Long tailed cage amines: Synthesis, metal complexation, and structure†

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Received 20th October 2009, Accepted 22nd January 2010
First published as an Advance Article on the web 22nd February 2010
DOI: 10.1039/b921930g

The generation of amphiphiles derived from macrobicyclic hexamines of the "sarcophagine" class can be prepared through efficient and selective reactions involving the reductive alkylation, using long-chain aldehydes, of amino-functionalised sarcophagines when bound to Cu(II) or Mg(II). The Mg(II) pathway is particularly convenient for the ultimate isolation of the free ligands, which can then be used to form metalloamphiphiles with a variety of metal ions. Structural studies have been made of one of the free (protonated) ligands and some of their complexes.

Introduction

Amphiphiles incorporating a complexed metal ion centre, metallosurfactants, are expected to find various specific applications,[1] known examples including those as components of luminescent[2] and magnetic materials,[3] as catalysts[4] and as MRI agents.[5] In the particular instance of the macrobicyclic hexamines termed "sarcophagines"[6] (Fig. 1) as the metal binding unit, relatively simple functionalisation has been shown to lead to amphiphiles with properties as diverse as those as vermicides,[7-9] as chiral anion sensors[10] and as photo- and electro-catalysts.[11] Such amphiphiles may also have the advantage of control of the form of their association through changes in overall charge.[12,13] Given that it is known that a wide range of metal ions can be used to form kinetically inert sarcophagine complexes and that these complexes are, for example, redox active over a total potential range of >2 V,[14] it remains an intriguing prospect to incorporate this wider range of metal ions into sarcophagine surfactants which have been, up to now, predominantly Co(III) derivatives. This implies the need for synthesis of the free ligands and the objective of the present work was thus to optimise, on the basis of varied preliminary observations, techniques for the preparation and isolation of alkyl-functionalised metal-free sarcophagines (Fig. 1) as one pathway to a new group of metallosurfactants.

A variety of methods are known for introduction of lipophilic substituents onto a sarcophagine unit but many of these involve aromatic entities which generally prove to reduce the solubility of the complexes in all solvents.[15] With long alkyl chains, the solubility in water is diminished (often dramatically) and solubility in apolar solvents can be achieved through the introduction of highly lipophilic groups, although this property is also strongly dependent on the counteranion.[16] It was for this reason that we chose to explore further the synthesis of free cages with long alkyl-group substituents, ultimately with an emphasis on chains of length C_7 or greater, since the amphiphilicity of such species (especially in their complexes) was expected to be most pronounced. Three methods that have proven successful for the synthesis of some such ligands in their complexed form are diazotization[7,8] and reductive alkylation (amination)[7,8,17,18] of amino-substituted cage complexes, and variations on the original template synthesis.[8,9] These have employed very largely Co(III) reactants, advantageously because of the protection of the six N-donors within the macrobicycle but disadvantageously in many instances because of the reduction of the nucleophilicity of pendent groups involved in the substituent introduction and the consequent need for the use of alkylating agents in large excess. Another major drawback to functionalising Co(III) cages is the difficulty in removing the metal ion from the complex after modification, this requiring rather stringent conditions in general and sometimes proving to be impossible.[19,20] In the face of such problems, it has been found that M(II) complexes of amino-functionalised cages are considerably stronger nucleophiles than their Co(III) analogues and that the use of Mg(II) in particular allows very ready isolation of the ligands from the product complexes, a procedure already developed for the synthesis of free cage ligands with $C_{13}H_{27}$ substituents.[17] The present work is a systematic exploitation of these developments for the synthesis of new amphiphilic cages using reductive alkylation of aminocage reactants (Fig. 1). The choice of different reactant species has enabled efficient and selective syntheses of mono- and di-alkylated cages to be developed.

Results and discussion

It is known that the free diaminosarcophagine ligand, $(NH_2)_2$sar (**L2**), reacts with alkylating agents, including aldehydes used in reductive alkylation procedures as presently employed, to give mixtures of species alkylated at both the primary and secondary N-centres, though with the latter predominating.[17] It was hoped initially that both this lack of selectivity and the preference for secondary-N alkylation might be overcome by the use of the partly protonated ligand (assuming preferential protonation of

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† Electronic supplementary information (ESI) available: Details of the synthesis of $[Cu(C_8H_{17}NH)_2sar]^{2+}$ and $[Cu\{(C_7H_{15})_2N\}(C_7H_{15}NH)sar]^{2+}$ and reductive demetallation of $[Cu(C_7H_{15}NH)_2sar]^{2+}$ with $NaBH_4$ and Pd/C are reported. CCDC reference numbers 688325 [**L1**], 738804 [**L7**], 738801 [**CuL4**], 738802 [**Cu(HL4)**], and 738803 [**ZnL5**]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b921930g

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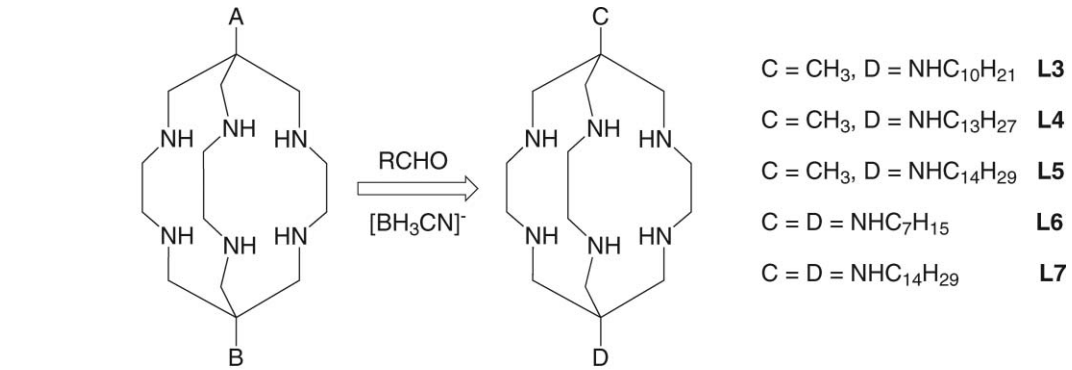


A = B = H = "sarcophagine" = sar
= 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane

A = CH_3, B = NH_2 = $(CH_3)(NH_2)$sar **L1**

A = B = NH_2 = $(NH_2)_2$sar **L2**

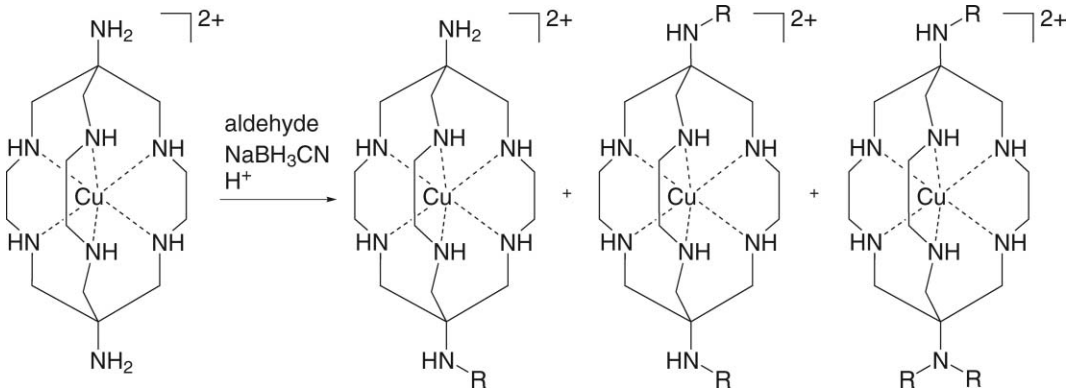
Fig. 1 Structures of the macrobicyclic ligands used and produced in this work.

secondary sites), as has proved successful in the reactions of some aminomonomacrocycles,[21] but this was not so. In fact, there is structural evidence that protonation of the primary sites in $(NH_2)_2$sar occurs early in the sequence of protonation steps[22] and while this strictly concerns the solid state, it is plausible that in solution also, protonation of the primary sites would provide the maximum distance between similarly-charged cationic centres.

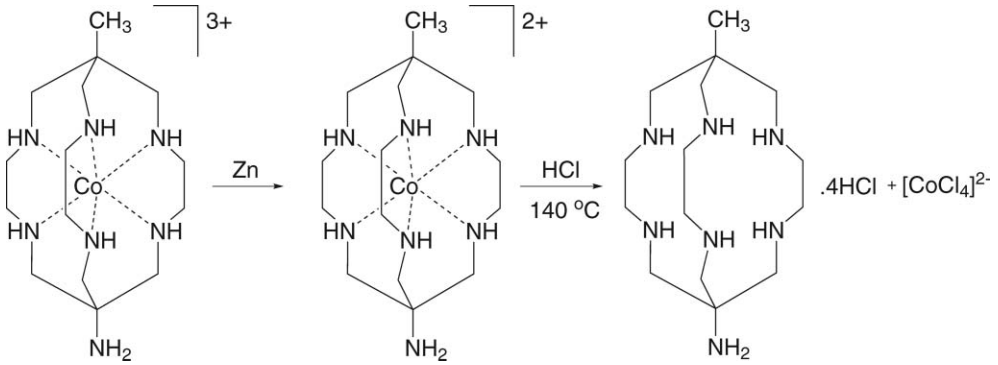
Cu(II) complexes

Mixtures of alkylation products, though here involving just the initially primary amino-group sites, were also obtained in preliminary experiments to conduct reductive alkylation of the Cu(II) complex of $(NH_2)_2$sar, $[Cu(NH_2)_2sar]^{2+}$ (**CuL2**), used as a species where these external amino substituents are known to be moderately nucleophilic.[19] Reactions were performed in EtOH in the presence of molecular sieves, $NaBH_3CN$, and acetic acid, conditions known to be effective in related syntheses[7,17] and less harsh than those seemingly required for complete formation of the intermediate imines followed by $NaBH_4$ reduction. Initial work using aldehyde to cage ratios of 1 : 1 and 2 : 1 in an attempt to maximise the yields of mono-alkylated and di-alkylated species, respectively, always gave mixtures of the two products and some starting material. While the properties of the Cu(II) complexes of mono- and di-tridecylated $(NH_2)_2$sar are markedly different,[17] present investigations of the use of chromatography (on silica, alumina or cation exchange columns) or fractional crystallisation to separate the product mixtures for this and other chains showed such methods to be tedious and inefficient. Fortunately, however, it was found possible to adapt the reaction conditions so as to obtain the (symmetrically 1,8-) di-alkylated derivatives alone in good yield. Thus, for octanal as the aldehyde, for example, use of a 6 : 1 octanal to cage ratio under refluxing conditions in EtOH allowed the exclusive isolation of $[Cu(C_8H_{17}NH)_2sar](ClO_4)_2 \cdot xHClO_4$ (identified *via* MS) after 30 min by precipitation from the reaction mixture by the addition of $HClO_4$. Higher alkylation products could also be prepared using greater excesses of aldehyde in the reaction mixture (Scheme 1, also see ESI†).

An obvious solution to the problem of inefficient formation of monoalkylated cage ligands in competition with higher alkylated species is to use a reactant cage but with a single alkylation site. This is available in the cage ligand $(CH_3)(NH_2)$sar (**L1**), formed *via* template synthesis[23] on the complex $[Co(sen)]^{3+}$.[24] The synthesis of $[Co(CH_3)(NH_3)sar]^{4+}$ is somewhat more laborious than that of



Scheme 1 The various products identified (*via* MS) during reductive alkylation procedures on **CuL2** (R = alkyl group).



Scheme 2 Isolation of **L1**·4HCl·2H_2O using hot, concentrated HCl under pressure.

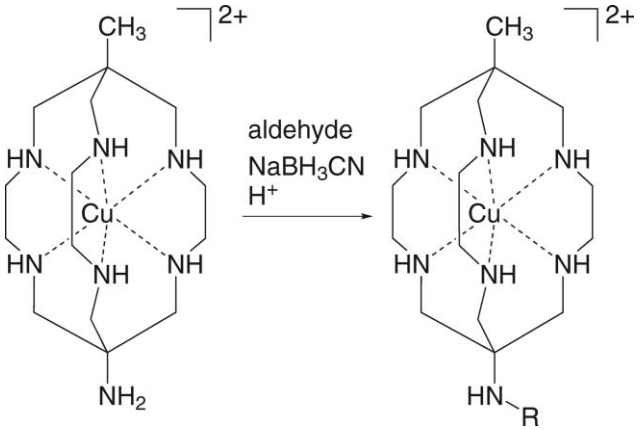
$[Co(NH_3)_2sar]^{5+}$ but the real disadvantage here was that the use of excess cyanide[22] to isolate **L1** gave rather poor yields.[25] It was of interest, therefore, to investigate another method for obtaining **L1** in the hope of increasing the yield of this rather precious starting material.

Using a procedure analogous to that for the isolation of $[(NH_3)_2sarH_3]Cl_5·4H_2O$,[22] $[Co(CH_3)(NH_2)sar]^{3+}$ was reduced to the more labile $[Co(CH_3)(NH_2)sar]^{2+}$ in deoxygenated water using Zn dust under an inert atmosphere (Scheme 2). After filtration and removal of the solvent under vacuum, deoxygenated concentrated HCl was added to the solid, the flask was sealed and the mixture heated to 140 °C for at least 12 h. The progress of the reaction was readily observed visually, as the dull green colour of the initially largely insoluble Co(II) cage complex gave place to the characteristic deep blue colour of $[CoCl_4]^{2-}$ in solution. After workup using cation exchange chromatography on Dowex, the protonated ligand $[(CH_3)(NH_3)sarH_3]Cl_4·2H_2O$ (**L1**·4HCl·2H_2O) could be isolated in 60–70% yield. Preparation of the Cu(II) and Mg(II) complexes of **L1** was readily achieved by heating an aqueous solution of the hydrochloride with a basic metal source ("$CuCO_3$" or MgO) followed by precipitation.

