Studies of Pendant-arm Macrocyclic Ligands. Part 2.[1] Comparison of the Nickel(II), Copper(II), and Zinc(II) Complexes of 11-(2'-Dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane, a Pyridine Analogue, and a Related New Tetra-aza Macrocycle, 11-Methyl-1,4,7,11-tetra-azacyclotetradecane

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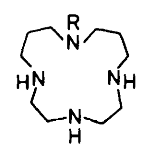
The complexes of Ni^{2+}, Cu^{2+}, and Zn^{2+} with two closely related pendant-arm penta-aza macrocycles 11-(2'-dimethylaminoethyl)-1,4,7,11-tetra-azacyclotetradecane, L^1, and 7-(2'-dimethylaminoethyl)-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene, L^2, have been characterised spectroscopically. The square-planar complex of the protonated ligand L^1, $[Ni(HL^1)][ClO_4]_3$, previously reported to be a mixture of two isomers, has been found to isomerise in hot aqueous solution to give two further isomers. Six-co-ordinate thiocyanato-complexes of formula $[Ni(L^1)(NCS)]ClO_4$ and $[Ni(HL^1)(NCS)_2]ClO_4$ have been isolated. For the protonated copper(II) complex of the ligand (L^1) (but not L^2), a temperature-dependent equilibrium of the type $[Cu(L^1)]^{2+} + H^+ \rightleftharpoons [Cu(HL^1)]^{3+}$ exists in aqueous solution, and a variable-temperature visible spectroscopic study shows that, at 298.2 K, $K = (2.2 \pm 0.3) \times 10^3$ dm^3 mol^{-1} and $\Delta G^\circ = -19.05 \pm 0.29$ kJ mol^{-1}. Isomerisation of the protonated copper complex was not observed. The complexes of formula $[Zn(L)][NO_3]_2$ (L = L^1 or L^2) were found to be single isomers which do not isomerise even at elevated temperatures. ^{13}C N.m.r. studies show that in $[Zn(L^1)][NO_3]_2$ the macrocycle is asymmetric whereas in $[Zn(L^2)][NO_3]_2$ the macrocycle is in a symmetric configuration. The new, related macrocycle, 11-methyl-1,4,7,11-tetra-azacyclotetradecane, L^3, and its complexes with Ni^{2+}, Cu^{2+}, and Zn^{2+} have been prepared. ^{13}C N.m.r. studies show that the diamagnetic, planar complex $[Ni(L^3)][ClO_4]_2$ is a single symmetric species, whereas $[Zn(L^3)][NO_3]_2$ is a 1 : 2 mixture of a symmetric and an asymmetric species.

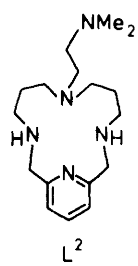
In Part 1 [1] we reported the synthesis of two new quinquedentate pendant-arm macrocycles L^1 and L^2 and their isomorphous complexes of Ni^{2+} and Cu^{2+}, $[M(L)][ClO_4]_2$ (L = L^1, M = Ni or Cu). Both ligands form trigonal-bipyramidal complexes in which the pendant arm occupies one of the three trigonal co-ordination sites, as revealed by a crystal structure determination of the nickel(II) complex. The complexes of Ni^{2+} and Cu^{2+} were found to undergo reversible protonation to form square-planar complexes in which the pendant arm is protonated and non-co-ordinating [reaction (i)].

$$[M(L)]^{2+} + H^+ \rightleftharpoons [M(HL)]^{3+} \qquad (i)$$

Now we report further studies of these systems, together with the synthesis of the zinc complexes of the ligands L^1 and L^2. The thermodynamic parameters associated with equilibrium (i) have been determined from a variable-temperature pH study of the copper(II) complex, and thiocyanato-complexes of $[Ni(L)]^{2+}$ and $[Ni(HL)]^{3+}$ have been isolated. We have prepared a further new related quadridentate tetra-aza macrocycle, L^3, together with its complexes of Ni^{2+}, Cu^{2+}, and Zn^{2+} for comparison with those of the macrocycles L^1 and L^2.



L^1 R = $CH_2CH_2NMe_2$
L^3 R = Me



L^2

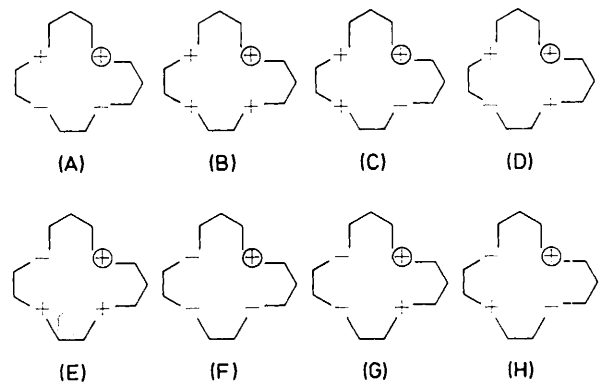


Figure 1. Schematic representation of the eight isomers of $[Ni(HL^1)]^{3+}$ or $[Ni(L^3)]^{2+}$. The pendant-arm position of L^1 and the NMe group of L^3 are circled, and + or − represents the position either of these groups, or of the NH groups, with respect to the macrocyclic plane. (C)/(E) and (A)/(G) are enantiomeric pairs. For $[Ni(HL^2)]^{3+}$ there are four isomers: (A)/(C), (B)/(D), (E)/(G), and (F)/(H)

