

Anion and cation binding by a pendant arm cyclam and its macrobicyclic derivatives

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A series of transition-metal complexes of *N,N',N'',N'''*-tetra(3-hydroxypropyl)cyclam (**L**¹) are reported. The X-ray structures of the compounds reveal pendant arm coordination of one of the alcohol groups to give square-pyramidal metal centres with simultaneous hydrogen bonding to the counter anions. Ligand **L**¹ has been elaborated to form a series of macrotricyclic derivatives that form 1 : 1 complexes with Cu(II) and Ni(II). The X-ray structure of the tetrahydrate and protonated forms of **L**¹ are also reported.

Introduction

There is growing current interest in the simultaneous recognition of anions and cations.^{1–3} For example, the macrobicyclic contact ion pair binding receptors pioneered by Smith and co-workers^{3,4} have proved particularly effective in this regard. In these systems a metal cation (usually an alkali metal) is bound within a diazacrown-ether like macrocyclic region, while anion recognition is imparted by a hydrogen-bonding unit such as an amide or pyrrole⁵ derivative strapped across the ring. These highly preorganised systems contrast to recent work by Loeb and co-workers,^{6–8} and Rice and co-workers^{9,10} as well as ourselves^{11–14} in which a metal cation acts as a core, tying together a number of independent unidentate ligands that possess anion binding functionality, resulting in a generally labile, multi-component [ML_n](X)_m assembly with some degree of second coordination sphere recognition of the anions 'X' by coordination complex ML_n^{m+}. Whatever the approach, in the case of anion binding by neutral host species the influence of the counter-cation is generally likely to be significant. It therefore makes sense to incorporate cation as well as anion recognition into a truly selective host species.¹

While macrobicycles are generally expected to exhibit the highest binding constants, they can be difficult to prepare and may exhibit slow binding and decomplexation kinetics.¹⁵ We have therefore sought to develop simple ligands in which a metal cation binding site is fortified by a number of flexible pendant arms with hydrogen-bonding functionality. This approach has been used highly successfully by Parker and co-workers for example, to develop a wide range of anion sensors based around lanthanoid complexes of the azamacrocyclic cyclen ([12]aneN₄).^{16,17} Complexes of the larger cyclam ([14]aneN₄) with pendant ammonium arms can bind nickel(II) within the macrocycle while hydrogen bonding to a coordinated anion *via* the pendant arms.¹⁸ Extensive work by Gokel and co-workers has concentrated on alkali-metal cation complexation by lariat ethers and bibrachial lariat ethers (BiBLEs) in which the pendant arms contribute to cation binding even when the binding functional group is an alkene or alkyne.^{19–23} We have carried out related work on Ag⁺ binding.^{24,25} We now report the results of our work on transition-metal salt binding by the pendant arm macrocycle *N,N',N'',N'''*-tetra(3-hydroxypropyl)cyclam²⁶ (*N,N',N'',N'''*-tetra(3-hydroxypropyl)[14]aneN₄, **L**¹) and its elaboration to form a series of macrobicyclic derivatives.

Results and discussion

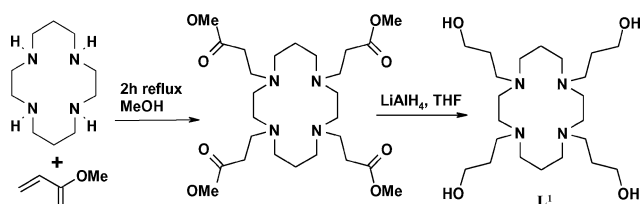
Synthesis

Transition-metal binding by both *N,N',N'',N'''*-tetra(3-hydroxypropyl)cyclam and its tetra(hydroxyethyl) homologue (**L**²) has been studied previously.^{26–28} Ligand **L**² was found to be selective for copper(II) and nickel(II). The X-ray crystal structure of the nickel complex shows that the macrocycle adopts the *trans*(III) conformation (of the Bosnich, Poon and Tobe classification²⁹) with the nickel centre in an octahedral arrangement, with two hydroxy groups bonding at the metal's axial sites.³⁰ In one molecule the remaining two arms hydrogen bond to the coordinated arms, while no such hydrogen bonds are observed in a second crystallographically independent complex. Coordination to the hydroxyl groups has been shown to be intimately involved in the metal complexation process.^{28,31,32} The propyl analogue **L**¹ is prepared through the high-pressure reaction of cyclam with trimethylene oxide.²⁶ Yields are almost quantitative due to the reactive nature of the oxetane molecule. Ligand **L**¹ binds metals less effectively than **L**² which was suggested to be due to a weaker pendant effect of the hydroxypropyl group than for the hydroxyethyl group which could be related, in turn, to increased intramolecular hydrogen bonding as evidenced in the crystal structure of free **L**¹.³³ Metal complexation by **L**¹ was investigated using solely UV-vis spectroscopy and magnetic studies although it was suggested without structural verification that the metal centre is octahedral with the two pendant arms completing the four-nitrogen coordination sphere, rather than perchlorate anions.²⁶

The oxetane synthesis of **L**¹ and ethylene oxide synthesis of **L**² along with a 2-hydroxypropyl derivative³⁴ are high yielding but require harsh and potentially dangerous reaction conditions. In contrast, reaction of cyclam with 3-bromo-1-propanol in the presence of a base under mild conditions gives only a disubstituted variant.³⁵ We elected to prepare **L**¹ by a novel method involving a Michael addition (Scheme 1). This method proved to be somewhat easier than the literature method, producing yields of *ca.* 65%, although these are not comparable to the quantitative yields of the original procedure.

Ligand structure

L¹ was characterised by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, elemental analysis and X-ray crystallography.



Scheme 1 Straightforward synthesis of L^1 .

Recrystallisation by vapour diffusion of diethyl ether into an ethanolic solution of the material resulted in the isolation of the same crystal form reported previously in which the macrocycle adopts a *trans*(IV) conformation.²⁶ However, recrystallisation from a variety of amine solvents such as aniline and triethylene tetramine resulted in the isolation of the pseudo-polymorph $L^1 \cdot 4H_2O$, Fig. 1. The structure incorporates an hydrogen-bonded network held together by a total of twelve unique interactions. The ligand exists as the *trans*(I) conformer. The intramolecular hydrogen bonding between the hydroxy arm and nitrogen atom on the same macrocycle is similar to the anhydrous form resulting in two arms wrapped over the macrocycle while two are splayed out. The supramolecular structure is based on a five-oxygen atom, $R_4^5(10)$ hydrogen-bonded ring (in graph set nomenclature³⁶) comprising four water molecules and O(1A) of one of the independent L^1 ligands. This ring then interacts with each of the remaining hydroxyl arms on the two independent half molecules.

