

# Copper(II) environments in some macrobicycle complexes at room and low temperatures: some novel binuclear chloro-bridged systems

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**Abstract** Single crystal X-ray studies are recorded for five copper(II) complexes of macrobicyclic ligands. In both [Cu(sar)][ZnCl<sub>4</sub>] (295, 170 K) determinations ('sar' = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) and [Cu(NH<sub>3</sub>)<sub>2</sub>sar]Cl<sub>4</sub>·6H<sub>2</sub>O (295 K), the ligand encapsulates the copper atom by coordinating through all six nitrogen atoms, though distortions of the primary coordination sphere from an octahedral array are both marked and quite different in the two cases. [Cu(sar)]<sup>2+</sup> undergoes a relatively facile detachment of one ligand strand in acid solution, giving a species with a different bound-N configuration to that of the

reactant and which may be crystallised in various forms. In the solid of composition Cu(ClO<sub>4</sub>)<sub>2</sub>·2HClO<sub>4</sub>·½HCl·H<sub>2</sub>O·sar (295 K) the complex present is binuclear '[Cu(sarH)CuClCu(sarH<sub>2</sub>)](ClO<sub>4</sub>)<sub>6</sub>·2H<sub>2</sub>O', with the linear CuClCu array comprising the apical bonds of a pair of square-pyramidal ClCuN<sub>4</sub> components. In mononuclear [Cu(sarH<sub>2</sub>)(O-NO<sub>2</sub>)](NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (295 K) two of the ligand strings coordinate in a quasi-square-planar array, with an approach of an anionic oxygen atom to one of the remaining opposed axial coordination sites. In the crystalline complex formed between copper(II) triflate (Cu(tfs)<sub>2</sub>; 'tfs' = F<sub>3</sub>CSO<sub>3</sub><sup>-</sup>) and the expanded macrobicycle Me<sub>5</sub>tricosaneN<sub>6</sub> (Me<sub>5</sub>tricosaneN<sub>6</sub> ≡ *fac*-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane), the ligand, despite the lack of any protonation, is found (295, 150 K) to be bound in a quinquedentate form, with one triflate-O occupying the sixth coordination site about the metal, in the mononuclear complex [Cu(Me<sub>5</sub>tricosaneN<sub>6</sub>)(O-tfs)](tfs). This contrasts with the perchlorate counterpart wherein all nitrogen atoms are coordinated within an encapsulating cage.

Alan M. Sargeson—Deceased.

Dedicated to Professor Leonard Lindoy, a multidentate chemist, like his ligands, on the occasion of his 75th birthday.

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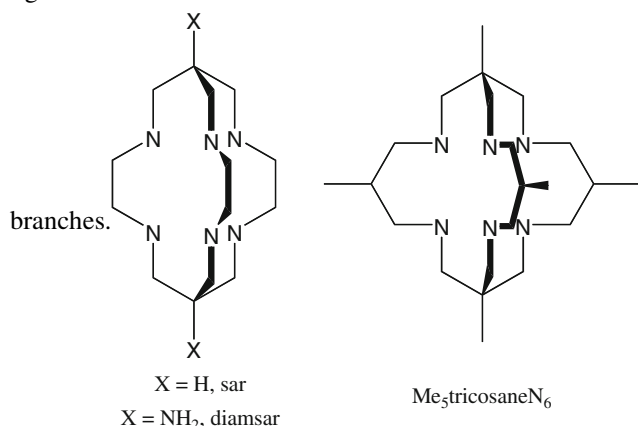
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## Introduction

Unless the metal atom is unusually small or large, complexes formed with the macrobicycle 'sar' (= 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane) and its derivatives [1–3], many of them being Cu(II) species of interest because of their physical properties [4–9], or the expanded 3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane (Me<sub>5</sub>tricosaneN<sub>6</sub>) ligands [10–13] (see below) usually satisfy tendencies toward the achievement of six-coordination,

encapsulating the metal atom in an  $N_6$  environment of  $D_3$ ,  $C_3$  or  $C_2$  symmetry, depending on the conformations of the ligand