Results and Discussion

Nickel(II) *Complexes*.—As shown previously, there are eight possible isomers for the protonated square-planar species $[M(HL)][ClO_4]_3$ (L = L^1; M = metal ion), Figure 1; (A) and (G), and (C) and (E) are enantiomeric pairs. The ^{13}C n.m.r. spectrum of $[Ni(HL^1)]^{3+}$ previously revealed the presence of two of these isomers, one of which was assigned structure (E) by comparison with the crystal structure of $[Ni(L^1)]^{2+}$, and the other assigned any of the symmetric structures (B), (D), (F), or (H).

Upon heating $[Ni(HL^1)]^{3+}$ in aqueous solution at *ca.* 80 °C

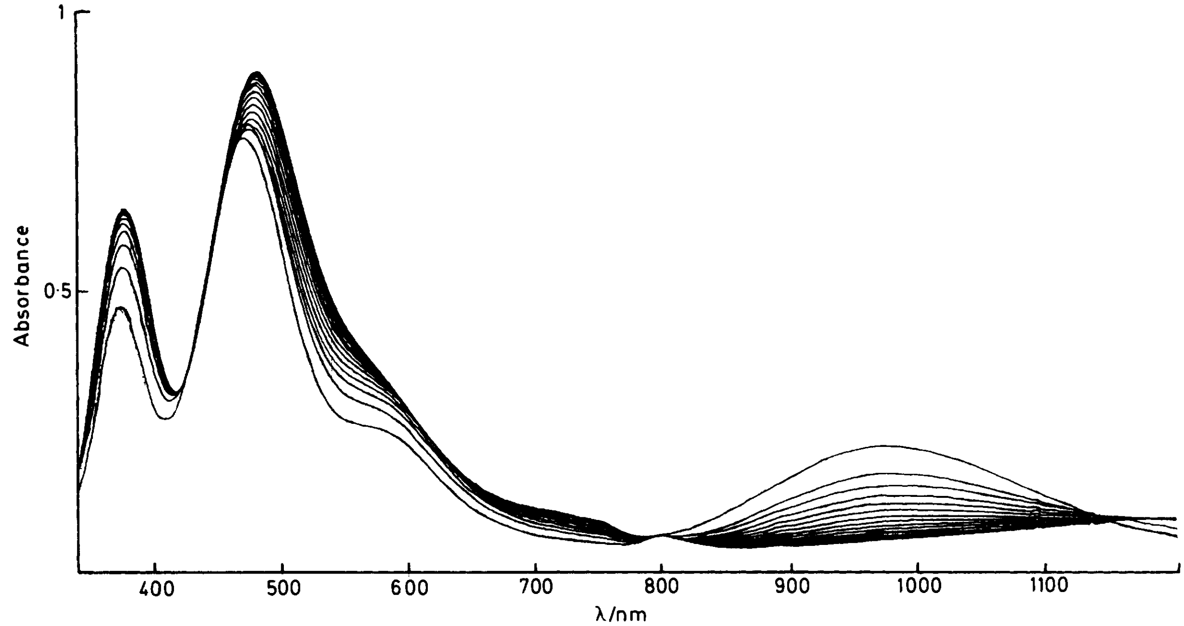


Figure 2. Visible spectral changes recorded at 5-min time intervals during the isomerisation of $[Ni(HL^1)][ClO_4]_3$ (2.7×10^{-3} mol dm^{-3}; 1-cm path length cell) at 323 K in water. The peak at *ca.* 970 nm decreases, and the one at *ca.* 480 nm increases with time

Table 1. ^{13}C N.m.r. data (δ/p.p.m.)[a] for $[Ni(HL^1)][ClO_4]_3$ and $[Ni(L^3)][ClO_4]_2$ (for tentative assignments refer to Figure 1)

$[Ni(HL^1)][ClO_4]_3$[a,b]	
Isomer (B)	22.9,[c] 45.6,[d] 46.0,[e] 47.7, 49.5, 50.1, 51.8, 55.6
Isomer (D) or (H) (*ca.* 85%)[f]	23.8(2),[c] 44.3(1),[d] 45.8(2),[e] 46.7(2), 47.8(2), 52.4(1),[g] 53.5(2), 54.9(2)
Isomer (C)/(E) (*ca.* 10%)[f]	20.5,[c] 23.7,[c] 44.6,[e] 44.9, 45.6, 49.5, 50.1, 50.6, 51.2, 51.8, 55.3, 55.5, 56.1
$[Ni(L^3)][ClO_4]_2$[a]	23.5,[c] 43.5,[h] 48.2, 49.3, 54.8, 61.7

[a] In CD_3NO_2 at 298 K with $SiMe_4$ as internal reference. [b] Some additional resonances for a minor species (<5%) were observed, $[Ni(HL^1)]^{3+}$, at δ 24.0, 26.6, 45.4, 48.9, and 51.9 p.p.m. [c] $C-CH_2-C$. [d] $-CH_2N^+HMe_2$. [e] $-N^+H(CH_3)_2$. [f] At equilibrium after heating in aqueous solution. [g] $-NCH_2CH_2N^+HMe_2$. [h] $-NCH_3$.

