for the complex. Crystals are orthorhombic, space group $Pna2_1$, with a = 14.559(3), b = 15.337(3), c = 10.322(3) Å, and Z = 4. The final R was 0.108 for 978 observed reflections with $I/\sigma(I) > 2.5$. The axial N–Ni–N bond angle is 172(1)°, and the equatorial bond angles are 107(2), 107(1), and 144(2)°. Ni–N distances range from 2.04(2) to 2.17(3) Å. The nickel(II) and copper(II) complexes of L^1 are isomorphous.

Few macrocyclic ligands have been reported which contain a 'pendant arm' capable of further co-ordination to a centrally placed metal ion.[1–7] Apart from the enhanced stability of metal complexes formed by such ligands,[1] it is to be expected that they will give rise to compounds in which the metal ion either shows an uncommon geometry, or exhibits interesting properties such as enhanced activity towards molecular oxygen resulting from the axial ligation by the pendant arm.



L^1



L^2 : R = H
L^3 : R = Me

In this work we report the synthesis of two such quinquedentate aza-macrocyclic ligands, L^1 and L^2, and the isolation and characterisation of their nickel(II) and copper(II) complexes in the solid state and in solution. The ligands were designed to ensure co-ordination of the pendant NMe_2 groups, and we have established whether the resulting complexes contain a square-pyramidal or trigonal-bipyramidal arrangement of the ligand. Novel, pH-dependent, reversible equilibria between trigonal-bipyramidal and square-planar geometries were observed in solution, with the planar arrangement existing at low pH where the pendant arm is protonated and non-co-ordinating [equilibrium (i): L = L^1 or L^2, M = Cu^{2+} or Ni^{2+}].

$$[ML]^{2+} + H^+ \rightleftharpoons [M(HL)]^{2+} \qquad (i)$$

The ligands and their complexes were investigated by u.v.-visible spectroscopy, ^1H and ^{13}C n.m.r., and magnetic susceptibility measurements in solution. The fast atom bombardment (f.a.b.) mass spectrum of the protonated nickel(II) complex of L^1 was obtained, and the crystal structure of the unprotonated nickel(II) complex of L^1 is also reported.

Results and Discussion

Ligand Syntheses.—Reaction of *NN*-dimethyl-1,2-diaminoethane with an excess of acrylonitrile leads to the production of the bis-adduct (1) (Scheme 1). This nitrile is smoothly reduced to the corresponding diamine (2) by sodium in ethanol. Other reagents which normally facilitate this reduction give either a complex mixture of products [*e.g.* $LiAlH_4$ in tetrahydrofuran (thf)], or no observed reaction (*e.g.* BH_3·thf). This latter observation is probably due to complexation of the boron to the tertiary amine moiety, resulting in a modification of the reducing ability. The diamine (2) was converted to the disulphonamide (3) using standard conditions.[8] The tris(methanesulphonyl) derivative of diethanolamine, (4), was prepared by reaction with methanesulphonyl chloride in dichloromethane using triethylamine as base.[9] Although the tris(*p*-toluenesulphonyl) derivative has been prepared previously[8] we have found that the methanesulphonates of diethanolamine and dipropanolamine are easier to prepare (< 15 min), with both being easily isolable crystalline materials. Standard Richman-Atkins conditions[10] were used for the coupling of compounds (3) and (4) to give the protected macrocycle (5). This material was not purified but was immediately hydrolysed with conc. H_2SO_4, and the new macrocycle L^1, 11-(2-dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane was isolated as a low-melting solid.

The second new macrocycle L^2 was prepared by a template method as shown in Scheme 2. The first step involves the cyclization of 2,6-pyridinedicarbaldehyde with the amine (2) in the presence of Ni^{2+} to give the macrocyclic di-imine com-

