DALTON

Selective derivatisation of aza macrocycles

Alexander J. Blake,[a,b] Ian A. Fallis,[b] Robert O. Gould,[b] Simon Parsons,[b] Steven A. Ross[b] and Martin Schröder*[a,b]

[a] *Department of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*

A range of selectively functionalised compounds derived from 1,4,7-triazacyclononane ([9]aneN$_3$), including 4,7-bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane-1-carbaldehyde (H_2L^1), 1-benzyl-4,7-bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane (H_2L^2) and 1,4-bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane (H_2L^3), has been prepared. The structure of H_2L^3·$CHCl_3$ shows a disordered macrocyclic ring with the major conformer refining to a site occupancy of 0.663(8), and both disordered rings adopting a [333] conformation. The pendant alcohol arms were not disordered and were found to be hydrogen bonded to a $CHCl_3$ solvate molecule with H · · · O(1) and H · · · O(4) distances of 1.73 and 1.81 Å respectively. The structure of $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$ shows the copper(II) centre in the $[Cu(H_2L^1)(NCMe)]^{2+}$ cation bound to two amine donors and two alcohol donors of H_2L^1 and to a MeCN molecule. The Cu–N bond lengths lie in the range 1.984(3)–2.015(3) Å. Both alcohol donors are protonated, with one short Cu–O(16) bond of 1.963(3) Å and one long Cu–O(21) bond of 2.252(3) Å. There is also a sixth longer-range interaction of the copper(II) centre with the amide N [N(1)] of H_2L^1 at a distance of 2.611(5) Å, confirmed by the loss of planarity of the C(2)–C(9)–N(1)–C(10)–O(11)–H(10) amide fragment to give a dihedral angle between the planes defined by C(2)–C(9)–N(1) and N(1)–C(10)–O(11)–H(10) of 27.1(4)°. The structure is completed by interaction of O(11) with a Na^+ ion which itself bridges to BF_4^- counter anions leading to a central infinite core of $[Na(BF_4)_2]^-$ aggregates onto which are attached the $[Cu(H_2L^1)(NCMe)]^{2+}$ cations. The complex $[Cu(H_2L^2)(OH_2)][NO_3]_2$ shows the six-co-ordinate copper(II) centre bound to the three amine and two alcohol donors of H_2L^2 and to one water molecule. There are four short bonds [to N(7), N(4), O(40) and O(1)] in the range 1.961(5)–2.073(6) Å and two longer bonds to N(1) and O(70) at 2.308(5) and 2.313(5) Å respectively. The H atoms of the water molecule [O(1)] and one of the pendant arms [O(40)] also make hydrogen-bonding contacts with the nitrate counter ions.

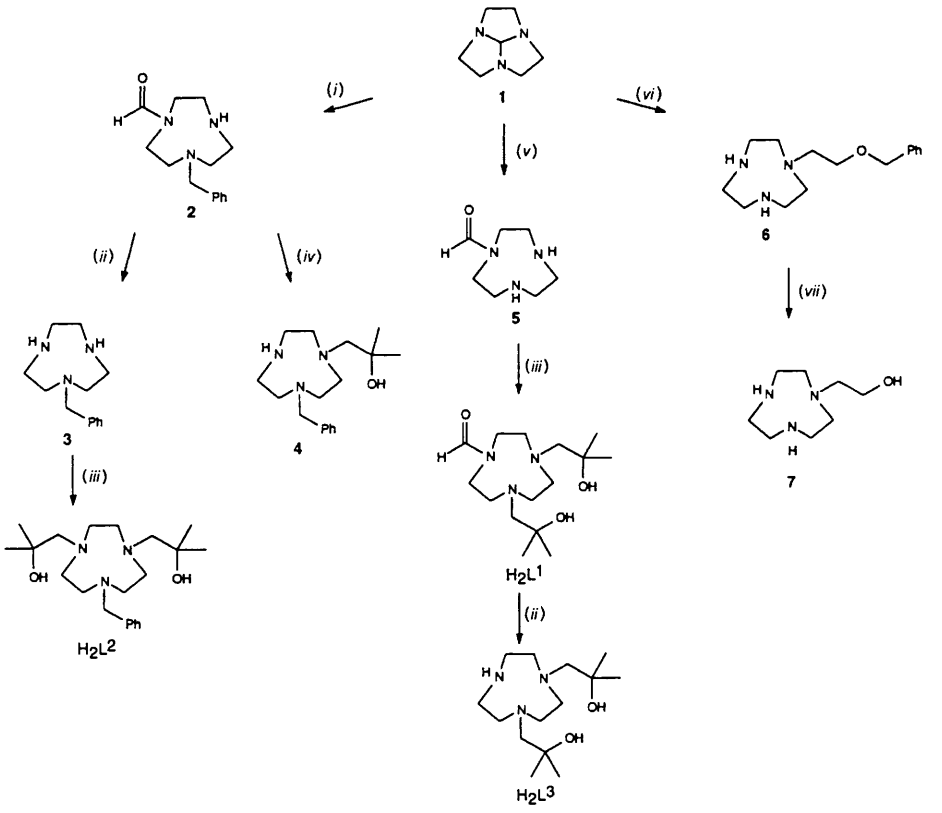
The co-ordination chemistry of the facially co-ordinating triazamacrocycle 1,4,7-triazacyclononane ([9]aneN$_3$) has been comprehensively established over the last twenty years.[1] Further N-functionalisation of [9]aneN$_3$ *via* incorporation of three pendant donor groups has afforded a wide range of new hexadentate compounds which can confer remarkable stability upon metal centres.[2,3] However, less work has been reported on selectively functionalised derivatives of [9]aneN$_3$ with only one or two pendant donors. This in part reflects the synthetic difficulties. Moore and co-workers[4] have reported the preparation of [9]aneN$_3$ with one pendant pyridine (or bipyridine) *via* reaction of an excess of [9]aneN$_3$ with 2-methylpyridyl chloride, whilst Spiccia and co-workers[5] have reported a similar compound with two pendant-arm pyridine groups. They reported an overall yield of 50% by reaction of 2 equivalents of 2-methylpyridyl chloride with 1 equivalent of [9]aneN$_3$ under aqueous conditions. Parker and co-workers[6] have also reported a derivative of [9]aneN$_3$ with one pendant methylene(methylphosphinic acid) group *via* a route where two of the ring N atoms are protected by a bridging CH_2 group.

We were interested in developing a route which would allow high-yield syntheses of mono- and di-functionalised derivatives of [9]aneN$_3$, and which would also allow for the preparation of compounds with more than one type of pendant group. Our approach[7] has been to expand upon the work initially reported by Weisman *et al.*,[8] which illustrated the suitability of orthoamide derivatives of [9]aneN$_3$ as precursors to functionalised macrocycles.

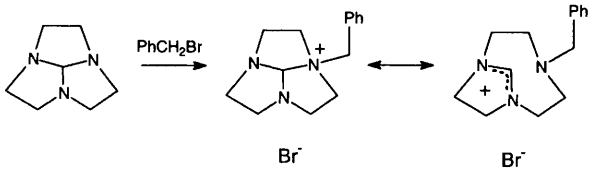
Results and Discussion

The preparation of functionalised derivatives of [9]aneN$_3$ is summarised in Scheme 1. The starting material was the orthoamide derivative 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane **1**,[9] the crystal structure of which has been reported recently.[10] Reaction of orthoamide **1** with $PhCH_2Br$ in tetrahydrofuran (thf), followed by aqueous hydrolysis, afforded 4-benzyl-1,4,7-triazacyclononane-1-carbaldehyde **2**, where all three N atoms of the ring have been distinguished from each other. The lack of further reactivity of the cationic intermediate in this reaction has been rationalised in terms of contributions from amidinium canonical forms,[11] as illustrated in Scheme 2. The amide group of **2** can be hydrolysed in ethanolic KOH solution to afford monofunctionalised 1-benzyl-1,4,7-triazacyclononane **3**, the co-ordination chemistry of which has been reported separately.[12] Reaction of **3** with an excess of isobutylene oxide in EtOH at room temperature gives H_2L^2 in high yield. Alternatively, **2** can be treated with isobutylene oxide prior to hydrolysis of the amide group, which affords the potentially tetradentate ligand 1-benzyl-4-(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane **4**.