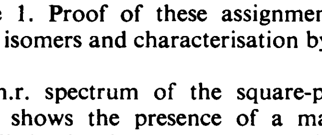
Table 2. Magnetic susceptibilities at 298 K in CD_3NO_2 solution *

Complex	χ/μ_B	Complex	χ/μ_B
$[Ni(L^1)][ClO_4]_2$	3.65	$[Cu(L^1)][ClO_4]_2$	2.26
$[Ni(HL^1)][ClO_4]_3$	Diamagnetic	$[Cu(HL^1)][ClO_4]_3$	2.10
$[Ni(L^1)(NCS)]ClO_4$	3.27	$[Cu(L^2)][ClO_4]_2$	2.35
$[Ni(L^2)][ClO_4]_2$	3.57	$[Cu(HL^2)][ClO_4]_3$	2.11
$[Ni(HL^2)][ClO_4]_3$	Diamagnetic	$[Cu(L^3)][ClO_4]_2$	1.89
$[Ni(L^3)][ClO_4]_2$	Diamagnetic		

* Determined by the method of D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

for several hours, isomerisation occurs to give a mixture of three isomers. The reaction was monitored by visible spectroscopy (Figure 2) which revealed the presence of an intermediate. ^{13}C N.m.r. studies show that a major new symmetric species (*ca.* 85%) is formed, leaving *ca.* 10% of isomer (E) and a new minor asymmetric species (<5%) tentatively assigned to (A)/(G).

We have recently shown how donor solvents assist nitrogen inversions in 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II) $\{[Ni(L^4)]^{2+}\}$ complexes.[2] A complex with a structure analogous to (B) is known to form when L^4 is added to Ni^{2+}, and this 'all-four-up' set of nitrogen configurations has also been shown to form for the nickel(II) complex of the 2,12-*C*-dimethyl analogue of the ligand L^2.[1] Starting from (B), successive single nitrogen inversions can give rise to the other isomers as shown in the Scheme.



Scheme.

If we assume by analogy with previous studies that structure (B) is initially present, a plausible explanation of our observations is that a symmetric structure (D) or (H) is formed by a single NH inversion from (B) or (C)/(E) respectively. Tentative assignments of the ^{13}C n.m.r. data on this basis are given in Table 1. Proof of these assignments must await isolation of the isomers and characterisation by *X*-ray crystallography.

The ^{13}C n.m.r. spectrum of the square-planar complex $[Ni(L^3)][ClO_4]_2$ shows the presence of a major symmetric species, but a distinction between structures (B), (D), (F), or (H) could not be made from the chemical shifts (Table 1).

Reaction of the trigonal-bipyramidal $[Ni(L)]^{2+}$ and square-planar $[Ni(HL)]^{3+}$ complexes ($L = L^1$ or L^2) with sodium thiocyanate gives the six-co-ordinate complexes $[Ni(L)(NCS)]^+$ and $[Ni(HL)(NCS)_2]^+$ respectively. The visible spectra of these complexes (Table 3) show them to be pseudo-octahedral, and the magnetic moment of $[Ni(L^1)(NCS)]ClO_4$ (Table 2) is as expected for such a geometry. There is no displacement of the pendant arm in $[Ni(L)]^{2+}$ even with a large excess of

