# Copper and Nickel Complexes of 1,8-Disubstituted Derivatives of 1,4,8,11-Tetraazacyclotetradecane†

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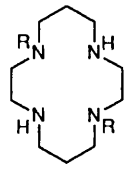
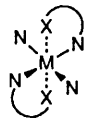
The stereoselective synthesis of various 1,8-disubstituted derivatives of 1,4,8,11-tetraazacyclotetradecane (cyclam) has been achieved and copper and nickel complexes prepared. For the 1,8-dibutyl derivative, the square-planar nickel(II) complex exists as two diastereoisomers, as revealed by crystallographic analysis. The structure of the copper(II) complex of this ligand confirmed that a strong in-plane ligand field was conserved in square-planar complexes notwithstanding the dialkylation at nitrogen. The structures of the copper(II) complexes of two 1,8-dicarboxymethyl derivatives of cyclam also reveal primary $N_4$ co-ordination with carboxyl oxygens occupying the elongated axial sites. The tricyclic ligand 1,5,8,12-tetraazatricyclo[10.2.2.2$^{5,8}$]octadecane is readily prepared from one of these diacids and the copper complex is kinetically stable in solution with respect to attack by hydrogen sulfide and to acid-catalysed dissociation.

The elaboration of the co-ordination chemistry of 1,4,8,11-tetraazacyclotetradecane (cyclam) has been a pivotal feature in the development of macrocyclic complexation chemistry.[1] Less work has been reported for monosubstituted derivatives of cyclam,[2] although the chemistry of both C- and N-substituted derivatives has been described in some detail.[3,4] Much less attention has been paid to the chemistry of disubstituted derivatives although they are intrinsically very interesting. For example the regioselective formation of 1,8-disubstituted derivatives,[5,6] **A**, in which the substituent may act as a donor to a metal allows the formation of octahedral complexes in which the two additional neutral or anionic donors X may adopt axial binding sites, **B** (X = $CO_2H$, $CONR_2$, $CO_2^-$ or $PMeO_2^-$). In



**A** R = alkyl or carboxyalkyl



**B**

such a complex destabilising steric interactions between the N-substituents and other ligand atoms or torsional ring-strain effects are likely to be minimised, and a small divalent ion such as $Cu^{2+}$ or $Ni^{2+}$ may still experience a strong ligand field from the four 'equatorial' ring nitrogens, comparable to that found in related complexes of cyclam itself. Such a situation may be compared with that found in the nickel(II) complex of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, where the low ligand-field strength observed[7] has been attributed to a stretching of all the Ni–N bonds to relatively long values (1.98–1.99 Å)[8,‡] due to van der Waals repulsions between N-methyl groups and proximate hydrogens. If the donor X in **B** is ionisable, then metal complexes with divalent ions will be charge neutral overall. Such complexes are likely to be somewhat lipophilic and this lipophilicity may be enhanced by alkylation of the 4,11 positions. There are additional reasons for studying lipophilic metal complexes. For example, kinetically stable complexes of $^{64}Cu$ ($\beta^+$, $t_{\frac{1}{2}}$ = 12.8 h) are required for *in vivo* use[9] in diagnostic medicine. Positron-emission tomography affords high-resolution detection of the tracer isotope *in vivo*,[10] and lipophilic complexes may exhibit tissue specificity in their biodistribution. A particularly attractive target is the brain, in which the problem of localisation is directly related to the ability of the complex to cross the blood-brain barrier. Low molecular weight (≤600), charge-neutral and relatively lipophilic complexes may transverse the membrane.[11] A second potential application of lipophilic metal complexes is in agrochemistry. The depletion of trace-metal cations in soils and plants is usually rectified by application of large quantities of their hydrophilic edta or dtpa complexes ($H_4$edta = ethylenediaminetetraacetic acid, $H_5$dtpa = diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid). It is possible that the more lipophilic complexes of these essential cations, *e.g.* $Mn^{2+}$, $Cu^{2+}$ or $Zn^{2+}$, may be much more readily taken up by plant roots thereby reducing the dosage required.

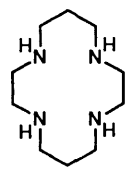
There have been only isolated reports of the stereoselective N-functionalisation of cyclam ($L^1$). For example, in the carboxymethylation of $L^2$, steric inhibition of electrophilic attack at the 4,11 positions leads to selective 1,8 functionalisation giving $L^3$.[12] When functionalising cyclam itself, it has been found that ditosylation occurs with selective formation of the 1,8-ditosylamide, $L^4$.[5,6] This compound has been used as the precursor for the formation of a series of 1,8-dialkylated derivatives $L^5$–$L^7$ and the structures of the nickel and copper complexes of $L^5$ are reported herein, together with the structures of the copper(II) complexes of $H_2L^8$ and $H_2L^9$ in each of which the primary co-ordination to copper involves the four ring nitrogen atoms with the oxygens of the carboxylates occupying the elongated axial sites. A preliminary account of part of this work has appeared.[5]

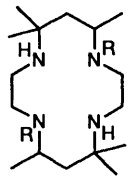
## Results and Discussion

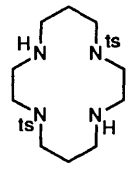
*Ligand Syntheses.*—Alkylation of the ditosylamide $L^4$ (BuI, MeCN, $Na_2CO_3$) afforded the dibutyl compound $L^{10}$ in moderate yield. Selective monoalkylation of $L^4$ occurred using

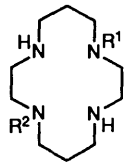
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

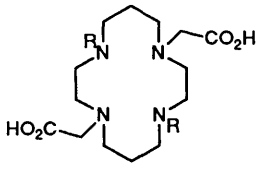
‡ These bond lengths may be compared with Ni–N bond lengths of 1.926 and 1.940(4) Å found[8b] in the structure of 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane $L^{17}$.

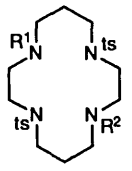

$L^1$

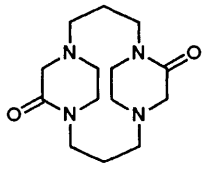

$L^2$ R = H
$H_2L^3$ R = $CH_2CO_2H$

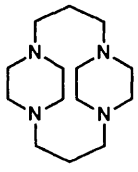

$L^4$

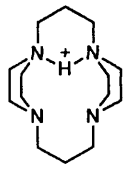

$L^5$ $R^1$ = $R^2$ = Bu
$L^6$ $R^1$ = $R^2$ = Me
$L^7$ $R^1$ = Bu, $R^2$ = Me

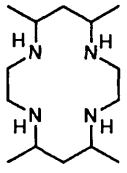

$H_2L^8$ R = H
$H_2L^9$ R = Me

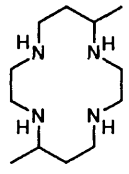

$L^{10}$ $R^1$ = $R^2$ = Bu
$L^{11}$ $R^1$ = $R^2$ = Me
$L^{12}$ $R^1$ = H, $R^2$ = Bu
$L^{13}$ $R^1$ = Me, $R^2$ = Bu


$L^{14}$


$L^{15}$


$HL^{15+}$


$L^{16}$


$L^{17}$

bromobutane instead of iodobutane under similar reaction conditions to give $L^{12}$. This was N-methylated under standard Eschweiler–Clarke conditions to yield $L^{13}$. Direct methylation of $L^4$ ($HCO_2H$, HCHO) afforded the dimethyl derivative $L^{11}$, completing the short series. Detosylation of $L^{10}$, $L^{11}$ and $L^{13}$ was effected smoothly and efficiently in excellent yield using HBr–$MeCO_2H$ in the presence of phenol giving the tetramines $L^5$, $L^6$ and $L^7$ which were isolated as their hydrobromide salts.