Hydrolysis of orthoamide **1** with dilute HCl(aq) affords the previously reported[8] 1,4,7-triazacyclononane-1-carbaldehyde **5**. The crystal structure of **5** in both its free base and protonated forms has been reported separately[13] along with its co-ordination chemistry and a range of other amide derivatives of [9]aneN$_3$. Reaction of **5** with an excess of isobutylene oxide in EtOH affords H_2L^1 in high yield. Hydrolysis of the amide group of H_2L^1 with ethanolic KOH yields the potentially pentadentate ligand 1,4-bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane H_2L^3. The ^1H and ^{13}C NMR spectra of **2**, **5** and H_2L^1 are complicated by the presence of the formyl amide group, the slow period of rotation of which leads to freezing out of conformational isomers in solution at room temperature.



Scheme 1 Functionalised derivatives of [9]aneN$_3$. Reagents and conditions: (*i*) (*a*) $PhCH_2Br$–thf, (*b*) water, reflux for 3.5 h; (*ii*) KOH–EtOH, reflux; (*iii*) isobutylene oxide–EtOH; (*iv*) (*a*) isobutylene oxide–EtOH, (*b*) KOH–EtOH; (*v*) 2.8 mol dm^{-3} HCl(aq); (*vi*) (*a*) $PhCH_2OCH_2CH_2Br$–diethyl ether, (*b*) water, reflux for 5 h, (*c*) KOH–EtOH, 72 h; (*vii*) Pd/C–H_2–$MeCO_2H$



Scheme 2 Resonance structures of cationic intermediate (**1** + $PhCH_2Br$)

The NMR spectra of related amide derivatives have been discussed.[13]

Compounds H_2L^1, H_2L^2 and H_2L^3 described above all have two pendant alcohol donor groups, whilst **4** has one pendant alcohol and one benzyl group. We wished to extend this work to the preparation of derivatives of [9]aneN$_3$ with only one pendant alcohol donor and no other functionality. Our initial approach was to treat orthoamide **1** with $BrCH_2CH_2OH$ in thf, which proved to be unsuccessful. We attributed the failure of this reaction to the elimination of HBr from $BrCH_2CH_2OH$ under basic conditions. We therefore decided to protect the alcohol group of $BrCH_2CH_2OH$ prior to reaction with **1** and found that an appropriate approach was to prepare a benzyl ether, which would not be susceptible to cleavage under acidic or basic conditions. Thus, reaction of $BrCH_2CH_2OCH_2Ph$ with **1** in Et_2O, followed by aqueous hydrolysis and then subsequent hydrolysis of the formyl amide group, afforded 1-(1-benzyloxyethyl)-1,4,7-triazacyclononane **6** in high yield. The benzyl group was then removed by hydrogenolysis with Pd/C in glacial acetic acid to yield the potentially tetradentate ligand 1,4,7-triazacyclononane-1-ethanol **7**. Czech and Bartsch[14] have reported that hydrogenolysis of benzyl ethers in the presence of amines can lead to poor yields and suggest that yields are higher if the reaction is carried out in acetic acid.

The general methodology described above can, in principle, be extended to prepare a range of tetra- and penta-dentate ligands with a different range of donor atoms. We were particularly interested in pentadentate ligands which could block off five sites at a metal centre leaving one site free for further reactivity. As part of these studies we decided to undertake a single-crystal structure determination of H_2L^3. The crystal structure of [9]aneN$_3$ has not been reported previously, in contrast to the wide range of thioether ligands.[15] This is perhaps due to its hygroscopic nature and difficulties involved in preparing single crystals. The structure of the trimethylated analogue, 1,4,7-trimethyl-1,4,7-triazacyclononane, has been reported as the monohydroperchlorate salt,[1] which shows the protonated amine donor to be hydrogen bonded to the two free amine donors. We undertook the structure determination of H_2L^3 in order to confirm the conformation of the macrocyclic ring of a derivative of [9]aneN$_3$ in the solid state.

A single crystal of H_2L^3 was obtained from the slow evaporation of a $CHCl_3$ solution of it. Details of the structure solution and refinement are given in the Experimental section: bonded distances and valence angles are within normal ranges and have been deposited. The determination confirms the expected structure and shows one molecule of $CHCl_3$ per asymmetric unit with long-range hydrogen-bonding contacts between $CHCl_3$ and both oxygen atoms of the pendant arms [H • • • O(1) 1.73 and H • • • O(4) 1.81 Å]. The macrocyclic ring was found to be disordered, with the major conformation denoted by primes (the minor conformation by double primes) refining to a site occupancy of 0.663(8). No disorder was apparent in the pendant arms. A view of the major conformer is given in Fig. 1. In each of the disordered rings the macrocycle adopts a [333] conformation and can be regarded as 'pre-organised' for complexation to a metal centre. However, the question of 'pre-organisation' is complicated by the presence of the pendant arms. The actual process of complexation may involve initial co-ordination of the alcohol donors to the metal, followed by the macrocyclic ring donors.

The co-ordination chemistry of the pentadentate compounds H_2L^1 and H_2L^2 with Cu^{II} is described below. We wished to observe how the presence of the amide group in H_2L^1 would affect the mode of binding. Amide groups usually bind to metal ions through their oxygen atom[16] since the lone pair on the

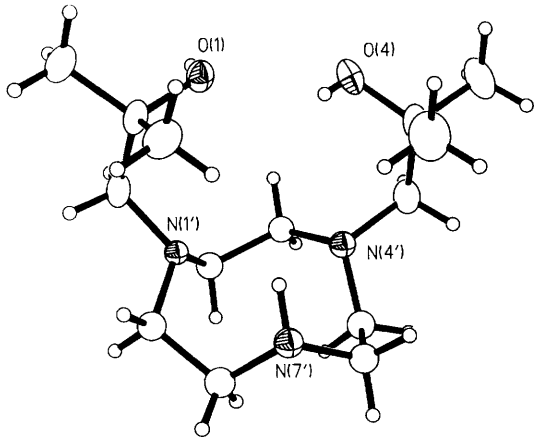


Fig. 1 View of structure of H_2L^3 with numbering scheme adopted

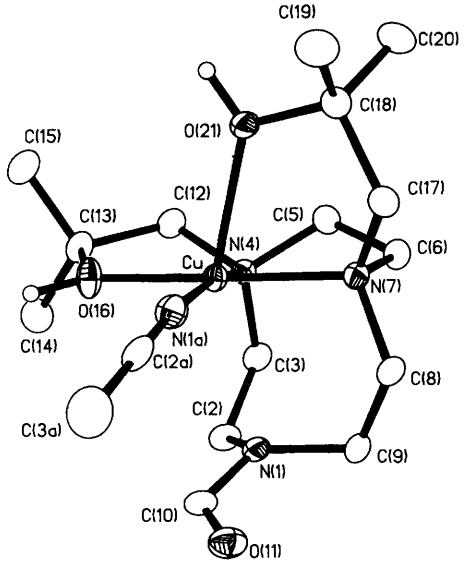


Fig. 2 View of the cation in $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$ with numbering scheme adopted

Table 1 Selected bond lengths (Å) and angles (°) for $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$

Cu–N(4)	2.002(3)	Cu–O(21)	2.252(3)
Cu–N(7)	2.015(3)	Cu–N(1a)	1.984(3)
Cu–O(16)	1.963(3)	Cu···N(1)	2.611(5)
N(4)–Cu–N(7)	86.95(12)	N(7)–Cu–O(21)	77.66(10)
N(4)–Cu–O(16)	82.12(11)	N(7)–Cu–N(1a)	97.85(12)
N(4)–Cu–O(21)	96.57(10)	O(16)–Cu–O(21)	103.37(10)
N(4)–Cu–N(1a)	168.40(12)	O(16)–Cu–N(1a)	92.92(12)
N(7)–Cu–O(16)	169.07(11)	O(21)–Cu–N(1a)	94.77(11)

nitrogen atom is delocalised and is not readily available for binding.[17] It was also of interest therefore to see how H_2L^2 would bind to a metal centre to compare with the mode of binding of H_2L^1.