Despite the presence of but a single, weakly nucleophilic "external" amino group in the complex $[\mathbf{CuL1}]^{2+}$, the use of large excesses of aldehyde and elevated temperatures in an attempt to maximise the yield of the mono-alkylated product proved ineffective as it led to di-alkylation and subsequent tedious separations. Fortunately, under milder conditions such as the use of one to two equivalents of aldehyde, the mono-alkylated products could be obtained in 60–70% yields (Scheme 3).

Since the Cu(II) complexes were extremely resistant to ligand removal by treatment with acid, they were first subjected to transmetallation with Zn metal.[26] It was anticipated that the Zn(II) complex could then be demetallated by treating the complex with acid, thus liberating the protonated free ligands.[27] However, heating solutions of either the mono- or di-alkylated copper complexes in the presence of Zn metal gave very sluggish reduction of the Cu(II) complex, as judged from the colour in solution, and even after extended reaction times a faint tinge of blue colour was always observed in solution, indicating incomplete reduction of the Cu(II) complex during the reaction (Scheme 4) or perhaps the presence (unexpected) of a stable Cu(I) species.

Ultimately, an alternative method[28] using $NaBH_4$ and Pd/C to reduce the Cu(II) species was found to be more effective at



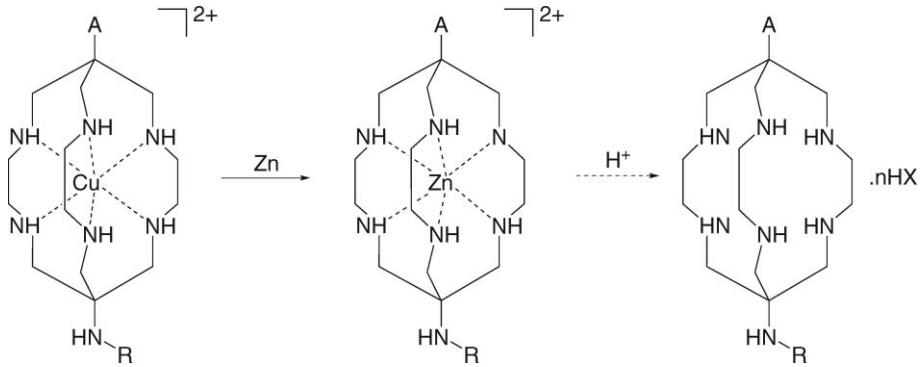
Scheme 3 Synthesis of mono-alkylated Cu-cage complexes. (R = $C_{10}H_{21}$, $C_{13}H_{27}$, $C_{14}H_{29}$).

completely removing the metal from the complex (Scheme 5, also see ESI†).

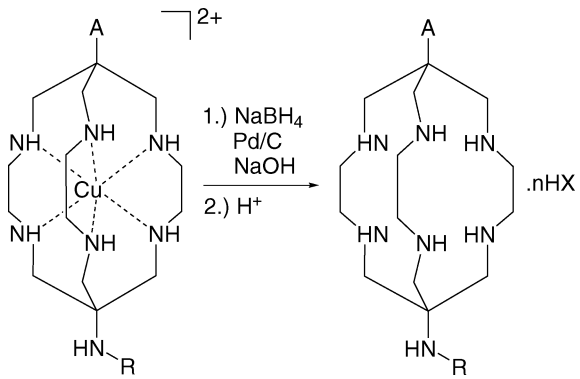
Thus, selective preparation of mono- and di-alkylated cage ligands could be achieved using Cu(II) complexes during the syntheses. Following the progress of the reactions of these paramagnetic complexes was, however, inconvenient, and a significant drawback was the difficulty of removing the ligands from the metal. Ultimately, these observations on the Cu(II) complexes were exploited in the development of more convenient syntheses of the free di-alkylated ligands based on the use of Mg(II) complexes.

Mg(II) cages

Success in the selective synthesis of mono- or di-alkylated Cu(II) cages provided the stimulus to examine the use of a more labile and diamagnetic metal complex such that the "free" ligands could be obtained relatively easily. Magnesium(II) cage complexes are appropriate in this respect, as they allow for the reactions to be monitored *via* NMR spectroscopy and are known to dissociate readily in acidic solution[17] thus allowing the alkylated ligands to be readily demetallated by lowering the pH. However, the lability of the Mg(II) complexes in acid is a potential drawback when considering their use in reductive alkylation reactions as these are typically performed at pH ~ 6–8, in order that rapid and selective reduction of the C=N double bond of the protonated imine intermediate (rather than the carbonyl group of any free aldehyde) is achieved with $[BH_3CN]^-$, but successful reductive



Scheme 4 Attempted reduction of Cu(II) complexes with Zn, and subsequent demetallation under acidic conditions. (A = CH_3 or NHR; R = alkyl group).

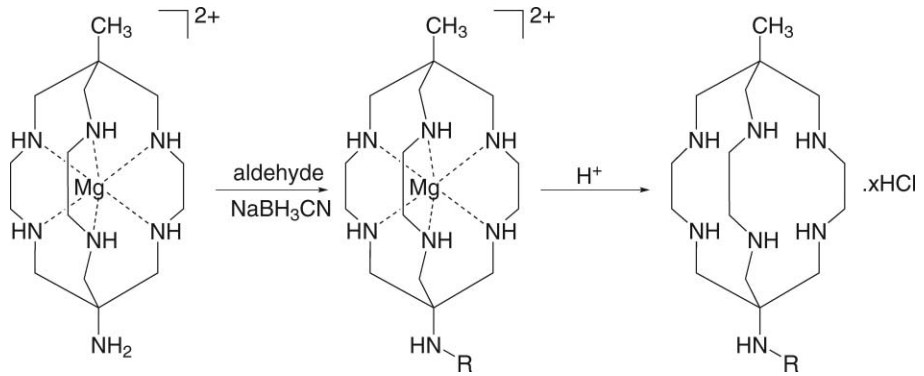


Scheme 5 Reduction of the copper complexes with $NaBH_4$ and Pd/C to give the free ligands. (A = CH_3 or NHR; R = alkyl group).

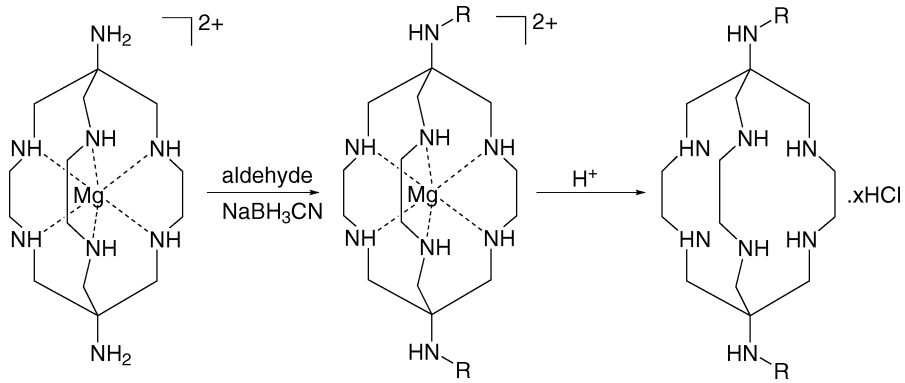
alkylation has been achieved under more basic conditions in other systems.[29] There is, of course, a compensating factor that attack of a hydridic nucleophile on a pendent imine should be facilitated by the cationic charge. Thus, the reductive alkylation of **MgL2**·$(OAc)_2$ and **MgL1**·$(OAc)_2$ was investigated under weakly basic conditions. NMR spectroscopic experiments indicated that alkylation of **MgL1**·$(OAc)_2$ to give the desired mono-alkylated species was readily achieved using 4–5 molar equivalents of the aldehyde in the presence of an excess of $[BH_3CN]^-$ at room temperature (Scheme 6). The synthesis of the symmetrically di-alkylated complexes was performed in an analogous manner, *via* reductive alkylation of **MgL2** with 8 molar equivalents of aldehyde in MeOH or MeOH–$CHCl_3$ (Scheme 7). Removal of magnesium from the alkylated cage was achieved by heating the material in concentrated HCl/MeOH or HCl/EtOH, and isolation of the metal free ligands was achieved after chromatography on Dowex cation exchange resin followed by recrystallisation to give the pure ligands in *ca.* 55–65% yields.

The mono-alkylated ligands **L3** and **L5** exhibit good solubility in water as their hydrochloride salts, displaying typical surfactant properties such as their propensity to form stable aqueous foams when agitated. The ability to form foams is lost upon symmetrical di-alkylation to give **L6**, which also coincides with a reduction in water solubility. The long chained derivative **L7** did not display any significant solubility in water, but showed favourable solubility in the polar alcoholic solvents MeOH and EtOH. Thus, it appears that the introduction of significant apolar groups, in this case the addition of two C_{14} tails on the ligand, is required to effect a meaningful change in the aqueous solubility of the free cage. However, even after dialkylation, the polar charged cage moiety still exerts a strong influence on the solubility of the ligand, favouring polar solvents, and it appears that the introduction of more lipophilic groups is required to achieve solubility in non-polar solvents.[16]

With these solubility properties in mind, synthesis of metal complexes from the free ligands is a relatively straightforward process, owing to the rapid complexation kinetics and stability of complexes of the cage amines.[22] Since the ligands were isolated in their protonated forms (**L3**·5HCl, **L5**·7HCl, **L6**·$4HNO_3$, **L7**·$4HCl·2H_2O$), it was convenient to simply heat the ligand with a



Scheme 6 Synthesis of the mono-alkylated ligands using 4–5 : 1 aldehyde to cage ratios. (R = $C_{10}H_{21}$, $C_{14}H_{29}$).



Scheme 7 Synthesis of the dialkylated ligands using 8 : 1 aldehyde to cage ratios. ($R = C_7H_{15}$, $C_{14}H_{29}$).

basic metal source such as a metal carbonate or acetate in a suitable solvent (water or MeOH), with oxygenation of the solutions required for the reactions with cobalt in order to oxidise the Co(II) to Co(III). This procedure is suitable for the metal complexes targeted (Cu, Ni, Zn and Co) but not general for all possible metal complexes of the ligand.[30] After filtration of any undissolved carbonate, the compounds were converted to their acetate salts (in order to avoid the potential complication of precipitating the complexes as mixed salts (*i.e.* mixture of Cl^-/ClO_4^- anions)[15,19]) by ion exchange on Dowex 1 × 8 anion exchange resin before being precipitated by the addition of perchloric acid. The only exception to this procedure was in the case of **CoL7**, where the product readily precipitated from the reaction mixture as the tri-chloride, allowing straightforward recovery of the complex.

The complexes displayed similar solubility characteristics to their ligand precursors. The mono-alkylated species exhibit good solubility in water as their acetate salts, and produced stable foams when agitated, but the addition of chloride, perchlorate or nitrate anions decreased their solubility in polar solvents significantly. The di-alkylated complexes derived from **L6** also exhibited good solubility in water as their acetates, but did not foam when agitated, as was observed for the ligand precursor. Unsurprisingly, complexes of the longer chain di-alkylated ligand **L7** proved to be completely insoluble in water, regardless of the anion present, and were most readily dissolved in MeCN. As part of our continuing efforts to prepare metallomesogens,[16] the thermotropic properties of these complexes were examined with a polarising optical microscope fitted with a hot stage, but unfortunately none of the complexes displayed any mesophases prior to decomposition. The surfactant properties of these complexes, including any lyotropic liquid crystalline behaviour are currently under investigation.

Single crystal X-ray structure determinations of L1, L7, CuL4, Cu(HL4) and ZnL5

The lattice of the crystalline ligand hydrochloride **L1**·4HCl·$^7/_3H_2O$, while complicated to describe in detail, shows that the tetra-protonated ligand is like analogous derivatives of $(NH_2)_2$sar[22] in adopting a form poised for reception of a metal ion by binding to the six secondary-N centres (Fig. 2(a)). In detail, the structure is remarkable for the fact that there are 24 molecules within the unit cell, the subtle differences between

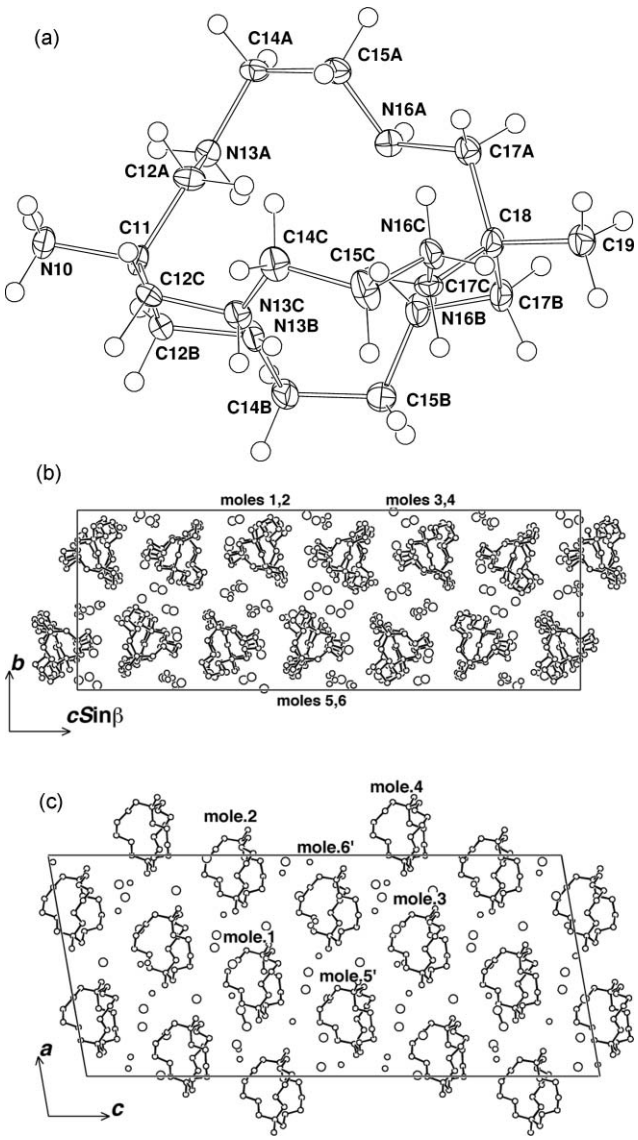


Fig. 2 (a) Molecular projection of one ligand molecule of **L1**·4HCl·$^7/_3H_2O$. Unit Cell of **L1**·4HCl·$^7/_3H_2O$. (b) Layers in the *ac* plane with pairs of different molecules (1,2 and 3,4, and 5,6) aligned parallel to the *a* axis. H-atoms omitted for clarity. (c) One of the layers from the *ac* plane. H-atoms omitted for clarity.