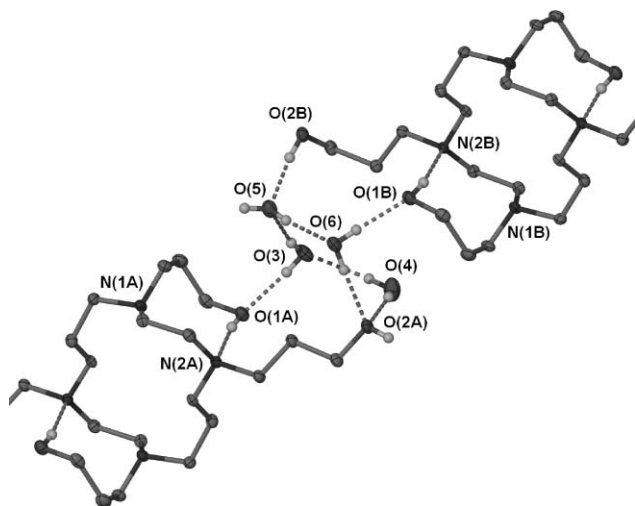


Fig. 1 Hydrogen bonding in $L^1 \cdot 4H_2O$ (thermal ellipsoids at 50% level).

Given the intramolecular $OH \cdots N$ interactions in both pseudo-polymorphs of L^1 it is of interest to examine the structure of the protonated form in which the amine lone pair is not available as a hydrogen-bond acceptor. Colourless cube-shaped crystals of $H_2L^1(BF_4)_2$ were obtained by crystallisation of the ligand in the presence of $Fe(BF_4)_2$. The structure demonstrates the reverse of the free ligand cases with intramolecular $S(9)^{36}$ motif and $NH^+ \cdots OH$ hydrogen bonding from the protonated tertiary amine nitrogen atoms on opposite sides of the macrocycle to the hydroxypropyl arms stemming from an adjacent nitrogen atom with an $N \cdots O$ distance of 2.816(2) Å. An interaction between the pendant arms and the tetrafluoroborate anion was observed with an $O \cdots F$ distance of 2.7963(19) Å. The same arm also forms an intermolecular interaction to another protonated macrocycle with an $O \cdots O$ distance of 2.7536(19) Å, Fig. 2. For comparison the uncharged intramolecular $OH \cdots N$ interactions in the unprotonated compound have $O \cdots N$ distances in the range 2.70–2.75 Å. An identical (isostructural) *trans*(III) form was observed for the diperchlorate salt $H_2L^1(ClO_4)_2$ isolated from decomposition of the $Ni(ClO_4)_2$ complex of L^1 , *vide infra*.

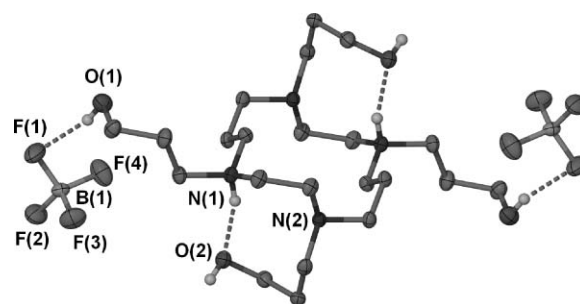


Fig. 2 Hydrogen bonding in the protonated $H_2L^1(BF_4)_2$ (thermal ellipsoids at 50% level).

Reactions with metal salts

The reactions of L^1 with nickel(II) perchlorate, nickel(II) nitrate, copper(II) nitrate, copper(II) tetrafluoroborate and copper(II) acetate were investigated resulting in the isolation of $[Ni(L^1)](ClO_4)_2$ (**1**), $[Ni(L^1)](NO_3)_2$ (**2**), $[Cu(L^1)](NO_3)_2$ (**3**), $[Cu(L^1)](BF_4)_2$ (**4**) and the mixed-anion complex $[Cu(L^1)](O_2CCH_3)_{1.3}Cl_{0.7} \cdot 0.2H_2O$ (**5**) in which the chloride arises from decomposition of chloroform solvent.

For the nickel(II) perchlorate complex, **1**, the complexation was performed by mixing ethanolic solutions of both ligand and metal salt and then refluxing for 2 h. The product precipitated as a green powder upon concentration of the solution. The IR spectrum of **1** in nujol showed the $\nu(OH)$ stretch at 3511 cm^{-1} suggesting a change in the coordination of the hydroxyl arm (*cf.* 3354 cm^{-1} for the free ligand). Two almost isostructural sets of diffraction quality crystals of composition $[Ni(L^1)](ClO_4)_2 \cdot CHCl_3 \cdot 0.5H_2O$ (**1a**) and $[Ni(L^1)](ClO_4)_2 \cdot MeCN$ (**1b**) were grown by vapour diffusion of chloroform in to acetonitrile solutions of the complex. In both cases the X-ray crystal structure showed severe disorder with the complex and anions residing in two different orientations with a rotation of 90° around the nickel ion. The disorder was resolved using fractional occupancy isotropic carbon atoms. The structure of **1a** is geometrically rather better than **1b** and discussion will be confined to this sample although the gross features are similar for both. Despite the disorder, qualitative structural information can be inferred from the analysis and is reinforced by the agreement between the two solvates. The nickel is found to be in a five-coordinate environment with one of the pendant arms bonding to the metal ion with an Ni–O distance of 2.026(4) Å (Fig. 3(a)). The cyclam ring adopts the usual *trans*(I) conformation and the nickel ion is found to be 0.24 Å above the mean plane of the nitrogen atoms with Ni–N bonds ranging from 2.120(5) to 2.216(8) Å. The perchlorate ions are positioned outside the primary metal coordination sphere. One anion is located on the opposite side of the nickel, but at a distance of 3.59 Å (closest Ni \cdots O distance), indicating an absence of any significant interaction. No significant hydrogen-bond contacts are formed between the anions to any of the pendant arms except for a bifurcated interaction from hydroxyl O(1) to O(9/10) with $O \cdots O$ distances 3.10–3.22 Å. The most significant intermolecular contact is between the nickel-bound oxygen atom and an arm from another molecule where the $O(2) \cdots O(4)$ distance is 2.650(6) Å, creating a hydrogen-bonded dimeric entity where one macrocycle caps another, Fig. 3(b). The same acceptor oxygen atom is involved as a donor and laterally hydrogen bonds to the arm of third macrocycle where the $O(4) \cdots O(3)$ distance is 2.660(7) Å. A chloroform molecule was also included in the asymmetric unit and forms a $C-H \cdots O$ interaction with one of the perchlorate anions with a $C \cdots O$ distance of 2.91(3) Å, which is a short distance for this type of contact.³⁷

Attempts were made to characterise the compound by 1H NMR spectroscopy. However, upon addition of D_2O to the pre-dried green solid, a purple solution immediately formed.