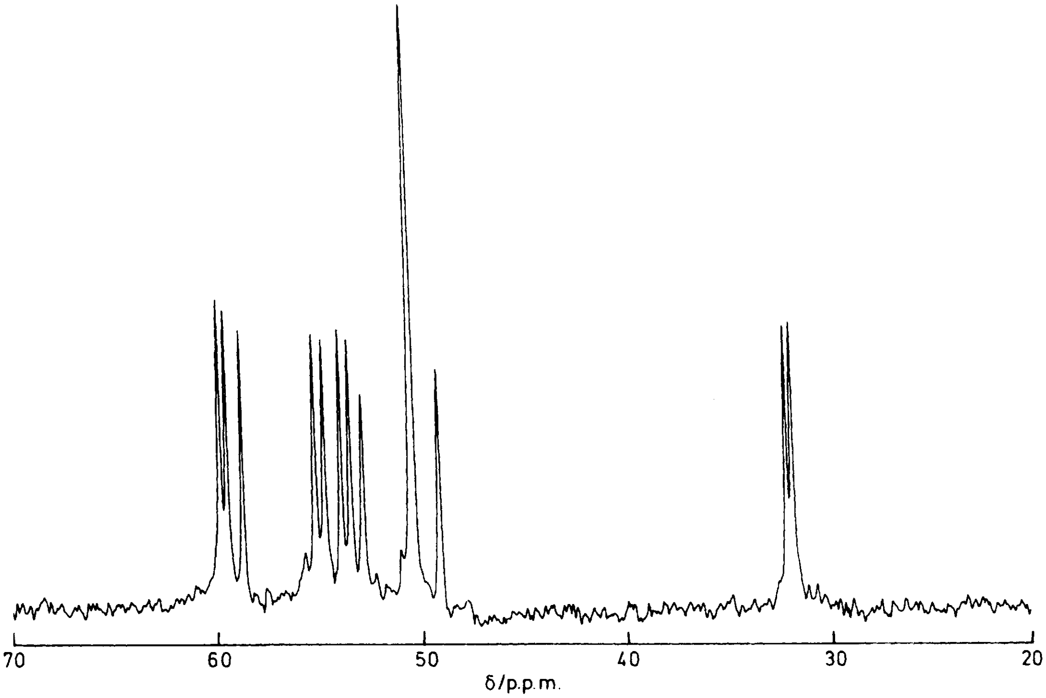


Figure 3. ^1H Decoupled ^{13}C n.m.r. spectrum of $[Zn(L^1)][NO_3]_2$

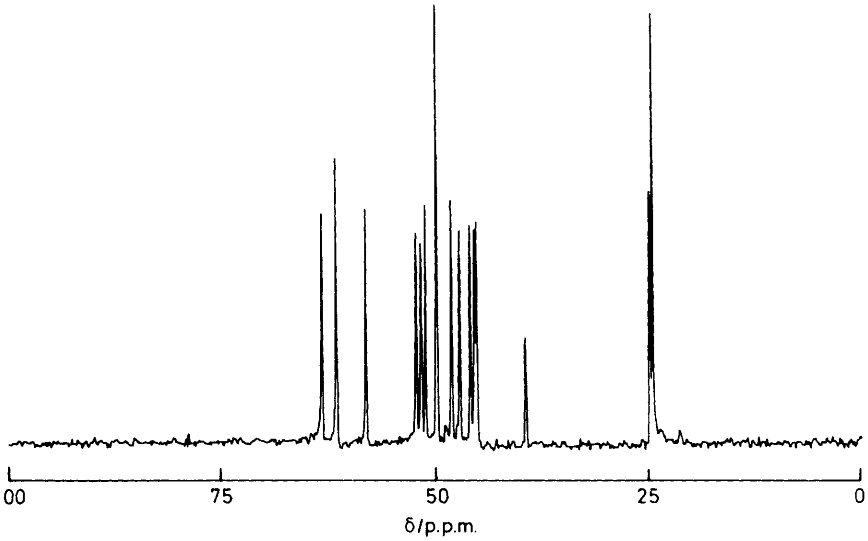


Figure 4. ^1H Decoupled ^{13}C n.m.r. spectrum of $[Zn(L^3)][NO_3]_2$

thiocyanate ion. The bis(thiocyanate) adducts of the protonated complexes have two nitrile i.r. bands (*e.g.* for the complex of L^1 at 2 105 and 2 080 cm^{-1}), and by comparison with recent results for $[Ni(L^4)(NCS)_2]$ [3,4] they probably have a *trans* geometry; $[Ni(L^4)(NCS)_2]$ was originally reported to have a *cis* structure,[3] but by comparison with a related crystal structure is now believed to have a *trans* configuration.[4]

Zinc(II) *Complexes*.—The macrocycles L^1, L^2, and L^3 all react with $Zn[NO_3]_2 \cdot 6H_2O$ to give the complexes $[Zn(L)][NO_3]_2$. The ^{13}C n.m.r. spectrum of $[Zn(L^1)][NO_3]_2$ (Figure 3) shows the presence of a single asymmetric species. This is supported by the ^1H n.m.r. spectrum which reveals the *N*-methyl groups to be non-equivalent (in D_2O, δ 2.50 and 2.66 p.p.m.). This is only possible if the pendant arm is co-ordinated to the Zn^{2+}. Assuming that this complex forms by the same mechanism as that for the nickel(II) complex, it is most likely that it has structure (C)/(E). The complex in D_2O is inert and undergoes very slow proton exchange as shown by three clearly visible N–H resonances at δ 4.05, 4.16, and 4.40 p.p.m. with couplings to adjacent protons.

The ^{13}C n.m.r. spectrum of $[Zn(L^2)][NO_3]_2$ is analogous to that of the nickel(II) complex, showing a single symmetric species to be present. This must be either isomer (B)/(D) or (F)/(H). Again, the N–H protons are in slow exchange in D_2O solution.