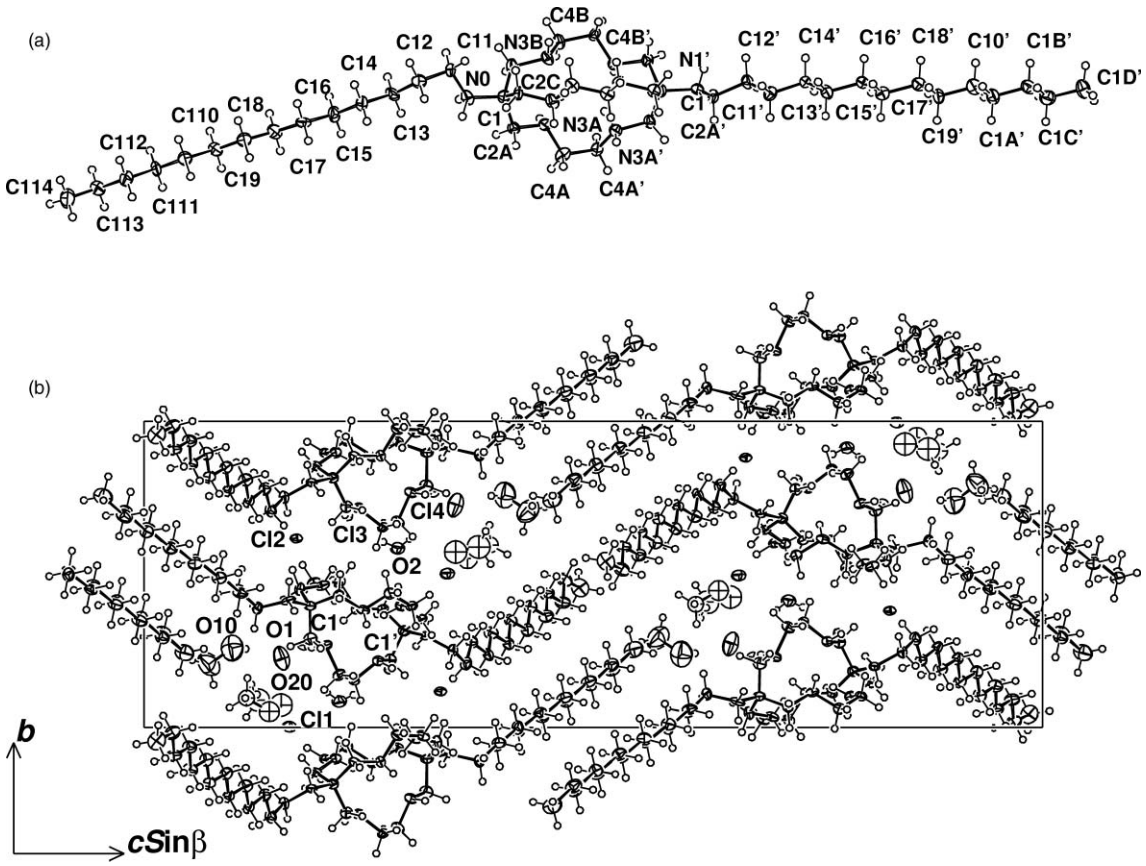


Fig. 3 (a) Projection of the cation of **L7**·4HCl·2H$_2$O·2CH$_3$OH. (b) Unit cell diagram for **L7**·4HCl·2H$_2$O·2CH$_3$OH projected down the *a* axis.

them being associated with conformational changes presumably consequential upon differences in H-bonding interactions. The differences are not due to inversion of configuration at any of the three (unprotonated) chiral N centres. The molecules are packed in the unit cell in layers in the *ac* plane with pairs of different molecules (1,2 and 3,4, and 5,6) aligned parallel to the *a* axis (see Fig. 2(b) with one layer shown in Fig. 2(c)). All of the molecules in the same layer are aligned with respect to the apical substituents. As could be expected there is present an extensive three dimensional hydrogen bonding array, involving most of the available hydrogen atoms, and is best visualized *in silico*.

The structure of the cation present in **L7**·4HCl·2H$_2$O·2CH$_3$OH is shown in Fig. 3(a) and is one of the few structures obtained on substituted, metal-free sarcophagines.[22,27] As observed in the solid state structures of some M(II) complexes[6] of (NH$_2$)$_2$sar, as well as the free ligand and its various protonated forms,[22] the cage core of the ligand adopts a conformation intermediate between octahedral and trigonal prismatic, with an average twist angle of 27°. Two protons are encapsulated by the cage, whereby a hydrogen on the protonated nitrogen of a given cap is involved in a bifurcated H-bonding arrangement with the other two nitrogens of the cap (H···NH 2.20–2.45 Å). The twist angle of 27° places the NH units of the cage itself too far apart to coordinate an anion (as is commonly observed in Co(III) complexes of the ligand),[31] and thus the "external" NH groups, including those of the cap substituents, act as donors to separate acceptors. Thus, four of the NH groups of the cage itself are involved in close contact with chloride anions (HN···Cl 3.31–3.47 Å), the other two in close contact with water molecules (HN···O 2.73–2.80 Å), with the nitrogens of both apical substituents interacting with two chloride anions each (HN···Cl 3.08–3.17 Å). This shows that the anions are acting to link the cages together in an intricate H-bonding network between the chlorides and solvent molecules. The packing of the ligand within the solid can be described as homochiral sheets of protonated cages, anions and solvent, with adjacent sheets alternating in chirality of the cage in a ΔΛΔΛ manner, separated by sheets of aliphatic tail groups, forming a herringbone type arrangement when viewed down *a* (Fig. 3(b)). The tails exist in a fully *trans*-extended arrangement, except for a *gauche* conformation for the first two carbons of the chain immediately attached to the apical nitrogen of the cage caps. The angle between the two apical chains as defined by the C(12)–C(113) and C(11′)–C(1C′) vectors is 26.8°. The angles between these and the axis of the cage, as defined by the N(0)–N(1′) vector, are 20.0 and 31.6°.

The packing of the tails within the lattice is a mixture of two modes, one in which two alkyl groups from adjacent sheets meet in an end-on manner, and the other in which the tails of adjacent sheets lie in a roughly parallel sheet-like arrangement. Dispersion interactions play a role in the packing of the lattice, with the alkyl chains displaying closest contacts (C···C 3.8–3.9 Å) for parallel tails of adjacent cation sheets, and (C···C 4.0–4.1 Å) within any given sheet.

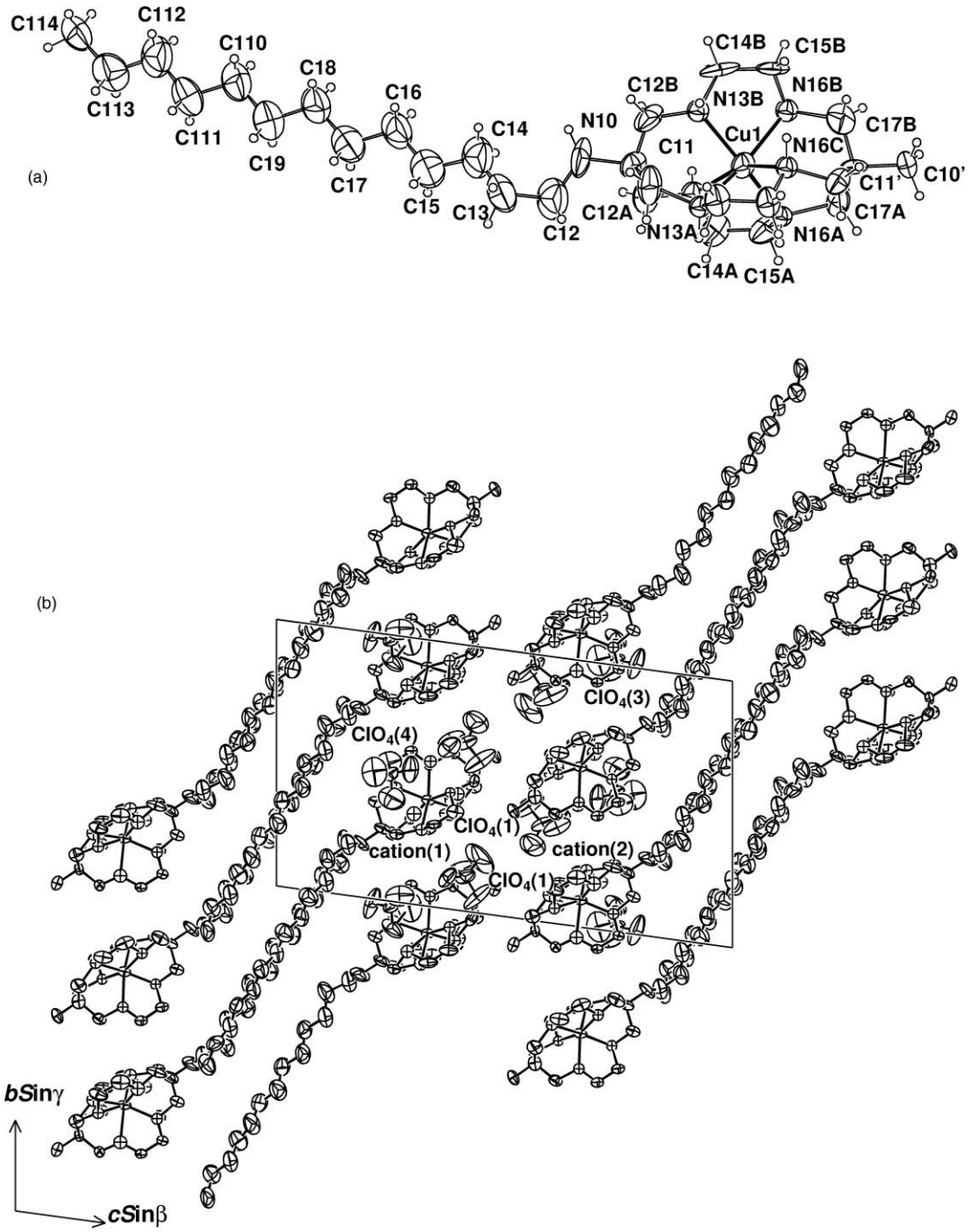


Fig. 4 (a) Projection of the cation of **CuL4**. Only one component of the disordered atoms is shown in this figure and in Fig. 4(b). (b) Unit cell of **CuL4** projected down the *a* axis. H-atoms omitted for clarity.

Compound **CuL4** crystallised from a dilute solution in water as the di-perchlorate and the coordination geometry about the Cu(II) ion is irregular and distorted, reflecting Jahn–Teller distortion consistent with other known Cu(II) cage complexes (Fig. 4a).[32] It should be noted that the model for this structural determination can be considered poor, as a result of twinning, and conclusions reached should be considered tenuous. An emerging theme for alkylated cage species[17,18] is found by considering the structure as sheets of cations and anions separated by sheets of aliphatic tails when viewed down *a* (Fig. 4b), with an equal distribution of enantiomers throughout the sheets. The packing of the molecules in the crystal lattice of **CuL4**·$(ClO_4)_2$ is (head–head–tail–tail), with the tails adopting an essentially transoid arrangement, and serve to link adjacent polar sheets *via* interdigitation with their associated tails, which display some close contacts of (C···C *ca.* 3.9–4.0 Å) indicative of relatively weak dispersion interactions. The perchlorate anions are located in sheets above and below the planes defined by the copper atoms within any given sheet. Perchlorates located nearest the methyl capped end of the cage serve to link three nearest neighbour cages together *via* hydrogen