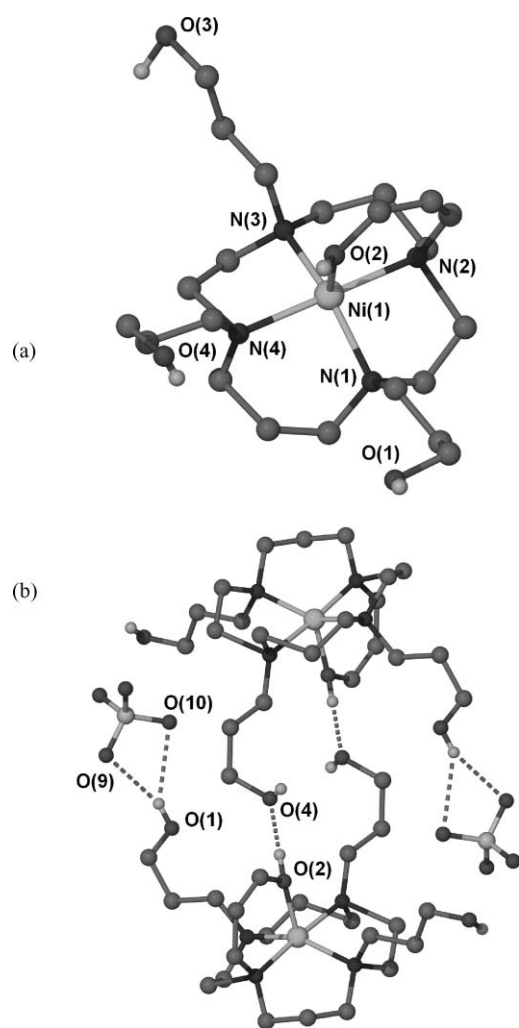


Fig. 3 (a) Molecular structure of **1a** showing pendant arm coordination in the major disorder component. Selected bond lengths (Å): Ni(1)–O(2) 2.026(4), Ni(1)–N(3) 2.124(5), Ni(1)–N(1) 2.120(5), Ni(1)–N(2) 2.145(6), Ni(1)–N(4) 2.216(8); (b) crystal packing in **1a**.

This solution yielded pale pink cube shaped crystals which were shown to be $\text{H}_2\text{L}^1(\text{ClO}_4)_2$ (cf. the isomorphous BF_4^- salt described above). The demetallation of the ligand was supported by IR evidence which shows the O–H stretch at 3320 cm^{-1} , close to the free ligand value (3354 cm^{-1}).

The procedure for the preparation of **1** was repeated for nickel(II) nitrate to give green crystals of $[\text{Ni}(\text{L}^1)](\text{NO}_3)_2$, complex **2**. FAB mass spectrometry showed a peak at m/z 489 corresponding to $[\text{Ni}(\text{L}^1 - \text{H})]^+$. Diffraction-quality crystals were produced by recrystallisation from ethanol and then vapour diffusion of diethyl ether into an ethanolic solution. The X-ray crystal structure showed the complexed ligand in a *trans*(I) conformation with a five-coordinate square-pyramidal nickel centre 0.286 Å above the mean plane of the nitrogen atoms and an Ni–O distance of $2.027(2)\text{ Å}$, Fig. 4. The complex was not disordered, allowing a much more precise determination. The Ni–N distances ranged from $2.137(2)$ to $2.143(3)\text{ Å}$. Neither of the two nitrate ions are bound to the nickel; one sits beneath the plane of the nitrogen atoms with the nearest contact to the nickel being 3.630 Å , too long to indicate any significant interaction. The other anion however, is hydrogen bonded to the nickel-coordinated pendant arm through two of its oxygen atoms with $\text{O}_{\text{arm}} \cdots \text{O}_{\text{anion}}$ distances of $2.720(3)$ and $3.044(3)\text{ Å}$.

The hydrogen atom located on the pendant arm points towards the further nitrate oxygen atom from it rather than to the closer oxygen atom. This is may be because of a hydrogen-bond interaction occurring from another separate cyclam moiety toward the other oxygen atom of the nitrate anion with an

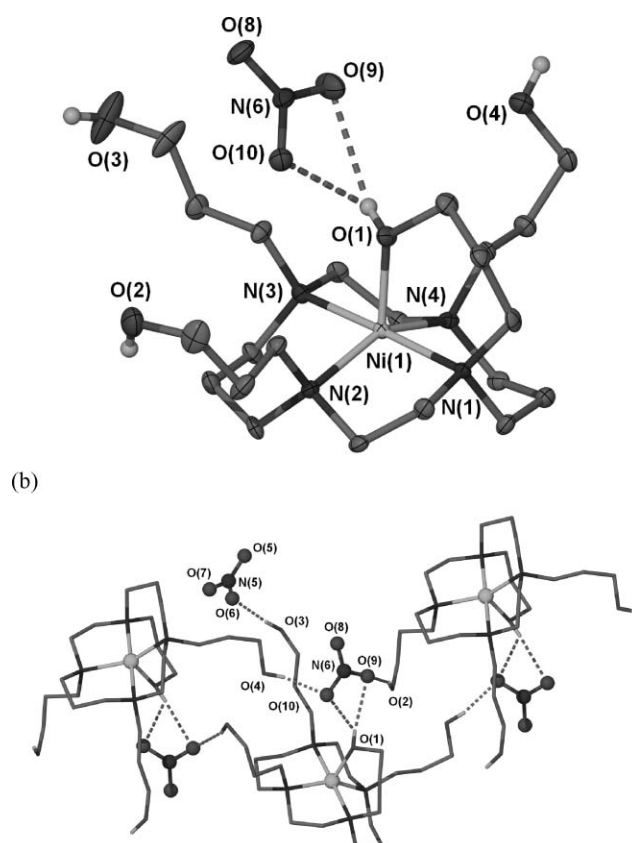


Fig. 4 X-Ray crystal structure of $[\text{Ni}(\text{L}^1)](\text{NO}_3)_2$ (**2**) showing (a) hydrogen bonding to the second-sphere nitrate anion and (b) extended structure (nitrate and Ni atoms as spheres of arbitrary radius, CH hydrogen atoms omitted for clarity). Selected bond lengths (Å): Ni(1)–O(1) $2.027(2)$, Ni(1)–N(1) $2.140(2)$, Ni(1)–N(2) $2.143(3)$, Ni(1)–N(3) $2.143(3)$, Ni(1)–N(4) $2.137(3)$. Hydrogen bond distances (Å): O(1) \cdots O(10)^I $2.720(3)$, O(4) \cdots O(10)^I $2.787(4)$, O(3) \cdots O(6)^{II} $2.855(4)$, O(2) \cdots O(9)^{III} $3.073(6)$. Symmetry transformations used to generate equivalent atoms: I $x, -y + 1, -z - 1/2$; II $x, -y - 1, z$, III $-x, -y, z + 1/2$.

O(4) \cdots O(10) distance of $2.787(4)\text{ Å}$. A second weak interaction is observed between O(9) and O(2) of a third cyclam unit with a distance of $3.073(6)\text{ Å}$ with the third carbon and oxygen atom disordered in two positions. The other position of the arm hydrogen bonds to another arm on the initial macrocycle with an O(2A) \cdots O(4) distance of $2.831(6)\text{ Å}$. The remaining pendant arm forms a hydrogen bond with the nitrate anion beneath the nitrogen atom plane with an O(3) \cdots O(6) distance of $2.855(4)\text{ Å}$.

The copper(II) nitrate complex was also synthesised and characterised as $[\text{Cu}(\text{L}^1)](\text{NO}_3)_2$ (**3**). Unfortunately, attempts to refine a structure from diffraction quality crystals led to highly disordered models. Information from the unit cell parameters, however shows the dimensions to be comparable to those of **2** ($a, b, c = 15.4796(6), 11.7954(6)$ and $15.1196(9)\text{ Å}$ for **2** and $15.4577(2), 11.8571(1)$ and $15.0999(2)\text{ Å}$ for **3**, respectively). The disordered model also shows the basic square-pyramidal copper centre with pendant arm coordination, further corroborating the isostructural nature of **2** and **3**. A similar situation was encountered for $[\text{Cu}(\text{L}^1)](\text{BF}_4)_2$ (**4**). This structure was also unrefinable to a satisfactory level, but shows the basic square-pyramidal metal centre with a single pendant arm bonding to the copper.