The synthesis of the diacid $H_2L^8$ and of the bicyclic lactam $L^{14}$ (derived from $H_2L^8$) was effected as reported earlier.[6] Although $H_2L^8$ lactamises at room temperature in aqueous solution (even in 6 mol $dm^{-3}$ HCl!) it may be methylated in good yield (HCHO, $HCO_2H$, 74%) giving $L^9$. Reduction of the lactam $L^{14}$ [$BH_3$·tetrahydrofuran (thf), 60%] permitted the synthesis of the tricyclic tetramine $L^{15}$. This ligand, a cryptand, may also be regarded as a 'structurally reinforced' macrocycle[13] in which the rigidity of the tricyclic system enforces the metal ion to bind in the plane of the donor atoms. In binding in such a manner, each of the piperazine rings needs to adopt a boat conformation which is energetically unfavourable and will contribute an unfavourable term to the enthalpy of metal complexation. The unfavourable nature of the chair–boat interconversion and the structural rigidity of the ligand as a whole are reflected in the observed protonation constants for $L^{15}$. Potentiometric titrations reveal successive p$K_a$ values of 8.33(3) and 3.02(2). The first of these values is very similar to that found for other piperazines or 1,4-diazabicyclooctane,[14] but the second protonation constant is rather low. The relatively high acidity of the diprotonated species $H_2L^{15\,2+}$ may be related to steric inhibition of protonation of the monoprotonated ligand. The $^1H$ NMR spectrum of the ligand was examined as a function of pH. At both high pH ($\geqslant$11) and in $CDCl_3$ or $CD_2Cl_2$, resonances were observed that were consistent with time-averaged $D_{2d}$ symmetry: a single quintet and triplet for the two $NCH_2CH_2CH_2N$ moieties and a pair of symmetrical multiplets for the piperazine ring protons. The spectrum of the tetracation was shifted to higher frequency (in 12 mol $dm^{-3}$ DCl–$D_2O$) but also had the same features (*e.g.* quintet for $NCH_2CH_2CH_2N$) suggesting that this species has similar high symmetry. At intermediate values of pH, broadened resonances were additionally observed and the spectra obtained were more complex. In a deuterioacetate buffer at pH 5, two multiplets in 1:1 ratio for the $NCH_2C\mathit{H}_2CH_2N$ resonances were observed suggesting the structure shown for the monocation $HL^{15+}$, while at pH 0 the broadened resonances of the protons in the six-membered rings had shifted to higher frequency and at least four resonances for the $NCH_2C\mathit{H}_2CH_2N$ protons were distinguished. Certainly the protonation behaviour of $L^{15}$ is quite different from that of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, and it is not behaving like two independent piperazines.

**Table 1** Visible absorption spectra ($H_2O$, 293 K) for nickel and copper complexes

| Complex cation | $\lambda_{max}$/$cm^{-1}$ | 10 $D_{q_{xy}}$ [a] |
|---|---|---|
| $[NiL^5]^{2+}$ | 21 691 | 1971[b] |
| | 21 141 | 1922[c] |
| $[NiL^6]^{2+}$ | 21 929 | 1993 |
| $[NiL^7]^{2+}$ | 21 820 | 1984 |
| $[NiL^{15}]^{2+}$ | 22 222 | 2020 |
| $[NiL^1]^{2+}$ [d] | 22 473 | 2043 |
| $[NiL^{18}]^{2+}$ [d,e] | 23 540 | 2140 |
| $[CuL^{18}]^{2+}$ [f] | 18 310 | |
| $[CuL^1]^{2+}$ [f] | 19 900 | |
| $[CuL^{15}]^{2+}$ | 18 587 | |
| $[CuL^5]^{2+}$ | 18 939 | |
| $[CuL^6]^{2+}$ | 18 315 | |
| $[CuL^7]^{2+}$ | 18 656 | |

[a] 10 $D_{q_{xy}}$ = $\nu_{d-d}$/11.0 (ref. 15). [b] *trans* Isomer. [c] *cis* Isomer. [d] Ref. 16. [e] $L^{18}$ = 1,4,7,10-tetraazacyclotridecane. [f] Ref. 7.

*Metal Complexes.*—Nickel- and copper-(II) complexes of ligands $L^5$–$L^7$ were prepared and the structures of the 1,8-dibutyl derivatives $[NiL^5]^{2+}$ and $[CuL^5]^{2+}$ determined by X-ray crystallography. In all of the nickel complexes, the position of the observed visible absorption band (Table 1) suggested that the nickel was square planar with a relatively strong ligand field. This was confirmed by the crystallographic analysis of $[NiL^5][ClO_4]_2$ in which the Ni–N bond lengths were 1.939(2) (to NH) and 1.970(2) Å (to NBu) (Table 2). In this centrosymmetric structure (Fig. 1), the perchlorate counter ions were fairly remote from the nickel [O(1) • • • Ni 3.072(8) Å], and were disordered over two sites. The ring adopted the expected quadrangular [3434] conformation with an *RSSR* configuration at the nitrogen stereogenic centres. For comparison, in the nickel complex of 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclo-

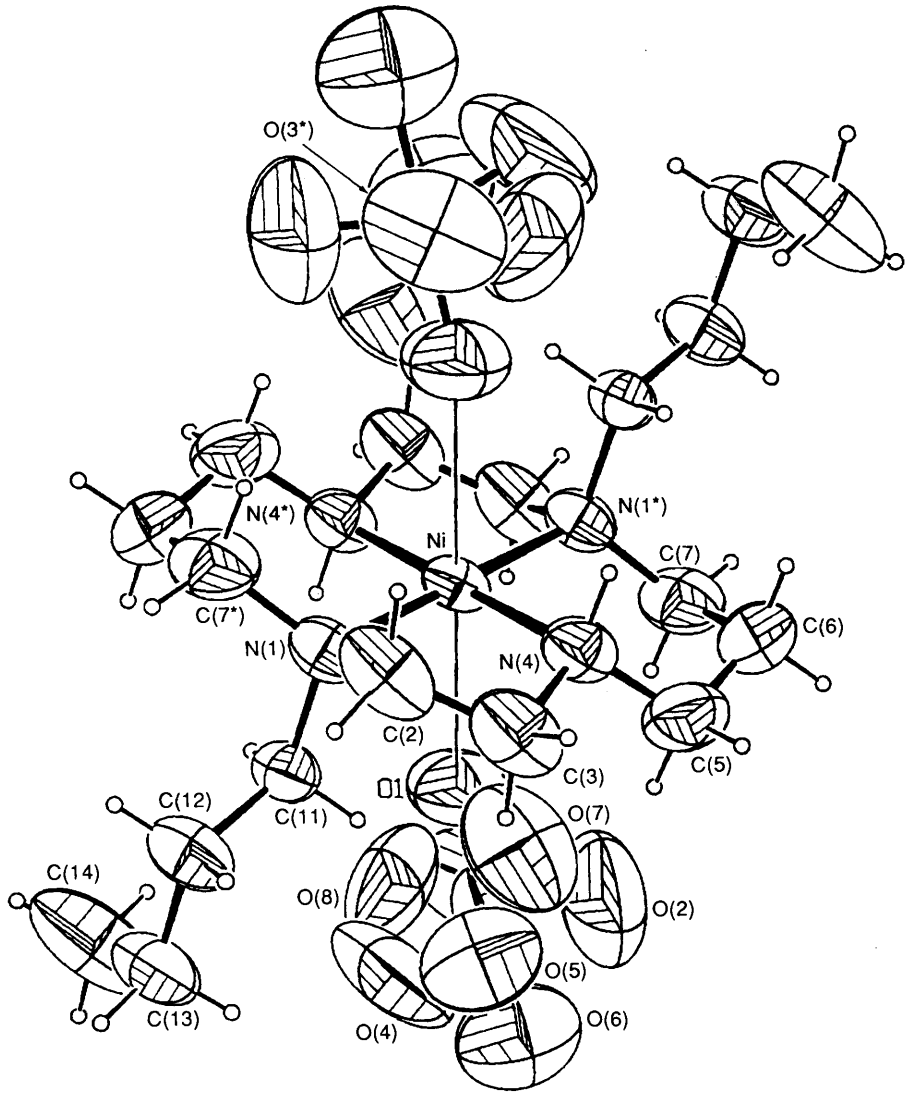



**Fig. 1** Structure of $[NiL^5][ClO_4]_2$ in the crystal. The perchlorate anions were disordered over two sites with equal occupancy

**Table 2** Selected molecular dimensions (distances in Å, angles in °) for $[NiL^5][ClO_4]_2$ with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Ni–N(1) | 1.970(2) | N(1)–Ni–N(4) | 87.45(9) |
| Ni–N(4) | 1.939(2) | Ni–N(1)–C(2) | 105.1(2) |
| O(1) · · · Ni | 3.072(8) | Ni–N(1)–C(7$^I$) | 115.8(2) |
| N(4) · · · O(3$^{II}$) | 3.150(9) | Ni–O(1)–Cl | 152.0(3) |
| N(4) · · · O(8$^{II}$) | 2.997(13) | N(4)–H(4)–O(3$^{II}$) | 139.4 |
| H(4) · · · O(3$^{II}$) | 2.37 | N(4)–H(4)–O(8$^{II}$) | 146.5 |
| H(4) · · · O(8$^{II}$) | 2.16 | | |