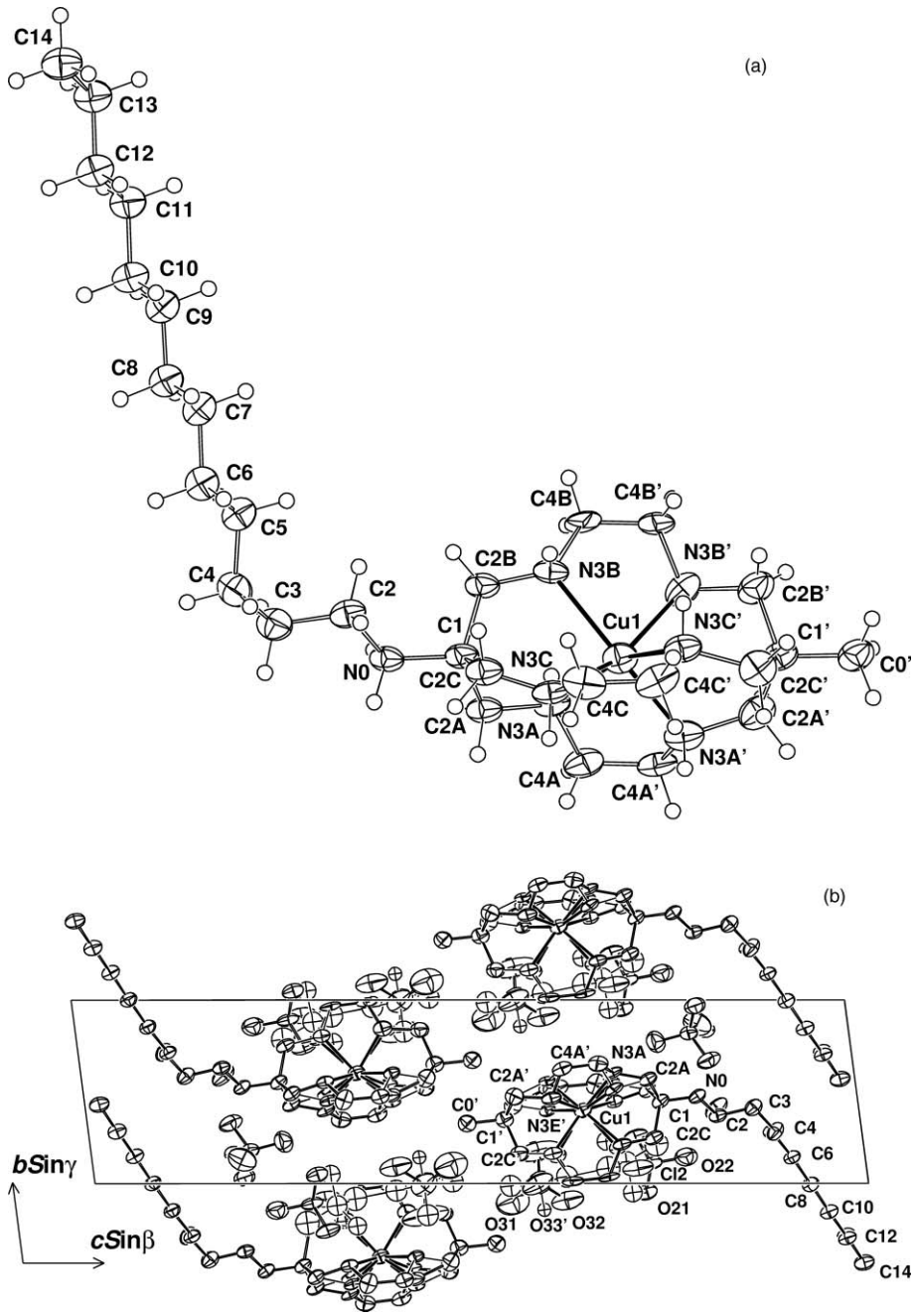


Fig. 5 (a) Projection of the cation of **Cu(HL4)**·$(ClO_4)_3$·$2H_2O$ showing one component of the disordered atoms only. (b) Unit cell contents of **Cu(HL4)**·$(ClO_4)_3$·$2H_2O$ projected down the *a* axis showing all disordered atoms. H-atoms omitted for clarity.

bonding with coordinated –NH-groups (O···NH *ca.* 3.0–3.4 Å). The other sheet of perchlorates links three nearest neighbour cages *via* close contacts with two coordinated –NH-groups (O···NH *ca.* 3.2–3.5 Å) and a relatively remote contact to the unprotonated apical –NH-group (O···NH *ca.* 3.6–3.9 Å). There are few close contacts between individual sheets of antiparallel cages, except for some relatively remote carbon–carbon contacts between the cage methyl group of one sheet and the cap methylenes of another (C···C *ca.* 3.9–4.0 Å). Protonation of the uncoordinated nitrogen is known to have a dramatic effect on the packing of the molecules in the lattice for the shorter chain complex **ZnL3**[18] by producing a polar crystal, and thus it was of interest to determine what effect it would have here. In the case of **CuL4**, protonation to give **Cu(HL4)**·$(ClO_4)_3$·$2H_2O$ (see Fig. 5) has a more subtle effect on the overall lattice, as the (head–head–tail–tail) arrangement of the cations is still present, but there is a significant bend of the tail away from the plane defined by the headgroup slabs, as seen for **ZnL3**. The tails do not appear to be involved in any significant interactions with one another, and thus the bend in the chain between C2 and C3 is again most probably a consequence

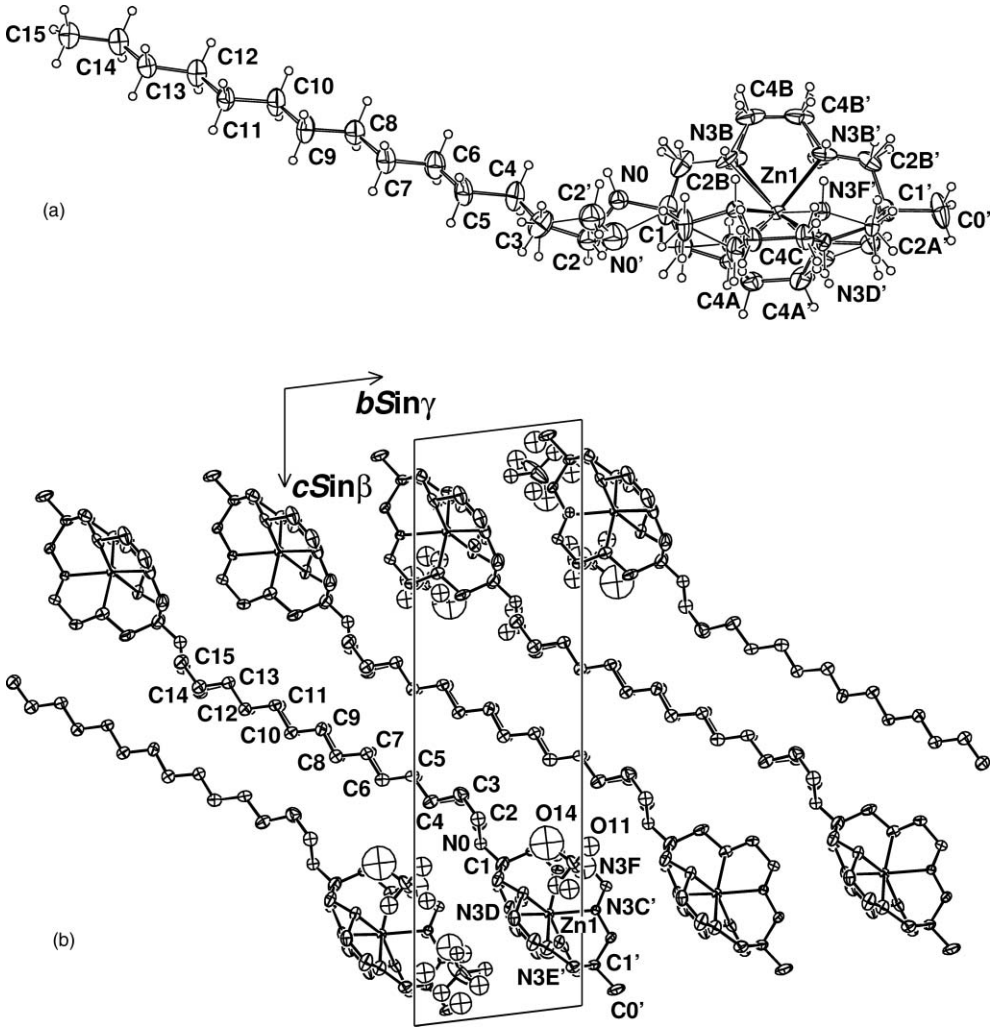


Fig. 6 (a) Projection of the cation of **ZnL5** showing both components of the disordered atoms. (b) Unit cell contents of **ZnL5** projected down the *a* axis. H-atoms omitted for clarity.

of the need to accommodate the extra anion within the headgroup region of the lattice, causing the cages to adopt a more nearly parallel arrangement.

The complex **ZnL5** (see Fig. 6) crystallised from water as the di-perchlorate and the coordination geometry about the Zn(II) ion is intermediate between octahedral and trigonal prismatic, with an average twist angle of 32°. The arrangement of the molecules in the lattice is similar to that observed in the case of **CuL4**, with the now familiar (head–head–tail–tail) arrangement of the cations to form polar sheets separated by apolar tails. The tails are almost fully *trans* extended, displaying very little close contact with other apolar units, except for a remote contact with cage methylene groups (C···C 4.0 Å), and the perchlorate anions serve to link the cage headgroups in a similar manner to that observed in the structure of **CuL4**, displaying close contacts (HN···O 3.2–3.5 Å).

Conclusions

Efficient methods have been developed that allow for the selective preparation of mono- and di-alkylated cage complexes by careful control over the reaction conditions, obviating the need for tedious and difficult separations. The preparation of mono-alkylated species is facilitated by the development of a high yielding synthesis of the free ligand **L1**, which will enable further exploitation of this useful ligand in future. Successful protection of the secondary amine centres has been achieved through coordination to a metal centre, with Mg(II) being preferred to Cu(II) due to the relative ease of monitoring the reaction progress and subsequent removal of the metal ion to give the desired free ligands. This method should be of tremendous utility in the preparation of functionalised free cage ligands, allowing for the facile exploitation of the numerous possible transition metal-sarcophagine complexes. This was demonstrated in the present case by the preparation of metal complexes (*i.e.* Co(III), Zn(II), Cu(II) and Ni(II)) of the new alkylated ligands in a simple and efficient manner.

The introduction of alkyl groups to the sarcophagines reduces the aqueous solubility of their complexes relative to their simple cage precursors, but only in the case of the complexes of the di-alkylated C_{14} ligand **L7** was solubility in water drastically reduced. The mono-alkylated species display typical surfactant behaviour (by forming stable aqueous foams), which is lost upon symmetrical 1,8-di-alkylation. Examination of the structures of the compounds

in the solid state indicate that both of the free ligands **L1** and **L7** display cage moieties poised for reception of a metal ion, and the packing of the cations in **L7**, **CuL4**, **CuHL4** and **ZnL5** exhibit a common theme whereby the polar and apolar moieties form alternating layers, reminiscent of a bilayer arrangement.

Experimental

Safety note

Perchlorate salts are potentially explosive. Although no problems were experienced with the compounds synthesised in this work, they should never be handled in large quantities, heated in the solid state, nor scraped from sintered glass frits.

General

Nuclear magnetic resonance (NMR) spectra were acquired using Bruker ARX 300 (^{1}H at 300 MHz and ^{13}C at 75.5 MHz), Bruker AV 500 (^{1}H at 500.13 MHz and ^{13}C at 125.8 MHz), or Bruker AV 600 (^{1}H at 600.13 MHz and ^{13}C at 150.9 MHz) instruments. All carbon spectra were proton decoupled. Chemical shifts for samples measured in D_2O are expressed in ppm relative to an internal standard of acetone which was taken as being 2.22 for ^{1}H NMR spectra and 30.89 for ^{13}C NMR spectra relative to TMS. Chemical shifts for samples measured in d_6-DMSO, $CDCl_3$ and d_3-MeCN were referenced to the residual solvent peak. Assignments were made with the aid of either the DEPT or HSQC techniques.

Mass spectra were recorded using the electrospray (positive ion trap) or fast-atom bombardment technique on a VG Autospec instrument or QSTAR XL-MS/MS.

Microanalyses for C, N, and H were carried out by The Australian National University Microanalytical Service. All samples were thoroughly dried under vacuum at 50 °C for at least 4 h prior to their analysis.

$[Co(CH_3)(NH_3)sar]Cl_4{\cdot}0.5H_2O$[23] (**CoL1**$\cdot Cl_4\cdot 0.5H_2O$) and $(NH_2)_2sar{\cdot}2H_2O$[22] (**L2**$\cdot 2H_2O$) were synthesised according to literature methods. Heptanal, octanal, decanal, tridecanal, $NaBH_3CN$, $NaBH_4$ (Aldrich), 10% Pd/C (Fluka), $Co(CH_3CO_2)_2{\cdot}4H_2O$, $Cu(CH_3CO_2)_2{\cdot}H_2O$, $CuCO_3.Cu(OH)_2$, $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ (Ajax), $CoCO_3{\cdot}xH_2O$, ZnO, MgO (BDH) were all used as received. Tetradecanal was synthesised from tetradecanol *via* pyridinium chlorochromate (PCC) oxidation.[33] "Absolute" EtOH and MeOH were stored over 3 Å molecular sieves prior to use in the following syntheses.