The reaction of L^1 with $\text{Cu}(\text{O}_2\text{CCH}_3)_2 \cdot \text{H}_2\text{O}$ followed the method used for synthesising **1**, yielding a deep blue solution from which crystals did not readily precipitate. A variety of attempts to grow diffraction quality crystals by vapour diffusion were made with the nitromethane–diethyl ether system ultimately yielding hygroscopic blue needles. These were found to be the mixed compound $[\text{Cu}(\text{L}^1)](\text{O}_2\text{CCH}_3)_{1.3}\text{Cl}_{0.7} \cdot 0.2\text{H}_2\text{O}$ (**5**). The X-ray structure of **5** showed no metal-coordinated anion,

but was reminiscent of **1–4** in terms of the metal coordination geometry. The anion environment is remarkable, however. One acetate is situated above the copper(II) ion, while a disordered anion site consisting of part acetate, part chloride (apparently a remnant of a previous crystallisation involving chloroform) is on the opposite side of the metal. Once again the ligand adopts a *trans*(1) form with a five-coordinate square-pyramidal copper(II) centre where the average Cu–N distance is 2.101(3) Å while the Cu–O distance was 2.252(2) Å. This is longer than the M–O_{arm} distances for the other complexes as a result of Jahn–Teller distortion. The copper ion is situated more deeply in the macrocyclic cavity being 0.242 Å above the mean nitrogen plane, a shorter distance than for complexes **1** and **2**. A hydrogen-bond contact is seen between the coordinated pendant arm and the acetate with an O(1)⋯O(5) distance of 2.675(3) Å. The distance from O(1) on this arm to O(6) on the acetate ion is 3.293(3) Å, which is too long to suggest a significant interaction. In turn, O(6) is hydrogen bonded to another pendant arm with an O(2)⋯O(6) distance of 2.737(4) Å. A third arm also bonds to the first acetate oxygen atom with an O(3)⋯O(5) distance of 2.722(3) Å. The fourth arm is found to be disordered over two positions. One oxygen atom position forms a hydrogen bond with another arm where O(4)⋯O(3) is 2.818(4) Å and the other position hydrogen bonds to a partial occupancy solvent water molecule where O(4A)⋯O(1S) is 2.807 Å, Fig. 5.

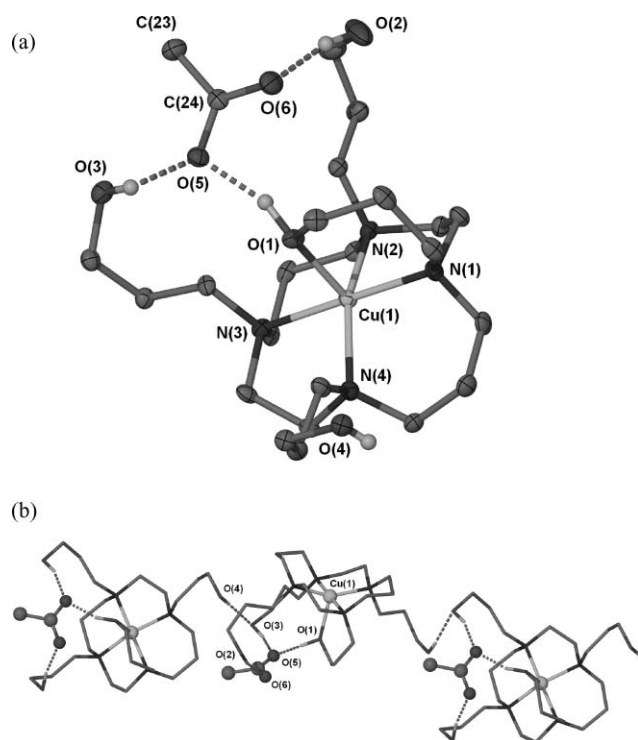
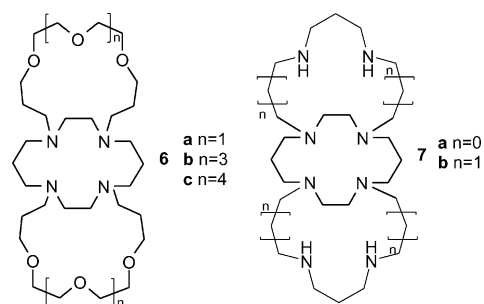


Fig. 5 Crystal structure of **5** showing the triple hydrogen-bonded acetate anion (a) repeat unit with 50% ellipsoids and (b) extended structure forming a linear hydrogen-bonded chain. Selected bond lengths (Å): Cu(1)–O(1) 2.252(2), Cu(1)–N(1) 2.111(3), Cu(1)–N(2) 2.093(3), Cu(1)–N(3) 2.118(3), Cu(1)–N(4) 2.080(3). Hydrogen-bond distances (Å): O(1)⋯O(5) 2.675(3), O(2)⋯O(6) 2.738(4), O(4)⋯O(3) 2.816(4). Symmetry transformation used to generate equivalent atoms: $x, -y + 3/2, z + 1/2$.

The ordered anion based on O(5) and O(6) is thus strongly hydrogen bonded by three of the four ligand pendant arms and might thus be expected to be tightly held. In support of this expectation FAB mass spectrometry showed a peak for a number of the complexes in the presence of one bound anion. This gas phase observation could be a result of the multiple pendant arm hydrogen bonds forming to the anions in a similar way to that observed in the crystal structure.

Formation and complexation of tricyclic ligands

While the flexible structure of **L**¹ allows the ligands to adapt to the coordination requirements of a variety of metals and anions, tying up the hydroxypropyl arms as part of a macrocyclic framework would impart a much higher degree of preorganisation. Studies by Beer have shown that certain difunctional macrocycles can bind both softer transition-metal ions at nitrogen atom moieties and harder alkali metal cations at oxygen atom-containing moieties.³⁸ Similar behaviour might be expected of ligands **6a–c** derived from **L**¹. Synthesis of related N-donor species has been achieved by Murase *et al.* who have taken a tetratosylated tetra(aminoethyl)cyclam core and substituted it with two equivalents of a ditosylated propyl group to form the novel tricycle **7a**.³⁹ The ligand forms complexes with copper(II) and cobalt(II) which were found to be bimetallic with a cavity between the two metal ions. In the cobalt(II) case a carbonate anion is coordinated between the two metals. The origin of this anion is thought to be the trapping of atmospheric CO₂. Wainwright and co-workers have synthesised a similar compound (**7b**), using tetraaminopropylcyclam as the core moiety on which to build the tricycle.⁴⁰ This ligand has been successfully complexed with cobalt(II), copper(II), zinc(II), cadmium(II) and lead(II) and found to have sequential occupation of the outer cycles rather than the single inner cavity. The two metallated compartments were found to be too distant from each other to bind any anions between them.