Symmetry operations: I $-x, -y, -z$; II $x, y, -1 + z$.

tetradecane, $L^{16}$, nickel–nitrogen bond lengths of 1.964(3) and 1.974(3) Å were found[17] in the square-planar complex with the perchlorate counter ion somewhat closer at 2.808(5) Å from nickel. In the related nickel(II) complex of $L^{17}$, Ni–NH bond lengths were 1.926 and 1.940 Å.[8] Crystallisation of the nickel complex of $L^5$ from aqueous solution gave prisms ($\lambda_{max}$ 461 nm) initially and plates on further concentration and slow evaporation of the aqueous solution ($\lambda_{max}$ 473 nm). The former complex was determined to be the *trans* isomer (Fig. 1), and it was assumed that the other complex was a diastereoisomer with the N-butyl groups *cis* related in the complex. Crystallographic analysis (both at 293 and 173 K) of these plates revealed severe disorder in the crystal lattice. There were two independent cations in the unit cell each lying across mirror planes. In each case the nickel atom and the two secondary nitrogens lie on the same mirror plane. This demands that the N–Bu groups are *cis* disposed. Electron-density maps revealed the nickel, nitrogen and the first two carbon atoms of the butyl chain but as a consequence of the mirror-imposed disorder the five- and six-membered chelate rings could not be distinguished and a composite was observed with ill defined density corresponding to a superposition of the five- and six-membered rings. In addition, all of the four perchlorate groups in the unit cell (each lying on a mirror plane) were disordered. The analysis is certainly sufficient to pinpoint the differences from the structure of the isomeric complex. It is very likely that the plates are indeed a *cis* diastereoisomer with an *RSRS* configuration at nitrogen. Although the formation of two isomeric copper–cyclam cationic complexes has been known for some time, the observation and structural determination of two diastereoisomeric square-planar nickel(II) complexes of a tetraaza macrocycle appears to be most uncommon.

The copper(II) complex of $L^5$ was isolated as its hexafluorophosphate salt (from MeCN–MeOH–$Pr^i_2O$) and crystallised in the same space group as $[NiL^5][ClO_4]_2$. Again the 14-membered ring adopted a [3434] quadrangular conformation with an *RSSR* configuration at each nitrogen (Fig. 2) and the two $PF_6$ counter ions occupied the axial sites. The nearest

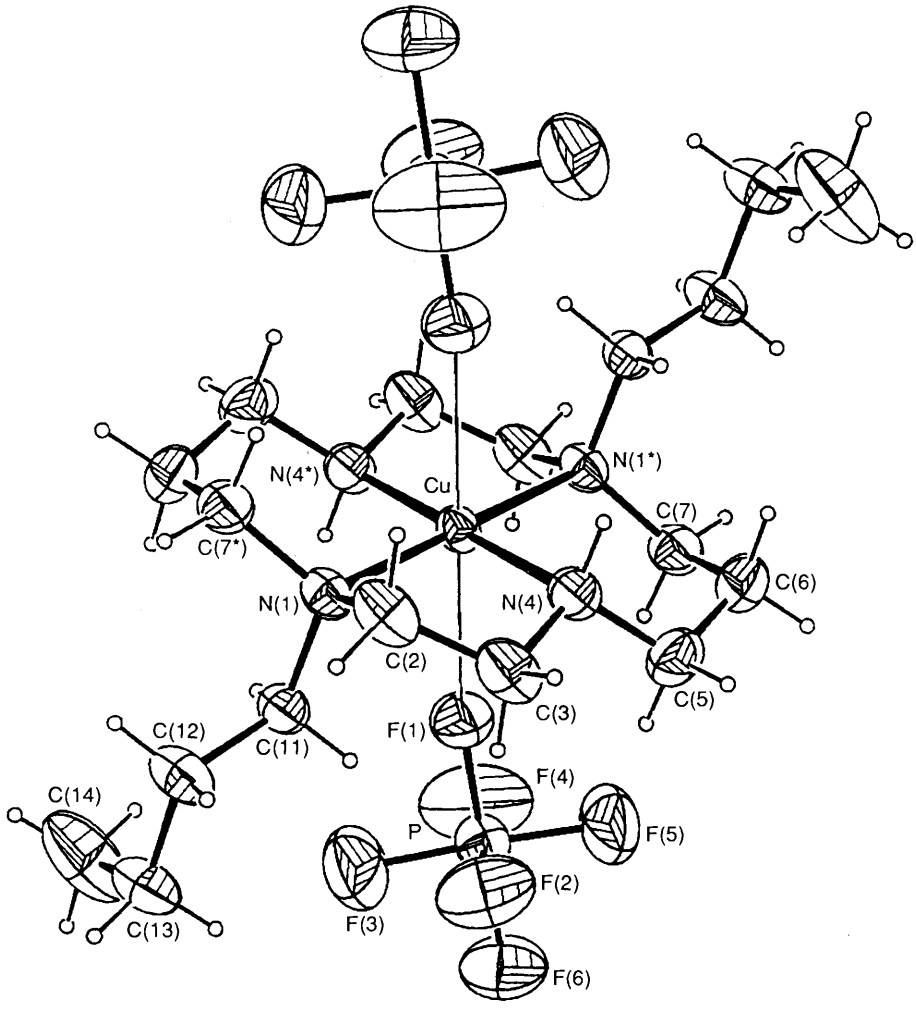



**Fig. 2** Structure of $[CuL^5][PF_6]_2$ in the crystal

**Table 3** Selected molecular dimensions (distances in Å, angles in °) for $[CuL^5][PF_6]_2$ with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Cu–N(1) | 2.062(2) | N(1)–Cu–N(4) | 86.61(8) |
| Cu–N(4) | 2.005(2) | Cu–F(1)–P | 158.48(9) |
| F(1)···Cu | 2.840(2) | N(4)–H(4)–F($1^{I}$) | 117.5 |
| N(4)···F($1^{II}$) | 3.303(4) | N(4)–H(4)–F($4^{II}$) | 147.5 |
| H(4)···F($1^{II}$) | 2.76 | | |
| N(4)···F($4^{II}$) | 3.221(4) | | |
| H(4)···F($4^{II}$) | 2.38 | | |

Symmetry operations: I $-x, -y, -z$; II $x, y, -z$.

**Table 4** Selected molecular dimensions (distances in Å, angles in °) for $[Cu(H_2L^9)][ClO_4]_2 \cdot 2H_2O$; with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Cu–N(1) | 2.070(3) | N(1)–Cu–N(4) | 87.1(1) |
| Cu–N(4) | 2.096(3) | N(1*)–Cu–N(4) | 92.9(1) |
| Cu–O(10) | 2.369(3) | N(1)–Cu–O(10) | 101.8(1) |
| | | N(1*)–Cu–O(10) | 78.2(1) |
| | | N(4)–Cu–O(10) | 91.9(1) |

Cu ··· F distance was 2.840(2) Å (Table 3). The Cu–N bond lengths of 2.005(2) (to NH), and 2.062(2) Å are quite short, and may be compared to values of 2.03 Å for a 'strain-free' Cu–NH bond [7] and 2.02 Å observed in the copper complex of cyclam.[18] The structural analyses of these nickel and copper complexes of $L^5$ together with the observed ligand-field strength (Table 1) certainly support the premise that 1,8-disubstitution of 1,4,8,11-tetraazacyclotetradecane does not compromise complex stability as a result of unfavourable steric interactions. Indeed the only obvious poor non-bonding interactions in the structures of the copper and nickel complexes are apparent in the six-membered chelate rings. There are unfavourable 1,3-synaxial interactions between the NBu group and an NH in each chair (Figs. 1 and 2).