Reaction of $Cu(NO_3)_2{\cdot}3H_2O$ with 1 molar equivalent of H_2L^1 in MeOH followed by addition of $NaBF_4$ and recrystallisation from MeCN–Et_2O afforded blue crystals. The IR spectrum of this material indicated the presence of H_2L^1 and both NO_3^- and BF_4^- counter ions, although the FAB mass spectrum showed no assignable peaks. The ν_{CO} amide stretch of H_2L^1 in this material was observed at 1654 cm^{-1}, which is not shifted substantially from that of free H_2L^1 which occurs at 1656 cm^{-1}. Analytical data were confusing, partly due to the presence of both NO_3^- and BF_4^- anions as confirmed by IR spectroscopy. This suggested a product with mixed counter ions, such as $[Cu(H_2L^1)(OH_2)][NO_3][BF_4]$, although the analytical data

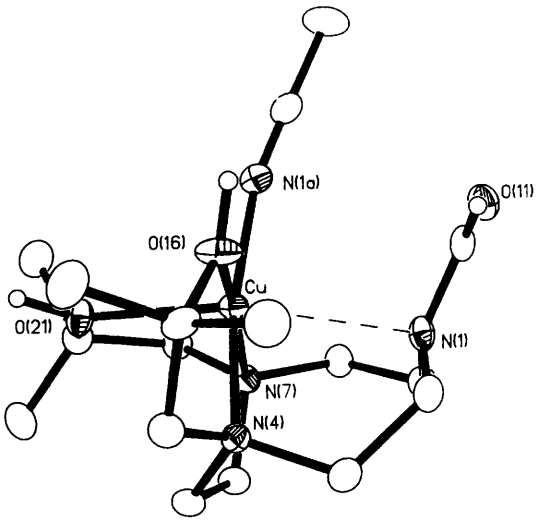


Fig. 3 Alternative view of the cation in $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$, illustrating the deviation from planarity of the amide group

did not agree with any predicted formulae. A single-crystal structure determination was therefore undertaken.

Deep blue prisms of X-ray quality were obtained from the diffusion of diethyl ether into a MeCN solution of the complex. Details of the structure solution and refinement are given in the Experimental section. Selected bond lengths and angles are given in Table 1 and a view of the cation in Fig. 2. The cation has the structure $[Cu(H_2L^1)(NCMe)]^{2+}$, with the copper(II) centre bound to two amine donors and two alcohol donors of H_2L^1 and also to a co-ordinated MeCN molecule. The Cu–N bond lengths lie in the range 1.984(3)–2.015(3) Å. Both alcohol donors are protonated, with one short Cu–O(16) bond of 1.963(3) Å and one long Cu–O(21) bond of 2.252(3) Å. The geometry at the O atom of the alcohols is such that the M–O(H)(C) fragment is planar.

In addition to these five bonds, there is also an unusual longer-range interaction of the metal centre with the amide N-donor [N(1)] of H_2L^1 at a distance of 2.611(5) Å. This is confirmed by the observed loss of planarity of the C(2)–C(9)–N(1)–C(10)–O(11)–H(10) amide fragment. Thus, the dihedral angle between the planes defined by C(2)–C(9)–N(1) and N(1)–C(10)–O(11)–H(10) is 27.1(4)°, which is illustrated by the view of the cation shown in Fig. 3.

The solid-state structure of $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$ also contains an aggregate of $[Na(BF_4)_2]^-$ units which form a polymeric chain structure. Each Na^- ion makes five contacts with F atoms (from BF_4^- ions) in the range 2.242(3)–2.424(3) Å. In addition, the amide O [O(11)] from the $[Cu(H_2L^1)(NCMe)]^{2+}$ cation forms a sixth interaction with the Na^+ ion at a distance of 2.321(3) Å.

The combined effect of the interactions described above is to create a supramolecular array of cations and anions which generates a stacked structure in the solid state. The structure is completed by nitrate counter ions which do not form any bonding interactions. Fig. 4 shows the structure viewed along the *b* axis and Fig. 5 along the *a* axis. The ion contacts and geometries around the Na^+ ions are given in Table 2, along with the operations used to generate symmetry-equivalent atoms.

The amide function of H_2L^1 thus interacts with two metal centres in this structure, namely Cu^{II} and Na^+. The interaction of amide O atoms with alkali metals is well documented,[16,17] while interaction of amide N atoms with metal centres usually occurs with concurrent deprotonation of the amide.[16,18] Since the amide function in H_2L^1 is a tertiary amide, deprotonation is not possible. As stated previously, the amide function deviates significantly from planarity. However, as the equivalent dihedral angle in an sp^3-hybridised donor to a metal centre (*e.g.*

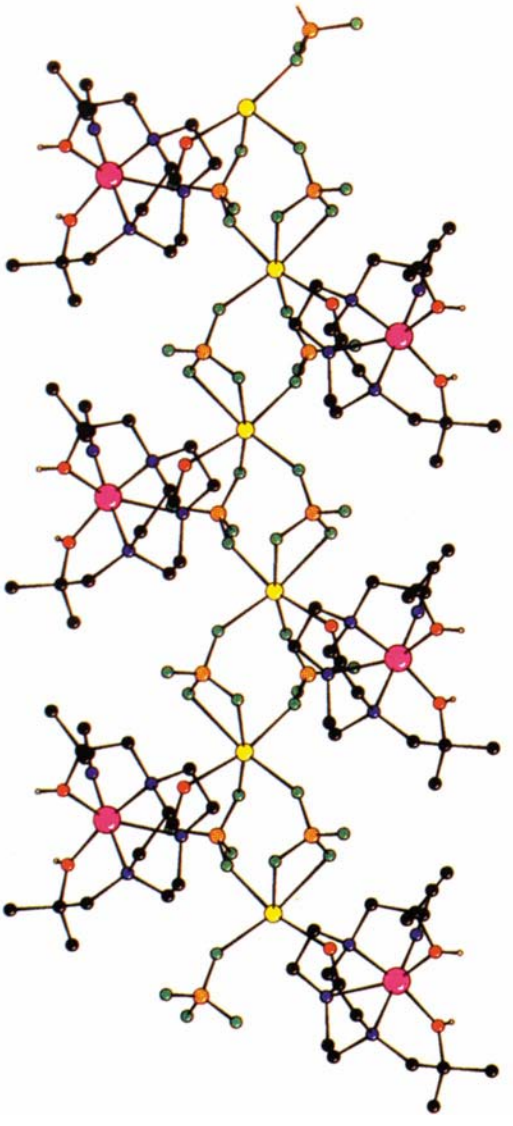


Fig. 4 View of $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$ along *b* axis (NO_3^- ions omitted for clarity). Key: Cu, magenta; Na, yellow; B, orange; F, turquoise; O, red; N, blue; C, black

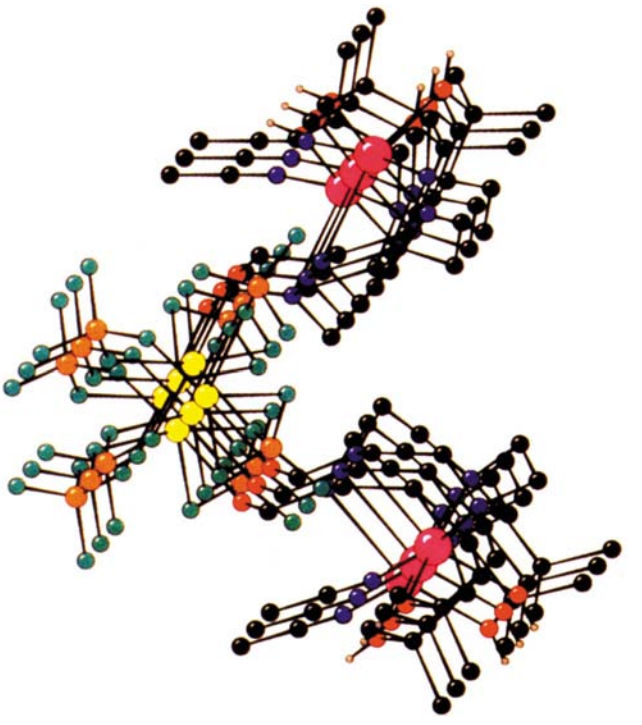


Fig. 5 View of $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$ along *a* axis. Details as in Fig. 4

Table 2 Sodium ion contacts (Å) and geometries (°) for $Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$