Compounds **6a–c** were prepared following the synthesis of Guillard and co-workers⁴¹ Diethylene glycol ditosylate was reacted with **L**¹ to form compound **6a**. Column chromatography was used to separate the ligand from unreacted and partially reacted starting materials. FAB mass spectrometry showed the presence of the desired ligand with a peak at m/z 573. The ¹H NMR spectrum of the material was complicated by the presence of many overlapping resonances for the aliphatic backbone of the molecule. While the presence of a number of isomers cannot be ruled out the most likely structure is the one shown with the polyether chains bridging the ethylene rather than the propylene portion of the cyclam core by analogy with compounds **7**. The ligand was successfully complexed with Cu(BF₄)₂ by mixing solutions of the ligand and metal in ethanol to form [Cu(**6a**)](BF₄)₂ (**8**). FAB mass spectrometry showed the complex cation with a peak at m/z 635 (40% intensity). Complexation was also achieved with Ni(ClO₄)₂ to provide [Ni(**6a**)](ClO₄)₂ as a reddish-pink material (in contrast to the green starting material). FAB mass spectrometry showed a peak for the complex cation at m/z 632 and also a peak at m/z 731 corresponding to the complex with one perchlorate anion.

The same procedure used for **6a** was used to synthesise **6b** and **6c**, but using tetraethylene glycol ditosylate and pentaethylene glycol ditosylate, respectively. FAB mass spectrometry showed the desired ligands at 749 and 837 m/z . ¹H NMR spectroscopy gave similar results to **6a** with poorly resolved spectra. Ligand **6b** was complexed with Cu(BF₄)₂ to yield [Cu(**6b**)](BF₄)₂ (**9**). FAB mass spectrometry revealed the complex with a peak at m/z 811 (5% intensity) assigned to [Cu(**6b**) – H]⁺. Similar complexations were attempted with Pb(NO₃)₂, Cs₂CO₃, but yielded no complexes. Ligand **6c** reacted also with Cu(BF₄)₂ with a distinct colour change to purple upon addition of the

metal salt to an ethanolic solution of the ligand. This solution was analysed using FAB mass spectrometry and confirmed the complex as $[\text{Cu}(\mathbf{6c})(\text{BF}_4)_2]$ (**10**) with a peak at m/z 918 (5% intensity) assigned to $[\text{Cu}(\mathbf{6c}) - \text{H}]^+$. Attempts were made to obtain diffraction quality crystals of all of the complexes **8–10** without success.

Summary and conclusion

The complexes of L^1 prepared and isolated with copper(II) and nickel(II) show that in the solid state the metals prefer to adopt a five-coordinate square-pyramidal structure with the ligand, contrary to previous studies which hinted at an octahedral geometry.^{26,33} The side arm is effective at coordinating the bound metal ion in an intramolecular fashion similar to a 'scorpion' complex.⁴² It has also been shown that the hydroxypropyl arms readily hydrogen bond to anions which do not coordinate to the metal ion. The molecule could potentially serve as a host for similar smaller anions and form comparable interactions.

A number of novel macrotricyclic species and their copper(II) and nickel(II) complexes have been synthesised and characterised. Although crystal structures have not been elucidated, mass spectrometry has shown that this family of ligands form 1 : 1 complexes with transition metals, unlike the related amino-based cyclam derivatives **7** which form 2 : 1 metal : ligand complexes.

Experimental

Instrumentation

^1H NMR spectra were recorded using a Bruker AM360 spectrometer at a frequency of 360 MHz. Mass Spectra were run on a Jeol AX505X spectrometer in FAB mode in either thioglycerol or nitrobenzyl alcohol (NBA). IR spectra were recorded using a Perkin-Elmer 983G Infrared spectrophotometer as Nujol mulls between sodium chloride plates. Microanalyses were performed at Birkbeck College and the University of North London. High-resolution mass spectrometry was performed at the School of Pharmacy, University of London. Cyclam was prepared using the method of Barefield *et al.*⁴³

CAUTION: Solid perchlorate salts should be assumed to be explosive and handled with great care, avoiding heat, friction or percussion.

Preparations

N, N', N'', N''' -1,4,8,11-Tetra(hydroxypropyl)-1,4,8,11-tetraazacyclotetradecane (L^1). L^1 was prepared using the method of Wainwright and co-workers.²⁶ Cyclam (4.0 g, 20 mmol) was dissolved in methanol (100 mL). This solution was brought to reflux and methyl acrylate (7.56 g, 96 mmol) added dropwise. This was refluxed for a further 2 h. The methanol and excess acrylate were evaporated and the resulting oil taken up in dry THF (100 mL). Lithium aluminium hydride (6.21 g, 164 mmol) was added and the suspension refluxed with stirring for 2 h. The reaction mixture was quenched with water (6.2 mL); 15% sodium hydroxide (6.2 mL) and excess water (18.6 mL), filtered through Celite, and evaporated to dryness under reduced pressure. The resulting white solid was recrystallised using ethanol to yield a white crystalline solid which was washed with diethyl ether and air-dried (5.64 g, 13 mmol, 65%). ^1H NMR (CDCl_3 , δ/ppm , J/Hz): 1.69 (m, 12 H, $\text{NCH}_2\text{CH}_2 + \text{CH}_2\text{CH}_2\text{CH}_2$), 2.43 (t, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$, $^2J = 7.0$), 2.56 (m, 16H, $\text{NCH}_2\text{CH}_2\text{N} + \text{NCH}_2\text{CH}_2\text{OH}$), 3.70 (t, 8H, $\text{NCH}_2\text{CH}_2\text{OH}$, $J = 5.5$), 4.84 (br. s, 4H, OH). MS (FAB): 433 (MH^+). IR: 3354, br. m, $\nu(\text{O-H})$. Anal. Calc. for $\text{C}_{22}\text{H}_{48}\text{N}_4\text{O}_4$: C, 61.08; H, 11.18; N, 12.95. Found: C, 61.00; H, 11.29; N, 12.95%.

$(N, N', N'', N'''$ -Tetra(3-hydroxypropyl)cyclam)nickel(II) diperchlorate (1**).** L^1 (0.20 g, 0.46 mmol) was dissolved in ethanol

(20 mL) and brought to reflux. Nickel(II) perchlorate hexahydrate (0.17 g, 0.46 mmol) was dissolved in ethanol (20 mL) and added dropwise to the ligand solution which was refluxed for 3 h. The resulting green solution was reduced in volume and left in the refrigerator at 4 °C overnight, which resulted in the precipitation of green crystals. These were filtered and washed with ether (2×20 mL) and dried *in vacuo* (0.236 g, 0.34 mmol, 74%). MS (FAB): 489 ($\text{L}^1 + \text{Ni}$), 433 (L^1). Anal. Calc. for $\text{C}_{22}\text{H}_{48}\text{Cl}_2\text{N}_4\text{NiO}_{12}$: C, 38.28; H, 7.01; N, 8.12. Found: C, 38.49; H, 7.04; N, 8.06%. IR (Nujol mull): 3630–3510, br, m; 1103, sh, s; 1073, sh, s.