With the *trans*-diacetate ligands $L^8$ and $L^9$, the carboxymethyl groups are able to bind to the metal ion in axial sites while retaining a strong ligand field in the plane of the ring. This view was confirmed by the position of the d–d absorption ($\lambda_{max}$ 565 and 573 nm respectively) and in the crystallographic analyses of the neutral copper(II) complexes, which crystallised from aqueous acidic solution. With the dimethyl ligand $H_2L^9$, the crystal structure (Fig. 3) revealed the copper to be six-co-ordinate with four short bonds to nitrogen [2.070(3) and 2.096(3) Å] and two longer bonds to oxygen [Cu–O 2.369(3) Å] with the copper at an inversion centre (Table 4). In the crystal lattice, a hydrated proton was hydrogen-bonded to each carbonyl oxygen and to a proximate perchlorate counter ion. The protonation of the complex on oxygen may account for the slight elongation of the Cu–O bonds, notwithstanding the Jahn–Teller distortion and the strong in-plane ligand field. Support for this idea comes from a comparison of the related structure of $[CuL^8]$ (Fig. 4), in which the Cu–O distance is shorter, 2.263(4) Å (Table 5), and the Cu–N bond lengths are similar, 2.095(3) (to $NCH_2CO_2$) and 2.014(4) Å, to the secondary nitrogens. The shorter Cu–NH bond in $[CuL^8]$ compared to the Cu–NMe bond in $[CuL^9]$ is expected. Numerous

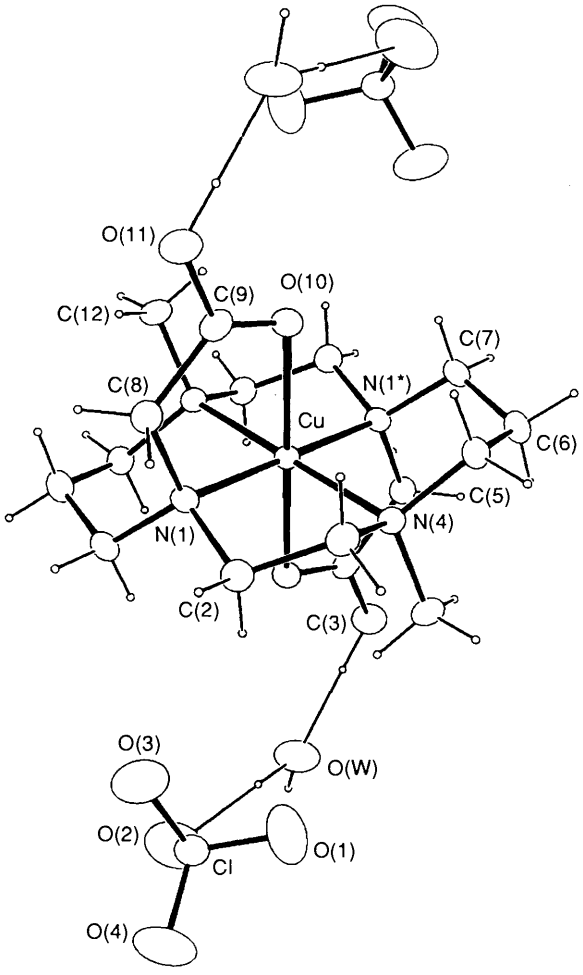



**Fig. 3** Structure of $[Cu(H_2L^9)][ClO_4]_2 \cdot 2H_2O$ in the crystal showing the pattern of hydrogen bonding

**Table 5** Selected molecular dimensions (distances in Å, angles in °) for $[CuL^8][ClO_4]_2 \cdot H_2L^{14}$ with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Cu–N(1A) | 2.095(3) | N(1A)–Cu–N(4A) | 86.3(1) |
| Cu–N(4A) | 2.014(4) | N(1A)–Cu–N(4A) | 93.7(1) |
| Cu–O(10A) | 2.263(3) | N(1A)–Cu–O(10A) | 79.7(1) |
| N(4A)–O(1) | 3.046(9) | N(4A)–Cu–O(10A) | 90.0(1) |
| HN(4A)–O(1) | 2.21 | | |
| HN(1B)–O(11A) | 1.76 | C(2B)–N(1B)–C(7B*) | 111.2(4) |
| N(1B)–O(11A) | 2.676(4) | C(2B)–N(1B)–C(8B) | 106.5(4) |
| N(4B)–C(9B) | 1.341(7) | N(1B)–C(2B)–C(3B) | 111.6(3) |
| N(4B)–C(5B) | 1.471(5) | C(2B)–C(3B)–N(4B) | 113.3(5) |
| C(9B)–O(10B) | 1.216(5) | C(3B)–N(4B)–C(5B) | 117.0(4) |
| N(1B)–C(2B) | 1.489(7) | C(3B)–N(4B)–C(9B) | 124.2(4) |
| C(3B)–N(4B) | 1.456(5) | N(4B)–C(9B)–O(10B) | 123.7(4) |

studies have demonstrated that metal–nitrogen bond lengths are increased by N-alkyl substitution[7,19] due to van der Waals repulsions between alkyl hydrogens and those elsewhere in the complex. For example in the bis(*N*,*N*-diethylethylenediamine)-copper(II) complex, values of 2.08 and 2.02 Å were found for copper tertiary- and secondary-nitrogen bonds, respectively.[19]

In each of the copper(II) complexes of $L^8$ and $L^9$, the macrocyclic ring adopts a [3434] conformation with the configuration at each nitrogen centre being *RRSS*. In the case of $[CuL^8]$, the complex crystallised with the diprotonated lactam $H_2L^{14}$ in the crystal lattice. In the unit cell, the lactam lay in the centre (at an inversion centre) with the copper complex at the four corners. The carbonyl oxygens of the copper complex were hydrogen-bonded to the protonated tertiary amines of the lactam and the

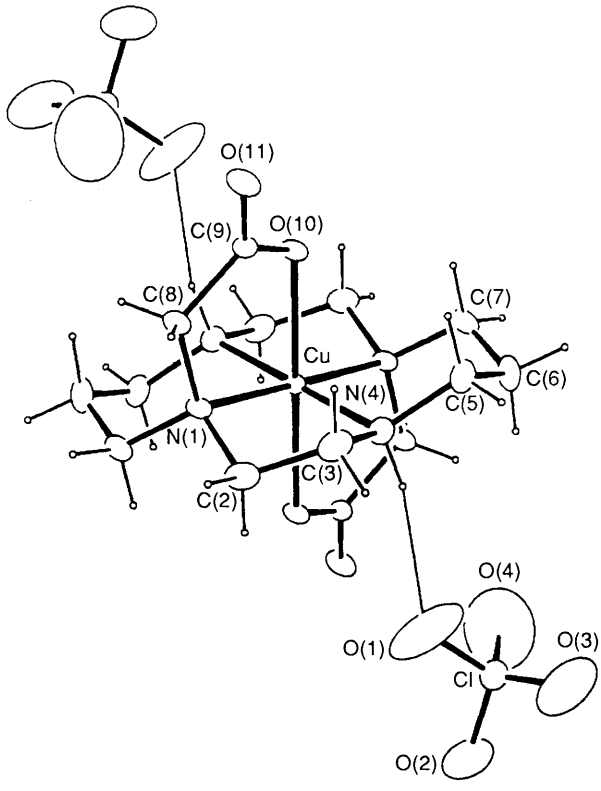



**Fig. 4** Structure of $[CuL^8]$ in the crystal showing the hydrogen bonding to the perchlorate anions of the protonated lactam $H_2L^{14\,2+}$

secondary N–H groups were hydrogen-bonded to perchlorate counter ions (Fig. 5).

These copper complex structures with ligands $L^8$ and $L^9$ may be contrasted with that reported with 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid, in which the primary co-ordination sphere involves $N_2O_2$ co-ordination and two ring nitrogen atoms occupy the elongated axial sites.[20] In this case a strong $N_4$ in-plane ligand field cannot be attained without severe non-bonding steric interactions and the complex relaxes to the lower-energy structure observed.

The copper and nickel complexes of the tricyclic tetraamine $L^{15}$ in aqueous solution give visible absorption spectra [$\lambda_{max}(H_2O)$ 538 and 450 nm respectively] typical of square-planar complexes with a strong ligand field (Table 1). The copper complex is resistant to attack by hydrogen sulfide in aqueous solution, consistent with high kinetic stability. The visible absorption spectrum was invariant in the range pH 1.4–11.4 showing that the complex was resistant to protonation over this range. In comparison $[CuL^1]^{2+}$ is also resistant to acid-catalysed decomplexation and dissociation may only be observed in 6 mol $dm^{-3}$ nitric acid.[21] In these square-planar complexes with $L^{15}$, the two piperazine rings must adopt boat conformations.