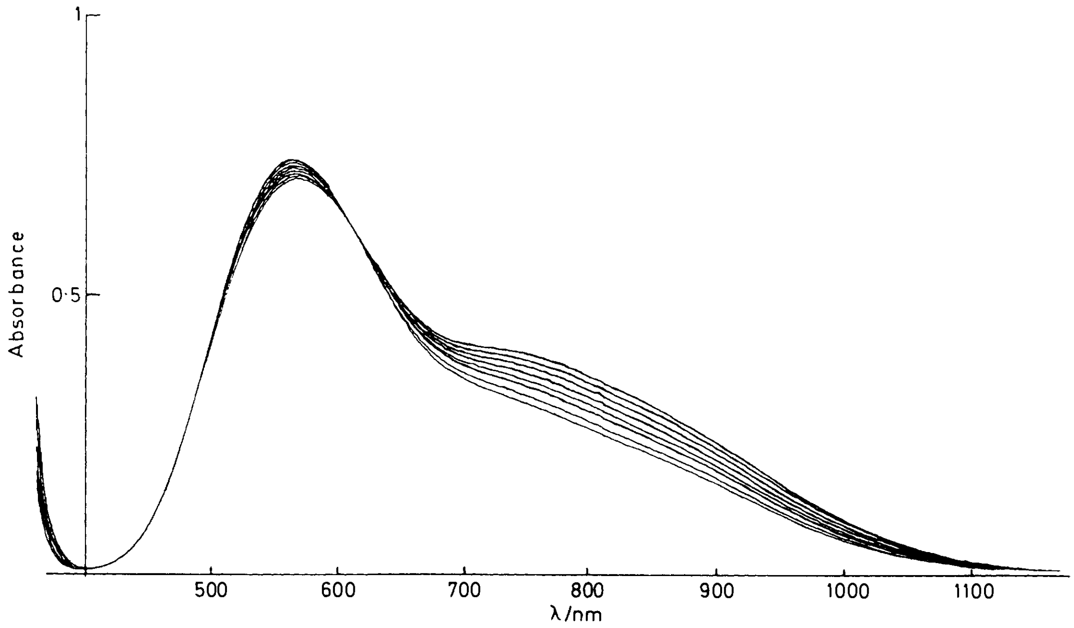


Figure 5. Visible spectral changes associated with equilibrium (i) for $[Cu(HL^1)][ClO_4]_3$ (4.92×10^{-3} mol dm^{-3}, 1-cm path length cell) in 0.1 mol dm^{-3} $LiClO_4$ at eight temperatures in the range 288.4—328.5 K. The absorbance at 820 nm decreases and that at 560 nm increases with increase in temperature

Table 3. Visible spectra of complexes

Complex	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1}) In CH_3NO_2	In H_2O
$[Ni(L^1)][ClO_4]_2$	368(sh), 584(42), 1 245(18)	375(78), 584(36), 1 240(14)
$[Ni(HL^1)][ClO_4]_3$	464(122)	370(20), 458(12.5), 588(10), 976(13)
$[Ni(HL^1)][ClO_4]_3$ [a]	482(129)	375(24), 480(33), 560(s), 1 220(4)
$[Ni(L^1)(NCS)]ClO_4$	572(16.5), 910(12.5)	
$[Ni(HL^1)(NCS)_2]ClO_4$	572(21), 948(25)	
$[Ni(L^2)][ClO_4]_2$	372(140), 568(44), 808(12), 1 375(15)	348(18), 560(16), 758(10)
$[Ni(HL^2)][ClO_4]_3$	469(152)	
$[Ni(L^2)(NCS)]ClO_4$	512(29), 756(16)	
$[Ni(HL^2)(NCS)_2]NCS$	530(27), 765(33)	
$[Ni(L^3)][ClO_4]_2$	480(146)	350(12), 475(91.6)
$[Cu(L^1)][ClO_4]_2$	625(5), 772(262)	640(5), 768(198) [b]
$[Cu(HL^1)][ClO_4]_3$	542(158)	558(143) [c]
$[Cu(L^2)][ClO_4]_2$	570(163), 760(5)	595(153.5), 780(5)
$[Cu(HL^2)][ClO_4]_3$	548(168.5)	565(174)
$[Cu(L^3)][ClO_4]_2$	536(166)	546(181)

[a] After isomerization. [b] Aqueous $LiClO_4$ (0.1 mol dm^{-3}) solution. [c] Aqueous $LiClO_4$ (0.1 mol dm^{-3}) solution plus $HClO_4$.

The ^{13}C n.m.r. spectrum of $[Zn(L^3)][NO_3]_2$ is shown in Figure 4. Two isomers are present, one symmetric and one asymmetric, in a ratio 1 : 2. This ratio does not change on heating an aqueous solution for several hours; the complex shows two N–Me ^1H resonances at δ 2.40 and 2.45 p.p.m. in the ratio 1 : 2. The N–H protons are also in slow exchange with D_2O.