Complexes of copper(II), by virtue of distortions contingent upon their  $d^9$  electron configurations, may be idiosyncratic in respect of the above [4–9, 14–17]. The metal atom environment may remain regular or distorted within the  $N_6$  cage of the ligand, or a branch of the ligand may detach with the remaining  $N_4$  donor component tending toward a (square-) planar array, either in itself or as the base of a square-pyramidal form. This may be in response to the effects of increased ligand complexity and competing interactions/forces contingent on that, or the presence of donors competitive with the more loosely bound N-donors, chloride in particular, either in isolation or as part of a more complex  $[MCl_4]^{n-}$  species.

The measured stability constants for metal ion complexes of macrobicyclic ligands of the sarcophagine (sar) type are high [18–20], indicating that metal ion release from the complex should be many orders of magnitude slower than complexation. Metal ion release can be observed in the presence of acid and/or coordinating anions and is in fact critical to the isolation of the free ligands after their formation in template reactions [21]. The extreme conditions required for the release of hexamine species, in particular, from Co(II) are not required in other cases and Mg(II) complexes, for example, provide relatively labile systems useful in the synthesis of cage amine derivatives [22]. Cages with at least some thiaether donor atoms are also rather readily removed from the metal [23]. Importantly, the cage ligands themselves are not prone to fragmentation which might facilitate metal ion dissociation and instances of such reactions are thus very few [24–26]. In the case of Cu(II) complexes of various cage hexamines, it is possible to observe an acid-catalysed partial unravelling of the ligand which is seemingly a consequence of a preference of the metal ion for four rather than six-coordination [27–29]. The nature of this process is of some interest, since the reactant has all N-atoms of the same chirality, whereas it would not be anticipated [30] that the

four coordinated N-atoms in a partially stripped product would retain this chirality and this is certainly not the case in such species as are obtained from carboxymethylamino cage derivatives [29]. An objective of the present work, therefore, was to establish the relative donor atom configurations of the Cu(II) complex(es) of the quadridentate form of sarcophagine itself, the complex  $[Cu(sar)]^{2+}$  being a species observed to rather readily change from a blue to a violet-red colour in acidic solution. Thus, attempts were made to crystallise the cations from solution at various stages of reaction, using various precipitating anions in the hope of isolating different species.

In the present contribution, we present the structural characterization of several adducts of copper(II) salts with sar, its 1,8-diamino derivative ‘diamsar’ (=  $(NH_2)_2sar$ ) and *fac*-Me<sub>5</sub>tricosane- $N_6$  (*facial*-1,5,9,13,20-pentamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricosane)—some at both room and low temperatures, which offer further interesting insights into factors controlling the structures of such systems as well as further characterising the coordination chemistry of these cage ligands.

## Experimental

### Synthesis

The syntheses of  $[Cu(sar)][ZnCl_4]$  and  $[Cu(diamsarH_2)]Cl_4 \cdot 6H_2O$  were based upon the literature procedures for the triflate [5] and nitrate [8], (see below, also) respectively, (see also [4]) with the minor variation of using  $CuCl_2$  as the reactant (with  $ZnCl_2$  also added after complexation in the first case). The complexes containing the sar macrobicycle in a quadridentate form were obtained by the addition of either  $HClO_4$  or  $HNO_3$  to solutions of  $[Cu(sar)][ZnCl_4]$  in dilute HCl after different periods of reaction.

$[Cu(sarH)][Co(CN)_6] \cdot 3H_2O$   $[Cu(sar)](CF_3SO_3)_2$  was dissolved in the minimal volume of 2 M  $HNO_3$  and immediately mixed with a saturated solution of  $K_3[Co(CN)_6]$ , which precipitated a purple microcrystalline powder. The powder was collected, washed with ethanol and diethyl-ether, and dried in the air. Anal. Calc. for  $[Cu(sarH)][Co(CN)_6] \cdot 3H_2O$ ,  $C_{20}H_{33}N_{12}CoCu \cdot 3H_2O$ : C, 38.87; H, 6.35; Co, 9.53; Cu, 10.20; N, 27.20. Found: C, 38.4; H, 6.1; Co, 9.8; Cu, 10.4; N, 27.1%.