Na–O(11)	2.321(3)	Na–F(4′)	2.242(3)
Na–F(2)	2.270(3)	Na–F(5″)	2.424(3)
Na–F(7)	2.257(3)	Na–F(6″)	2.353(3)
C(10)–O(11)–Na	141.2(3)	F(2)–Na–F(6″)	86.93(9)
B(1)–F(2)–Na	153.5(3)	F(7)–Na–F(4′)	98.15(9)
B(2)–F(7)–Na	144.4(3)	F(7)–Na–F(5″)	149.06(10)
O(11)–Na–F(2)	167.25(11)	F(7)–Na–F(6″)	93.53(9)
O(11)–Na–F(7)	95.24(10)	F(4′)–Na–F(5″)	112.04(9)
O(11)–Na–F(4′)	92.69(10)	F(4′)–Na–F(6″)	168.19(10)
O(11)–Na–F(5″)	77.36(9)	F(5″)–Na–F(6″)	56.15(8)
O(11)–Na–F(6″)	84.49(9)	Na–F(4′)–B(1′)	132.2(2)
F(2)–Na–F(7)	94.68(10)	Na–F(5″)–B(2′)	96.6(2)
F(2)–Na–F(4′)	93.80(10)	Na–F(6″)–B(2′)	99.7(2)
F(2)–Na–F(5″)	90.03(9)		

Primed atoms are related by the symmetry operation $-\frac{1}{2} + x, \frac{1}{2} - y, z$; doubly primed ones by $\frac{1}{2} + x, \frac{1}{2} - y, z$.

an amine donor) is about 55°, the N atom of the amide group appears to be midway between sp^2 and sp^3 hybridised. This can be viewed as a compromise between donation of the amide N-donor lone pair to the copper(II) Lewis acid and the stability gained from delocalisation of the lone pair onto the O atom, thereby optimising interaction with the Na^+ ion. Interestingly, Crabtree and co-workers[19] have reported very recently an example of N-donor co-ordination of an amide to an iridium centre. This complex, like the system described herein,[7] uses a conformationally hindered polychelate ligand to control and enforce metal–ligand interactions.

Co-ordination of amide O atoms to metal centres is normally accompanied by a decrease in the ν_{CO} stretching frequency of *ca.* 30 cm^{-1} which has not been seen for this structure. This can be taken as further evidence for the amide N atom interacting with the copper(II) centre. The copper–amide interaction should disrupt delocalisation of the amide N lone pair onto the O atom, which is normally responsible for the lowering of the amide ν_{CO} stretching frequency. Since the ν_{CO} stretching frequency is not lowered, this suggests that the N atom of the amide is weakly bound to the Cu^{II}. Thus, binding of amide *via* O and N atoms has opposing effects with respect to the ν_{CO} stretching vibration.

Reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with 1 molar equivalent of H_2L^2 in ethanol gave a deep blue solution, which upon evaporation afforded a blue microcrystalline solid. This was recrystallised from hot CH_2Cl_2. The FAB mass spectrum of this material showed peaks for $[Cu(H_2L^2)]^+$ and also for $[Cu(H_2L^2)(NO_3)]^+$. The compound H_2L^2 is potentially a pentadentate donor, through three amine and two alcohol donor atoms. The sixth co-ordination site of this material could therefore be filled by a water or nitrate ligand, elemental analysis of the sample suggesting the presence of water. In order to ascertain the co-ordination geometry of the metal centre a single-crystal structure determination was undertaken.

Crystals suitable for X-ray studies were obtained from the evaporation of a solution of the complex in CH_2Cl_2. Details of the structure solution and refinement are given in the Experimental section. Selected bond lengths and angles are given in Table 3 and a view of the cation is shown in Fig. 6. The copper(II) centre is six-co-ordinate, bonding to the three amine and two alcohol donors of H_2L^2 as well as to a water molecule. There are four short bonds [to N(7), N(4), O(40) and O(1)] in the range 1.961(5)–2.073(6) Å and two longer bonds [to N(1) and O(70)] at 2.308(5) and 2.313(5) Å respectively. The H atoms of the water molecule [O(1)] and one of the pendant arms [O(40)] are

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu(H_2L^1)(OH_2)][NO_3]_2$

Cu–O(1)	1.961(5)	Cu–O(40)	2.002(5)
Cu–N(4)	2.010(6)	Cu–N(7)	2.073(6)
Cu–N(1)	2.308(5)	Cu–O(70)	2.313(5)
O(1)–Cu–O(40)	90.1(2)	O(1)–Cu–N(4)	171.6(2)
O(40)–Cu–N(4)	81.5(2)	O(1)–Cu–N(7)	101.9(2)
O(40)–Cu–N(7)	167.6(2)	N(4)–Cu–N(7)	86.4(2)
O(1)–Cu–N(1)	98.2(2)	O(40)–Cu–N(1)	99.8(2)
N(4)–Cu–N(1)	84.2(2)	N(7)–Cu–N(1)	81.7(2)
O(1)–Cu–O(70)	87.7(2)	O(40)–Cu–O(70)	103.8(2)
N(4)–Cu–O(70)	93.5(2)	N(7)–Cu–O(70)	74.0(2)
N(1)–Cu–O(70)	155.7(2)		

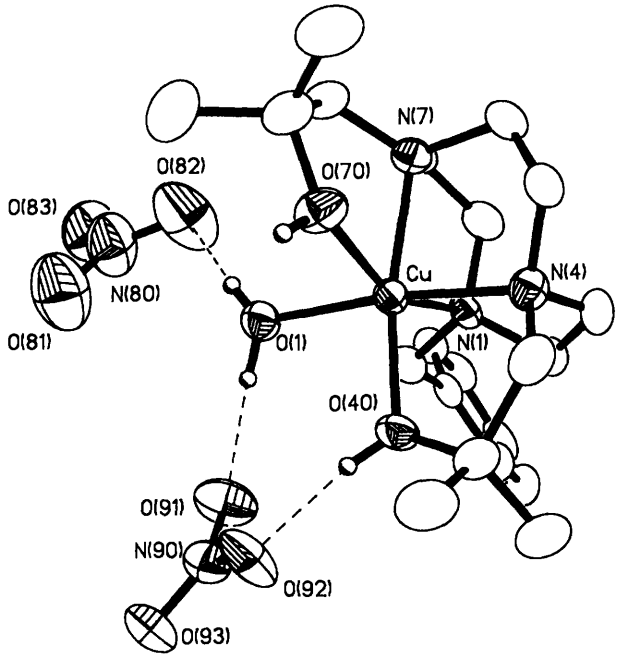


Fig. 6 View of the structure of $[Cu(H_2L^2)(OH_2)][NO_3]_2$ with the numbering scheme adopted

found to make hydrogen-bonding contacts with the nitrate counter ions. Three such contacts are made, H(40) · · · O(92) at 1.85, H(1a) · · · O(91) at 1.92 and H(1b) · · · O(82) at 1.75 Å, which can be observed in Fig. 6. Such association between the nitrate ions and the cation in solution may help to explain the unexpected solubility of this material in CH_2Cl_2.

Fig. 7 illustrates the packing for $[Cu(H_2L^2)(OH_2)][NO_3]_2$. The aromatic benzyl groups of H_2L^2 are seen to lie above each other in the solid state with a vertical separation of 3.334(5) Å and a centroid–centroid distance of 3.658(5) Å, which may be indicative of a π–π stacking interaction. However, care must be taken to distinguish π–π stacking forces from simple crystal-packing forces. Much work has been devoted recently to the development of molecular receptors which utilise aromatic π–π stacking (in conjunction with hydrogen bonding) to bind molecules such as nucleotide bases and phenols.[20]

As mentioned earlier, H_2L^1 and H_2L^2 have similiar donor arrays, the difference being the functional group attached to N(1), which is a formyl group in H_2L^1 and a benzyl group in H_2L^2. Comparison of the Cu–N(1) bond lengths in the two structures shows a substantial difference, with a Cu–N(1) distance of 2.308(5) Å in $[Cu(H_2L^2)(OH_2)]^{2+}$ and 2.611(5) Å in $[Cu(H_2L^1)(NCMe)]^{2+}$. This substantiates further the idea that the interaction of the amide with the copper(II) centre in $[Cu(H_2L^1)(NCMe)]^{2+}$ is not as strong as a copper(II)–amine interaction.