Copper(II) *Complexes*.—The complex $[Cu(L^1)][ClO_4]_2$ was found previously to be isomorphous with $[Ni(L^1)][ClO_4]_2$, and like the nickel(II) complex undergoes protonation to give $[Cu(HL^1)][ClO_4]_3$ [reaction (i)].[1] However, unlike the nickel complex, no isomerisation was detected in aqueous solution at elevated temperatures. One further difference is that equilibrium (i) lies to the right only in strongly acidic solutions. The visible spectra of $[Cu(HL^1)]^{3+}$ were recorded in 0.1 mol dm^{-3} $LiClO_4$ between 288 and 328 K, and these spectra are shown in Figure 5. Isosbestic points are evident at 610 and 445 nm. The absorbances at 820 and 900 nm were fitted by equations (ii)—(iv), based on equilibrium (i).

$$K = \exp(-\Delta G^{\circ}/RT) = [Cu(HL)^{3+}]/\{[Cu(L)^{2+}][H^+]\} \quad \text{(ii)}$$

$$[Cu]_T = [Cu(L)^{2+}] + [Cu(HL)^{3+}] \quad \text{(iii)}$$

$$A = \varepsilon_{CuL}[CuL^{2+}] + \varepsilon_{CuHL}[Cu(HL)^{3+}] \quad \text{(iv)}$$

Values of the absorption coefficient for the protonated complex, ε_{CuHL}, were determined at very low pH where $[CuL^{2+}] = 0$; $\varepsilon_{CuHL} = 27.85$ and 13.2 dm^3 mol^{-1} cm^{-1} at 820 and 900 nm respectively. Values of absorbances, A, at the two wavelengths as a function of temperature were fitted simultaneously by non-linear regression analysis using equations (ii)—(iv), treating ΔG° (or K at 298.2 K) and the absorption coefficient of $[Cu(L)]^{2+}$ as unknown parameters.[5] This gave $K = (2.2 \pm 0.3) \times 10^3$ dm^3 mol^{-1}, $\Delta G^{\circ} = -19.05 \pm 0.29$ kJ mol^{-1}, and $\varepsilon_{CuL} = 166.6 \pm 7.1$ and 181.3 ± 7.1 dm^3 mol^{-1} cm^{-1} at the two wavelengths. At a total copper concentration of 5×10^{-3} mol dm^{-3}, $[Cu(L)^{2+}] = 4.36 \times 10^{-3}$ and $[Cu(HL)^{2+}] = 6.38 \times 10^{-4}$ mol dm^{-3} at 298.2 K; *i.e.* there is 87.2% closure of the pendant-arm ring at this concentration, showing the greater affinity of Cu^{2+} for the pendant Me_2N group compared with a proton. The analogous complex, $[Cu(HL^2)]^{3+}$, was not observed to ring-close in this way, and the copper chelate ring formed by the pendant arm of the macrocycle L^2 is, therefore, less stable than that formed by the macrocycle L^1.

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 either at 100.6 MHz using a Bruker WH400 Fourier-transform spectrometer, or at 22.6 MHz using a Bruker WH90 Fourier-transform spectrometer. ^{1}H N.m.r. spectra were recorded using a Bruker WH400 Fourier-transform spectrometer or a Perkin-Elmer (model R34) 220-MHz spectrometer. I.r. spectra were recorded using a Perkin-Elmer (model 580B) 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. Compounds L^1, L^2, $[Ni(L)][ClO_4]_2$ ($L = L^1$ or L^2), $[Ni(HL)][ClO_4]_3$ ($L = L^1$ or L^2), $[Cu(L^1)][ClO_4]_2$, $[Cu(HL^1)][ClO_4]_3$, and *NOO'*-tris(methylsulphonyl)diethanolamine were prepared as previously described.[1]

Preparation of the Ligand L^3.—A solution of *NN*-bis(3-*p*-tolylsulphonylaminopropyl)methylamine (43.5 g, 96 mmol) in *NN*-dimethylformamide (dmf) (250 cm^3) was stirred under nitrogen during the addition of sodium hydride (4.6 g, 192 mmol). When gas evolution had ceased the solution was heated to 110 °C and a solution of *NOO'*-tris(methylsulphonyl)-diethanolamine (32.6 g, 96 mmol) in dmf (200 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 removed by evaporation under reduced pressure; the resulting viscous brown oil was dissolved in concentrated H_2SO_4 (150 cm^3) and the solution heated at 100 °C for 24 h. After cooling the solution was poured into ethanol (300 cm^3) and diethyl ether (500 cm^3) added. The resulting dark brown precipitate was collected by filtration 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 yellow oil. Distillation (kügelrohr apparatus) gave a colourless oil which solidified on standing to give the ligand L^3, 11-methyl-1,4,7,11-tetra-azacyclotetradecane (4.5 g, 21 mmol), b.p. 120—122 °C at 0.05 mmHg, (*ca.* 6—7 Pa), m.p. 38—40 °C, in *ca.* 22% yield. N.m.r., ^{1}H ($CDCl_3$), δ 1.71 (4 H, quintet), 2.13 (3 H, s), 2.40 (4 H, t), and 2.72 p.p.m. (15 H, m); ^{13}C (CD_3NO_2), δ 28.0 (2 $C\text{-}CH_2\text{-}C$), 41.6 (NMe), 47.3 (2C), 47.4 (2C), 49.7 (2C), and 57.6 (2C) p.p.m. I.r. (thin film): 3 290 cm^{-1} (N–H). Electron-impact mass spectrum; *m/z* 214 (M^+).