The synthesis and discussion of the complex **ZnL3** are given elsewhere.[18]

Synthesis

$[(CH_3)(NH_3)sarH_3]Cl_4{\cdot}2H_2O$ (L1·4HCl·2H$_2$O). Under argon, $[Co(CH_3)(NH_3)sar]Cl_4{\cdot}0.5H_2O$ (8.77 g, 17 mmol) was dissolved in deoxygenated water (*ca.* 75 mL) and an excess of Zn powder (5 g) was added to the orange solution. The solution colour rapidly changed to a dull green and the mixture was stirred for 2 h to complete reduction before being filtered *via* a cannula into a thick-walled 150 mL Schlenk flask fitted with a RotaFlo® tap. The solvent was removed under vacuum and replaced with deoxygenated, conc. HCl (*ca.* 75 mL), most of the dull green solid initially remaining insoluble. The tap to the flask was closed and the stirred mixture heated to 140 °C using a heater stirrer and an oil bath (**CAUTION**: This reaction must be conducted behind a suitable blast shield). The solution colour became deep blue within 1 h but heating was continued for 18 h to ensure equilibration. On cooling, the solution was exposed to the normal atmosphere, diluted to 1 L with water and passed through a column of Dowex 50W×2 cation exchange resin, this procedure allowing retention of the protonated ligand and a small amount of unreacted complex (now in its Co(III) form), with much of the released Co(II) passing through. Elution with 1 mol L^{-1} HCl (500 mL) removed any residual Co(II) and the column was then washed with water (500 mL) before the ligand was removed by elution with 0.2 mol L^{-1} NaOH (1 L). The ligand eluate was acidified with glacial acetic acid and reapplied to a column of H^+ form Dowex 50W×2 cation exchange resin, which was washed with water (500 mL) and then 1 mol L^{-1} HCl (500 mL) to remove Na^+, and finally with 5 mol L^{-1} HCl (1 L) to remove the ligand hydrochloride. This final eluate was taken to near-dryness under vacuum before ethanol was added to precipitate the crude product. Recrystallisation from hot 3 mol L^{-1} HCl by the addition of ethanol gave colourless, weakly hygroscopic crystals of $[(CH_3)(NH_3)sarH_3]Cl_4{\cdot}2H_2O$ (**L1**·4HCl·2H$_2$O) (5.80 g, 12 mmol, 71%). ^{1}H NMR (D_2O, 300 MHz): δ 1.0 (s, 3H, -CH_3), 3.1–3.5 (m, 24H, cage–CH_2-). ^{13}C NMR (D_2O, 75 MHz): δ 19.41 (-CH_3), 37.14 (C of methyl cage cap), 46.42, 48.32, 50.63, 54.12 (cage–CH_2-), 56.62 (C of amine cage cap). MS(ES) (*m*/*z*): 314.3 $[C_{15}H_{35}N_7 + H]^+$; 157.5 $[C_{15}H_{35}N_7 + 2H]^{2+}$. Anal. Calcd for $C_{15}H_{43}N_7Cl_4O_2$: C, 36.37; H, 8.75; N, 19.79. Found C, 36.67; H, 8.53; N, 19.70. Crystals suitable for an X-ray structure determination were grown by addition of EtOH to a hot 3 M HCl solution of the ligand followed by slow cooling. The structure solution was modelled as **L1**·4HCl·7/3H$_2$O.

$[Mg(CH_3)(NH_3)sar]Cl_3{\cdot}2.5H_2O$ (MgL1·Cl$_2$·HCl·2.5H$_2$O). MgO (0.08 g, 2.0 mmol) was added to a solution of $(CH_3)(NH_2)sar{\cdot}4HCl{\cdot}2H_2O$ (0.50 g, 1.0 mmol) in water (*ca.* 20 mL) and the mixture heated on a steam bath for 8 h, with periodic addition of water to maintain the volume of the solution. The mixture was then filtered, concentrated to a volume of *ca.* 5 mL on the rotary evaporator and cooled on ice as a few drops of 5 M HCl were added to the solution, followed quickly by the addition of EtOH to precipitate a white powder which was collected and washed with EtOH then Et_2O to give $[Mg(CH_3)(NH_3)sar]{\cdot}Cl_3{\cdot}2.5H_2O$ (**MgL1**$\cdot Cl_2\cdot HCl\cdot 2.5H_2O$) (0.38 g, 0.78 mmol, 78%). MS(FAB) (*m*/*z*): 372.0 $[MgC_{15}H_{35}N_7 + Cl]^+$; 336.0 $[MgC_{15}H_{35}N_7 - H]^+$. Anal. Calcd for $MgC_{15}H_{41}N_7Cl_3O_{2.5}$: C, 36.75; H, 8.43; N, 20.00. Found C, 37.05; H, 8.96; N, 19.93. NMR spectra of the complex in D_2O indicated a gradual demetallation of the ligand, thus a convenient method for obtaining NMR spectra was to convert the complex to its acetate salt by passing through a column of Dowex 1 × 8 anion exchange resin (acetate form) and evaporating to dryness. This material was also more useful for the subsequent reductive alkylation reactions in alcohol solvents.

$[Mg(CH_3)(NH_2)sar](CH_3CO_2)_2$ (MgL1·(CH$_3$CO$_2$)$_2$). ^{1}H NMR (D_2O, 600 MHz): δ 0.67 (s, 3H, cage–CH_3), 1.90 (s, 6H, 2(CH_3CO_2)), 2.30–3.20 (m, 24H, cage–CH_2-), 3.41 (m, 3H, cage–NH-), 3.60 (m, 3H, cage–NH-). ^{13}C NMR (D_2O, 150 MHz): δ 23.95 (CH_3CO_2), 23.96 (cage–CH_3), 35.71 (C of methyl cage

cap), 49.87, 50.09 (cage–CH_2-), 50.73 (C of amine cage cap), 58.44, 59.09 (cage–CH_2-), 182.07 (CH_3CO_2).

[Cu(CH_3)(NH_2)sar](ClO_4)$_2$·0.5$HClO_4$ (CuL1·(ClO_4)$_2$·0.5$HClO_4$). $CuCO_3$·Cu(OH)$_2$ (0.60 g, 2.7 mmol) was added to a solution of (CH_3)(NH_2)sar·4HCl·2H_2O (1.20 g, 2.28 mmol) in H_2O (*ca.* 10 mL), causing immediate effervescence and a deep blue colour to appear in the solution. The mixture was heated on a steam bath for 4 h, filtered and the solution was diluted to 500 mL with water and applied to a column of H^+ Dowex 50W×2 cation exchange resin. The column was washed with water (500 mL), 1 M HCl (500 mL) and the complex, now violet in colour, was eluted from the column with 3 M HCl. The solvent was removed from the rotary evaporator, leaving a green-brown solid, which persisted even after repeated evaporation of water. The green-brown solid was dissolved in water to give a light blue solution, which was slurried with *ca.* 5 g of Dowex 1×8 anion exchange resin (acetate form) for 15 min before being loaded onto a column of the same resin. Elution with water removed a deep blue solution, which was brought to dryness on the rotary evaporator. The blue solid was dissolved in EtOH (*ca.* 10 mL), filtered and cooled on ice before conc. $HClO_4$ (*ca.* 4 mL) was added dropwise until no further deposition of a blue solid was observed. The blue solid was collected, washed with cold EtOH and finally Et_2O to give [Cu(CH_3)(NH_2)sar](ClO_4)$_2$·0.5$HClO_4$ (**CuL1**·(ClO_4)$_2$·0.5$HClO_4$) (0.63 g, 1.0 mmol, 44%). MS(ES) (*m*/*z*): 475.17 [$CuC_{15}H_{35}N_7$ + ClO_4]$^+$. Anal. Calcd for $CuC_{15}H_{35.5}N_7Cl_{2.5}O_{10}$: C, 28.77; H, 5.71; N, 15.66. Found C, 28.47; H, 5.13; N, 15.40. The compound was converted to the acetate salt *via* passage through a column of Dowex 1×8 anion exchange resin (acetate form) and evaporating the solution to dryness.

[Mg(NH_2)$_2$sar](CH_3CO_2)$_2$·3.5H_2O (MgL2·(CH_3CO_2)$_2$·3.5H_2O). (NH_2)$_2$sar·2H_2O (L2) (0.50 g, 1.4 mmol) and Mg(CH_3CO_2)$_2$·4H_2O (0.32 g, 1.5 mmol) were dissolved in EtOH (*ca.* 10 mL) and the solution was gently heated for 30 min, with small portions of EtOH added periodically to maintain the volume of solution. Et_2O was added to the warm solution until the first traces of precipitate were observed, and the mixture cooled at –20 °C overnight. The white solid thus obtained was collected, washed with cold EtOH–Et_2O (50/50 v/v) and Et_2O to give [Mg(NH_2)$_2$sar](CH_3CO_2)$_2$·3.5H_2O (**MgL2**·(CH_3CO_2)$_2$·3.5H_2O) (0.49 g, 0.94 mmol, 67%). ^{1}H NMR (D_2O, 300 MHz): δ 1.91 (s, 6H, 2(CH_3CO_2)), 2.3–3.3 (m, 24H, cage–CH_2-), 3.62 (m, 6H, cage–NH-). ^{13}C NMR (D_2O, 75 MHz): δ 23.95 (CH_3CO_2), 49.97 (cage–CH_2-), 50.71 (cage C), 59.04 (cage–CH_2-). MS(ES) (*m*/*z*): 397.29 [$MgC_{14}H_{34}N_8$ + CH_3CO_2]$^+$. Anal. Calcd for $MgC_{18}H_{47}N_8O_{7.5}$: C, 41.58; H, 9.11; N, 21.55. Found C, 41.52; H, 8.72; N, 21.38.

[($C_{10}H_{21}NH_2$)(CH_3)sarH_4]Cl_5 (L3·5HCl). To a solution of [Mg(CH_3)(NH_2)sar](OAc)$_2$ (1.0 g, 2.2 mmol) in dry MeOH (20 mL) was added $NaBH_3CN$ (0.30 g, 4.8 mmol), causing some effervescence. After 10 min, decanal (1.4 g, 8.8 mmol) was added, causing more effervescence and the solution became noticeably warm. The mixture was stirred at RT for 1.5 h, before conc. HCl was added, causing vigorous effervescence and the precipitation of a white solid. The solvent was removed on a rotary evaporator, and the white solid obtained was extracted with n-hexane (3 × 100 mL), the organic extracts discarded, and the solid dissolved in 100 mL of MeOH/conc. HCl (50 : 50 v:v) and heated at reflux for 5 h. The solvent was then removed on a rotary evaporator and the solid residue dissolved in MeOH and applied to a column of H^+ Dowex 50W×2 cation exchange resin which was washed successively with MeOH, H_2O, 1M HCl, H_2O, MeOH (500 mL each) and the ligand was eluted with a mixture of conc. HCl/MeOH (50 : 50 v/v, 500 mL). The solvent was removed on a rotary evaporator giving an off-white tacky film. Crystallisation of the product was found to be hampered by the presence of water, so the product was repeatedly dissolved in MeOH and evaporated to dryness (5 times) and finally the product was crystallised by dissolving in hot MeOH, filtering and then allowing to cool to RT before being stored at –20 °C. The solid was collected under N_2 to give [($C_{10}H_{21}NH_2$)(CH_3)sarH_4]Cl_5 (**L3**·5HCl) (0.84 g, 1.3 mmol, 59%) as a semicrystalline white powder. ^{1}H NMR (D_2O, 600 MHz): δ 0.85 (t, 3H, -CH_3), 1.00 (s, 3H, cage–CH_3), 1.20–1.35 (m, 12H, 6(-CH_2-), 1.38 (apparent p, 2H, -CH_2-), 1.69 (apparent p, 2H, -CH_2-), 3.05–3.45 (m, 26H, (-CH_2–N + cage–CH_2-)). ^{13}C NMR (D_2O, 150 MHz): δ 14.04 (-CH_3), 19.36 (cage–CH_3), 22.66, 26.23, 26.69, 28.74, 29.03, 29.05, 29.20, 31.78 (-CH_2-), 37.00 (C of methyl cage cap), 43.20 (-CH_2–N), 46.66, 48.31, 49.35, 54.18 (cage -CH_2-), 60.98 (C of amino cage cap). MS(ES) (*m*/*z*) 454.29 [$C_{25}H_{55}N_7$ + H]$^+$; 227.59 [$C_{25}H_{55}N_7$ + 2H]$^{2+}$. Anal. Calcd for $C_{25}H_{60}N_7Cl_5$: C, 47.21; H, 9.51; N, 15.41. Found C, 46.64; H, 8.83; N, 15.41.

[Co($C_{10}H_{21}NH_2$)(CH_3)sar](ClO_4)$_4$·2H_2O (CoL3·(ClO_4)$_3$·$HClO_4$·2H_2O). Excess $CoCO_3$ (0.20 g, 1.7 mmol) was added to a solution of [($C_{10}H_{21}NH_2$)(CH_3)sarH_4]Cl_5 (0.40 g, 0.63 mmol) in water (*ca.* 10 mL) and heated on a steam bath for 8 h, whilst bubbling air through the mixture in order to oxidise the Co(II) to Co(III). The mixture was then filtered, and the filtrate passed through a column of Dowex 1×8 anion exchange resin (acetate form) using MeOH as the eluant. The solvent was then removed on the rotary evaporator, and the orange residue dissolved in *ca.* 5 mL of MeOH, and cooled on ice before the addition of conc. $HClO_4$, which produced a yellow-orange precipitate. The solid was filtered and washed with ice-cold water to give [Co($C_{10}H_{21}NH_2$)(CH_3)sar](ClO_4)$_4$·2H_2O (**CoL3**·(ClO_4)$_3$·$HClO_4$·2H_2O) (0.42 g, 0.44 mmol, 70%) as a yellow-orange solid. The sample was recrystallised from hot MeOH. ^{1}H NMR (CD_3CN, 500 MHz): δ 0.88 (t, 3H, -CH_3), 0.91 (s, 3H, cage–CH_3), 1.25–1.40 (m, 14H, 7(–CH_2-)), 1.64 (apparent p, 2H, -CH_2-), 2.4–3.6 (m, 26 H, (-CH_2–N + cage–CH_2-), 5.61 (b, 3H, cage–NH-), 5.80 (b, 3H, cage–NH-), 7.46 (b, 2H, -$^+NH_2$-). ^{13}C NMR (CD_3CN, 125 MHz): δ 14.38 (-CH_3), 20.10 (cage–CH_3), 23.36, 26.68, 26.84, 29.38, 29.94, 29.97, 30.12, 32.59 (tail–CH_2-), 43.13 (C of methyl cage cap), 45.11 (tail–CH_2–N), 51.44, 55.27, 55.34, 55.62 (cage–CH_2-), 62.39 (C of amine cage cap). MS(ES) (*m*/*z*): 510.3694 [$CoC_{25}H_{55}N_7$ – 2H]$^+$; 610.1562 [$CoC_{25}H_{55}N_7$ – H + ClO_4]$^+$; 255.6242 [$CoC_{25}H_{55}N_7$ – H]$^{2+}$. Anal. Calcd for $CoC_{25}H_{60}N_7Cl_4O_{18}$: C, 31.69; H, 6.38; N, 10.35. Found C, 31.31; H, 5.87; N, 10.11.