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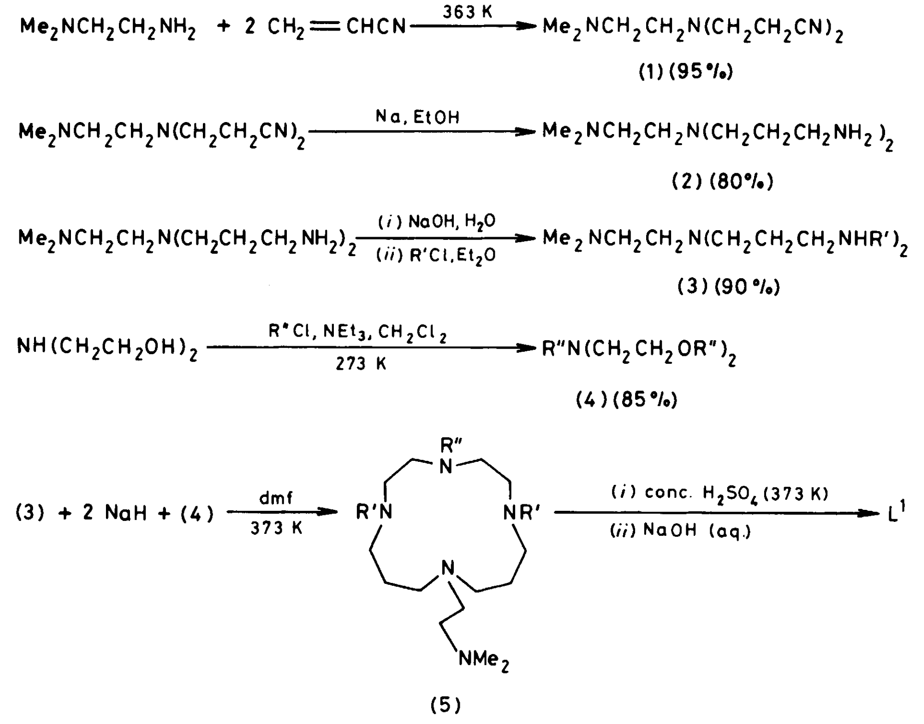
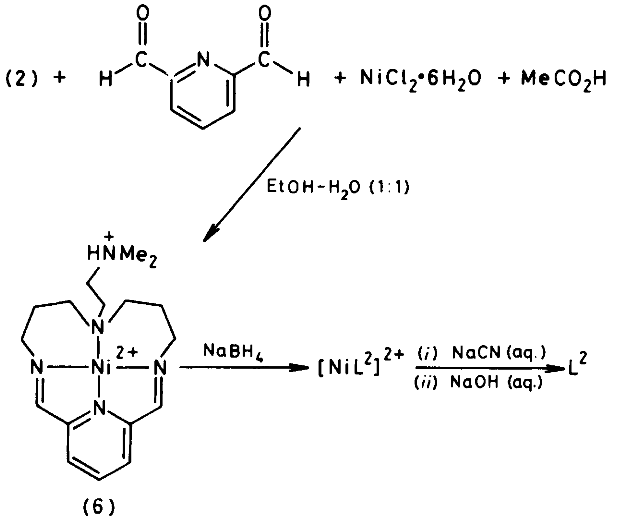
† *Supplementary data available* (No. SUP 23976, 16 pp.): full bond length and angle listing, structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: B.M. ≈ 9.27 × 10^{-24} J T^{-1}, mmHg ≈ 133 Pa.



Scheme 1. R' = $-O_2SC_6H_4Me$-*p*, R" = $-O_2SMe$



Scheme 2.

plex (6).[4] Several methods are available for the oxidation of 2,6-pyridinedimethanol to 2,6-pyridinedicarbaldehyde [MnO_2, $Pb(O_2CMe)_4$],[11,12] but we have found that selenium dioxide [13] in dioxane is an excellent reagent for this transformation, the product being easily isolated in high yield.

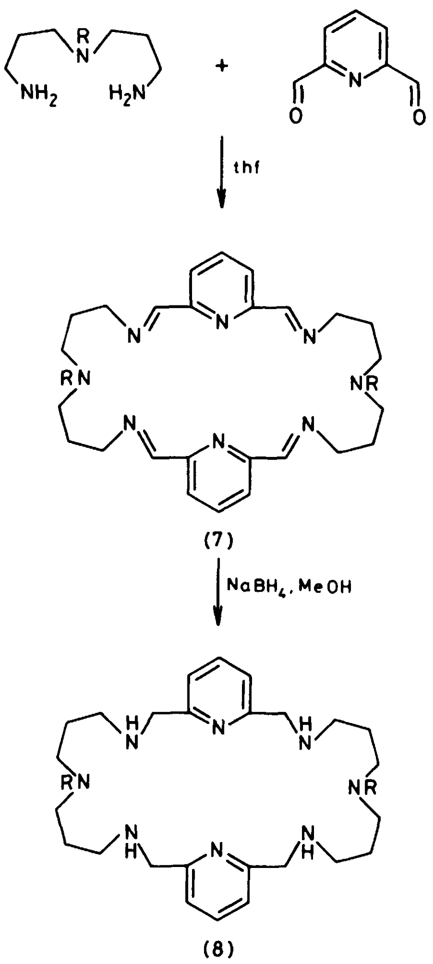
The importance of Ni^{2+} in the cyclization reaction was shown by performing a direct condensation reaction between 2,6-pyridinedicarbaldehyde and bis(3-aminopropyl)methylamine in thf solution. A colourless crystalline material precipitated after *ca.* 1 h at room temperature and was characterised as the imine compound (7) in Scheme 3. Reduction with sodium tetrahydroborate in methanol gave the corresponding amine, (8).

Compound (6) was reduced *in situ* with $NaBH_4$, and the ligand L^2 was liberated by treatment with excess sodium cyanide. The ligand L^2 has an advantage over L^3 in that it has no diastereomeric forms.[4]

Synthesis and Characterisation of Metal Complexes.— On mixing methanolic solutions of L^1 or L^2 with $[Ni(dmso)_6][ClO_4]_2$ (dmso = dimethyl sulphoxide),[14] or hydrated copper(II) perchlorate in a 1 : 1 molar ratio, complexes of formula $M(L)(ClO_4)_2$ (M = Ni or Cu, L = L^1 or L^2) precipitate and can be recrystallised from nitromethane–ethanol.

The blue nickel(II) complex of L^1 is paramagnetic (μ_B = 3.65 B.M.) and five-co-ordinate, as shown by its visible spectrum (Table 1). An *X*-ray structural analysis (Figure 1) reveals an approximately trigonal-bipyramidal geometry, with the pendant $-NMe_2$ group co-ordinated to the Ni^{2+} at one of the equatorial sites. The macrocycle is folded about the dashed line shown in the structure of L^1, such that the other four co-ordination sites of the trigonal pyramid are occupied by macrocyclic N-donor atoms. The Cu^{2+} and Ni^{2+} complexes of L^1 are isomorphous. The Ni^{2+} complexes of L^2 are very similar to those of L^1 as shown by their visible spectra (Table 1). However, in this case, folding of the macrocycle must occur about the alternative dashed line shown in the structure of L^2. The analogous compound of L^3 where R = Me is reported to be six-co-ordinate.[5] This unexpected difference is confirmed by the visible spectra (Table 1).