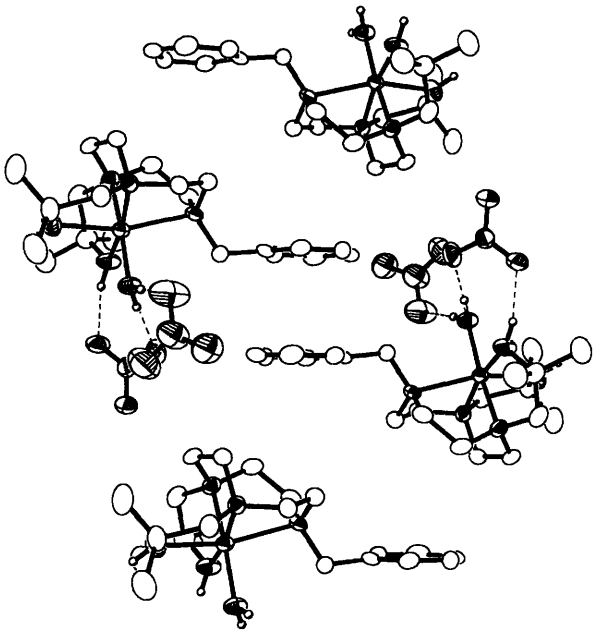


Fig. 7 View of the packing for $[Cu(H_2L^2)(OH_2)][NO_3]_2$

Experimental

All solvents were dried and purified using standard procedures.[21] Tetrahydrofuran ('HPLC-grade', Fisons) was distilled from sodium–benzophenone. Dimethylformamide used for macrocycle cyclisation reactions was always taken from a fresh bottle. Standard chemicals were used as commercially supplied. The $PhCH_2Br$ (BDH) was distilled on a shortway distillation apparatus then stored at −20 °C prior to use. Infrared spectra were recorded as KBr discs or thin films between CsI plates on a Perkin-Elmer 1600 Series Fourier-transform spectrometer, fast atom bombardment (FAB) and electron ionisation (EI) mass spectra on a Kratos MS 50TC spectrometer, with FAB spectra in a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by the University of Edinburgh Chemistry Department microanalytical service. Proton NMR spectra were recorded on Brüker WP80, WP200 and AC250 spectrometers, operating at 80.13, 200.13 and 250.13 MHz respectively, ^{13}C NMR spectra on Brüker WP200 and AC250 spectrometers, operating at 50.32 and 62.89 MHz respectively. 1,4,7-Triazacyclononane was prepared by a standard literature procedure.[22] The preparation of 1,4,7-Triazatricyclo[5.2.1.$0^{4,10}$]decane **1** from 1,4,7-triazacyclononane was carried out according to the method reported by Atkins.[9]

Syntheses

4-Benzyl-1,4,7-triazacyclononane-1-carbaldehyde 2. This compound was prepared according to the method of Weisman *et al.*[8] 1,4,7-Triazatricyclo[5.2.1.$0^{4,10}$]decane **1** (0.50 g, 0.0036 mol) and benzyl bromide (0.615 g, 0.0036 mol) were stirred together in thf (2 cm^3) for 1 h to yield a thick paste (the reaction time of 24 h quoted by Weisman was found to be unnecessary). Diethyl ether (10 cm^3) was then added and the solution filtered to give a white solid which was dissolved in water (10 cm^3) and refluxed for 3.5 h. The solution was adjusted to pH 12 with NaOH solution (5 mol dm^{-3}) and the product extracted with $CHCl_3$ (5 × 50 cm^3). The combined extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to give the product as a yellow oil, which was stored as a standard solution in ethanol at −20 °C (0.80 g, 89.9%). NMR ($CDCl_3$): ^1H (200.13 MHz), δ 2.35–3.25 (12 H, m, NCH_2, ring), 3.49 (2 H, s, NCH_2Ph), 7.13 (5 H, br s, aryl H), 7.79 and 7.93 (1 H, s, NCHO, from alternative isomers); ^{13}C (50.32 MHz), δ 45.93, 46.03, 46.37, 47.13, 47.33, 48.19, 49.39, 51.45, 52.12, 54.73,

56.51 (NCH_2, ring, from alternative isomers, assuming one coincidence), 61.54 (NCH_2Ph, assuming both isomers coincident), 126.33, 126.53, 127.59, 127.70, 128.26 (aromatic CH, assuming one coincidence), 138.04 (aromatic quaternary, assuming both isomers coincident), 163.01 and 163.17 (NCHO, from alternative isomers) (Found: C, 67.4; H, 9.10; N, 16.9. $C_{14}H_{21}N_3O$ requires C, 68.0; H, 8.55; N, 17.0%).

1-Benzyl-1,4,7-triazacyclononane 3. Compound **2** (0.3 g, 0.0012 mol) was added to a solution of potassium hydroxide (1.48 g, 0.026 mol) in EtOH (10 cm^3) and the mixture refluxed for 24 h. The solvent was removed *in vacuo* and the residue taken up in water (5 cm^3). The solution was extracted with $CHCl_3$ (5 × 25 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a yellow oil. This was distilled on a shortway bulb-to-bulb distillation apparatus to give the product as a clear viscous oil which was stored as a standard solution in ethanol at −20 °C (0.251 g, 95.1%). NMR ($CDCl_3$): ^1H (200.13 MHz), δ 2.46–2.59 (12 H, m, NCH_2 ring), 3.53 (2 H, s, NCH_2Ph) and 7.14 (5 H, m, aryl H); ^{13}C (50.32 MHz), δ 45.77, 45.96, 52.08 (NCH_2, ring), 60.97 (NCH_2Ph), 126.37, 127.65, 128.32 (aromatic CH) and 139.08 (aromatic quaternary). EI mass spectrum: *m/z* 219 (M^+).

1-Benzyl-4,7-bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane (H_2L^2). Compound **3** (0.420 g, 0.0019 mol) and isobutylene oxide (0.552 g, 0.0076 mol) were dissolved in EtOH (5 cm^3) in a round-bottomed flask (10 cm^3). The flask was sealed with a greased stopper and then left for 10 d at 20 °C. Removal of the solvent and excess of isobutylene oxide *in vacuo* afforded the product as a pale yellow oil. No further purification was necessary, as the NMR spectra showed no starting materials to be present and confirmed the acceptable purity of the product (0.695 g, essentially quantitative). NMR ($CDCl_3$): ^1H (80.13 MHz), δ 1.08 (12 H, s, CH_3), 2.43 (4 H, s, CH_2 arm), 2.72 (8 H, m, CH_2 ring), 2.88 (4 H, s, CH_2 ring), 3.60 (2 H, s, NCH_2Ph), 4.45 (2 H, br s, OH) and 7.21–7.25 (5 H, m, aryl H); ^{13}C (50.32 MHz), δ 27.77 (CH_3), 57.52, 59.14, 59.78 (CH_2, ring), 62.55 (CH_2, arm), 69.56 [$C(CH_3)_2OH$], 126.46, 127.79, 128.60 (aromatic CH) and 139.37 (aromatic quaternary) (Found: C, 69.0; H, 10.9; N, 10.3. $C_{21}H_{37}N_3O_2$ requires C, 69.4; H, 10.3; N, 11.6%). EI mass spectrum: *m/z* 363 (M^+).

1-Benzyl-4-(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane 4. Compound **2** (0.30 g, 0.0012 mol) and isobutylene oxide (0.250 g, 0.0026 mol) were dissolved in ethanol (5 cm^3) in a well sealed flask and left for 10 d at 20 °C. The solvent and excess of oxirane were removed *in vacuo* and the remaining oil redissolved in ethanol. Potassium hydroxide (1.7 g, 0.030 mol) was added to the flask and the mixture was refluxed for 30 h. The ethanol was removed under reduced pressure and the residue taken up in water (5 cm^3). The solution was extracted with $CHCl_3$ (5 × 25 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give the product as a pale yellow oil, which was stored as a standard solution in EtOH at −20 °C (0.308 g, 88.3%). NMR ($CDCl_3$): ^1H (80.13 MHz), δ 1.15 (6 H, s, CH_3), 2.55–2.77 (14 H, m, NCH_2 ring and arm), 3.68 (2 H, s, NCH_2Ph), 4.41 (1 H, s, OH) and 7.25 (5 H, s, aryl H); ^{13}C (50.32 MHz), δ 27.98 (CH_3), 45.18, 47.35, 49.41, 54.06, 54.88 (NCH_2 ring, assuming one coincidence), 62.08 (NCH_2Ph), 69.29 (NCH_2 arm), 69.96 [$C(CH_3)_2OH$], 126.98, 128.08, 129.30 (aromatic CH) and 138.42 (aromatic quaternary). EI mass spectrum: *m/z* 291 (M^+).