[Cu($C_{10}H_{21}NH_2$)(CH_3)sar](ClO_4)$_3$·H_2O (CuL3·(ClO_4)$_2$·$HClO_4$·H_2O). [Cu(CH_3)(NH_2)sar](CH_3CO_2)$_2$ (1.0 g, 2.0 mmol), decanal (0.48 g, 3.0 mmol), acetic acid (0.3 mL) and $NaBH_3CN$ (0.22 g, 3.5 mmol) were dissolved in EtOH containing molecular sieves (3 Å, *ca.* 2 g) and the mixture stirred at RT for 15 min. After this period, the mixture was decanted and conc. HCl added to the blue solution, causing vigorous effervescence. The solvent was removed on the rotary evaporator and the purple solid was suspended in

H_2O and extracted with $CHCl_3$ (4 × 100 mL), and the organic extracts discarded. The aqueous fraction was concentrated on the rotary evaporator, then the product was precipitated by the addition of a saturated aqueous solution of $NaClO_4$, which was collected and washed with ice-cold water. The solid thus obtained was recrystallised from acetone/n-hexane, collected and then washed with n-hexane to give $[Cu(C_{10}H_{21}NH_2)(CH_3)sar](ClO_4)_3{\cdot}H_2O$ (**CuL3**·$(ClO_4)_2{\cdot}HClO_4{\cdot}H_2O$) (1.06 g, 1.3 mmol, 65%) as a blue powder. MS(ES) (*m*/*z*): 616.1 $[CuC_{25}H_{55}N_7 + ClO_4]$; 299.2 $[CuC_{25}H_{55}N_7 + 2CH_3CN]^{2+}$. Anal. Calcd for $CuC_{25}H_{58}N_7Cl_3O_{13}$: C, 35.97; H, 7.00; N, 11.75. Found C, 35.98; H, 6.25; N, 11.66.

$[Cu(C_{13}H_{27}NH_2)(CH_3)sar](ClO_4)_3$ (CuL4·$(ClO_4)_2{\cdot}HClO_4$). $[Cu(CH_3)(NH_2)sar](CH_3CO_2)_2$ (0.70 g, 1.4 mmol), tridecanal (0.48 g, 2.4 mmol) and acetic acid (0.25 mL) were dissolved in EtOH (20 mL) at 55 °C. Molecular sieves were added (3 Å, *ca*. 1 g) and the mixture stirred for 10 min before $NaBH_3CN$ (0.16 g, 2.5 mmol) was added, producing some effervescence. The reaction was allowed to continue for 30 min, TLC on silica (NH_4Cl/MeOH) indicating the reaction was complete, at which time $NaBH_4$ was added, followed 10 min later by conc. HCl, causing vigorous effervescence and a purple colour to appear in solution. The mixture was filtered through Celite, and the filtrate brought to dryness on the rotary evaporator. The purple residue was suspended in MeOH, which was extracted with n-hexane (3 × 50 mL), and the n-hexane extracts discarded. The MeOH solution was again brought to dryness on the rotary evaporator and the residue dissolved in hot water, the solution filtered, and the product precipitated by the dropwise addition of a saturated aqueous solution of $NaClO_4$, *the solid* collected and washed with ice-cold water. Recrystallisation from hot MeCN by the addition of H_2O gave $[Cu(C_{13}H_{27}NH_2)(CH_3)sar](ClO_4)_3$ (**CuL4**·$(ClO_4)_2{\cdot}HClO_4$) (0.72 g, 0.84 mmol, 60%) as a blue opalescent solid. MS(ES) (*m*/*z*): 657.2 $[CuC_{28}H_{61}N_7 + ClO_4]^+$; 299.7 $[CuC_{28}H_{61}N_7 + CH_3CN]^{2+}$; 320.3 $[CuC_{28}H_{61}N_7 + 2CH_3CN]^{2+}$. Anal. Calcd for $CuC_{28}H_{62}N_7Cl_3O_{12}$: C, 39.16; H, 7.28; N, 11.42. Found C, 39.17; H, 7.34; N, 11.10. Crystals suitable for the X-ray work were grown using two methods. Method 1 involved the slow deposition of crystals from a hot dilute aqueous solution of the complex in a branched tube flask, the structure solution indicating a composition of **CuL4**·$(ClO_4)_2$. Method 2 was identical to Method 1 except for the addition of a few drops of conc. $HClO_4$ to the aqueous solution; in this case, the structure solution indicating a composition of **CuL4**·$(ClO_4)_2{\cdot}HClO_4{\cdot}2H_2O$ (*i.e.* **CuHL4**).

$[(C_{14}H_{29}NH_2)(CH_3)sarH_6]Cl_7$ (L5·7HCl). To a solution of $[Mg(NH_2)(CH_3)sar](OAc)_2$ (1.0 g, 2.2 mmol) in dry MeOH (20 mL) was added $NaBH_3CN$ (0.30 g, 4.8 mmol), causing some effervescence. After 10 min, tetradecanal (2.33 g, 11 mmol) in $CHCl_3$ (15 mL) was added to the solution, causing some effervescence and warming of the solution. The mixture was stirred for 12 h before conc. HCl (*ca*. 20 mL) was added, causing vigorous effervescence and the precipitation of a white solid. The mixture was brought to dryness on the rotary evaporator, and the white solid thus obtained was extracted with n-hexane (3 × 100 mL) before conc. HCl/MeOH (50 : 50 v/v, *ca*. 250 mL) was added and the mixture heated at 70 °C for 8 h, causing most of the initially insoluble white material to dissolve within *ca*. 1 h. The solvent was then removed on the rotary evaporator, and the white solid dissolved in MeOH and applied to a column of H^+ Dowex 50W×2 cation exchange resin. The column was washed successively with MeOH, H_2O, 1 M $HCl_{(aq)}$ and the ligand eluted with conc. HCl/MeOH (50 : 50 v/v, 1 L). The solvent was removed on the rotary evaporator, with regular addition of EtOH required in order to suppress the extensive formation of foam in the apparatus. The tacky clear solid obtained was then dissolved in dry MeOH and precipitated by pouring into a rapidly stirred flask of dry MeCN, giving a fine off-white powder which was collected under N_2 on a Schlenk line and washed with more dry MeCN before being dried under vacuum to give $[(C_{14}H_{29}NH_2)(CH_3)sarH_6]Cl_7$ (**L5**·7HCl) as an off white solid (0.90 g, 1.2 mmol, 55%). ^{1}H NMR (D_2O, 600 MHz): δ 0.74 (t, 3H, -CH_3), 0.89 (s, 3H, cage–CH_3), 1.10–1.24 (m, 20H, 10(-CH_2-)), 1.27 (apparent p, 2H, -CH_2-), 1.59 (apparent p, 2H, -CH_2-), 3.02 (m, 2H, -CH_2-), 3.04–3.31 (m, 24 H, cage–CH_2-). ^{13}C NMR (D_2O, 150 MHz): δ 14.19 (-CH_3), 19.35 (cage–CH_3), 22.82, 26.41, 26.78, 29.01, 29.29, 29.36, 29.50, 29.65, 32.01 (-CH_2-), 37.00 (C of methyl cage cap), 43.20 (-CH_2–N), 46.67, 48.32, 49.34, 54.17 (cage–CH_2-), 61.02 (C of amine cage cap). MS(FAB) (*m*/*z*): 510.53 $[C_{29}H_{63}N_7 + H]^+$. Anal. Calcd for $C_{29}H_{70}N_7Cl_7$: C, 45.53; H, 9.22; N, 12.82. Found C, 45.23; H, 9.10; N, 12.21.

$[Zn((C_{14}H_{29}NH_2)(CH_3)sar)](ClO_4)_3$ (ZnL5·$(ClO_4)_2{\cdot}HClO_4$). ZnO (0.16 g, 2.0 mmol) was added to a solution of $[(C_{14}H_{29}NH_2)(CH_3)sarH_6]Cl_7$ (0.40 g, 0.52 mmol) in water (*ca*. 20 mL) and the mixture heated on a steam bath for 8 h, during which time water was added periodically to maintain the volume of solution. The mixture was then filtered, and the filtrate passed through a column of Dowex 1×8 anion exchange resin (acetate form). The solution was concentrated on a rotary evaporator to a volume of *ca*. 20 mL before being cooled on ice, and acidified by dropwise addition of conc. $HClO_4$ (*ca.* 3 mL), producing a white precipitate immediately. The solid was filtered and washed with ice-cold water to give $[Zn(C_{14}H_{29}NH_2)(CH_3)sar](ClO_4)_3$ (**ZnL5**·$(ClO_4)_2{\cdot}HClO_4$) (0.42 g, 0.48 mmol, 92%) as a white powder. The sample was recrystallised from hot water, giving a white opalescent semi-crystalline solid. ^{1}H NMR (CD_3CN, 500 MHz): 0.64 (s, 3H, cage–CH_3), 0.88 (t, 3H, -CH_3), 1.20–1.40 (m, 22H, 11(-CH_2-)), 1.60 (apparent p, 2H, -CH_2-), 2.40–3.60 (m, 32H, (-CH_2–N + cage–NH- + cage–CH_2-)), 6.95 (br, 1H, -$^+$N(H)H-$(CH_2)_n$-), 7.05 (br, 1H, -$^+$N(H)H-$(CH_2)_n$-). ^{13}C NMR (CD_3CN, 125 MHz): 14.39 (-CH_3), 23.39 (-CH_2-), 24.31 (cage–CH_3), 26.84, 27.04, 29.51, 29.99, 30.07, 30.20, 30.33, 30.36, 30.38, 30.40, 32.64 (-CH_2-), 34.76 (C of methyl cage cap), 43.47, 49.36, 49.62, 53.48 (cage -CH_2-), 57.93 (C of amine cage cap), 59.05 (cage–CH_2-). MS(ES) (*m*/*z*): 672.38 $[ZnC_{29}H_{63}N_7 + ClO_4]^+$; 327.69 $[ZnC_{29}H_{63}N_7 + 2CH_3CN]^{2+}$; 307.10 $[ZnC_{29}H_{63}N_7 + CH_3CN]^{2+}$. Anal. Calcd for $ZnC_{29}H_{64}N_7Cl_3O_{12}$: C, 39.82; H, 7.38; N, 11.21. Found C, 39.82; H, 6.85; N, 10.75. Crystals suitable for the X-ray work were grown by slow cooling of a hot aqueous solution of the complex, indicating a composition of **ZnL5**·$(ClO_4)_2$.

$[Co((C_{14}H_{29}NH_2)(CH_3)sar)](ClO_4)_4{\cdot}H_2O$ (CoL5·$(ClO_4)_3{\cdot}HClO_4{\cdot}H_2O$). $CoCO_3$ (0.075 g, 0.63 mmol) was added to a solution of $[(C_{14}H_{29}NH_2)(CH_3)sarH_6]Cl_7$ (0.30 g, 0.39 mmol) in water (*ca*. 10 mL) and the mixture heated at 50 °C for 8 h whilst a stream of air was bubbled through the solution. The workup procedure was identical to that described above for **ZnL5** to give $[Co((C_{14}H_{29}NH_2)(CH_3)sar)](ClO_4)_4{\cdot}H_2O$

(**CoL5**·$(ClO_4)_3$·$HClO_4$·H_2O) (0.28 g, 0.28 mmol, 72%) as an orange waxy solid. The sample was recrystallised from hot water. ^{1}H NMR (CD_3CN, 600 MHz): δ 0.88 (t, 3H, -CH_3), 0.91 (s, 3H, cage–CH_3), 1.22–1.37 (br, 22 H, 11(-CH_2-)), 1.61 (apparent p, 2H, -CH_2-), 2.4–3.6 (m, 26 H, (-CH_2–N + cage–CH_2-)), 5.60 (br, 3H, cage–NH-), 5.77 (br, 3H, cage–NH-). ^{13}C NMR (CD_3CN, 150 MHz): δ 14.39 (-CH_3), 20.11 (cage–CH_3), 23.38, 26.80, 27.29, 29.48, 30.00, 30.06, 30.21, 30.33, 30.35, 30.38, 30.39, 32.63 (-CH_2-), 43.12 (C of methyl cage cap), 44.85 (-CH_2–N), 51.78, 55.32, 55.37, 55.65 (cage–CH_2-), 62.31 (C of amino cage cap). MS(ES) (*m*/*z*): 766.46 $[CoC_{29}H_{63}N_7 + 2ClO_4]^+$; 283.78 $[CoC_{29}H_{63}N_7 - H]^{2+}$; 304.29 $[CoC_{29}H_{63}N_7 - H + CH_3CN]^{2+}$; 324.79 $[CoC_{29}H_{63}N_7 - H + 2CH_3CN]^{2+}$; 666.49 $[CoC_{29}H_{63}N_7$–$H + ClO_4]^+$. Anal. Calcd for $CoC_{29}H_{66}N_7Cl_4O_{17}$: C, 35.34; H, 6.75; N, 9.95. Found C, 35.49; H, 6.93; N, 9.76.

[Cu($C_{14}H_{29}NH_2$)(CH_3)sar](ClO_4)$_3$·H_2O (CuL5·(ClO_4)$_2$·$HClO_4$·H_2O).

Method A. [Cu(CH_3)(NH_2)sar](OAc)$_2$ (1.0 g, 2.0 mmol), tetradecanal (0.66 g, 3.1 mmol), and acetic acid (0.3 mL) were dissolved in EtOH (50 mL) which contained molecular sieves (3 Å, *ca.* 2 g) and the mixture stirred at 60 °C. After 15 min, the reaction was quenched with HCl and the product isolated in an analogous manner to that described for compound **CuL4** to give [Cu($C_{14}H_{29}NH_2$)(CH_3)sar](ClO_4)$_3$·H_2O (**CuL5**·(ClO_4)$_2$·$HClO_4$·H_2O) (1.3 g, 1.5 mmol, 75%) as a blue opalescent solid.