Acidification of the Ni^{2+} and Cu^{2+} complexes of L^1 or the Ni^{2+} complex of L^2 gives immediate colour changes which are associated with rapid protonation of the pendant arms, followed by formation of square-planar complexes with only the macrocyclic N atoms co-ordinated [equilibrium (i)].[4] This is reversible. Careful increase of the pH to 6—7, with a suitable base, leads to deprotonation of the protonated pendant arms, regenerating the five-co-ordinate complexes immediately. In the case of Ni^{2+}, reaction (i) is accompanied by a spin change from the blue paramagnetic form (S = 1) to the yellow diamagnetic form (S = 0). These reactions were found



Scheme 3. R = Me or $Me_2NCH_2CH_2$

Table 1. Visible spectra (peak maxima/nm) of Ni^{2+} and Cu^{2+} complexes of L^1—L^3 (ε/dm^3 mol^{-1} cm^{-1} in parentheses)

Complex	Solvent MeNO$_2$	Me$_2$CO	H$_2$O
[NiL^1][ClO$_4$]$_2$	368(5)		375 (78)
(blue)	584 (42)		584 (36)
	1 245 (18)		1 240 (14)
[NiL^2][ClO$_4$]$_2$	372 (140) [a]		348 (18) [a]
(blue)	568 (44)		560 (16)
	808 (12)		758 (10)
	1 375 (15)		
[NiL^3][ClO$_4$]$_2$ [b]		367 (sh)	355 (sh)
		480 (15)	534 (9.6)
		632 (11)	746 (11)
		754 (13)	
[NiL^3][ClO$_4$]$_2$ [b]		350 (sh)	358 (194)
(second isomer)		528 (18)	464 (18)
		603 (15)	560 (24)
		745 (13)	ca. 750 (12)
[Ni(HL^1)][ClO$_4$]$_3$	464 (122)		370 (20) [c]
(yellow)			458 (12.5)
			588 (10)
			976 (13)
[Ni(HL^2)][ClO$_4$]$_3$	469 (152)		
(yellow)			
[Ni(HL^3)][ClO$_4$]$_3$ [b]		370 (sh)	350 (sh)
		476 (120)	476 (45)
[Ni(HL^3)][ClO$_4$]$_3$ [b]		370 (sh)	
(second isomer)		469 (113)	464 (82)
[CuL^1][ClO$_4$]$_2$	625 (sh)		
(blue)	772 (262)		
[Cu(HL^1)][ClO$_4$]$_3$	542 (158)		
(purple)			
[CuL^3][ClO$_4$]$_2$ [b]		612 (80)	
[Cu(HL^3)][ClO$_4$]$_3$ [b]		590 (82)	

[a] Approximate due to close proximity of solvent cut-off. [b] Ref. 2. [c] Pale blue due to water co-ordination; green in dmso, $\lambda_{max.}$ 374 (36), 460 (12.5), 590 (17), 1 100 nm (15.5 dm^3 mol^{-1} cm^{-1}).

Table 2. ^{13}C N.m.r. data (relative to $SiMe_4$) for [Ni(HL^1)][ClO$_4$]$_3$ and [Ni(HL^2)][ClO$_4$]$_3$

[Ni(HL^1)]$^{3+}$ Isomer (E) δ [a]/p.p.m.	Isomer (B) or (H) δ [b]/p.p.m.	[Ni(HL^2)]$^{3+}$ δ [c]/p.p.m.
20.4 [d]	22.9 [d]	24.2 (2) [d]
23.5 [d]	45.6	45.9 (2)
43.6	46.0 (2) [e]	46.4 (1)
44.6 (2) [e]		49.6 (2)
45.4	49.5	51.6 (1)
48.2	50.1	55.5 (2)
50.4	51.8	60.8 (2)
50.9	55.6	122.3 (2) [f]
51.4		143.2 (1) [g]
54.9		158.7 (2) [h]
55.2		
56.0		

[a] In CD_3NO_2–CD_3OH (9 : 1) at 230 K. Under these conditions resonances for isomer (B)/(H) become very broad. [b] In CD_3NO_2 at 298 K. [c] Some additional resonances for a minor species were observed. [d] C–CH_2–C. [e] $\overset{+}{H}N(CH_3)_2$. [f] Pyridine C^{β}. [g] Pyridine C^{γ}. [h] Pyridine C^{α}.