$(N, N', N'', N'''$ -Tetra(3-hydroxypropyl)cyclam)nickel(II) dinitrate (2**).** L^1 (0.20 g, 0.46 mmol) was dissolved in ethanol (20 mL) and brought to reflux. Nickel(II) nitrate hexahydrate (0.13 g, 0.46 mmol) was dissolved in ethanol (10 mL) and added dropwise to the L^1 solution and the deep green solution was refluxed for 3 h. Crystals did not immediately precipitate and the solution was evaporated to dryness yielding a green solid, which was dissolved in the minimum amount of ethanol. Diffraction quality crystals were grown by vapour diffusion of diethyl ether into an ethanolic solution of the green solid. These were mechanically isolated and washed with diethyl ether (0.049 g, 0.08 mmol, 17%). MS (FAB): 489 ($\text{L}^1 + \text{Ni} - \text{H}$), 433 (L^1). Anal. Calc. for $\text{C}_{22}\text{H}_{48}\text{N}_6\text{O}_{10}\text{Ni}$: C, 42.94; H, 7.86; N, 13.66. Found: C, 42.92; H, 7.90; N, 13.66%.

$(N, N', N'', N'''$ -Tetra(3-hydroxypropyl)cyclam)copper(II) dinitrate (3**).** L^1 (0.20 g, 0.46 mmol) was dissolved in ethanol (20 mL) and brought to reflux. Copper(II) nitrate trihydrate (0.11 g, 0.46 mmol) was dissolved in ethanol (10 mL) and added dropwise to the L^1 solution to give a deep blue solution. This was refluxed for 1 h and stirred at room temperature overnight. The solution was then cooled in a refrigerator at 4 °C overnight resulting in formation of blue crystals which were filtered off and washed with diethyl ether (0.226 g, 0.36 mmol, 79%). MS (FAB): 557 ($\text{L}^1 + \text{Cu} + \text{NO}_3$), 495 ($\text{L}^1 + \text{Cu}$), 433 (L^1). Anal. Calc. for $\text{C}_{22}\text{H}_{48}\text{N}_6\text{O}_{10}\text{Cu}$: C, 42.61; H, 7.80; N, 13.55. Found: C, 42.71; H, 7.89; N, 13.44%.

$(N, N', N'', N'''$ -Tetra(3-hydroxypropyl)cyclam)copper(II) bis-(tetrafluoroborate) (4**).** L^1 (0.10 g, 0.23 mmol) was dissolved in ethanol (10 mL). Copper(II) tetrafluoroborate hexahydrate (0.08 g, 0.23 mmol) was dissolved in ethanol (10 mL) and added dropwise to the ligand solution to create a deep blue solution. The solution was then concentrated by evaporating under reduced pressure and cooled in a refrigerator overnight to 4 °C. The resulting blue crystals filtered and washed with diethyl ether and air-dried (0.092 g, 0.14 mmol, 56%). MS (FAB): 581 ($\text{L}^1 + \text{Cu} + \text{BF}_4$), 495 ($\text{L}^1 + \text{Cu}$), 433 (L^1). Anal. Calc. for $\text{C}_{22}\text{H}_{48}\text{N}_4\text{O}_4\text{BF}_4\text{Cu}$: C, 39.44; H, 8.37; N, 7.23. Found: C, 39.52; H, 8.28; N, 7.38%.

$(N, N', N'', N'''$ -Tetra(3-hydroxypropyl)cyclam)copper(II) mixed acetate/chloride salt (5**).** L^1 (0.20 g, 0.46 mmol) was dissolved in ethanol (20 mL) and brought to reflux. Copper(II) acetate monohydrate (0.09 g, 0.46 mmol) was dissolved in ethanol (10 mL) and added dropwise to the ligand solution and the resulting aquamarine solution refluxed for 3 h. Blue needle crystals were grown by vapour diffusion of diethyl ether into a nitromethane solution of the complex following prior recrystallisation from chloroform. MS (FAB): 495 ($\text{L}^1 + \text{Cu}$), 433 (L^1).

8,11,14,25,28,31-Hexaoxa-1,4,18,21-tetraazatricyclo[19.13.3.3^{4,18}]tetracotane (6a**).** L^1 (0.25 g, 0.58 mmol) was dissolved in dry THF (50 mL) under nitrogen. Sodium hydride (1.80 g, 78 mmol) was added to the solution and the suspension stirred at room temperature for 1 h. Diethylene glycol ditosylate (0.48 g, 1.16 mmol) was dissolved in dry THF (25 mL) and added dropwise to the refluxing suspension. This was refluxed for 48 h under nitrogen and then cooled to room temperature. The pale

yellow mixture was quenched with water (50 mL) and resulting solution filtered through Celite and evaporated under reduced pressure. The residue was taken up in chloroform (50 mL) and acidified with 2 M hydrochloric acid (10 mL) and washed with water (50 mL). The aqueous layer was kept and basified (pH 14) with 2 M sodium hydroxide. This was washed with chloroform (2 × 25 mL) and the organic layer dried over anhydrous magnesium sulfate. This was filtered and evaporated under reduced pressure to yield an orange oil. This was purified using column chromatography (Al₂O₃: 9 : 1 chloroform–methanol) to yield a pale yellow oil (0.08 g, 0.14 mmol, 24%). IR (thin film): 2924, s, 1456, sh, s; 1259, sh, s; 1111, sh, s. ¹H NMR (CDCl₃, δ/ppm, J/Hz): 3.65 (m, 24H, NCH₂CH₂CH₂O + OCH₂CH₂O), 2.57 (m, 24H, NCH₂CH₂CH₂O + NCH₂CH₂N + NCH₂CH₂CH₂N), 1.75 (m, 12H, NCH₂CH₂CH₂N + NCH₂CH₂CH₂O). MS (FAB): 573 (MH⁺).

8,11,14,17,21,33,36,39,42,45-Decaoxa-1,4,25,29-tetraazatricyclo[25.19.3.3^{4,25}]tetrapentacontane (6b). L¹ (0.5 g, 1.16 mmol) was dissolved in dry THF (50 mL) under nitrogen. Sodium hydride (0.161 g, 7.0 mmol) was added to the solution and the suspension stirred at room temperature for 1 h. Tetraethylene glycol ditosylate (1.16 g, 2.31 mmol) was dissolved in dry THF (25 mL) and added dropwise to the refluxing suspension. This was refluxed for 48 h under nitrogen and then cooled to room temperature. The pale yellow mixture was quenched with water (50 mL) and resulting solution filtered on a sintered glass funnel and evaporated under reduced pressure. The residue was taken up in chloroform (50 mL) and acidified with 2 M hydrochloric acid (10 mL) and washed with water (50 mL). The aqueous layer was kept and basified (pH 14) with 2 M sodium hydroxide. This was washed with chloroform (2 × 50 mL) and the organic layer dried with magnesium sulfate. This was filtered and evaporated under reduced pressure to yield a yellow–brown oil (0.52 g, 0.68 mmol, 60%). ¹³C{¹H} NMR (CDCl₃, δ/ppm): 27.49 (NCH₂CH₂CH₂N), 27.71 (NCH₂CH₂CH₂N), 50.76 (NCH₂CH₂N), 51.41 (NCH₂CH₂CH₂O), 52.04 (NCH₂CH₂CH₂O), 61.30 (NCH₂CH₂CH₂O), 69.28–72.60 (OCH₂CH₂O). MS (FAB) 749 (MH⁺). IR (thin film): 2865, s; 1458, sh, s; 1248, sh, s; 1115, sh, s. Anal. Calc. for C₃₈H₇₆N₄O₁₀·H₂O·CHCl₃: C, 52.84; H, 8.98; N, 6.32. Found: C, 52.72; H, 8.96; N, 6.32%.