1,4,7-Triazacyclononane-1-carbaldehyde 5. This was prepared according to the method of Weisman *et al.*[8] 1,4,7-Triazatricyclo[5.2.1.$0^{4,10}$]decane **1** (5 g, 0.036 mol) was stirred in HCl (20 cm^3, 2.8 mol dm^{-3}) at room temperature for 8 h. The solution was then cooled to 0 °C and adjusted to pH 12 with NaOH solution (5 mol dm^{-3}). The product was extracted immediately with $CHCl_3$ (5 × 50 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a clear, viscous oil which crystallised upon standing. Recrystallisation from $CHCl_3$–hexane gave white needles (2.61 g, 44.6%). NMR ($CDCl_3$): ^1H (200.13 MHz), δ 2.01 (2 H, s, NH), 2.65–2.77 (4 H, m, CH_2), 2.98–3.10 (4 H, m, CH_2), 3.31–3.44 (4 H, m, CH_2) and 8.11 (1 H, s, NCHO); ^{13}C (50.32 MHz), δ 46.58, 48.14, 48.62, 49.20, 49.73, 52.59 (CH_2) and 163.79 (NCHO) (Found: C, 54.4; H, 10.1; N, 26.4. $C_7H_{15}N_3O$ requires C, 53.5; H, 9.60; N, 26.7%). IR (KBr disc): 3321s (NH), 2879s (CH), 1656vs (CO), 1450s, 1161s, 971m and 762s cm^{-1}. EI mass spectrum: *m/z* 157 (M^+).

4,7-Bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane-1-carbaldehyde (H_2L^1). Compound **5** (0.60 g, 0.0038 mol) and isobutylene oxide (1.20 g, 0.016 mol) were dissolved in EtOH (5 cm^3) in a round-bottomed flask (10 cm^3). The flask was sealed with a greased stopper and then left for 10 d. Removal of the solvent and excess of oxirane *in vacuo* afforded the product as a pale yellow oil. No further purification was necessary, as the NMR spectra showed no starting materials and no other products to be present (1.14 g, quantitative). NMR ($CDCl_3$): ^1H (200.13 MHz), δ 1.11 (6 H, s, CH_3), 1.13 (6 H, s, CH_3), 2.51 (4 H, s, CH_2, arm), 2.65 (4 H, s, CH_2, ring), 2.93 (4 H, m, CH_2, ring), 3.47 (4 H, m, CH_2, ring), 4.51 (2 H, br s, OH) and 8.10 (1 H, s, NCHO); ^{13}C (distortionless enhancements of polarisation transfer, DEPT, 3π/4, 50.32 MHz), δ 27.85, 28.09 (CH_3), 50.06, 52.66, 56.76, 58.60, 58.80, 59.04 (CH_2, ring), 70.27 and 71.73 (CH_2, arm) (Found: C, 59.0; H, 9.75; N, 14.9. $C_{15}H_{31}N_3O_3$ requires C, 59.8; H, 10.4; N, 13.9%). EI mass spectrum: *m/z* 302 (M^+). IR spectrum: ν_{CO} 1656 cm^{-1}.

1,4-Bis(2-hydroxy-2-methylpropyl)-1,4,7-triazacyclononane (H_2L^3). Compound H_2L^1 (0.450 g, 0.0013 mol) was added to KOH (1.48 g, 0.026 mol) in EtOH (10 cm^3) and this mixture was refluxed for 24 h. The solvent was then removed *in vacuo* and the residue taken up in water (5 cm^3). The solution was extracted with $CHCl_3$ (5 × 25 cm^3), the combined extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure to give the product as a pale yellow oil, which was stored at −20 °C (0.350 g, 96.4%). NMR ($CDCl_3$): ^1H (200.13 MHz), δ 1.15 (12 H, s, CH_3), 2.54 (4 H, s, CH_2, arm), 2.73–2.83 (12 H, m, CH_2, ring) and 3.50 (2 H, br s, OH); ^{13}C (50.32 MHz), δ 28.17 (CH_3), 48.51, 56.91, 57.23 (CH_2, ring), 70.05 (CH_2, arm) and 70.81 [$C(CH_3)_2OH$] (Found: C, 59.4; H, 11.9; N, 14.9. $C_{14}H_{31}N_3O_2$ requires C, 61.5; H, 11.4; N, 15.4%). EI mass spectrum: *m/z* 274 (M^+).

2-Benzyloxyethyl bromide. Tribromophosphine (1.55 g, 0.0057 mol) and pyridine (0.5 cm^3) were added to freshly distilled benzene (3 cm^3) at 6 °C under N_2. 2-Benzyloxyethanol (2.5 g, 0.0165 mol) was then added dropwise over 5 min. The reaction mixture was allowed to warm to room temperature and stirred for 48 h, which gave rise to an orange precipitate. Benzene (20 cm^3) was added, the solution was washed with HCl (0.5 mol), $NaHCO_3$ (1.0 mol) and water. Chloroform (20 cm^3) was added, the solution was dried over $MgSO_4$, concentrated *in vacuo* and distilled on a shortway bulb-to-bulb distillation apparatus. Thin-layer chromatography and NMR spectroscopy showed this to be a 4:1 mixture of the required product and benzyl bromide. This mixture was purified by flash column chromatography on silica (hexane–diethyl ether, 10:1) to give the final product as a clear oil (1.68 g, 47.4%); R_f = 0.35 (hexane–diethyl ether, 10:1 on silica). NMR ($CDCl_3$): ^1H (250.13 MHz), δ 3.50 (2 H, t, OCH_2CH_2Br), 3.79 (2 H, t, OCH_2CH_2Br), 4.59 (2 H, s, $PhCH_2O$) and 7.35 (5 H, m, aryl H); ^{13}C (62.89 MHz), δ 30.32 (OCH_2CH_2Br), 69.78 (OCH_2CH_2Br), 72.95 ($PhCH_2O$), 127.58, 127.68, 128.31 (aromatic CH)

and 137.56 (aromatic quaternary). EI mass spectrum: *m/z* 215 (M^+).

1-(1-Benzyloxyethyl)-1,4,7-triazacyclononane 6. Compound **1** (0.50 g, 0.0036 mol) and 2-benzyloxyethyl bromide (0.773 g, 0.0036 mol) were stirred in freshly distilled ether (10 cm^3) for 5 d. The solvent was then removed *in vacuo* and the residue was refluxed in water (15 cm^3) for 5 h. The water was removed *in vacuo*, potassium hydroxide (1.6 g, 0.028 mol) in EtOH (10 cm^3) was added and the mixture was refluxed for 3 d. The solvent was removed *in vacuo*, water (5 cm^3) added, and the solution was extracted with $CHCl_3$ (5 × 25 cm^3). The organic layer was dried ($MgSO_4$) and the solvent removed to yield the product as a pale yellow oil (0.610 g, 64.4%). NMR ($CDCl_3$): ^1H (250.13 MHz), δ 2.63 (8 H, dt, J = 2.82, NCH_2CH_2N), 2.70 (4 H, s, NCH_2CH_2N), 2.77 (2 H, t, J = 5.78, NCH_2CH_2O), 3.29 (2 H, br s, NH), 3.49 (2 H, t, J = 5.78 Hz, NCH_2CH_2O), 4.45 (2 H, s, $PhCH_2O$) and 7.24 (5 H, m, aryl H); ^{13}C (62.89 MHz), δ 45.92, 46.04, 52.77 (NCH_2, ring), 55.84 (NCH_2CH_2O), 68.58 (NCH_2CH_2O), 72.90 ($PhCH_2O$), 127.34, 127.46, 128.11 (aromatic CH) and 137.95 (aromatic quaternary). EI mass spectrum: *m/z* 263 (M^+).

1,4,7-Triazacyclononane-1-ethanol 7. Compound **6** (0.50 g, 0.0019 mol) was added to a suspension of Pd on charcoal (5%, 1.20 g) in glacial acetic acid (150 cm^3). Hydrogen gas was vigorously bubbled through this solution for 5 min and then slowly passed over the solution for 78 h.[14] The Pd/C was filtered off (glass microfibre filter-paper), washed with glacial acetic acid and the filtrate concentrated *in vacuo*. Potassium hydroxide solution was added to the residue to pH 14, toluene was added and the mixture transferred to a round-bottomed flask fitted with a Dean and Stark trap. The solution was refluxed for 24 h to remove water and the toluene was filtered and concentrated *in vacuo* to yield the product as a pale yellow oil (0.293 g, 89.1%). NMR ($CDCl_3$): ^1H (250.13 MHz), δ 2.44 (14 H, m, NCH_2 ring and NCH_2CH_2OH) and 3.32 (2 H, t, J = 5.5 Hz, NCH_2CH_2OH); ^{13}C (62.89 MHz), δ 45.80, 46.15, 52.06 (NCH_2 ring), 58.07 (NCH_2CH_2OH) and 59.40 (NCH_2CH_2OH). EI mass spectrum: *m/z* 173 (M^+).

$Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$. Compound H_2L^1 (0.050 g, 0.00016 mol) and $Cu(NO_3)_2·3H_2O$ (0.038 g, 0.00016 mol) were each dissolved in MeOH (5 cm^3) and the two solutions were mixed. This gave a change from pale to intense blue. Upon standing for several days the solution evaporated to yield a blue glass. This was dissolved in the minimum volume of water, and $NaBF_4$ (0.040 g, 0.00036 mol) added. No precipitate formed upon standing, whereupon the water was removed *in vacuo* and the residue recrystallised by diffusion of Et_2O into a MeCN solution of the product to afford blue crystals (0.035 g, 33.1%) (Found: C, 29.9; H, 6.01; N, 10.5. $C_{17}H_{34}B_2CuF_8N_5NaO_6$ requires C, 30.7; H, 5.15; N, 10.5%). IR (KBr disc): 2977m, 1654s, 1474m, 1383s and 1028m cm^{-1}. FAB mass spectrum: no assignable peaks.

$[Cu(H_2L^2)(OH_2)][NO_3]_2$. Compound H_2L^2 (0.180 g, 0.0005 mol) and $Cu(NO_3)_2·3H_2O$ (0.108 g, 0.00045 mol) were each dissolved in EtOH (3 cm^3) and the solutions mixed to give a deep blue solution. Evaporation over several days afforded blue crystals, which were recrystallised from hot CH_2Cl_2 (0.209 g, 81.6%) (Found: C, 44.4; H, 6.05; N, 12.2. $C_{21}H_{39}CuN_5O_9$ requires C, 44.3; H, 6.85; N, 12.3%). FAB mass spectrum: *m/z* 425 $[Cu(H_2L^2)]$, 488 $[Cu(H_2L^2)(NO_3)]$ and 550 $[Cu(H_2L^2)(NO_3)_2]$.

Crystallography

Crystal data and details of the structure determinations appear

Table 4 Summary of crystal data

Formula	$C_{14}H_{31}N_3O_2·CHCl_3$	$C_{17}H_{34}B_2CuF_8N_5NaO_6$	$C_{21}H_{39}CuN_5O_9$
M	404.8	664.52	569.11
Crystal size/mm	0.80 × 0.56 × 0.12	0.58 × 0.42 × 0.17	0.40 × 0.15 × 0.12
Crystal appearance	Colourless plate	Deep blue prism	Deep blue lath
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2_1/a$	$C2/c$
a/Å	11.813(6)	9.637(2)	17.863(5)
b/Å	11.300(6)	30.814(12)	10.114(3)
c/Å	15.231(9)	10.104(2)	30.685(8)
β/°		114.43(22)	109.37(3)
U/Å^3	2033.1	2732	5230
No. reflections used	32	25	34
measured at ±ω/°	25–27	30–32	23–32
D_c/g cm^{-3}	1.28	1.615	1.446
Z	4	4	8
T/K	150	150	260
μ(Mo-Kα)/mm^{-1}	0.46	0.909	0.890
F(000)	840	1364	2408
hkl Ranges	0–14, 0–13, −18 to 0	−10 to 9, 0–33, 0–10	−19 to 18, 0–10, 0–33
Unique reflections	1858	3449	3366
Reflections used	1638	3239	3314
Absorption corrections	None	ψ Scans	ψ Scans
(maximum, minimum)	—	0.789, 0.703	0.867, 0.794
Parameters refined	217	376	363
x in weighting scheme $w^{-1} = \sigma^2(F) + xF^2$	—	0.000 035	—
x, y in $w^{-1} = \sigma^2(F_o^2) + (xP)^2 + yP$, $P = \frac{1}{3}[\max(F_o^2, 0) + 2F_c^2]$	0.004 64, 1.65	—	0.050, 78.3
R, R' (SHELX 76)		0.0342, 0.0449	—
R, wR (SHELXL 93)	0.047, 0.104	—	0.0607, 0.160
S	1.11	1.037	1.073
Minimum, maximum residues in final ΔF synthesis/e Å^{-3}	+0.30, −0.30	+0.45, −0.42	+0.88, −0.96

Common parameters: Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems low-temperature device;[23] Mo-Kα radiation, λ = 0.710 73 Å; ω–2θ scans using on-line profile fitting,[24] $2\theta_{max}$ = 45°. Except where stated otherwise, non-H atoms were refined anisotropically and H atoms were introduced at calculated positions. Phenyl rings, where present, were refined as idealised hexagons.

in Table 4 and only special features of the analyses are noted here.

$H_2L^3 \cdot CHCl_3$. The structure was solved by direct methods using SHELXS 86[25] and refined on F^2 using SHELXL 93.[26] Substantial disorder in the macrocyclic ring was modelled by allowing isotropic refinement of two interpenetrant rings with constrained values of C–C and C–N bonds which converged at 1.515(7) and 1.472(3) Å respectively. The major and minor conformers were found to have occupancies of 0.663(8) and 0.337(8) respectively. Affected non-H atoms were refined isotropically while other non-H atoms were refined with anisotropic thermal parameters, H atoms bound to N and O atoms were refined positionally and other H atoms were included in calculated positions. Molecular plots were generated using SHELXTL-PC.[27]

$Na[Cu(H_2L^1)(NCMe)][BF_4]_2[NO_3]$. Deep blue prisms of diffraction quality were obtained by diffusion of ether into an acetonitrile solution of the complex. A correction for crystal decay (3%) was applied during data processing.

The Cu atom was located from a Patterson synthesis, and the structure was then developed using iterative rounds of least-squares refinement and Fourier-difference synthesis using SHELX 76.[28] All non-H atoms were refined with anisotropic thermal parameters and all H atoms were fixed in calculated positions except H(16) and H(21) which were located and allowed to ride at a fixed distance of 0.96 Å. During refinement the CH_3 group of the MeCN molecule was found to be disordered by rotation around the C–C–N axis. This was modelled using two distinct, equally occupied orientations with restrained C–H and H···H distances. Molecular plots were generated using SHELXTL-PC[27] and CAMERON.[29]

$[Cu(H_2L^2)(OH_2)][NO_3]_2$. Deep blue laths suitable for diffraction studies were obtained from evaporation of a solution of the complex in CH_2Cl_2. A correction for crystal decay (4%) was applied as part of the data reduction procedure.

The structure was solved by direct methods using SIR 92[30] and refined using CRYSTALS.[31] During refinement one of the nitrate ions was found to be disordered due to tilting of the O_3 plane about the N atom. This was modelled by restraining the N and O atoms to lie on a plane and refining two distinct orientations of the O atoms. All non-H atoms were refined with anisotropic thermal parameters and all H atoms were fixed in calculated positions, except those on the water molecule. These were located and then allowed to refine with restraints on the O–H distances and H–O–H angle. The final cycles of least squares were performed against F^2 using SHELXL 93.[26] Molecular plots were generated using SHELXTL-PC.[27]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/203.

Acknowledgements

We thank the University of Edinburgh for a studentship (to S. A. R.), and the EPSRC and The Royal Society for support.