## Experimental

Reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Commercial solvents were distilled from an appropriate drying agent prior to use according to standard procedures. Proton and carbon-13 NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.1 and 62.9 MHz respectively. Chemical shifts are given in ppm relative to $SiMe_4$ ($\delta$ 0). Infrared spectra were recorded as KBr discs or as a mull in Nujol with a Perkin-Elmer 577 spectrometer or a Mattson-Sirius 100 FT spectrometer. Mass spectra were recorded on a VG 7070 E spectrometer with a FAB, CI, EI or DCI ionization mode (FAB, fast atom

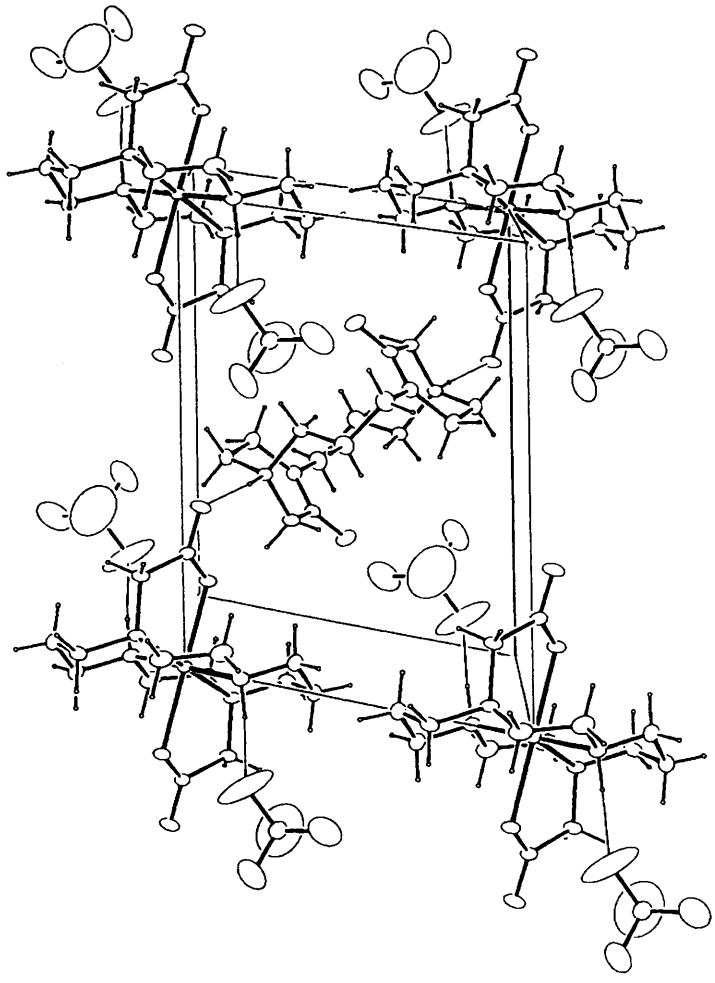


**Fig. 5** View of the unit cell showing the protonated lactam $H_2L^{14\,2+}$ at the inversion centre

bombardment; CI, chemical ionization; EI, electron impact; DCI, desorption chemical ionization), as stated.

pH-*Metric Titrations*.—(*i*) *Apparatus*. The titration cell was a double-walled glass vessel (capacity 5 $cm^3$) which was maintained at 25 °C, using a Techne Tempette Junior TE-8J. Titration solutions were stirred using a magnetic stirrer and kept under an atmosphere of nitrogen. Titrations were performed using an automatic titrator (Mettler DL20, 1 $cm^3$ capacity) and burette functions (volume increments and equilibration time) were controlled by a BBC microprocessor. The pH was measured using a Corning 001854 combination microelectrode which was calibrated using buffer solutions at pH 4.008 ($HO_2CC_6H_4CO_2K$, 0.05 mol $dm^{-3}$) and pH 6.865 [$KH_2PO_4$ (0.025 mol $dm^{-3}$)–$Na_2HPO_4$ (0.025 mol $dm^{-3}$)]. Data were stored on the BBC microprocessor and transferred to the MTS mainframe using KERMIT and subsequently analysed by two non-linear least-squares programs SCOGS-2 and SUPERQUAD.[22]

(*ii*) *Acid-dissociation constants*. Stock solutions of the ligand $L^{15}$ (0.002 mol $dm^{-3}$) in Milli-Q water (25.0 $cm^3$) with nitric acid (0.004 mol $dm^3$) and tetramethylammonium nitrate ($I$ = 0.10 mol $dm^{-3}$) were prepared. In each titration 3.5 $cm^3$ of the stock ligand solution was titrated with tetramethylammonium hydroxide (0.109 mol $dm^{-3}$), the exact molarity of the which was determined by titration against hydrochloric acid (0.100 mol $dm^3$).

*Synthesis of Ligands*.—1,8-*Dimethyl*-4,11-*bis*(*toluene*-p-*sulfonyl*)-1,4,8,11-*tetraazacyclotetradecane*, $L^{11}$. A mixture of 1,8-bis(toluene-*p*-sulfonyl)-1,4,8,11-tetraazacyclotetradecane $L^4$ (0.51 g, 0.1 mmol), formaldehyde (1 $cm^3$, 30% aqueous solution) and formic acid (1.2 $cm^3$) was heated at 90° for 4 h. After cooling hydrochloric acid was added (5 $cm^3$, 6 mol $dm^{-3}$) and the solution was evaporated. The residue was taken up in water (5 $cm^3$), the pH adjusted to ⩾13 (KOH) and the solution extracted with dichloromethane (4 × 10 $cm^3$). After evaporation and drying ($K_2CO_3$) a colourless oil was obtained (0.48 g, 86%); $R_f$ (10% MeOH–$CH_2Cl_2$) 0.70; *m*/*z* (DCI) 538 $[M + 2]^+$ and 537 $[M + 1]^+$; $\delta_C(CDCl_3)$ 143.1 (s), 136.7 (s), 129.5, 126.9 (d), 55.7, 55.4 (t), 47.6, 46.9 ($CH_2N$), 43.1 ($CH_3N$), 26.3 ($CH_2C$) and 21.3 ($CH_3$–aryl); $\delta_H(CDCl_3)$ 7.65 (4 H, d, ortho aryl H, $J$ 7.7 Hz), 7.25 (4 H, d), 3.19 [8 H, t + t, $CH_2N$(ts)], 2.49 (4 H, t, $CH_2N$), 2.40 (6 H, s, $CH_3$-aryl), 2.35 (4 H, t, $CH_2N$), 2.15 (6 H, s, $CH_3N$) and 1.73 (4 H, qnt, $CH_2C$).

1,8-*Dibutyl*-4,11-*bis*(*toluene*-p-*sulfonyl*)-1,4,8,11-*tetraazacyclotetradecane*, $L^{10}$. To a solution of $L^4$ (0.51 g, 0.1 mmol) in acetonitrile (15 $cm^3$) was added anhydrous potassium carbonate (0.26 g) and 1-iodobutane (0.39 g, 2.12 mmol), and the mixture was heated to reflux for 48 h. After filtration and removal of solvent, the residue was chromatographed on silica (2% MeOH–$CH_2Cl_2$) to yield a colourless oil (0.27 g, 43%), which crystallised on standing, m.p. 108–110 °C; *m*/*z* (DCI) 622 $[M + 2]^+$ and 621 $[M + 1]^+$; $\delta_C(CDCl_3)$ 143.0, 136.6 (s), 129.5, 127.0 (d), 55.0, 53.2, 51.2, 47.9, 47.3 ($CH_2N$), 28.9, 26.3 ($CH_2C$), 21.3 ($CH_3$–aryl) and 13.9 ($CH_3CH_2$); $\delta_H$ 7.65 (4 H, d), 7.30 (4 H, d), 3.22 [4 H, t, $CH_2N$(ts)], 3.12 [4 H, t, $CH_2N$(ts)], 2.56 (4 H, t), 2.41 (6 H, s, $CH_3$-aryl), 2.31 (4 H, t), 1.70 (4 H, t), 1.28 (8 H, m, $CH_2CH_2$) and 0.89 (6 H, t, $CH_3CH_2$).