8,11,14,17,20,23,34,37,40,43,46,49-Dodecaoxa-1,4,27,30-tetraazatricyclo[28.22.3.3^{4,27}]octapentacontane (6c). L¹ (0.45 g, 1.0 mmol) was dissolved in dry THF (100 mL) under nitrogen. Sodium hydride (0.161 g, 7.0 mmol) was added to the solution and the suspension stirred at room temperature for 1 h. Tetraethylene glycol ditosylate (1.14 g, 2.0 mmol) was dissolved in dry THF (25 mL) and added dropwise to the refluxing suspension. This was refluxed for 48 h under nitrogen and then cooled to room temperature. The pale yellow mixture was quenched with water (50 mL) and resulting solution filtered on a sintered glass funnel and evaporated under reduced pressure. The residue was taken up in chloroform (50 mL) and acidified with 2 M hydrochloric acid (10 mL) and washed with water (50 mL). The aqueous layer was kept and basified (pH 14) with 2 M sodium hydroxide. This was washed with chloroform (2 × 50 mL) and the organic layer dried with magnesium sulfate. This was filtered and evaporated under reduced pressure to yield a colourless, viscous oil (0.52 g, 0.68 mmol, 60%). ¹H NMR (CDCl₃, δ/ppm, J/Hz): 3.65 (m, 48H, NCH₂CH₂CH₂O + OCH₂CH₂O), 2.50 (m, 24H, NCH₂CH₂CH₂O + NCH₂CH₂N + NCH₂CH₂CH₂N), 1.70 (m, 12H, NCH₂CH₂CH₂N + NCH₂CH₂CH₂O). MS (FAB) 837 (MH⁺).

Crystallography

Crystals were mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100–120 K using an Oxford

Cryostream low-temperature attachment. Approximate unit cell dimensions were determined by the Nonius Collect program⁴⁴ from five index frames of width 2° in ϕ using a Nonius ^{Kappa}CCD diffractometer and Mo-K α radiation, $\lambda = 0.71073$ Å, with a detector to crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5% completeness for $\theta = 27.5^\circ$ using a combination of 0.5–2° ϕ and ω scans of 10–60 s degree^{−1} exposure time (depending on crystal quality). Crystals were indexed using the DENZO-SMN package⁴⁵ and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack⁴⁵) resulted in unique data sets corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97⁴⁶ and developed *via* alternating least-squares cycles and difference Fourier synthesis (SHELXL-97⁴⁷) with the aid of the program X-Seed.⁴⁸ In general, unless stated, all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride, except for acidic protons which were located on the final difference Fourier map and refined freely where possible. See individual sections for specific data.

Crystal data for H₂L¹(ClO₄)₂. C₂₂H₅₀Cl₂N₄O₁₂, $M = 633.56$, pale pink cube, $0.90 \times 0.80 \times 0.70$ mm³, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.9260(4)$, $b = 11.9504(8)$, $c = 11.5955(6)$ Å, $\beta = 104.449(3)^\circ$, $V = 1466.14(14)$ Å³, $Z = 2$, $D_c = 1.435$ g cm^{−3}, $F_{000} = 680$, $T = 100(2)$ K, $2\theta_{\max} = 50.0^\circ$, 7090 reflections collected, 2574 unique ($R_{\text{int}} = 0.0585$). Final GooF = 1.051, $R_1 = 0.0333$, $wR_2 = 0.0833$, R indices based on 2278 reflections with $I > 2\sigma(I)$ (refinement on F^2), 183 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.288$ mm^{−1}. Hydroxy and amine protons were located on the final difference Fourier map and refined freely where possible.

Crystal data for H₂L¹(BF₄)₂. C₂₂H₅₀B₂F₈N₄O₄, $M = 608.28$, colourless cube, $2.00 \times 2.00 \times 2.00$ mm³, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.8652(10)$, $b = 11.9557(8)$, $c = 11.4131(9)$ Å, $\beta = 103.732(4)^\circ$, $V = 1440.2(2)$ Å³, $Z = 2$, $D_c = 1.403$ g cm^{−3}, $F_{000} = 648$, $T = 120(2)$ K, $2\theta_{\max} = 55.0^\circ$, 7921 reflections collected, 3193 unique ($R_{\text{int}} = 0.0717$). Final GooF = 1.047, $R_1 = 0.0501$, $wR_2 = 0.1238$, R indices based on 2177 reflections with $I > 2\sigma(I)$ (refinement on F^2), 188 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.127$ mm^{−1}. Hydroxy and amine protons were located on the final difference Fourier map and refined freely where possible.

Crystal data for 1a. C₂₃H₅₀Cl₅N₄NiO_{12.5}, $M = 818.63$, green plate, $0.80 \times 0.30 \times 0.02$ mm³, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.7140(11)$, $b = 10.3555(7)$, $c = 18.0585(13)$ Å, $a = 101.519(5)^\circ$, $\beta = 104.520(5)^\circ$, $\gamma = 100.024(5)^\circ$, $V = 1674.3(3)$ Å³, $Z = 2$, $D_c = 1.624$ g cm^{−3}, $F_{000} = 858$, $T = 100(2)$ K, $2\theta_{\max} = 50.0^\circ$, 9847 reflections collected, 5882 unique ($R_{\text{int}} = 0.0903$). Final GooF = 1.028, $R_1 = 0.0837$, $wR_2 = 0.1958$, R indices based on 4328 reflections with $I > 2\sigma(I)$ (refinement on F^2), 431 parameters, 186 restraints. Lp and absorption corrections applied, $\mu = 1.044$ mm^{−1}. The structure proved to be disordered with a 90° rotation of the macrocycle core. Disordered atoms were modelled isotropically with a common occupancy factor for each disordered component, constrained to sum to 100%. The refined proportion of the two components was 66 : 34. A similar disorder was encountered for 1b.

Crystal data for 2. C₂₂H₄₈N₆NiO₁₀, $M = 615.37$, green plate, $0.50 \times 0.30 \times 0.09$ mm³, orthorhombic, space group $Pca2_1$ (no. 29), $a = 15.4796(6)$, $b = 11.7954(6)$, $c = 15.1196(9)$ Å, $V = 2760.7(2)$ Å³, $Z = 4$, $D_c = 1.481$ g cm^{−3}, $F_{000} = 1320$, $T = 100(2)$ K, $2\theta_{\max} = 55.0^\circ$, 16338 reflections collected, 6211 unique ($R_{\text{int}} = 0.1075$). Final GooF = 1.004, $R_1 = 0.0509$, $wR_2 = 0.0839$, R

indices based on 4793 reflections with $I > 2\sigma(I)$ (refinement on F^2), 378 parameters, 25 restraints. Lp and absorption corrections applied, $\mu = 0.767 \text{ mm}^{-1}$. Absolute structure parameter = $-0.016(12)$.⁴⁹

Crystal data for 5. $\text{C}_{24.6}\text{H}_{52.3}\text{Cl}_{0.7}\text{CuN}_4\text{O}_{6.8}$, $M = 601.36$, blue plate, $0.50 \times 0.40 \times 0.10 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.0421(15)$, $b = 8.2819(6)$, $c = 20.5152(15) \text{ \AA}$, $\beta = 105.080(4)^\circ$, $V = 2795.8(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.429 \text{ g cm}^{-3}$, $F_{000} = 1293$, $T = 100(2) \text{ K}$, $2\theta_{\text{max}} = 55.0^\circ$, 17013 reflections collected, 6347 unique ($R_{\text{int}} = 0.0999$). Final GooF = 1.066, $R1 = 0.0696$, $wR2 = 0.1069$, R indices based on 4427 reflections with $I > 2\sigma(I)$ (refinement on F^2), 336 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.897 \text{ mm}^{-1}$. One anion was disordered 70% Cl^- and 30% acetate. The 30% occupancy methyl group of the acetate anion could not be located.