Isomerisation of $[Ni(HL^1)][ClO_4]_3$.—The complex $[Ni(HL^1)][ClO_4]_3$ (110 mg, 0.17 mmol) was dissolved in distilled water and the solution heated at 70 °C overnight. Removal of the solvent gave a quantitative yield of isomerised material.

$[Ni(L^1)(NCS)]ClO_4$.—The complex $[Ni(L^1)][ClO_4]_2$ (0.1 g, 0.19 mmol) was stirred in ethanol during the addition of a solution of NaSCN (0.022 g, 0.19 mmol) in ethanol. The pale purple precipitate was collected by filtration, washed with ethanol then diethyl ether, and dried *in vacuo* to give $[Ni(L^1)(NCS)]ClO_4$ (91 mg, 0.18 mmol) in *ca.* 95% yield (Found: C, 35.9; H, 6.8; N, 16.3. $C_{15}H_{33}ClN_6NiO_4S\cdot H_2O$ requires C, 35.6; H, 7.0; N, 16.6%). I.r. (Nujol mull): 3 330, 3 300 (N–H), 2 074 (SCN), and 1 100 cm^{-1} (ClO_4).

$[Ni(HL^1)(NCS)_2]ClO_4$.—The complex $[Ni(HL^1)][ClO_4]_3$ (50 mg, 80 µmol) was stirred in ethanol during the addition of NaSCN (18.6 mg, 160 µmol). The resulting pale purple precipitate was filtered off, washed with ethanol and diethyl ether, then dried *in vacuo* to give $[Ni(HL^1)(NCS)_2]ClO_4$ (42 mg, 74 µmol) in *ca.* 93% yield (Found: C, 34.45; H, 6.1; N, 17.4. $C_{16}H_{34}ClN_7NiO_4S_2\cdot H_2O$ requires C, 34.05; H, 6.4; N, 17.4%). I.r. (Nujol mull): 3 310, 3 265, 3 210 (N–H), 2 105, 2 080 (NCS), and 1 096 cm^{-1} (ClO_4).

$[Ni(L^2)(NCS)]ClO_4$.—The complex $[Ni(L^2)][ClO_4]_2$ (30 mg, 53 µmol) was stirred in ethanol during the addition of NaSCN (6.5 mg, 55 µmol). The resulting purple precipitate was filtered off, washed with ethanol–diethyl ether, and dried *in vacuo* to give $[Ni(L^2)(NCS)]ClO_4$ (25 mg, 48 µmol) in *ca.* 90% yield (Found: C, 41.3; H, 5.9; N, 15.9. $C_{18}H_{31}ClN_6NiO_4S$ requires C, 41.4; H, 6.0; N, 16.1%). I.r. (Nujol mull): 3 330, 3 310 (N–H), 2 080 (SCN), 1 605, 1 582 (pyridine), and 1 110 cm^{-1} (ClO_4).

$[Ni(HL^2)(NCS)_2]NCS$.—The complex $[Ni(HL^2)][ClO_4]_3$ (20 mg, 30 µmol) was stirred in ethanol during the addition of NaSCN (10.6 mg, 90 µmol) in ethanol. The pale purple precipitate was filtered off, washed with ethanol–diethyl ether and dried *in vacuo* to give $[Ni(HL^2)(NCS)_2]NCS$ (15 mg, 28 µmol) in *ca.* 93% yield (Found: C, 42.7; H, 5.7; N, 19.9. $C_{20}H_{32}N_8NiS_3\cdot H_2O$ requires C, 43.1; H, 6.15; N, 20.1%). I.r. (Nujol mull): 3 400, 3 200 (N–H), 2 082 (SCN), 2 060(sh), 1 603, and 1 578 cm^{-1} (pyridine).

$[Ni(L^3)][ClO_4]_2$.—11-Methyl-1,4,7,11-tetra-azacyclotetradecane L^3 (0.25 g, 1.2 mmol) was dissolved in ethanol and added to a solution of $[Ni(dmso)_6][ClO_4]_2$ (dmso = dimethyl sulphoxide) (0.85 g, 1.2 mmol) in ethanol. The resulting orange precipitate was filtered off, washed with ethanol–diethyl ether, and dried *in vacuo* to give $[Ni(L^3)][ClO_4]_2$ (0.50 g, 1.10 mmol) in *ca.* 90% yield (Found: C, 28.1; H, 5.5; N, 11.7. $C_{11}H_{26}Cl_2N_4NiO_8$ requires C, 28.0; H, 5.55; N, 11.9%). I.r. (Nujol mull): 3 205, 3 190 (N–H), and 1 080 cm^{-1} (ClO_4). ^{1}H N.m.r. (CD_3NO_2): δ 1.76 (4 H, m), 2.12 (2 H, m), 2.40 (2 H, m), 2.65 (8 H, m), 2.70 (3 H, s), 2.98 (2 H, m), 3.13 (2 H, qnt), and 3.50 p.p.m. (3 H, N–H).