$[Cu(sarH_2)](NO_3)_4 \cdot 4H_2O$   $[Cu(sar)]Cl_2 \cdot 4H_2O$  (100 mg) was dissolved in 1 M  $HNO_3$ , 4 M  $LiNO_3$  solution (2 ml). The solution immediately changed colour to purple followed by a gradual change to red over hours. After standing for at least 7 days at  $\sim 20^\circ C$  with slow evaporation of the solvent, dark red crystals formed. These were collected, washed with ethanol and diethylether, and dried

in air. Anal. Calc. for  $[\text{Cu}(\text{sarH}_2)](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{C}_{14}\text{H}_{32}\text{N}_{10}\text{O}_{12}\text{Cu} \cdot 4\text{H}_2\text{O}$ : C, 25.17; H, 6.03; N, 20.97. Found: C, 25.3; H, 6.4; N, 21.2%.

$[\text{Cu}(\text{sarH})]_2(\text{ClO}_4)_6 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$   $[\text{Cu}(\text{sar})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  (10 mg) was dissolved in 4 M  $\text{HNO}_3$  (5 ml). After 2 min, the resulting purple solution was pipetted carefully on top of a saturated  $\text{NaClO}_4$  solution. Within 30–60 min, purple crystals formed in the contact area. These were collected and dried on filter paper. Washing with ethanol or leaving the crystals in the air changed the colour of the crystals from purple to blue. Anal. Calc. for  $[\text{Cu}(\text{sarH})]_2(\text{ClO}_4)_6 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{C}_{28}\text{H}_{67}\text{N}_{17}\text{Cl}_7\text{O}_{24}\text{Cu}_2 \cdot 2\text{H}_2\text{O}$ : C, 24.60; H, 5.23; N, 12.29. Found: C, 24.1; H, 5.2; N, 11.9%.

If  $[\text{Cu}(\text{sar})](\text{ClO}_4)_6$  (10 mg) was dissolved in 5 M  $\text{HClO}_4$  (3 ml) a purple then pink solution resulted but no crystals formed. However, addition of  $\text{NaCl}$  to the pink solution yielded purple crystals of  $[\text{Cu}(\text{sarH})]_2(\text{ClO}_4)_6 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ .

$[\text{Cu}(\text{Me}_5\text{tricosaneN}_6)](\text{F}_3\text{CSO}_3)_2$  was obtained by a procedure identical to that described for the perchlorate and tetrafluoroborate by the use of sodium triflate as precipitant.  $\text{Me}_5\text{tricosaneN}_6 \cdot 6\text{HCl} \cdot 2\text{H}_2\text{O}$  (206 mg; 0.32 mmol) was dissolved in 10 ml distilled water.  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (63 mg; 0.32 mmol) was also dissolved in 10 ml distilled water, and the resulting solution added to the solution of ligand. 0.5 ml concentrated ammonia solution was then added, and the solution stirred for 10 min, before being split into two equal portions. To one half an excess of solid sodium triflate was added, precipitating a dark blue solid. This was then purified by  $\text{CH}_2\text{Cl}_2/\text{THF}$  vapour diffusion, which yielded a blue crystalline material that was washed with THF and dried in air. Yield 11 mg. Anal. Calc. for  $[\text{Cu}(\text{Me}_5\text{tricosaneN}_6)](\text{F}_3\text{CSO}_3)_2$ ,  $\text{C}_{24}\text{H}_{48}\text{N}_6\text{O}_6\text{CuF}_6\text{S}_2$ : C, 38.01; H, 6.38; Cu, 8.38; N, 11.08. Found: C, 37.9; H, 6.7; Cu, 7.9; N, 10.8%.