to be too rapid for kinetic observation by stopped-flow spectrophotometry at 278 K, which was unexpected in view of the kinetic results obtained for the acidolysis of five-co-ordinate $[Ni\{(Me_2NCH_2CH_2)_3N\}(OH_2)]^{2+}$ and other polyamine-nickel(II) complexes.[15,16] This points either to considerable strain in the five-co-ordinate species, or to a large positive entropy of activation associated with desolvation during the geometric rearrangements.^{13}C N.m.r. spectra (Table 2) of the diamagnetic yellow Ni^{2+} complexes, $[Ni(HL)]^{3+}$, reveal the presence of one major and one minor isomer for both L^1 and L^2. These isomers arise from the different configurations of the co-ordinated N–H groups, either above or below the macrocyclic plane. Eight isomers are possible as shown diagrammatically in Figure 2; (A) and (G), and (C) and (E) are enantiomeric pairs. The crystal structure of $[NiL]^{2+}$ (Figure 1; L = L^1) shows a structure related to (E), with three nitrogen configurations (+) and one (−). This strongly suggests structure (E) for $[Ni(HL)]^{3+}$ (Figure 2) as this would not require any nitrogen inversion on formation of $[Ni(HL)]^{3+}$ from $[NiL]^{2+}$ or *vice versa*. Structure (E) is also consistent with the ^{13}C n.m.r. spectrum of the major component (Table 2). The ^{13}C n.m.r. of the minor isomer of $[Ni(HL)]^{3+}$ is consistent with any of the symmetric structures (B), (D), (F), or (H). In the case of the four-co-ordinate complex of L^2 the minor species is less symmetric than the major species (as shown by the splitting of each n.m.r. resonance into a pair). Kaden [4,6] has reported several more isomers for complexes of L^3 arising from the additional complication of different C–Me positions.[4,6] The crystal structure of $[Ni(HL^3)]^{3+}$ has been reported,[6] and shows the N-configuration (B) of Figure 2. In addition, convincing ^{13}C n.m.r. evidence for N-configurations (H) and (C) has been reported for two further isolable isomers of $[Ni(HL^3)]^{3+}$. These isomers can be interconverted by base catalysis.[4,6]

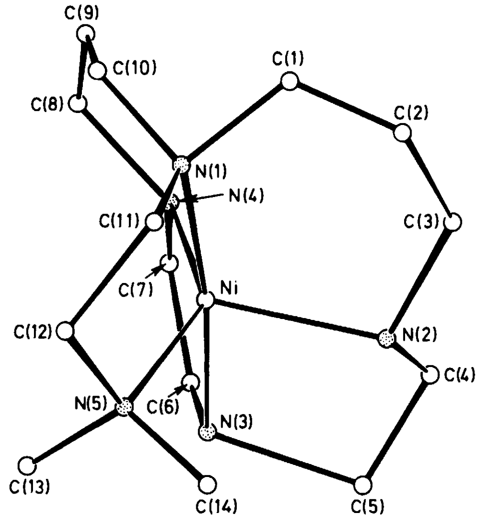


Figure 1. The $[NiL^1]^{2+}$ cation, showing the atomic numbering; only one set of positions is shown for the disordered atoms

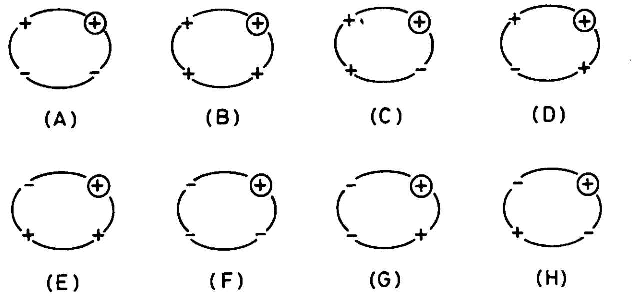


Figure 2. Schematic representation of the eight isomers of square-planar $[Ni(HL)]^{3+}$ ($L = L^1$); (+) or (−) indicates that the proton or dangling arm is attached to N respectively *above* or *below* the macrocycle plane. Structures (A) and (G), and (C) and (E) are enantiomers. The pendant arm positions are circled. For $L = L^2$ there are four isomers, (A)/(C), (B)/(D), (E)/(G), and (F)/(H)

Although the precision of the present crystal structure determination is relatively low (see Experimental section), it establishes the co-ordination geometry as trigonal bipyramidal, with the pendant arm occupying an equatorial position. The axial N(1)–Ni–N(3) angle is 172(1)° (Table 3), with the bend being towards the pendant arm (Figure 1). This probably indicates that this $-(CH_2)_2-$ arm is slightly too short to span from the axial to the equatorial co-ordination position. The other notable distortion is in the equatorial plane, where the angle N(4)–Ni–N(5) is 144(2)°. This is probably just the result of flexibility in this plane which would of course accommodate four ligand atoms, in an octahedral complex. The 107° angles for N(2)–Ni–N(4) and N(2)–Ni–N(5) probably impose no significant strain on the complex. The Ni–N distances are rather irregular, ranging from 2.04(2) to 2.17(3) Å. These differences are not due to a distinction between axial and equatorial positions, but may be a result of strain involving the pendant arm, as the two longest distances are to the arm nitrogen, and to its point of attachment. These distances are broadly comparable to the range of Ni–N distances found in other trigonal-bipyramidal high-spin Ni^{II} complexes, *e.g.* 2.04(2)—2.13(2) Å in $[Ni\{(Et_2NCH_2CH_2)_3N\}(NCS)_2]$.[17] However, a close comparison is not possible partly because of the rather low precision of the present study, and partly because it is the only example of this co-ordination geometry yet examined that has five N-ligand atoms all of amine type.