1,8-*Dibutyl*-1,4,8,11-*tetraazacyclotetradecane*, $L^5$. The di-

**Table 6** Summary of cell data, data collection and refinement details

| Compound | *trans*-[NiL$^5$][ClO$_4$]$_2$ | *cis*-[NiL$^5$][ClO$_4$]$_2$ | [CuL$^5$][PF$_6$]$_2$ | [Cu(H$_2$L$^9$)][ClO$_4$]$_2$·2H$_2$O | [CuL$^8$][H$_2$L$^{14}$][ClO$_4$]$_2$ |
|---|---|---|---|---|---|
| Formula | $C_{18}H_{40}Cl_2NiN_4O_8$ | $C_{18}H_{40}Cl_2NiN_4O_8$ | $C_{18}H_{40}CuF_{12}N_4P_2$ | $C_{16}H_{36}Cl_2CuN_4O_{14}$ | $C_{28}H_{52}Cl_2CuN_8O_{14}$ |
| *M* | 570.2 | 570.2 | 666.0 | 642.9 | 859.2 |
| Colour, habit | Yellow, block | Orange, plate | Pink, diamond | Blue, block | Deep blue, plate |
| Crystal size/mm | 0.29 × 0.33 × 0.57 | 0.15 × 0.41 × 0.55 | 0.07 × 0.56 × 0.65 | 0.14 × 0.32 × 0.38 | 0.30 × 0.25 × 0.24 |
| Crystal system | Triclinic | Orthorhombic | Triclinic | Monoclinic | Triclinic |
| *a*/Å | 9.214(2) | 15.047(3) | 9.357(2) | 8.089(4) | 9.547(2) |
| *b*/Å | 9.315(2) | 12.689(3) | 9.297(2) | 9.269(2) | 12.014(2) |
| *c*/Å | 8.507(2) | 26.471(5) | 8.552(2) | 17.552(4) | 8.929(1) |
| α/° | 113.90(1) | | 112.60(2) | | 98.97(1) |
| β/° | 104.64(2) | | 103.63(2) | 96.34(3) | 114.56(1) |
| γ/° | 75.52(1) | | 77.31(1) | | 80.44(2) |
| *U*/Å$^3$ | 636.9(4) | 5054(2) | 660.6(4) | 1308(1) | 914.2(6) |
| Space group | $P\bar{1}$ | *Pnma*/*Pn*2$_1$*a* | $P\bar{1}$ | *P*2$_1$/*c* | $P\bar{1}$ |
| *Z* | 1 | 8 | 1 | 2 | 1 |
| Molecular symmetry | $\bar{1}$ | | $\bar{1}$ | $\bar{1}$ | $\bar{1}$ |
| *F*(000) | 302 | 2416 | 343 | 670 | 451 |
| $D_{calc}$/g cm$^{-3}$ | 1.49 | 1.50 | 1.67 | 1.63 | 1.56 |
| μ/cm$^{-1}$ | 10.2 | 10.3 | 10.5 | 11.1 | 8.2 |
| Min., max. absorption correction | 0.69, 0.79 | | 0.59, 0.93 | 0.71, 0.86 | 0.70, 0.82 |
| 2θ range/° | 4 to 54 | 4 to 48 | 4 to 54 | 4 to 54 | 4 to 54 |
| *T*/°C | 21 | −100 | 21 | 21 | 21 |
| Reflections measured | 2857 | 3800 | 2944 | 3320 | 4097 |
| Unique reflections | 2857 | | 2423 | 2848 | 3985 |
| Reflections with $I > 3\sigma(I)$ | 2331 | 2109 | 2420 | 1934 | 2643 |
| No. variables in least squares | 187 | | 170 | 169 | 241 |
| *p* in weighting scheme | 0.057 | | 0.07 | 0.08 | 0.05 |
| *R*, *R*′ | 0.049, 0.072 | | 0.044, 0.064 | 0.053, 0.075 | 0.053, 0.081 |
| Density in final difference map/e Å$^{-3}$ | 0.54 | | 0.65 | 0.67 | 0.92 |
| Final shift/error ratio | 0.02 | | 0.01 | 0.01 | 0.02 |

tosylamide L$^{10}$ (0.34 g, 0.55 mmol) was treated with HBr–MeCO$_2$H (15 cm$^3$, 40%) and phenol (0.3 g) was added. The mixture was heated to 120 °C for 48 h, then cooled and filtered to yield a colourless precipitate of the tetrahydrobromide salt which was washed with diethyl ether (3 × 10 cm$^3$) and dried (0.1 mm Hg, *ca.* 13.3 Pa), 0.32 g (93%), m.p. > 250 °C (Found: C, 31.4; H, 6.85; N, 7.65. $C_{18}H_{40}N_4$·4HBr·3H$_2$O requires C, 31.3; H, 6.95; N, 8.10%); *m*/*z* (DCI) 314 [*M* + 2]$^+$ and 313 [*M* + 1]$^+$; $\delta_C$(D$_2$O) 54.5, 46.3, 42.9, 39.7, 35.2 (CH$_2$N), 24.8, 17.9, 16.6 (CH$_2$C) and 11.5 (CH$_3$); $\delta_H$(D$_2$O) 3.71 (8 H, br m, CH$_2$N), 3.54 (4 H, br t, CH$_2$N), 3.45 (4 H, t, CH$_2$N), 3.31 (4 H, m, CH$_2$N ring), 2.16 (4 H, m, CH$_2$CH$_2$N), 1.75 (6 H, NH$^+$C*H*$_2$CH$_3$), 1.40 (4 H, qnt, CH$_2$C) and 0.92 (6 H, t, CH$_3$).

1,8-*Dimethyl*-1,4,8,11-*tetraazacyclotetradecane*, L$^6$. This was prepared in an analogous manner to the dibutyl compound L$^5$ in 87% yield; m.p. ≥240 °C (as fully protonated hydrobromide salt) (Found: C, 25.6; H, 5.95; N, 10.00. $C_{12}H_{28}N_4$·4HBr·H$_2$O requires C, 25.2; H, 5.95; N, 9.80%); *m*/*z* (DCI) 229 [*M* + 1]$^+$, $\delta_C$(D$_2$O) 49.8, 45.8, 42.6, 40.8 (CH$_2$N), 36.5 (CH$_3$N) and 18.0 (CH$_2$C); $\delta_H$(D$_2$O) 3.73 (8 H, br s, CH$_2$N), 3.49 (8 H, m, CH$_2$N), 3.03 (6 H, s, CH$_3$N) and 2.18 (4 H, br qnt, CH$_2$C).

4-*Butyl*-1,8-*bis*(*toluene*-p-*sulfonyl*)-1,4,8,11-*tetraazacyclotetradecane*, L$^{12}$. To a solution of the ditosylamide L$^4$ (0.25 g, 0.05 mmol) in acetonitrile (10 cm$^3$) was added anhydrous sodium carbonate (0.11 g) and 1-bromobutane (0.14 g, 1.02 mmol) and the mixture was heated to reflux for 48 h. After filtering and removing solvent, the residue was chromatographed on silica (5% MeOH–CH$_2$Cl$_2$) to yield a colourless gummy solid (0.11 g, 40%); $R_f$ (SiO$_2$, 10% MeOH–CH$_2$Cl$_2$) 0.48; *m*/*z* (DCI) 566 [*M* + 2]$^+$, 565 [*M* + 1]$^+$ and 564 [*M*]$^+$; $\delta_C$(CDCl$_3$) 143.5, 134.1 (s), 129.5, 127.2 (d), 53.7, 52.5, 50.7, 49.6, 49.1, 48.8, 47.3, 46.0, 45.1 (CH$_2$N), 27.2, 25.8 (CH$_2$C), 21.3 (CH$_3$–aryl), 20.3 (CH$_2$C) and 13.8 (CH$_3$CH$_2$); $\delta_H$(CDCl$_3$) 7.63 (4 H, d + d, *o* aryl H), 7.33 (4 H, d + d, *m* aryl H), 3.23 (4 H, t, CH$_2$N), 3.08 (4 H, t, CH$_2$N), 2.71 (4 H, t, CH$_2$N), 2.68 (4 H, t, CH$_2$N), 2.43 (6 H, s, CH$_3$–aryl), 1.92 (4 H, qnt, CH$_2$C), 1.28 (4 H, m, CH$_2$C) and 0.92 (3 H, t, C*H*$_3$CH$_2$).

1-*Butyl*-8-*methyl*-4,11-*bis*(*toluene*-p-*sulfonyl*)-1,4,8,11-*tetraazacyclotetradecane*, L$^{13}$. This was prepared from L$^{12}$ using HCO$_2$H–HCHO as described for L$^{11}$ in 89% yield; *m*/*z* (DCI) 580 [*M* + 2]$^+$, 579 [*M* + 1]$^+$ and 578 [*M*]$^+$; $\delta_H$(CDCl$_3$) 7.65 (4 H, d, *J* = 8.1 Hz), 7.31 (4 H, d), 3.24 (4 H, t, CH$_2$N), 3.15 (4 H, t, CH$_2$N), 2.49 (4 H, t, CH$_2$N), 2.42 (6 H, s, CH$_3$–aryl), 2.35 (4 H, t, CH$_2$N), 2.15 (3 H, s, CH$_3$N), 1.73 (4 H, qnt, CH$_2$C), 1.28 (4 H, m, CH$_2$C) and 0.90 (3 H, t, CH$_3$).