References

1 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 329; K. Wieghardt, *Pure Appl. Chem.*, 1988, **60**, 509.
2 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297; J. L. Sessler, J. Hugdahl, H. Kurosaki and Y. Sasaki, *J. Coord. Chem.*, 1988, **18**, 93; S. G. Taylor, M. R. Snow and T. W. Hambley, *Aust. J. Chem.*, 1983, **36**, 2359; K. Wieghardt, W. Schmidt, W. Herrmann and H. J. Küppers, *Inorg. Chem.*, 1983, **22**, 2953; M. J. Van der Merve, J. C. A. Boeyens and R. D. Hancock, *Inorg. Chem.*, 1985, **24**, 1208; A. Riessen, T. A. Kaden, W. Ritter and H. R. Macke, *J. Chem. Soc., Chem. Commun.*, 1989, 460; D. Moore, P. E. Fanwick and M. J. Welch, *Inorg. Chem.*, 1989, **28**, 1504; R. C. Matthews, D. Parker, G. Ferguson, B. Kaitner, A. Harrison and L. Royle, *Polyhedron*, 1991, **10**, 1951; U. Bossek, D. Hanke and K. Wieghardt, *Polyhedron*, 1993, **12**, 1; D. A. Moore, P. E. Fanwick and M. J. Welch, *Inorg. Chem.*, 1990, **29**, 672; T. Beissel, K. S. Bürger, G. Voigt, K. Wieghardt, C. Butzlaff and A. X. Trautwein, *Inorg. Chem.*, 1993, **32**, 124; M. A. Konstantinovskaya, K. B. Yatsimirskii, B. K. Shcherbakov, Y. M. Polikarpov, T. Y. Medved and M. I. Kabachnik, *Russ. J. Inorg. Chem.*, 1985, **30**, 1463; U. Auerbach, J. Weiss, K. Wieghardt, B. Nuber, E. Bill, C. Butzlaff and A. X. Trautwein, *Inorg. Chem.*, 1993, **32**, 508; O. Schlager, K. Wieghardt, H. Grondey, A. Rufinska and B. Nuber, *Inorg. Chem.*, 1995, **34**, 6440; O. Schlager, K. Wieghardt and B. Nuber, *Inorg. Chem.*, 1995, **34**, 6449; 6456.
3 A. A. Belal, L. J. Farrugia, R. D. Peacock and J. J. Robb, *J. Chem. Soc., Dalton Trans.*, 1989, 931; A. A. Belal, P. Chaudhuri, I. Fallis, L. J. Farrugia, R. Hartung, N. M. Macdonald, B. Nuber, R. D. Peacock, J. Weiss and K. Wieghardt, *Inorg. Chem.*, 1991, **30**, 4397; I. Fallis, L. J. Farrugia, N. M. Macdonald and R. D. Peacock, *Inorg. Chem.*, 1993, **32**, 779; *J. Chem. Soc., Dalton Trans.*, 1993, 2759; H. Al-Sagher, I. Fallis, L. J. Farrugia and R. D. Peacock, *J. Chem. Soc., Chem. Commun.*, 1993, 1499.
4 N. W. Alcock, F. McLaren, P. Moore, G. A. Pike and S. M. Roe, *J. Chem. Soc., Chem. Commun.*, 1989, 629; N. W. Alcock, F. McLaren, P. Moore and A. M. Wynn, *J. Chem. Soc., Chem. Commun.*, 1989, 798; E. Kimura, I. Nakamura, T. Koike, M. Shionoya, Y. Kodama, T. Ikeda and M. Shiro, *J. Am. Chem. Soc.*, 1994, **116**, 4764; Z. Kovacs and A. D. Sherry, *Tetrahedron Lett.*, 1995, **36**, 9269; J. Huskens and A. D. Sherry, *J. Am. Chem. Soc.*, 1996, **118**, 4396.
5 G. A. McLachlan, S. J. Brudenell, G. D. Fallon, R. L. Martin, L. Spiccia and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1995, 439; G. A. McLachlan, G. D. Fallon, R. L. Martin, B. Mourabaki, K. S. Murray and L. Spiccia, *Inorg. Chem.*, 1994, **33**, 4663; G. A. McLachlan, G. D. Fallon, R. L. Martin and L. Spiccia, *Inorg. Chem.*, 1995, **34**, 254; L. R. Gahan, G. A. Lawrance and A. M. Sargeson, *Aust. J. Chem.*, 1982, **35**, 1119; C. Flassbeck, K. Wieghardt, E. Bill, C. Butzlaff, A. X. Trautwein, B. Nuber and J. Weiss, *Inorg. Chem.*, 1992, **31**, 21.
6 C. J. Broan, K. J. Jankowski, R. Kataky and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1990, 1738; see also, W. Clegg, P. B. Iveson and J. C. Lockhart, *J. Chem. Soc., Dalton Trans.*, 1992, 3291; C. S. John, C. E. Costello and E. O. Schlemper, *Polyhedron*, 1992, **11**, 2651; M. Studer and T. A. Kaden, *Helv. Chim. Acta*, 1986, **69**, 2081; M. Studer, A. Riesen and T. A. Kaden, *Helv. Chim. Acta*, 1989, **72**, 307; H.-Z. Cai and T. A. Kaden, *Helv. Chim. Acta*, 1993, **76**, 557; J. L. Sessler and J. W. Sibert, *Tetrahedron*, 1993, **49**, 8727.
7 A. J. Blake, I. A. Fallis, R. O. Gould, S. Parsons, S. A. Ross and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1994, 2467.
8 G. R. Weisman, D. J. Vachon, V. B. Johnson and D. A. Gronbeck, *J. Chem. Soc., Chem. Commun.*, 1987, 886.
9 T. J. Atkins, *J. Am. Chem. Soc.*, 1980, **102**, 6364; J. M. Erhardt, E. R. Grover and J. D. Wuest, *J. Am. Chem. Soc.*, 1980, **102**, 6365.
10 A. J. Blake, I. A. Fallis, R. O. Gould, S. G. Harris, S. Parsons, S. A. Ross and M. Schröder, *Acta Crystallogr., Sect. C*, 1995, **51**, 738.
11 L. J. Farrugia, P. A. Lovett and R. D. Peacock, *Acta Crystallogr., Sect. C*, 1993, **49**, 2164.
12 A. J. Blake, I. A. Fallis, S. Parsons, S. A. Ross and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1996, 525.
13 A. J. Blake, I. A. Fallis, S. Parsons, A. Heppeler, S. A. Ross and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1996, 31.
14 B. P. Czech and R. A. Bartsch, *J. Org. Chem.*, 1984, **49**, 4076.
15 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.
16 H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385.
17 P. L. Goggin, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, sect. 15.8; H. R. Das and S. C. Shome, *Anal. Chim. Acta*, 1962, **27**, 545; B. C. Challis and J. A. Challis, in *Comprehensive Organic Chemistry*, ed. I. O. Sutherland, Pergamon, Oxford, 1979, ch. 9.9; J. March, *Advanced Organic Chemistry*, 4th edn., Wiley-Interscience, New York, 1992, ch. 3; *The Chemistry of Amides*, ed. J. Zabicky, Interscience, London, 1970; W. E. Stewart and T. H. Siddall, *Chem. Rev.*, 1970, **70**, 517; T. E. Creighton, *Proteins: Structures and Molecular Properties*, 2nd edn., W. H. Freeman, New York, 1993; E. Gross and J. Meienhofer, *The Peptides*, Academic Press, New York, 1981, vol. 4.
18 T. Yatsunami, A. Sakonaka and E. Kimura, *Anal. Chem.*, 1981, **53**, 47; M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1979, 325; M. Kodama, T. Yatsunami and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1979, 1783.

19 J. C. Lee, B. Muller, P. Pregosin, G. P. A. Yap, A. L. Rheingold and R. H. Crabtree, *Inorg. Chem.*, 1995, **34**, 6295.
20 S. C. Zimmerman and W. Wu, *J. Am. Chem. Soc.*, 1989, **111**, 8054; J. C. Adrian, jun. and C. S. Wilcox, *J. Am. Chem. Soc.*, 1989, **111**, 8055, B. J. Whitlock and H. W. Whitlock, *J. Am. Chem. Soc.*, 1990, **112**, 3910; S. C. Zimmerman, W. Wu and Z. Zeng, *J. Am. Chem. Soc.*, 1991, **113**, 196; R. E. Sheridan and H. W. Whitlock, *J. Am. Chem. Soc.*, 1988, **110**, 4071; 1986, **108**, 7210; C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1079.
21 D. D. Perrin, D. R. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1980.
22 H. Koyama and T. Yoshino, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 481; J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, 1974, **96**, 2268.
23 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
24 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
25 G. M. Sheldrick, SHELXS 86, program for crystal structure solution, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
26 G. M. Sheldrick, SHELXL 93, program for crystal structure refinement, University of Göttingen, 1993.
27 G. M. Sheldrick, SHELXTL-PC, version 4.3, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1992.
28 G. M. Sheldrick, SHELX 76, program for crystal structure determination, University of Cambridge, 1976.
29 L. J. Pearce and D. J. Watkin, CAMERON, a program for molecular graphics, University of Oxford, 1985.
30 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, SIR 92, *J. Appl. Crystallogr.*, 1993, **26**, 343.
31 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide*, Issue 8, Chemical Crystallography Laboratory, University of Oxford, 1985.

Received 19*th April* 1996; *Paper* 6/02745H