Table 3. Bond lengths (Å) and angles (°) around nickel in $[NiL^1][ClO_4]_2$

Ni–N(1)	2.05(5)	Ni–N(4)	2.07(4)
Ni–N(2)	2.04(2)	Ni–N(5)	2.17(2)
Ni–N(3)	2.17(3)		
		N(2)–Ni–N(4)	107(2)
N(1)–Ni–N(2)	104(2)	N(2)–Ni–N(5)	107(1)
N(1)–Ni–N(3)	172(1)	N(3)–Ni–N(4)	80(1)
N(1)–Ni–N(4)	94(1)	N(3)–Ni–N(5)	96(1)
N(1)–Ni–N(5)	85(1)	N(4)–Ni–N(5)	144(2)
N(2)–Ni–N(3)	82(1)		

Currently we are synthesising pendant-arm macrocycles derived from 16-membered rings, and investigating whether they form square-pyramidal complexes rather than the trigonal-bipyramidal structures observed here. Once a folded structure of the type found in this study is formed, approach of a ligand (*e.g.* molecular O_2) in a *trans* position to the pendant arm is hindered by the backbone of the macrocycle. Further interaction with ligands (*e.g.* activation of molecular oxygen) will be easier in a square-pyramidal complex.

Experimental

Materials and Methods.—All chemicals used were of the highest available purity. ^1H-Decoupled, natural-abundance ^{13}C n.m.r. spectra were recorded at 100.6 MHz with dioxane ($\delta = 67.4$ p.p.m.) as reference, using a Bruker WH400 Fourier-transform spectrometer. ^1H N.m.r. spectra were recorded using a Perkin-Elmer (model R34) 220-MHz ^1H n.m.r. spectrometer, with $SiMe_4$ as reference. Infrared spectra were recorded using a Perkin-Elmer (model 580B) i.r. spectrometer, equipped with an internal reference. U.v.–visible spectra were recorded with a Shimadzu (model 365) spectrophotometer. Mass spectra were recorded using a Kratos (model MS80) instrument.

Preparation of Compound (1).—*NN*-Dimethyl-1,2-diaminoethane (50 g, 0.57 mol) was stirred at room temperature during the dropwise addition of acrylonitrile (120.4 g, 2.28 mol). The resulting solution was heated to 90 °C and monitored by ^1H n.m.r. spectroscopy until completion. Fractional distillation gave *NN*-bis(2-cyanoethyl)-*N'N'*-dimethyl-1,2-diaminoethane, (1) (105 g, 0.54 mol), b.p. 145—150 °C (0.05 mmHg) in *ca.* 95% yield. ^1H N.m.r. ($CDCl_3$): δ 2.24 (6 H, s), 2.40 (2 H, t), 2.50 (4 H, t), 2.69 (2 H, t), 2.92 p.p.m. (4 H, t). I.r. (thin film): 2 258 cm^{-1} ($-C{\equiv}N$).

Preparation of Compound (2).—Compound (1) (25 g, 0.13 mol) was dissolved in dry ethanol (400 cm^3) and stirred under nitrogen during the addition of sodium metal (50 g, 2.17 mol). The resulting solution was heated to reflux for 8 h and then poured into an equal volume of distilled water. Extraction with CH_2Cl_2 (5 × 200 cm^3), followed by drying ($MgSO_4$), filtration, and concentration gave a crude orange oil (23 g). Careful fractional distillation gave compound (2), *NN*-bis(3-aminopropyl)-*N'N'*-dimethyl-1,2-diaminoethane (20.8 g, 0.103 mol), b.p. 150—170 °C (0.05 mmHg), in *ca.* 80% yield. ^1H N.m.r. ($CDCl_3$): δ 1.32 (4 H, s, N–H), 1.60 (4 H, pentet), 2.22 (6 H, s), 2.35 (2 H, m), 2.48 (6 H, m), 2.72 p.p.m. (4 H, t). I.r. (thin film): 3 350 and 3 280 cm^{-1} (N–H).

Preparation of Compound (3).—Compound (2) (20 g, 98.8 mmol) and sodium hydroxide (7.9 g, 0.197 mol) were dissolved in distilled water (100 cm^3) and stirred vigorously during the dropwise addition of *p*-toluenesulphonyl chloride (37.7 g, 0.197 mol) in diethyl ether (400 cm^3). The resulting solution was stirred vigorously for 4 h and then dichloromethane (100 cm^3) was added. Separation of the organic layer, followed by drying ($MgSO_4$), afiltrtion, and evaporation gave (3), *NN*-dimethyl-*N'N'*-bis(3-*p*-toluenesulphonylaminopropyl)-1,2-diaminoethane (45.4 g, 88.9 mmol) as a colourless glass in *ca.* 90% yield. ^{1}H N.m.r. ($CDCl_3$): δ 1.52 (4 H, pentet), 2.20 (6 H, s), 2.25 (2 H, m), 2.35 (6 H, m), 2.40 (6 H, s), 2.94 (4 H, t), 6.90 (2 H, N–H), 7.29 (4 H, d), 7.73 p.p.m. (4 H, d).

Preparation of Compound (4).—Diethanolamine (15 g, 0.143 mol) and triethylamine (57.7 g, 0.57 mol) were dissolved in dichloromethane (300 cm^3) and stirred at 0 °C during the dropwise addition of methanesulphonyl chloride (49.05 g, 0.43 mol) in dichloromethane (50 cm^3). The resulting solution was stirred at 0 °C for 15 min and then poured into an equal volume of n-pentane. The resulting precipitate was filtered and washed well with distilled water. Drying over silica gel gave compound (4), *NOO'*-tris(methanesulphonyl)diethanolamine (41.16 g, 0.123 mol) as a white solid, m.p. 110—112 °C, in *ca.* 85% yield. ^{1}H N.m.r. (CD_3CN): δ 2.94 (3 H, s), 3.05 (6 H, s), 3.58 (4 H, t), 4.33 p.p.m. (4 H, t). I.r.: no N–H or O–H stretch observed. Mass spectrum (chemical ionisation, NH_3): found 357; calc. 357 (339 + 18).