1-*Butyl*-8-*methyl*-1,4,8,11-*tetraazacyclotetradecane*, L$^7$. The ditosylamide L$^{13}$ was detosylated as described for L$^5$, to yield the tetrahydrobromide salt as a colourless solid (90%) m.p. ≥240 °C (Found: C, 28.3; H, 6.80; N, 9.00. $C_{15}H_{34}N_4$·4HBr·2H$_2$O requires C, 28.6; H, 6.65; N, 8.90%); *m*/*z* (DCI) 271 [*M* + 1]$^+$ and 270 [*M*]$^+$; $\delta_H$(CDCl$_3$) 3.71 (8 H, m, CH$_2$N), 3.44 (4 H, m, CH$_2$N), 3.32 (4 H, m, CH$_2$N), 3.04 (5 H, qnt + t, CH$_3$N + CH$_2$N), 2.30 (4 H, qnt, CH$_2$), 1.42 (4 H, m, CH$_2$C) and 0.94 (3 H, t, CH$_3$). The diamide 6,13-dioxo-1,5,8,12-tetraazatricyclo[10.2.2.2$^{5.8}$]octadecane L$^{14}$ was prepared as described earlier.[6]

1,5,8,12-*Tetraazatricyclo*[10.2.2.2$^{5.8}$]*octadecane*, L$^{15}$. 6,13-Dioxo-1,5,8,12-tetraazatricyclo[10.2.2.2$^{5.8}$]octadecane (0.28 g, 0.1 mmol) was treated with a solution of BH$_3$·thf (40 cm$^3$, 1.0 mol dm$^{-3}$ solution) in thf and the mixture was boiled under reflux for 36 h. After cooling to 0 °C, methanol (2 cm$^3$) was slowly added and solvent was removed under reduced pressure. The residue was treated with 6 mol dm$^{-3}$ HCl (20 cm$^3$, 3 h), then evaporated to dryness and the residue redissolved in potassium hydroxide solution (10 cm$^3$, 6 mol dm$^{-3}$), extracted with dichloromethane (3 × 20 cm$^3$), dried (K$_2$CO$_3$) and solvent evaporated to yield a colourless solid (0.15 g, 60%); m.p. 80–82 °C (Found: C, 66.5; H, 11.4; N, 22.0. $C_{19}H_{28}N_4$ requires C,

**Table 7** Positional parameters for $[NiL^5][ClO_4]_2$ with estimated standard deviations (e.s.d.s) in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ni | 0.0 | 0.0 | 0.0 |
| N(1) | 0.1971(3) | −0.1446(3) | −0.0079(3) |
| C(2) | 0.1896(5) | −0.2560(4) | −0.1933(4) |
| C(3) | 0.0370(6) | −0.3056(4) | −0.2581(5) |
| N(4) | −0.0774(3) | −0.1579(3) | −0.2181(3) |
| C(5) | −0.2272(5) | −0.1979(4) | −0.2375(5) |
| C(6) | −0.3544(4) | −0.0554(4) | −0.2159(5) |
| C(7) | −0.3339(4) | 0.0680(4) | −0.0385(4) |
| C(11) | 0.2048(3) | −0.2311(3) | 0.1109(3) |
| C(12) | 0.3382(4) | −0.3629(4) | 0.1118(4) |
| C(13) | 0.3379(5) | −0.4394(4) | 0.2378(5) |
| C(14) | 0.3577(8) | −0.3381(6) | 0.4188(6) |
| Cl | 0.1786(1) | 0.2044(1) | −0.2915(1) |
| O(1)* | 0.1149(7) | 0.0911(6) | −0.2505(8) |
| O(2)* | 0.3152(8) | 0.199(1) | −0.186(1) |
| O(3)* | 0.231(1) | 0.088(1) | −0.439(1) |
| O(4)* | 0.057(1) | 0.2930(8) | −0.352(1) |
| O(5)* | 0.105(1) | 0.343(1) | −0.154(1) |
| O(6)* | 0.244(1) | 0.330(1) | −0.325(1) |
| O(7)* | 0.163(2) | 0.197(2) | −0.147(1) |
| O(8)* | 0.095(1) | 0.134(1) | −0.437(1) |

* The disordered oxygen atoms had occupancy factors of 0.55, 0.74, 0.40, 0.63, 0.50, 0.50, 0.32 and 0.36 for O(1)–O(8) respectively.

**Table 8** Positional parameters for $[CuL^5][PF_6]_2$ with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu | 0.0 | 0.0 | 0.0 |
| N(1) | 0.197 5(2) | −0.151 8(2) | −0.011 1(3) |
| C(2) | 0.180 9(4) | −0.259 3(3) | −0.193 6(4) |
| C(3) | 0.028 1(4) | −0.306 6(3) | −0.251 3(4) |
| N(4) | −0.081 9(3) | −0.162 4(2) | −0.218 4(3) |
| C(5) | −0.231 8(4) | −0.196 9(3) | −0.228 2(4) |
| C(6) | −0.349 5(3) | −0.054 0(4) | −0.204 1(4) |
| C(7) | −0.328 6(3) | 0.069 7(3) | −0.027 8(4) |
| C(11) | 0.210 2(3) | −0.237 8(3) | 0.109 4(3) |
| C(12) | 0.349 1(4) | −0.358 6(3) | 0.115 9(4) |
| C(13) | 0.352 8(4) | −0.434 8(4) | 0.244 8(4) |
| C(14) | 0.383 7(7) | −0.327 8(6) | 0.427 5(5) |
| P | −0.162 76(9) | −0.213 67(9) | 0.284 62(9) |
| F(1) | −0.101 2(2) | −0.101 2(2) | 0.223 6(2) |
| F(2) | −0.103 2(3) | −0.360 6(3) | 0.131 0(3) |
| F(3) | −0.008 9(3) | −0.240 2(3) | 0.399 5(3) |
| F(4) | −0.216 2(4) | −0.075 0(3) | 0.441 0(3) |
| F(5) | −0.314 7(3) | −0.196 8(3) | 0.167 9(3) |
| F(6) | −0.222 8(3) | −0.332 7(3) | 0.342 8(3) |

66.7; H, 11.1; N, 22.2%); *m*/z (DCI) 254 $[M + 2]^+$ 253 $[M + 1]^+$ (100%) and 252 $[M]^+$; $\delta_C(CDCl_3)$ 55.8, 49.4 ($CH_2N$) and 23.5 ($CH_2C$); $\delta_H(CD_2Cl_2)$ 3.14 (8 H, m, $CH_2N$ piperazine), 2.70 (8 H, t, *J* 5.5 Hz, $CH_2CH_2N$), 2.39 (8 H, m, $CH_2N$ piperazine) and 1.62 (4 H, qnt, $CH_2CH_2CH_2$).

1,8-*N*,*N*′-Bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane, $H_2L^8$, was prepared as reported previously.[6]

1,8-N,N′-*Bis*(*carboxymethyl*)-4,11-*dimethyl*-1,4,8,11-*tetraazacyclotetradecane*, $H_2L^9$. The diacid $H_2L^8$ (0.1 g, 0.32 mmol) was heated to reflux with formaldehyde solution (37%, 1.5 $cm^3$) and formic acid (1.7 $cm^3$) for 4 h. Hydrochloric acid (1 mol $dm^{-3}$, 20 $cm^3$) was added to the cooled solution and the mixture was heated for a further 10 min. On cooling a crystalline solid (the dihydrochloride salt) formed which was collected by filtration and dried (98 mg, 74%), m.p. ≥240 °C; *m*/*z* (DCI) 346 $[M + 2]^+$ and 345 $[M + 1]^+$; $\delta_H(D_2O)$ 2.05 (4 H, qnt, $CH_2C$), 2.89 (6 H, s, $CH_3N$), 3.00 (4 H, t, $CH_2N$), 3.23 (4 H, t, $CH_2N$), 3.48 (8 H, m, $CH_2N$) and 3.64 (4 H, s, $CH_2CO$).