$[Cu(L^2)][ClO_4]_2$.—The ligand L^2 (140 mg, 0.46 mmol) was dissolved in ethanol and added to a solution of $Cu[ClO_4]_2\cdot 6H_2O$ in ethanol. The resulting blue-purple precipitate was filtered off, washed with cold ethanol, and dried *in vacuo* to give $[Cu(L^2)][ClO_4]_2$ (0.15 g, 0.27 mmol) in *ca.* 60% yield. I.r. (Nujol mull): 3 580 (O–H), 3 240 (N–H), 1 615, 1 590 (pyridine), and 1 110 cm^{-1} (ClO_4).

$[Cu(HL^2)][ClO_4]_3$.—The complex $[Cu(L^2)][ClO_4]_2$ (100 mg, 0.176 mmol) was stirred in ethanol during the addition of a slight excess of $HClO_4$ (70% aqueous). The resulting purple precipitate was filtered off, washed with ethanol, and dried *in vacuo* to give $[Cu(HL^2)][ClO_4]_3$ (0.1 g, 0.15 mmol) in *ca.* 85% yield (Found: C, 29.1; H, 4.8; N, 9.7. $C_{17}H_{32}Cl_3CuN_5O_{12}\cdot 2H_2O$ requires C, 29.0; H, 5.1; N, 9.9%). I.r. (Nujol mull): 3 560 (O–H), 3 240 (N–H), 1 615, 1 585 (pyridine), and 1 100 cm^{-1} (ClO_4).

$[Cu(L^3)][ClO_4]_2$.—11-Methyl-1,4,7,11-tetra-azacyclotetradecane L^3 (0.1 g, 0.47 mmol) was dissolved in ethanol and stirred during the addition of $Cu[ClO_4]_2\cdot 6H_2O$ (0.173 g, 0.47 mmol). The resulting purple precipitate was filtered off, washed with cold ethanol and diethyl ether, then dried *in vacuo* to give $[Cu(L^3)][ClO_4]_2$ (0.19 g, 0.4 mmol) in *ca.* 85% yield (Found: C, 27.95; H, 5.5; N, 11.8. $C_{11}H_{26}Cl_2N_4O_8$ requires C, 27.7; H, 5.5; N, 11.75%). I.r. (Nujol mull): 3 220 (N–H) and 1 090 cm^{-1} (ClO_4).

$[Zn(L^1)][NO_3]_2$.—The ligand L^1 (50 mg, 0.18 mmol) was dissolved in ethanol and $Zn[NO_3]_2\cdot 6H_2O$ (54.8 mg, 0.18 mmol) in ethanol was added. Addition of diethyl ether gave a white precipitate which was filtered off, washed with ether, and dried in *vacuo* to give $[Zn(L^1)][NO_3]_2$ (80 mg, 0.17 mmol) in 94% yield (Found: C, 34.6; H, 7.0; N, 19.6. $C_{14}H_{33}N_7O_6Zn\cdot1.5H_2O$ requires C, 34.8; H, 7.4; N, 20.1%). I.r. (Nujol mull): 3 260 and 3 160 cm^{-1} (N–H).

$[Zn(L^2)][NO_3]_2$.—The ligand L^2 (50 mg, 0.16 mmol) was dissolved in ethanol and added to $Zn[NO_3]_2\cdot6H_2O$ (48.6 mg, 0.16 mmol) in ethanol. The product was precipitated by addition of diethyl ether, filtered off, and dried in *vacuo* to give $[Zn(L^2)][NO_3]_2$ (74 mg, 0.15 mmol) in *ca.* 92% yield (Found: C, 41.1; H, 6.4; N, 19.6. $C_{17}H_{31}N_7O_6Zn$ requires C, 41.3; H, 6.3; N, 19.8%). I.r. (Nujol mull): 3 280 cm^{-1} (N–H). N.m.r. (D_2O): ^1H, δ 2.11 (4 H, m), 2.70 (6 H, s), 2.91 (4 H, m), 3.05 (4 H, m), 3.18 (4 H, m), 4.00 (2 H, d), 4.36 (1 H, d), 4.45 (1 H, t), 4.50 (1 H, m), 4.56 (1 H, m), 7.56 (2 H, d), and 8.14 p.p.m. (1 H, t); ^{13}C, δ 22.6 (2 × C–CH$_2$–C), 47.2 (2 C), 47.6 (2 C), 51.2 (1 C), 51.5 (NMe$_2$), 53.2 (2 C), 56.5 (1 C), 123.6 (2 β-C), 143.0 (γ-C), and 154.2 p.p.m. (2 α-C).

$[Zn(L^3)][NO_3]_2$.—This compound was prepared as described for L^2, from the ligand L^3 (0.4 g, 1.87 mmol) and $Zn[NO_3]_2\cdot6H_2O$ (0.56 g, 1.87 mmol) in ethanol: yield 0.75 g, 1.74 mmol, *ca.* 93% (Found: C, 32.9; H, 6.5; N, 20.6. $C_{11}H_{26}N_6O_6Zn$ requires C, 32.7; H, 6.5; H, 20.8%). I.r. (Nujol mull): 3 270 and 3 190 cm^{-1} (N–H).

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