Preparation of L^1.—Compound (3) (15.5 g, 30.4 mmol) was dissolved in *NN*-dimethylformamide (dmf) (150 cm^3) and stirred under nitrogen during the addition of sodium hydride (1.46, 60.8 mmol). When gas evolution ceased the solution was heated to 110 °C and a solution of compound (4) (10.3 g, 30.4 mmol) in dmf (100 cm^3) was added dropwise over 2 h. The resulting solution was heated at 110 °C for 12 h and then poured into an equal volume of water. The whole of the solvent was then removed by evaporation to leave a viscous brown oil * which was then dissolved in concentrated H_2SO_4 (75 cm^3) and heated at 100 °C for 24 h. After cooling, the solution was poured into ethanol (120 cm^3), followed by the addition of diethyl ether (400 cm^3). The resulting dark brown precipitate was collected by decantation and dissolved in the minimum amount of distilled water. The pH of the solution was adjusted to *ca.* 10 with 20% NaOH (aq.) followed by extraction with dichloromethane (5 × 100 cm^3). The combined extracts were dried ($MgSO_4$), filtered and evaporated to leave a pale yellow oil. Distillation (Kügelröhr apparatus) gave a colourless oil which slowly crystallised to give L^1 (2.1 g, 7.74 mmol, *ca.* 26% yield), b.p. 120—125 °C (0.1 mmHg), m.p. 33—35 °C. ^{1}H N.m.r. ($CDCl_3$): δ 1.75 (4 H, pentet), 2.23 (6 H, s), 2.49 (9 H, m), 2.69 (10 H, m), 2.78 (4 H, t). ^{13}C N.m.r. (CD_3NO_2) (intensities in parentheses): δ 26.8 ($C{-}CH_2{-}C \times 2$), 45.9 ($-NMe_2$), 46.3 (2), 48.5(2), 49.1 (2), 51.2 (1), 54.7 (2), 57.4 (1) p.p.m. I.r. (thin film): 3 290 cm^{-1} (N–H). Mass spectrum (electron impact): M^+, found 271.2738; calc. 271.2735. Combustion analysis (Found: C, 61.3; H, 12.0; N, 25.45. Calc. for $C_{14}H_{33}N_5$: C, 62.0; H, 12.15; N, 25.8%).

$[NiL^1][ClO_4]_2$.—$[Ni(dmso)_6][ClO_4]_2$ (0.67 g, 0.92 mmol) was dissolved in ethanol (5 cm^3) and added to a solution of L^1 (0.25 g, 0.92 mmol) in ethanol (5 cm^3). The resulting blue precipitate was filtered off, washed with ethanol then diethyl ether, and dried *in vacuo* to give $[NiL^1][ClO_4]_2$ (0.448 g, 0.85 mmol, *ca.* 92% yield) (Found: C, 31.9, H, 6.20, N, 12.9. $C_{14}H_{33}Cl_2N_5NiO_8$ requires C, 31.8; H, 6.25; N, 13.25%).

$[Ni(HL^1)][ClO_4]_3$.—$[NiL^1][ClO_4]_2$ (0.3 g, 0.57 mmol) was stirred in ethanol during the dropwise addition of 70% perchloric acid. When the blue to orange conversion was complete the resulting orange-yellow precipitate was removed by filtration, washed with ethanol then ether, and dried *in vacuo* to give $[Ni(HL^1)][ClO_4]_3$ (0.32 g, 0.51 mmol, *ca.* 89% yield) (Found: C, 26.95; H, 5.45; N, 11.2. $C_{14}H_{34}Cl_3N_5NiO_{12}$ requires C, 26.7; H, 5.45; N, 11.15%).

Table 4. Comparison of parts of the observed f.a.b. mass spectrum of $[Ni(HL^1)][ClO_4]_3$ with values calculated for various fragment ions *

$[Ni(HL^1)(ClO_4)_2]^+$					
Observed *m/z*	528	529	530	531	532
Relative height	94	35	100	34	45
Calculated *m/z*	528	529	530	531	532
Relative height	94	17	100	20	42
$[NiL^1(ClO_4)]^+$					
Observed *m/z*	428	429	430	431	432
Relative height	100	33	72	21	19
Calculated *m/z*	428	429	430	431	432
Relative height	100	18	73	15	20
$[NiL^1 - H)]^+$					
Observed *m/z*	328	329	330	331	
Relative height	100	65	46	25	
Calculated *m/z*	328	329	330	331	
Relative height	100	18	40	9	

* The relative heights of the peaks at *m/z* 328, 428, and 530 were 100 : 70 : 20, and other large peaks were evident at *m/z* 277, 242, 185, 157, and 115.

The f.a.b. mass spectrum of $[Ni(HL^1)][ClO_4]_3$ gave an isotope pattern consistent with $[Ni(HL^1)(ClO_4)_2]^+$ as shown in Table 4. In addition to the pattern centred at *m/z* 530, there were isotope patterns centred at *m/z* 428 and 328 consistent with successive loss of $HClO_4$ to give $[NiL^1(ClO_4)]^+$ and $[Ni(L^1 - H)]^+$, together with signs of a pattern near to *m/z* 629 as expected for the parent ion. The latter was too weak for accurate assignment.