Method B. $CuCO_3$·$Cu(OH)_2$ (0.05 g, 0.23 mmol) was added to a solution of [($C_{14}H_{29}NH_2$)(CH_3)sarH_6]Cl_7 (0.062 g, 0.081 mmol) in water (*ca.* 10 mL) causing immediate effervescence and a deep blue colour to appear in solution. The mixture was heated on the steam bath for *ca*. 4 h, and the workup procedure conducted as described for **ZnL5** to give [Cu($C_{14}H_{29}NH_2$)(CH_3)sar](ClO_4)$_3$·H_2O (**CuL5**·(ClO_4)$_2$·$HClO_4$·H_2O) (0.039 g, 0.044 mmol, 54%) as a waxy blue solid. The sample was recrystallised from hot water. MS(ES) (*m*/*z*): 671.45 $[CuC_{29}H_{63}N_7 + ClO_4]^+$; 306.77 $[CuC_{29}H_{63}N_7 + CH_3CN]^{2+}$; 327.29 $[CuC_{29}H_{63}N_7 + 2CH_3CN]^{2+}$. Anal. Calcd for $CuC_{29}H_{66}N_7Cl_3O_{13}$: C, 39.10; H, 7.47; N, 11.01. Found C, 39.29; H, 7.43; N, 10.75.

[Ni($C_{14}H_{29}NH_2$)(CH_3)sar](ClO_4)$_3$·H_2O (NiL5·(ClO_4)$_2$·$HClO_4$·H_2O). $NiCO_3$ (0.02 g, 0.2 mmol) was added to a solution of [($C_{14}H_{29}NH_2$)(CH_3)sarH_6]Cl_7 (0.066 g, 0.086 mmol) in water (*ca.* 10 mL), producing some effervescence. The mixture was heated on the steam bath for *ca*. 8 h, at which time the peach coloured solution was filtered and the workup procedure conducted as described for **ZnL5** to give [Ni($C_{14}H_{29}NH_2$)(CH_3)sar](ClO_4)$_3$·H_2O (**NiL5**·(ClO_4)$_2$·$HClO_4$·H_2O) (0.044 g, 0.050 mmol, 58%) as a pale pink waxy solid. The sample was recrystallised from hot water. MS(ES) (*m*/*z*): 666.47 $[NiC_{29}H_{63}N_7 + ClO_4]^+$; 304.28 $[NiC_{29}H_{63}N_7 + CH_3CN]^{2+}$; 324.79 $[NiC_{29}H_{63}N_7 + 2CH_3CN]^{2+}$. Anal. Calcd for $NiC_{29}H_{66}N_7Cl_3O_{13}$: C, 39.32; H, 7.51; N, 11.07. Found C, 39.52; H, 7.41; N, 10.83.

[($C_7H_{15}NH_2$)$_2$sarH_2](NO_3)$_4$ (L6·4HNO_3). [Mg(NH_2)$_2$sar](OAc)$_2$·3.5H_2O (MgL2) (2.0 g, 4.4 mmol) was dissolved in dry MeOH (30 mL) in a round bottomed flask, and to this was added $NaBH_3CN$ (1.1 g, 18 mmol) producing some effervescence. After 10 min, heptanal (4.0 g, 35 mmol) was added to the solution and the flask was stoppered and left to stand at RT for 24 h. Concentrated HCl was then added (*ca.* 20 mL) producing vigorous effervescence and a white precipitate, and the solvent was removed on a rotary evaporator. The white solid thus obtained was extracted with $CHCl_3$ (3 × 100 mL), the organic layers decanted and discarded, and the remaining solid dissolved in MeOH/conc. HCl (50 : 50 v/v), the solution heated at reflux for 5 h, then brought to dryness on the rotary evaporator. The white solid thus obtained was dissolved in MeOH and applied to a column of Dowex 50W×2 cation exchange resin, washed with H_2O, 1M HCl (500 mL each), and finally the ligand was eluted from the column with a mixture of conc. HCl/MeOH (50 : 50 v/v, 500 mL). The solvent from this fraction was removed on the rotary evaporator, the white solid thus obtained dissolved in MeOH, cooled on ice, and the ligand precipitated by the addition of 4M HNO_3(aq) and cooling in the freezer. The precipitate was collected by suction filtration to give [($C_7H_{15}NH_2$)$_2$sarH_2](NO_3)$_4$ (**L6**·4HNO_3) (2.2 g, 2.9 mmol, 66%) as a white solid. The sample was recrystallised from hot H_2O. ^{1}H NMR (d_6-DMSO, 300 MHz): δ 0.85 (t, 6H, 2(-CH_3)), 1.25 (m, 16 H, 8(-CH_2-)), 1.52 (m, 4H, 2(-CH_2-)), 2.85 (br s, 16 H, (2(-CH_2-) + (cage–CH_2-))), 3.15 (br s, 12H, (cage–CH_2-)), 5.5–7.5 (br, 6H, cage–NH-). ^{13}C NMR (d_6-DMSO, 75 MHz): δ 13.95 (-CH_3), 21.96, 25.96, 26.48, 28.14, 31.08, 41.11 (-CH_2-), 47.26, 51.42 (cage-CH_2-), 55.90 (cage C). MS(ES) (*m*/*z*): 511.52 $[C_{28}H_{62}N_8 + H]^+$; 256.26 $[C_{28}H_{62}N_8 + 2H]^{2+}$. Anal. Calcd for $C_{28}H_{66}N_{12}O_{12}$: C, 44.08; H, 8.72; N, 22.03. Found C, 44.00; H, 8.52; N, 21.86.

[Co($C_7H_{15}NH$)($C_7H_{15}NH_2$)sar](ClO_4)$_4$·3H_2O (CoL6·(ClO_4)$_3$·$HClO_4$·3H_2O). Co(CH_3CO_2)$_2$·4H_2O (0.40 g, 1.6 mmol) was added to a hot aqueous solution (*ca.* 20 mL) of [($C_7H_{15}NH_2$)$_2$sarH_2](NO_3)$_4$ (0.40 g, 0.53 mmol), producing a deep pink solution, which was heated on the steam bath for 5 h. Compressed air was periodically bubbled through the solution to ensure it was fully oxygenated, producing a deep orange solution within 1 h. After the heating step, the solution was slurried with Dowex 1×8 anion exchange resin (acetate form) for 30 min before the slurry was loaded onto a column of the same material, and the orange solution eluted with water. The solvent was removed on the rotary evaporator to give a pink-orange solid which was slurried in EtOH and cooled on ice. To this mixture was added conc. $HClO_4$, causing the precipitation of the complex, which was collected and washed with cold EtOH and Et_2O to give [Co($C_7H_{15}NH$)$_2$sar](ClO_4)$_4$·3H_2O (**CoL6**·(ClO_4)$_3$·$HClO_4$·3H_2O) (0.36 g, 0.35 mmol, 66%) as a waxy orange powder. The sample was recrystallised from warm MeCN by the addition of EtOH and allowed to cool to room temperature. ^{1}H NMR (CD_3CN, 300 MHz): δ 0.90 (t, 6H, 2(-CH_3)), 1.20–1.45 (m, 16H, 8(-CH_2-)), 1.62 (apparent p, 4H, 2(-CH_2-)), 2.85–3.15 (m, 28H, (2(-CH_2–N) + cage–CH_2-), 6.37 (br, 6H, cage–NH-). ^{13}C NMR (CD_3CN, 75 MHz): δ 14.32 (-CH_3), 23.19, 26.80, 27.33, 29.17, 32.18, 44.69 (-CH_2-), 51.11, 54.22 (cage -CH_2-), 62.15 (cage C). MS(ES) (*m*/*z*): 284.21 $[CoC_{28}H_{62}N_8 - H]^{2+}$; 767.34 $[CoC_{28}H_{62}N_8 + 2ClO_4]^+$. Anal. Calcd for $CoC_{28}H_{69}N_8Cl_4O_{19}$: C, 32.89; H, 6.80; N, 10.96. Found C, 32.46; H, 6.38; N, 10.90.

[Zn($C_7H_{15}NH_2$)$_2$sar](ClO_4)$_4$·2H_2O (ZnL6·(ClO_4)$_2$·2$HClO_4$·2H_2O). An excess of ZnO (0.14 g, 1.7 mmol) was added to a hot aqueous solution (*ca.* 10 mL) of [($C_7H_{15}NH_2$)$_2$sarH_2](NO_3)$_4$ (0.50 g, 0.66 mmol) and the mixture heated on the steam bath for

6 h. The mixture was then filtered, and the filtrate diluted with water (*ca.* 100 mL) and passed through a column of Dowex 1×8 anion exchange resin (acetate form) using water as the eluant. The solution was brought to dryness on a rotary evaporator, and the white residue was dissolved in EtOH, which was cooled on ice before the addition of a saturated aqueous solution of $NaClO_4$ (*ca.* 5 mL) followed by dropwise addition of conc. $HClO_4$, producing a white precipitate immediately. Addition of $HClO_4$ was continued until no further precipitation was observed (*ca.* 1 mL), and the mixture was cooled at −20 °C before being filtered and washed with cold EtOH to give $[Zn(C_7H_{15}NH_2)_2sar](ClO_4)_4\cdot 2H_2O$ (**ZnL6**·$(ClO_4)_2\cdot 2HClO_4\cdot 2H_2O$) (0.60 g, 0.59 mmol, 89%) as a white opalescent solid. The sample was recrystallised from hot MeCN by the addition of EtOH and cooling at −20 °C. ^{1}H NMR (CD_3CN, 300 MHz): δ 0.89 (t, 6H, 2(-CH_3)), 1.20–1.40 (m, 16H, 8(-CH_2-)), 1.59 (apparent p, 4H, 2(-CH_2-)), 2.45–3.65 (m, 32H, (2(-CH_2–N) + cage–CH_2- + cage–NH-)). ^{13}C NMR (CD_3CN, 75 MHz): δ 14.30 (-CH_3), 23.18, 26.76, 26.97, 29.14, 32.14, 43.44 (-CH_2-), 49.21, 53.24 (cage -CH_2-), 57.59 (cage C). MS(ES) (*m*/*z*): 287.22 $[ZnC_{28}H_{62}N_8]^{2+}$; 673.38 $[ZnC_{28}H_{62}N_8 + ClO_4]^+$. Anal. Calcd for $ZnC_{28}H_{68}N_8Cl_4O_{18}$: C, 33.23; H, 6.77; N, 11.07. Found C, 33.37; H, 6.27; N, 10.77.

$[Ni(C_7H_{15}NH_2)_2sar](ClO_4)_4\cdot 2H_2O$ ($NiL6\cdot(ClO_4)_2\cdot 2HClO_4\cdot 2H_2O$). $NiCO_3$ (0.02 g, 0.17 mmol) was added to a solution of $[(C_7H_{15}NH_2)_2sarH_2](NO_3)_4$ (0.05 g, 0.07 mmol) in water (*ca.* 10 mL) and the mixture heated on the steam bath for 8 h giving a peach coloured solution. The mixture was filtered, and the filtrate passed through a column of Dowex 1×8 anion exchange resin (acetate form) using water as the eluant. The eluate was reduced to dryness on the rotary evaporator before the residue was dissolved in MeOH, the solution cooled on ice, and conc. $HClO_4$ added dropwise causing the immediate precipitation of a solid which was collected and washed with ice cold MeOH to give $[Ni(C_7H_{15}NH_2)_2sar](ClO_4)_4\cdot 2H_2O$ (**NiL6**·$(ClO_4)_2\cdot 2HClO_4\cdot 2H_2O$) (0.046 g, 0.046 mmol, 66%) as a waxy pink solid. The sample was recrystallised from hot water. MS(ES) (*m*/*z*): 667.40 $[NiC_{28}H_{62}N_8 + ClO_4]^+$; 284.22 $[NiC_{28}H_{62}N_8]^{2+}$. Anal. Calcd for $NiC_{28}H_{68}N_8Cl_4O_{18}$: C, 33.45; H, 6.82; N, 11.15. Found C, 33.31; H, 6.89; N, 10.92.

$[Cu(C_7H_{15}NH_2)_2sar](ClO_4)_4$ ($CuL6\cdot(ClO_4)_2\cdot 2HClO_4\cdot 6H_2O$). $CuCO_3\cdot Cu(OH)_2$ (0.03 g, 0.14 mmol) was added to a solution of $[(C_7H_{15}NH_2)_2sarH_2]\cdot(NO_3)_4$ (0.05 g, 0.07 mmol) in hot H_2O (*ca.* 5 mL) and the mixture heated on the steam bath for *ca.* 2 h, to give a deep blue solution. The workup procedure was identical to that described for **NiL6** to give $[Cu(C_7H_{15}NH_2)_2sar](ClO_4)_4\cdot 6H_2O$ (**CuL6**·$(ClO_4)_2\cdot 2HClO_4\cdot 6H_2O$) (0.042 g, 0.04 mmol, 57%) as a waxy blue solid. The sample was recrystallised from hot water. MS(ES) (*m*/*z*): 672.39 $[CuC_{28}H_{62}N_8 + ClO_4]^+$; 286.72 $[CuC_{28}H_{62}N_8]^{2+}$. Anal. Calcd for $CuC_{28}H_{76}N_8Cl_4O_{22}$: C, 31.07; H, 7.08; N, 10.35. Found C, 31.19; H, 6.58; N, 9.81.