#### Structure determinations

Unique data sets (single counter instrument ( $2\theta/\theta$  scan mode)) or full spheres (CCD instrument; ( $\omega$ -scans)) (both: monochromatic Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) were measured. For the CCD data,  $N_{(\text{total})}$  reflections were acquired, these merging to  $N$  unique after ‘empirical’/multiscan absorption correction ( $R_{\text{int}}$  cited). For the single counter instrument data, gaussian, analytical or spherical corrections were applied. In all determinations the full unique data sets were used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model (reflection weights:  $(\sigma^2(F_o^2) + (aP)^2 + (bP))^2$ ) $^{-1}$  ( $P = (F_o^2 + 2F_c^2)/3$ )).  $N_o$  reflections with  $I > 2\sigma(I)$  were considered ‘observed’. Neutral atom complex scattering factors were employed within the

SHELXL program [31]. Pertinent results are presented below and in the Tables and Figures, the latter showing non-hydrogen atoms with 20% (room-temperature) or 50% (low-temperature) probability amplitude displacement envelopes. Full.cif depositions (excluding structure factor amplitudes) reside with the Cambridge Crystallographic Data Centre, CCDC 689582–689586, 800991, 800992.

#### Crystal/refinement data

$[\text{Cu}(\text{sar})][\text{ZnCl}_4] \equiv \text{C}_{14}\text{H}_{32}\text{Cl}_4\text{CuN}_6\text{Zn}$ ,  $M = 555.2$ . Monoclinic, space group  $Cc$  ( $C_s^4$ , No. 9),  $Z = 4$ .

- (a)  $T$  ca. 295 K (single counter instrument).  $a = 10.012(5)$ ,  $b = 15.122(4)$ ,  $c = 14.516(8) \text{ \AA}$ ,  $\beta = 90.68(5)^\circ$ ,  $V = 2198 \text{ \AA}^3$ .  $D_c = 1.678 \text{ g cm}^{-3}$ .  $\mu_{\text{Mo}} = 2.6 \text{ mm}^{-1}$ ; specimen:  $= 0.24 \times 0.16 \times 0.12 \text{ mm}$ ;  $T_{\text{min/max}} = 0.87$ .  $2\theta_{\text{max}} = 50^\circ$ ;  $N = 1786$ ,  $N_o = 1750$ ;  $R1 = 0.044$ ,  $wR2 = 0.113$  ( $a = 0.095$ ),  $S = 1.00$ ;  $x_{\text{abs}} = 0.09(3)$ ;  $|\Delta\rho_{\text{max}}| = 0.93 \text{ e \AA}^{-3}$ .
- (b)  $T$  ca. 170 K (CCD instrument).  $a = 9.995(2)$ ,  $b = 15.099(2)$ ,  $c = 14.439(2) \text{ \AA}$ ,  $\beta = 90.822(2)^\circ$ ,  $V = 2179 \text{ \AA}^3$ .  $D_c = 1.692 \text{ g cm}^{-3}$ .  $\mu_{\text{Mo}} = 2.6 \text{ mm}^{-1}$ ; specimen:  $= 0.28 \times 0.27 \times 0.13 \text{ mm}$ ;  $T_{\text{min/max}} = 0.69$ .  $2\theta_{\text{max}} = 60^\circ$ ;  $N_t = 8776$ ,  $N = 2658$  ( $R_{\text{int}} = 0.045$ ),  $N_o = 2548$ ;  $R1 = 0.037$ ,  $wR2 = 0.092$  ( $a = 0.050$ ,  $b = 4.2$ ),  $S = 1.01$ ;  $x_{\text{abs}} = 0.16(2)$ .  $|\Delta\rho_{\text{max}}| = 1.11 \text{ e \AA}^{-3}$ .