$[CuL^1][ClO_4]_2$.—$Cu(ClO_4)_2{\cdot}6H_2O$ (0.34 g, 0.92 mmol) was dissolved in ethanol (5 cm^3) and added to a solution of L^1 (0.25 g, 0.92 mmol) in ethanol (5 cm^3). The resulting solution was cooled to 0 °C and the blue precipitate was collected by filtration, washed with a little cold ethanol and ether, then dried *in vacuo* to give $[CuL^1][ClO_4]_2$ (0.42 g, 0.79 mmol, *ca.* 85% yield) (Found: C, 31.85; H, 6.20; N, 13.05. $C_{14}H_{33}Cl_2CuN_5O_8$ requires C, 31.5; H, 6.25; N, 13.1%).

$[Cu(HL^1)][ClO_4]_3$.—$[CuL^1][ClO_4]_2$ (0.3 g, 0.56 mmol) was stirred in ethanol during the dropwise addition of 70% perchloric acid, sufficient to cause the complete conversion from blue to purple. The resulting purple precipitate was filtered off, washed with ethanol and diethyl ether, then dried *in vacuo* to give $[Cu(HL^1)][ClO_4]_3$ (0.34 g, 0.54 mmol, *ca.* 96% yield) (Found: C, 26.5; H, 5.25; N, 10.85. $C_{14}H_{34}Cl_3CuN_5O_{12}$ requires C, 26.5; H, 5.40; N, 11.05%).

Preparation of 2,6-*Pyridinedicarbaldehyde*.—2,6-Pyridinedimethanol (19 g, 0.137 mol) and selenium dioxide (15.15 g, 0.137 mol) were dissolved in dioxane (300 cm^3) and heated to reflux for 4 h. The solution was filtered and the solvent was removed by evaporation. The crude product was recrystallised from chloroform–light petroleum (b.p. 40—60 °C) to give the product (16 g, 0.117 mol, *ca.* 85% yield) m.p. 115—117 °C. ^{1}H N.m.r. ($CDCl_3$): δ 8.15 (3 H, m), 10.16 p.p.m. (2 H, s). I.r. (hexachlorobutadiene mull): 3 080, 3 060, 3 020 (pyridine C–H), 2 865 (formyl C–H), 1 725 cm^{-1} (C=O).

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* ^{1}H N.m.r. confirmed this oil to be compound (5).

Table 5. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	2 201(2)	657(2)	0	C(8)	1 125(22)	2 346(21)	222(43)
N(1)	1 876(26)	892(23)	1 897(50)	C(9)	1 140(25)	2 356(26)	1 470(39)
N(2)	3 588(14)	453(14)	13(41)	C(10)	1 114(28)	1 507(26)	2 173(42)
N(3)	2 396(23)	513(25)	−2 073(28)	C(11)	1 626(33)	−21(27)	2 441(42)
N(4)	1 978(48)	1 929(26)	−582(33)	C(12)	1 070(27)	−554(31)	1 516(41)
N(5)	1 544(15)	−593(18)	303(24)	C(13)	2 208(19)	−1 318(17)	307(35)
C(1)	2 766(52)	1 217(45)	2 675(47)	C(14)	866(25)	−661(25)	−670(31)
C(2)	3 630(48)	674(45)	2 539(73)	Cl(1)	234(6)	3 189(6)	5 511(14)
C(3)	4 085(85)	924(32)	1 136(53)	O(11)	727(17)	2 390(11)	5 538(42)
C(41) *	3 999(87)	881(76)	−707(129)	O(12)	443(27)	3 645(23)	4 351(45)
C(4) *	3 983	635	—1 274	O(13)	489(33)	3 705(30)	6 594(25)
C(51) *	3 732(49)	665(40)	−2 035(66)	O(14)	−723(10)	3 015(19)	5 560(51)
C(5) *	3 437	189	—2 285	Cl(2)	3 473(7)	3 777(7)	446(13)
C(6) *	2 106(51)	1 295(48)	−2 932(77)	O(21)	4 133(17)	4 443(17)	660(48)
C(61) *	2 539(78)	1 371(74)	−2 533(95)	O(22)	3 860(23)	3 120(17)	−355(51)
C(7) *	2 315(64)	1 986(56)	−1 860(85)	O(23)	2 690(24)	4 138(26)	−173(39)
C(71) *	1 539(87)	1 969(78)	−1 855(117)	O(24)	3 210(31)	3 407(34)	1 650(24)

* Occupancy 0.5.

Preparation of L^2.—$NiCl_2{\cdot}6H_2O$ (2.35 g, 9.9 mmol) was dissolved in ethanol–water (1 : 1, 30 cm³), with compound (2) (2 g, 9.9 mmol) to give a blue solution. 2,6-Pyridinedicarbaldehyde (1.34 g, 9.9 mmol) was then added followed by acetic acid (0.8 cm³) .The resulting brown solution was stirred for 2 h then heated at 80 °C for 6 h. The solution was then cooled in ice and sodium tetrahydroborate (1.5 g, 39.7 mmol) was added over 30 min. The reaction mixture was stirred at room temperature until effervescence ceased and then heated at 80 °C for 2 h. The ethanol was removed by evaporation and sodium cyanide (4 g, 81.6 mmol) was added. After heating at 80 °C for 1 h the reaction was cooled and basified with 15% NaOH (aq.) to *ca.* pH 10. The solution was extracted with dichloromethane (3 × 50 cm³) and the combined extracts were dried ($MgSO_4$). Filtration, evaporation, and distillation (Kügelröhr apparatus) gave L^2 (1.2 g, 3.9 mmol, *ca.* 40% yield) as a colourless oil, b.p. 150—155 °C (0.1 mmHg). This oil slowly crystallised to a colourless solid, m.p. 72—74 °C. ^{13}C N.m.r. (CD_3NO_2): δ 29.0 (2), 46.3 (2), 47.3 (2), 52.4 (1), 53.9 (2), 55.3 (2), 58.1 (1), 121.8 (2), 137.9 (1), 161.6 p.p.m. (2). ^1H N.m.r. ($CDCl_3$): δ 1.70 (4 H, pentet), 2.18 (6 H, s), 2.23 (4 H, m), 2.40 (6 H, m, includes NH), 2.52 (4 H, t), 3.88 (4 H, s), 7.00 (2 H, d), 7.55 p.p.m. (1 H, t). I.r. (thin film): 3 280 (N–H); 3 060, 1 595, 1 580 cm⁻¹ (pyridine). Mass spectrum (chemical ionisation, NH_3): found 323; calc. 323 (305 + 18).