$[(C_{14}H_{29}NH_2)_2sarH_2]Cl_4\cdot 2H_2O$ ($L7\cdot 4HCl\cdot 2H_2O$). [Mg-$(NH_2)_2sar](CH_3CO_2)_2\cdot 3.5H_2O$ (1.42 g, 3.1 mmol) was dissolved in dry MeOH (25 mL), and to this solution was added $NaBH_3CN$ (0.85 g, 13 mmol), causing some effervescence. After 10 min, tetradecanal (5.30 g, 25 mmol) was added to the solution, and $CHCl_3$ added to the mixture until all of the solid had dissolved (*ca.* 10 mL). This mixture was stirred for 15 h, after which time conc. HCl (*ca.* 10 mL) was added, causing vigorous effervescence. The solvents were removed on the rotary evaporator, the thick white slurry extracted with n-hexane (5 × 100 mL), and the organic extracts discarded. The white solid was then suspended in EtOH/conc. HCl (500 mL, 50 : 50 v/v) before being heated at reflux for 12 h, during which time most of the white solid dissolved. After this period, the solvent was removed on the rotary evaporator, and the white solid dissolved in MeOH and applied to a column of H^+ Dowex 50W×2 cation exchange resin. The column was washed with MeOH, H_2O, and 1 M HCl (500 mL each). Elution with MeOH or EtOH/conc. HCl (50 : 50 v/v) proved to elute the product very slowly from the column, owing to the low solubility of the ligand in this solvent mixture at RT, and thus the resin was placed into a large conical flask, and stirred in MeOH/conc. HCl (1 L, 50 : 50 v/v) heated to 50–60 °C on a heater-stirrer. After filtration, the solvent was removed on the rotary evaporator to give an off-white solid, which was recrystallised by dissolving in hot MeOH, filtering and allowing to cool to RT before being stored at −20 °C for a few hours to give $[(C_{14}H_{29}NH_2)_2sarH_2]Cl_4\cdot 2H_2O$ (**L7**·$4HCl\cdot 2H_2O$) (1.62 g, 1.8 mmol, 58%) as an off-white powder. ^{1}H NMR (CD_3OD, 600 MHz): δ 0.90 (t, 6H, 2(-CH_3)), 1.25–1.45 (m, 44H, 22(-CH_2-)), 1.70 (apparent p, 4H, 2(-CH_2-)), 3.06 (m, 4H, 2(-CH_2–N)), 3.13 (br s, 12 H, 6(cage–CH_2-)), 3.42 (br s, 4H, 6(cage–CH_2-)). ^{13}C NMR (CD_3OD, 150 MHz): δ 14.43 (-CH_3), 23.72, 27.57, 27.94, 30.19, 30.46, 30.50, 30.62, 30.73, 30.75, 30.76, 30.78, 33.06, 43.23 (-CH_2-), 48.78, 52.88 (cage–CH_2-), 57.93 (cage C). MS(FAB) (*m*/*z*): 707.21 $[C_{42}H_{90}N_8 + H]^+$. Anal. Calcd for $C_{42}H_{98}N_8Cl_4O_2$: C, 56.74; H, 11.11; N, 12.60. Found C, 56.59; H, 10.92; N, 12.28. Crystals suitable for the X-ray work were grown by slow evaporation of a MeOH solution of the ligand. The structure solution was modelled as $[(C_{14}H_{29}NH_2)_2sarH_2]Cl_4\cdot 2H_2O\cdot 2CH_3OH$.

$[Zn(C_{14}H_{29}NH_2)_2sar](ClO_4)_4\cdot 4H_2O$ ($ZnL7\cdot(ClO_4)_2\cdot 2HClO_4\cdot 4H_2O$). ZnO (0.06 g, 0.7 mmol) was added to a solution of $[(C_{14}H_{29}NH_2)_2sarH_2]Cl_4\cdot 2H_2O$ (0.30 g, 0.34 mmol) in MeOH (*ca.* 20 mL) and the mixture heated at reflux for 8 h causing a white precipitate to form. The mixture was diluted to *ca.* 200 mL by the addition of MeOH, filtered and the filtrate passed through a column of Dowex 1×8 anion exchange resin (acetate form), which was washed with further MeOH. The eluate was concentrated on the rotary evaporator to a volume of *ca.* 10 mL, cooled on ice and the complex precipitated by the addition of conc. $HClO_4$. The solid was filtered and washed with cold water to give $[Zn(C_{14}H_{29}NH_2)_2sar](ClO_4)_4\cdot 4H_2O$ (**ZnL7**·$(ClO_4)_2\cdot 2HClO_4\cdot 4H_2O$) (0.39 g, 0.31 mmol, 91%) as a white opalescent waxy solid. The sample was recrystallised from MeCN by the addition of MeOH and cooling on ice. ^{1}H NMR (CD_3CN, 500 MHz): δ 0.88 (t, 6H, 2(-CH_3)), 1.20–1.40 (m, 44H, 22(-CH_2-)), 1.60 (apparent p, 4H, 2(-CH_2-)), 2.55–3.60 (m, 30H, (cage–CH_2- + cage–NH-)), 2.89 (m, 2H, 2(-C(H)H–N)), 3.09 (m, 2H, 2(-C(H)H–N)). ^{13}C NMR (CD_3CN, 125 MHz): δ 14.39 (-CH_3), 23.39, 26.84, 27.00, 29.50, 29.99, 30.07, 30.21, 30.33, 30.36, 30.38, 30.40, 32.64 (-CH_2-), 43.54 (-CH_2–N), 49.26, 53.27 (cage–CH_2-), 57.73 (C). MS(ES) (*m*/*z*): 405.7825 $[ZnC_{42}H_{90}N_8 + CH_3CN]^{2+}$; 385.3299 $[ZnC_{42}H_{90}N_8]^{2+}$. Anal. Calcd for $ZnC_{42}H_{100}N_8Cl_4O_{20}$: C, 40.54; H, 8.10; N, 9.00. Found C, 40.67; H, 7.69; N, 8.76.

Table 1 Selected X-ray data collection and refinement data for the ligands and complexes

	L1·4HCl·7/3H_2O	**L7**· 4HCl·2H_2O·2CH_3OH	**CuL4**·$(ClO_4)_2$	**Cu(HL4)**·$(ClO_4)_2$·$HClO_4$·2H_2O	**ZnL5**·$(ClO_4)_2$
Empirical formula	$C_{15}H_{43.67}Cl_4N_7O_{2.33}$	$C_{44}H_{106}Cl_4N_8O_4$	$C_{28}H_{61}Cl_2CuN_7O_8$	$C_{28}H_{66}Cl_3CuN_7O_{14}$	$C_{29}H_{63}Cl_2N_7O_8Zn$
Formula weight	501.37	953.17	758.28	894.77	774.13
T/K	150(2)	100(2)	100(2)	100(2)	110(2)
Wavelength/Å	0.71073	0.71073	1.54178	0.76600	0.49594
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	20.116(5)	9.3572(3)	8.803(3)	8.5910(10)	8.7770(10)
b/Å	16.196(4)	14.2614(5)	17.759(4)	8.6340(10)	8.8680(10)
c/Å	45.918(11)	42.0780(10)	27.012(10)	31.316(5)	27.515(3)
α (°)	90	90	91.86(2)	95.803(10)	93.830(3)
β (°)	99.887(3)°	96.001(3)	99.60(2)	91.411(10)	94.964(3)
γ (°)	90	90	119.65(2)	119.620(10)	117.163(3)
V/Å^3	14738(6)	5584.4(3)	3586(2)	2001.5(5)	1884.6(4)
Z	24	4	4	2	2
ρ_c/g cm^{-3}	1.356	1.134	1.405	1.485	1.364
μ/mm^{-1}	0.509	0.256	2.694	0.816	0.848
F(000)	6464	2104	1620	950	828
Crystal size/mm	0.28 × 0.27 × 0.17	0.19 × 0.17 × 0.03	0.28 × 0.16 × 0.13	0.25 × 0.10 × 0.08	0.11 × 0.09 × 0.06
θ range (°)	0.90–25.87	2.49–25.00	2.89–66.04	2.12–27.50	4.06–17.18
Resolution d_{max} (Å)	0.81	0.84	0.84	0.83	0.84
Reflections collected	93467	47180	38793	29344	28352
Ind. reflections [R_{int}]	25982 [0.049]	9783 [0.149]	12163 [0.043]	6666 [0.084]	6365 [0.043]
Abs. correction	Multi-scan	Multi-scan	Multi-scan	Sphere	None
Max./min. *trans.*	1.00/0.84	0.99/0.83	0.70/0.40	0.95/0.92	—
Data/restr./paramet.	25982/18/1636	9783/8/564	12163/488/788	6666/20/569	6365/225/467
GOF on F^2	1.120	0.896	1.892	1.043	1.047
R_1, wR_2 [$I > 2\sigma(I)$]	0.0847, 0.2005	0.0747, 0.1389	0.1840, 0.3883	0.0908, 0.2458	0.1170, 0.3430
R_1, wR_2 (all data)	0.1129, 0.2125	0.1965, 0.1618	0.2142, 0.4259	0.0917, 0.2467	0.1278, 0.3452
Largest diff. peak and hole e Å^{-3}	1.602, –1.054	1.047, –0.484	2.864, –0.613	1.175, –0.855	2.037, –1.431

[Co($C_{14}H_{29}NH)_2$sar]Cl_3·2H_2O (CoL7·Cl_3·2H_2O). Co$(OAc)_2$·4H_2O (0.075 g, 0.30 mmol) was added to a solution of [$(C_{14}H_{29}NH_2)_2$sarH_2]Cl_4·2H_2O (0.20 g, 0.23 mmol) in MeOH (*ca.* 20 mL), causing a rapid colour change in solution to a deep orange-brown colour. The solution was heated at 50 °C for 5 h whilst air was gently bubbled through the solution continuously. After this time, the solution was allowed to cool to RT before the flask was placed in an ice bath as an orange precipitate began to form. The solid was collected on a sintered glass frit and washed with ice cold MeOH and water. The sample was dissolved in hot MeOH, filtered and recrystallised by cooling to RT and finally in an ice bath, then filtered and washed with ice cold MeOH and dried under vacuum to give [Co($C_{14}H_{29}NH)_2$sar]Cl_3·2H_2O (**CoL7**·Cl_3·2H_2O) (0.11 g, 0.12 mmol, 52%) as an orange semi-crystalline solid. ^{1}H NMR (d_6-DMSO, 600 MHz): δ 0.85 (t, 6H, 2(-CH_3)), 1.18–1.30 (br, 48H, 24(-CH_2-)), 1.87 (m, 2H, 2(-NH-)), 2.30–3.05 (m, 26 H, (2(-CH_2–N) + cage–CH_2-)), 8.18 (br, 6H, cage–NH-). ^{13}C NMR (d_6-DMSO, 150 MHz): δ 13.95 (-CH_3), 22.08, 26.63, 28.69, 28.92, 29.00, 29.01, 29.04, 29.05, 29.06, 30.48, 31.28 (-CH_2-), 40.99 (-CH_2–N), 52.13, 54.32 (cage–CH_2-), 60.76 (C). MS(ES) (m/z): 799.69 [$CoC_{42}H_{90}N_8$–H + Cl]$^+$. Anal. Calcd for $CoC_{42}H_{94}N_8Cl_3O_2$: C, 55.52; H, 10.43; N, 12.33. Found C, 55.89; H, 10.20; N, 12.16.

Crystal structural determinations

Crystallographic data for **ZnL5** and **L7** were collected on Bruker Smart and Oxford Diffraction Xcalibur diffractometers respectively with graphite-monochromated Mo-Kα radiation. Data for **CuL4** were collected on an Oxford Diffraction Gemini diffractometer with Cu-Kα radiation. Data for **Cu(HL4)** and **ZnL5** were collected on synchrotrons. The structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.[34] Except where stated, anisotropic displacement factors were employed throughout for the non-hydrogen atoms with H atoms added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on that of the parent atom. Pertinent details are given in Table 1 and Fig. 1–5 where the ellipsoids are drawn at the 30% probability level for **CuL4** and **ZnCl5** and at the 50% level for the remainder. For **L1**, assignments of the NH_3 and NH_2 groups were made on the basis of refinement and H-bonding considerations. The O atoms of the perchlorate anions were modeled as being disordered over two sets of sites with occupancy factors set to 0.5 (for ClO_4(1)) after trial refinement and 0.816(5) and its complement for ClO_4(2). For **L7**, the solvent was modeled as two water molecules and two MeOH molecules. One MeOH was disordered over two sites with occupancy factors refined to 0.692(7) and its complement. H atoms for one H_2O and for the MeOH molecules were not included. For **CuL4**, the geometries of the C atoms of the $C_{13}H_{28}N$ chains and of the perchlorate anions were restrained to ideal values. For **CuL4**, **Cu(HL4)** and **ZnL5**, the coordinating N atoms were modeled as being disordered over two sets of sites with occupancy factors set at 0.5 with these being refined with isotropic displacement parameters only for **CuL4**. For **Cu(HL4)**, the O atoms of the perchlorate anions (2) and (3) were modeled as being disordered over two sets of sites with occupancy factors of 0.878(5) and its complement and with geometries restrained to ideal values. For

ZnL5 the O atoms of both perchlorate anions were modeled as being disordered over two sets of sites with occupancy factors set to 0.5 after trial refinement. Geometries were again restrained to ideal values.

Acknowledgements

GLN was the holder of an Australian Postgraduate Award. Data for **Cu(HL4)** were collected on the PX1 beamline at the Australian Synchrotron, Victoria, Australia. The views expressed herein are those of the authors and are not necessarily those of the owner or operator of the Australian Synchrotron. Use of the ChemMatCARS Sector 15 at the Advanced Photon Source, for **ZnL5**, was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. ChemMatCARS Sector 15 is also supported by the National Science Foundation/Department of Energy under grant numbers CHE9522232 and CHE0087817 and by the Illinois board of higher education. The Advanced Photon Source is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

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