Crystal data for $\text{L}^1 \cdot 4\text{H}_2\text{O}$. $\text{C}_{22}\text{H}_{56}\text{N}_4\text{O}_8$, $M = 504.71$, colourless plate, $1.00 \times 0.40 \times 0.07 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.7258(15)$, $b = 7.9552(16)$, $c = 25.987(5) \text{ \AA}$, $\alpha = 91.77(3)^\circ$, $\beta = 90.64(3)^\circ$, $\gamma = 111.41(3)^\circ$, $V = 1485.8(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.128 \text{ g cm}^{-3}$, $F_{000} = 560$, $T = 100(2) \text{ K}$, $2\theta_{\text{max}} = 55.0^\circ$, 7779 reflections collected, 5589 unique ($R_{\text{int}} = 0.0398$). Final GooF = 1.255, $R1 = 0.0574$, $wR2 = 0.1349$, R indices based on 4283 reflections with $I > 2\sigma(I)$ (refinement on F^2), 532 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.084 \text{ mm}^{-1}$.

CCDC reference numbers 267665–267670.

See <http://www.rsc.org/suppdata/dt/b5/b504561d/> for crystallographic data in CIF or other electronic format.

References

- M. T. Reetz, 'Simultaneous binding of Cations and Anions' in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Pergamon, Oxford, 1996.
- T. Tuntulani, S. Poompradub, P. Thavornnyutikarn, N. Jaiboon, V. Ruangpornvisuti, N. Chachit, Z. Asfari and J. Vicens, *Tetrahedron Lett.*, 2001, **42**, 5541.
- A. V. Koulou, J. M. Mahoney and B. D. Smith, *Org. Biomol. Chem.*, 2003, **1**, 27.
- B. D. Smith and T. N. Lambert, *Chem. Commun.*, 2003, 2261.
- J. M. Mahoney, R. A. Marshall, A. M. Beatty, B. D. Smith, S. Camiolo and P. A. Gale, *J. Supramol. Chem.*, 2001, **1**, 289.
- C. R. Bondy, P. A. Gale and S. J. Loeb, *Chem. Commun.*, 2001, 729.
- C. R. Bondy and S. J. Loeb, *Coord. Chem. Rev.*, 2003, **240**, 77.
- C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Am. Chem. Soc.*, 2004, **126**, 5030.
- L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. T. Zeng, *Dalton Trans.*, 2004, 2396.
- L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. T. Zeng, *Chem. Commun.*, 2004, 654.
- D. R. Turner, B. Smith, E. C. Spencer, A. E. Goeta, I. R. Evans, D. A. Tocher, J. A. K. Howard and J. W. Steed, *New J. Chem.*, 2005, **29**, 90.
- D. R. Turner, E. C. Spencer, J. A. K. Howard, D. A. Tocher and J. W. Steed, *Chem. Commun.*, 2004, 1352.
- K. J. Wallace, R. Daari, W. J. Belcher, L. O. Abouderbala, M. G. Boutelle and J. W. Steed, *J. Organomet. Chem.*, 2003, **666**, 63.
- L. Applegarth, A. E. Goeta and J. W. Steed, *Chem. Commun.*, 2005, 2405.
- J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, Chichester, 1st edn., 2000.
- C. D. Edlin, S. Faulkner, D. Parker and M. P. Wilkinson, *Chem. Commun.*, 1996, 1249.
- D. Parker, R. S. Dickins, H. Puschmann, C. Crossland and J. A. K. Howard, *Chem. Rev.*, 2002, **102**, 1977.
- K. P. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1983, 1149.
- J. X. Hu, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 2001, **123**, 9486.
- J. X. Hu, L. J. Barbour and G. W. Gokel, *Chem. Commun.*, 2001, 1858.
- E. S. Meadows, S. L. De Wall, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 2001, **123**, 3092.
- G. W. Gokel, L. J. Barbour, R. Ferdani and J. Hu, *Acc. Chem. Res.*, 2002, **35**, 878.
- G. W. Gokel, L. J. Barbour, S. L. De Wall and E. S. Meadows, *Coord. Chem. Rev.*, 2001, **222**, 127.
- P. Arya, A. Channa, P. J. Cragg, P. D. Prince and J. W. Steed, *New J. Chem.*, 2002, **26**, 440.
- P. D. Prince and J. W. Steed, *Supramol. Chem.*, 1998, **10**, 155.
- P. J. Davies, M. R. Taylor, K. P. Wainwright, P. Harriott and P. A. Duckworth, *Inorg. Chim. Acta*, 1996, **246**, 1.
- C. M. Madeyski, J. P. Micheal and R. D. Hancock, *Inorg. Chem.*, 1984, **23**, 1487.
- P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
- B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
- M. I. Soldini, *Acta Crystallogr., Sect. C*, 1991, **47**, 2239.
- J. C. A. Boeyens, L. Cook, P. A. Duckworth, S. B. Rahardjo, M. R. Taylor and K. P. Wainwright, *Inorg. Chim. Acta*, 1996, **246**, 321.
- S. B. Rahardjo and K. P. Wainwright, *Inorg. Chim. Acta*, 1997, **255**, 29.
- P. J. Davies and K. P. Wainwright, *Inorg. Chim. Acta*, 1999, **294**, 103.
- R. W. Hay and M. M. Hassan, *Polyhedron*, 1997, **16**, 2205.
- K.-Y. Choi, H.-H. Lee, I.-H. Suh, J.-G. Kim and U.-S. Shin, *Inorg. Chim. Acta*, 2001, **321**, 221.
- J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555.
- G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441.
- P. D. Beer, *Chem. Soc. Rev.*, 1989, **18**, 409.
- I. Murase, G. Vuckovic, M. Kodera, H. Harada, N. Matsumoto and S. Kida, *Inorg. Chem.*, 1991, **30**, 728.
- A. Damsyik, P. J. Davies, C. I. Keeble, M. R. Taylor and K. P. Wainwright, *J. Chem. Soc., Dalton Trans.*, 1998, 703.
- S. Brandes, S. Lacour, F. Denat, P. Pullumbi and R. Guillard, *J. Chem. Soc., Perkin Trans. 1*, 1998, 639.
- P. S. Pallavicini, A. Perotti, A. Poggi, B. Seghi and L. Fabbri, *J. Am. Chem. Soc.*, 1987, **109**, 5139.
- E. K. Barefield, F. Wagner, A. W. Herlinger and A. R. Dahl, *Inorg. Synth.*, 1976, **26**, 220.
- R. Hooft, 'Collect', Nonius B.V., Delft, 1998.
- Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, London, 1997, p. 307.
- G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, 1997.
- G. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, 1997.
- L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.
- H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.