$[NiL^2][ClO_4]_2$.—The ligand L^2 (0.8 g, 2.6 mmol), was dissolved in ethanol (5 cm³) and added to a solution of $[Ni(dmso)_6][ClO_4]_2$ (1.9 g, 2.6 mmol) in ethanol. The resulting purple precipitate was filtered off, washed with ethanol–ether, and dried *in vacuo* to give $[NiL^2][ClO_4]_2{\cdot}H_2O$ (1.36 g, 2.3 mmol, *ca.* 89% yield) (Found: C, 34.75; H, 5.35; N, 11.85. $C_{17}H_{31}Cl_2N_5NiO_8{\cdot}H_2O$ requires C, 35.15; H, 5.70; N, 12.05%).

$[Ni(HL^2)][ClO_4]_3$.—$[NiL^2][ClO_4]_2{\cdot}H_2O$ (1.0 g, 1.7 mmol) was stirred in ethanol (10 cm³) during the dropwise addition of 70% perchloric acid, sufficient to cause the complete conversion from purple to orange-yellow colouration. The precipitate was removed by filtration and washed with ethanol, then ether. Drying *in vacuo* gave $[Ni(HL^2)][ClO_4]_3$ (1.05 g, 1.58 mmol, *ca.* 93% yield) (Found: C, 30.35; H, 4.75; N, 10.4. $C_{17}H_{32}Cl_3N_5NiO_{12}$ requires C, 30.75; H, 4.85; N, 10.55%).

Crystal Data for $[NiL^1][ClO_4]_2$.—$C_{14}H_{33}Cl_2N_5NiO_8$, M = 529.0, orthorhombic, space group $Pna2_1$, a = 14.559(3), b = 15.337(3), c = 10.322(3) Å, U = 2 305 Å³, D_m = 1.6 g cm⁻³, Z = 4, D_c = 1.52 g cm⁻³, $F(000)$ = 1 100, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 11.3 cm⁻¹.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range ±1.0° (2θ) around the $K_{\alpha1}$—$K_{\alpha2}$ 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. Three standard reflections were monitored every 300 reflections and showed significant decay during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 978 Observed reflections [$I/\sigma(I) > 2.5$] were used in refinement (2 342 total) and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR; [18] maximum and minimum transmission factors were 0.87 and 0.86. Because of the crystal deterioration and the weak diffraction, the data were considered likely to be of relatively poor quality.

The Cu compound is apparently isomorphous with the Ni compound, although its crystals were of even lower quality. Unit-cell dimensions are as follows: a = 14.761(3), b = 15.072(3), c = 10.371(3) Å, U = 2 307 Å³.

Systematic absences $0kl$, $k + l \neq 2n$; $h0l$, $h \neq 2n$ for both compounds indicate space group $Pna2_1$ or $Pnam$ (non-standard setting of $Pnma$, no. 62). The space group $Pnam$ would require the cations to have site symmetry $\bar{1}$ (impossible) or m; the latter was judged unlikely, though it would be possible if the pendant arm was either planar or somewhat disordered. Location of a Ni atom position was straightforward from a Patterson synthesis, but a full structure solution proved difficult. The centrosymmetric space group was discarded, because an initial Fourier synthesis did not show feasible anion or ligand positions, and a solution in space group $Pna2_1$ was eventually achieved from a Fourier synthesis after refining the Ni and one Cl position. Refinement to $R \approx 0.18$ revealed the molecule, but showed extra peaks around the chlorine atoms. Various models were tried for this disorder, but the most satisfactory was to hold the oxygen atoms as a regular tetrahedron, but refine them with anisotropic thermal parameters, which reached high values in some directions. Refinement to $R \approx 0.14$ then showed alternative positions for the carbon atoms between N(2) and N(4). Final refinement was by least-squares methods with unit weights, in large blocks. The largest peaks on a final difference-Fourier synthesis were in the vicinity of the

$[NiL^1]^{2+}$ ion suggesting that some further disorder was still present. The rather high final R value of 0.108 is not unexpected in view of the poor data quality, and the disorder, for which a better model would require a very large number of parameters. Computing was with the *X*-RAY 76 system,[19] on a Burroughs B6700 computer. Scattering factors in the analytical form were taken from ref. 20. Final atomic co-ordinates are given in Table 5, and bond lengths and angles around Ni are in Table 3. Bond lengths and angles for light atoms have normal values, allowing for the large e.s.d.s [0.10 Å for C–C, 3° for C–C–C (ordered atoms; higher for disordered ones)].

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