**Table 9** Positional parameters for $[Cu(H_2L^9)][ClO_4]_2 \cdot 2H_2O$ with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu | 0.000 0 | 0.000 0 | 0.000 0 |
| N(1) | −0.071 4(4) | −0.181 3(4) | −0.064 2(2) |
| C(2) | 0.011 0(6) | −0.300 9(5) | −0.017 3(3) |
| C(3) | 0.185 7(6) | −0.259 7(5) | 0.011 5(3) |
| N(4) | 0.181 5(4) | −0.129 7(4) | 0.060 8(2) |
| C(5) | 0.348 8(5) | −0.058 3(5) | 0.065 8(3) |
| C(6) | 0.356 5(5) | 0.084 5(5) | 0.109 2(3) |
| C(7) | 0.255 0(5) | 0.204 6(5) | 0.070 5(3) |
| C(8) | 0.011 4(6) | 0.180 0(5) | 0.141 4(2) |
| C(9) | −0.125 5(5) | 0.070 3(5) | 0.148 7(2) |
| O(10) | −0.174 4(4) | −0.014 1(3) | 0.099 6(2) |
| O(11) | −0.177 6(5) | 0.075 8(4) | 0.217 0(2) |
| O(12) | 0.151 4(6) | −0.177 9(5) | 0.138 9(3) |
| O(W) | −0.369 6(5) | −0.129 1(4) | 0.245 7(2) |
| Cl | −0.336 0(2) | −0.471 7(1) | 0.138 98(7) |
| O(1) | −0.183 5(9) | −0.436 1(9) | 0.179 1(5) |
| O(2) | −0.467 0(7) | −0.390 6(6) | 0.165 5(4) |
| O(3) | −0.325 5(9) | −0.448 8(7) | 0.062 5(3) |
| O(4) | −0.368 3(6) | −0.618 4(5) | 0.151 3(3) |

**Table 10** Positional parameters for $[CuL^8][H_2L^{14}][ClO_4]_2$ with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu | 0.0 | 0.0 | 0.0 |
| N(1A) | −0.1294(4) | −0.0848(3) | −0.2280(4) |
| C(2A) | −0.0518(6) | −0.0636(4) | −0.3313(5) |
| C(3A) | 0.1199(6) | −0.0857(4) | −0.2431(6) |
| N(4A) | 0.1683(4) | −0.0133(3) | −0.0843(4) |
| C(5A) | 0.3260(5) | −0.0505(4) | 0.0340(7) |
| C(6A) | 0.3794(5) | 0.0309(4) | 0.1857(7) |
| C(7A) | 0.2962(5) | 0.0364(4) | 0.2994(6) |
| C(8A) | −0.1160(5) | −0.2084(3) | −0.2147(5) |
| C(9A) | 0.0159(4) | −0.2508(3) | −0.0597(5) |
| O(10A) | 0.0700(3) | −0.1819(2) | 0.0624(3) |
| O(11A) | 0.0580(4) | −0.3550(2) | −0.0657(4) |
| N(1B) | 0.2408(4) | 0.5914(3) | 0.2410(4) |
| C(2B) | 0.1224(5) | 0.5774(4) | 0.3025(6) |
| C(3B) | 0.1959(5) | 0.5535(4) | 0.4818(6) |
| N(4B) | 0.3218(4) | 0.6214(3) | 0.5832(4) |
| C(5B) | 0.3961(5) | 0.6070(4) | 0.7611(5) |
| C(6B) | 0.5191(5) | 0.5048(4) | 0.7975(5) |
| C(7B) | 0.6498(5) | 0.5152(3) | 0.7513(5) |
| C(8B) | 0.3160(5) | 0.6932(3) | 0.3382(5) |
| C(9B) | 0.3788(5) | 0.6903(3) | 0.5231(5) |
| O(10B) | 0.4813(4) | 0.7488(3) | 0.6090(4) |
| Cl | 0.2726(1) | 0.2566(1) | −0.2260(1) |
| O(1) | 0.1836(8) | 0.1722(5) | −0.2721(8) |
| O(2) | 0.1978(7) | 0.3377(6) | −0.3264(9) |
| O(3) | 0.4084(7) | 0.2358(7) | −0.2352(11) |
| O(4) | 0.2750(14) | 0.2849(10) | −0.0819(9) |

*Complex Formation.*—The following examples are representative.

$[NiL^5][ClO_4]_2$. To a solution of the ligand $L^5$ (62 mg, 0.2 mmol) in methanol (4 $cm^3$) was added a solution of nickel perchlorate hexahydrate (74 mg, 0.2 mmol) in methanol (1 $cm^3$). After removal of solvent, the orange residue crystallised from water during slow evaporation to yield orange prismatic crystals (75 mg, 66%) (Found: C, 37.6; H, 7.20; Cl, 12.2; N, 10.1; Ni, 10.1. $C_{18}H_{40}Cl_2N_4NiO_8$ requires C, 37.9; H, 7.00; Cl, 12.45; N, 9.80; Ni, 10.3%); *m*/*z* (FAB, *m*-nitrobenzyl alcohol matrix) 571 $[M + 1]^+$; $\lambda_{max}(H_2O)$ 461 nm (ε 50 $dm^3$ $mol^{-1}$ $cm^{-1}$).

On further concentration of the mother-liquors and allowing the solution to evaporate slowly, plate-shaped crystals were deposited over a period of 7 d; $\lambda_{max}(H_2O)$ 473 nm (ε 48 $dm^3$ $mol^{-1}$ $cm^{-1}$) (Found: C, 38.0; H, 7.30; N, 9.65. $C_{18}H_{40}Cl_2N_4NiO_8$ requires C, 37.9; H, 7.00; N, 9.80%).

$[CuL^9][ClO_4]_2$. To a solution of the $H_2L^9 \cdot 2HCl$ (26 mg, 0.05 mmol) in water (2 $cm^3$) was added a solution of copper(II) perchlorate hexahydrate (19 mg, 0.05 mmol) in water (1 $cm^3$). The pH was raised to 3 by careful addition of dilute potassium hydroxide solution, the mixture filtered and the solution allowed to stand. After 48 h at room temperature, blue crystals had deposited, which were collected by filtration, washed with cold water and dried in air (25 mg, 78%) (Found: C, 29.6; H, 5.80; Cl, 11.2; N, 8.60. $C_{16}H_{36}Cl_2CuN_4O_{14}$ requires C, 29.9; H, 5.60; Cl, 11.0; N, 8.70%); $\lambda_{max}(H_2O)$ 573 nm ($\varepsilon$ 75 $dm^3$ $mol^{-1}$ $cm^{-1}$).

*Structural Analyses.*—Details of the X-ray experimental conditions, cell data, data collection and refinement are summarised in Table 6. For compounds *trans*-$[NiL^5][ClO_4]_2$, $[CuL^5][PF_6]_2$, $[Cu(H_2L^9)][ClO_4]_2 \cdot 2H_2O$ and $[CuL^8][H_2L^{14}][ClO_4]_2$, complete structural analyses are reported. The cell and intensity data were collected with an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-K$\alpha$ radiation. All calculations were carried out on a PDP11-73 computer system using the SDP-Plus system of programs and data therein.[23] The structures were solved by the heavy-atom method. Hydrogen atoms (visible in difference maps) were allowed for, and refinement was by full-matrix least-squares calculations with all non-H atoms allowed anisotropic motion. Selected dimensions are in Tables 2–5, fractional coordinates are in Tables 7–10.

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

The structure of *cis*-$[NiL^5][ClO_4]_2$ presented some difficulties (as noted in the Discussion section). The crystals only diffracted poorly at room temperature and even at −100 °C we could not obtain enough data adequately to define the structure (presumably because of disorder in the crystal lattice). The systematic absences allow the space group to be either *Pnma* or $Pn2_1a$. A satisfactory solution to the Patterson function was found in the centrosymmetric space group with the asymmetric unit containing two independent half-cations having their Ni atoms on mirror planes and four 'half' perchlorate anions with the chlorine atoms on mirror planes. This situation then demands that the cations be disordered. Solution in the non-centrosymmetric space group was also considered (in this case there would be two independent cations in the asymmetric unit) but led to the same impasse as with the centrosymmetric solution (with a pseudo-centrosymmetric map and very poor resolution). Work on this structure was then abandoned.

## Acknowledgements

We thank the SERC and WR Grace for support under the CASE scheme and the Natural Science and Engineering Research Council (Canada) for continued support *via* operating grants. Drs. P. McArdle and D. Cunningham (University College, Galway) are also thanked for their assistance in collecting an intensity data set at −100 °C for *cis*-$[NiL^5][ClO_4]_2$.

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*Received* 24*th July* 1991; *Paper* 1/03807I