$[\text{Cu}(\text{diamsarH}_2)]\text{Cl}_4 \cdot 6\text{H}_2\text{O} \equiv \text{C}_{14}\text{H}_{48}\text{Cl}_4\text{CuN}_8\text{O}_6$ ,  $M = 629.9$ .  $T$  ca. 295 K (single counter instrument). Monoclinic, space group  $C2/c$  ( $C_{2h}^6$ , No. 15),  $a = 15.19(2)$ ,  $b = 10.99(2)$ ,  $c = 18.50(2) \text{ \AA}$ ,  $\beta = 113.44(10)^\circ$ ,  $V = 2833$ .  $D_c$  ( $Z = 4$ ) =  $1.477 \text{ g cm}^{-3}$ .  $\mu_{\text{Mo}} = 1.19 \text{ mm}^{-1}$ ; specimen:  $0.40 \times 0.35 \times 0.35 \text{ mm}$ ;  $T_{\text{min/max}} = 0.96$ .  $2\theta_{\text{max}} = 50^\circ$ ;  $N = 2507$ ,  $N_o = 1903$ ;  $R1 = 0.058$ ,  $wR2 = 0.163$  ( $a = 0.090$ ,  $b = 8.00$ );  $S = 1.00$ .  $|\Delta\rho_{\text{max}}| = 0.79 \text{ e \AA}^{-3}$ .

#### Variata

Two of the chloride counterions were modelled as disordered over pairs of sites in the vicinity of a pair of the water molecules, similarly disordered. Occupancies were set at 0.5 after trial refinement. Hydrogen atoms of most of the water molecules were not located.

$[(\text{sarH})\text{CuClCu}(\text{sarH}_2)](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O} \equiv \text{C}_{28}\text{H}_{71}\text{Cl}_7\text{Cu}_2\text{N}_{12}\text{O}_{26}$ ,  $M = 1367.2$ .  $T$  ca. 295 K (single counter instrument.) Orthorhombic, space group  $Cmca$  ( $D_{2h}^{18}$ , No. 64),  $a = 34.476(7)$ ,  $b = 16.350(4)$ ,  $c = 9.175(2) \text{ \AA}$ ,  $V = 5172 \text{ \AA}^3$ .  $D_c$  ( $Z = 4$ ) =  $1.756 \text{ g cm}^{-3}$ .  $\mu_{\text{Mo}} = 1.28 \text{ mm}^{-1}$ ; specimen:  $0.22 \times 0.18 \times 0.06 \text{ mm}$ ;  $T_{\text{min/max}} = 0.89$ .  $2\theta_{\text{max}} = 45^\circ$ ;  $N_t = 3125$ ,  $N = 1717$  ( $R_{\text{int}} = 0.073$ ),  $N_o = 910$ ;  $R1 =$

0.10,  $wR2 = 0.34$  ( $a = 0.20$ ,  $b = 52$ ),  $S = 1.01$ .  $|\Delta\rho_{\max}| = 1.01 \text{ e } \text{\AA}^{-3}$ .

#### Comment

Data were weak and limited in scope. The specimen was preserved and, with the acquisition of CCD instrumentation, the data were remeasured at low temperature, but with no improvement in precision. There is a suggestion of slight disorder, unresolvable, in the envelope of the perchlorate oxygen nearest the uncoordinated nitrogen atom, consistent with the partial protonation of the latter required by the stoichiometry.

$[Cu(sarH_2)(ONO_2)](NO_3)_3 \cdot 3H_2O \equiv C_{14}H_{40}CuN_{10}O_{15}$ ,  $M = 652.1$ .  $T$  ca. 295 K (single counter instrument). Triclinic, space group  $P\bar{1}$  ( $C_i^1$ , No. 2),  $a = 12.326(4)$ ,  $b = 11.022(4)$ ,  $c = 10.172(4)$  \AA,  $\alpha = 109.11(3)$ ,  $\beta = 95.30(3)$ ,  $\gamma = 91.05(3)^\circ$ ,  $V = 1298.4$ .  $D_c$  ( $Z = 2$ ) =  $1.66_8 \text{ g cm}^{-3}$ .  $\mu_{Mo} = 0.93 \text{ mm}^{-1}$ ; specimen:  $0.30 \times 0.10 \times 0.10 \text{ mm}$ ;  $T_{\min/\max} = 0.93$ .  $2\theta_{\max} = 50^\circ$ ;  $N = 4367$ ;  $N_o = 3351$ ;  $R1 = 0.051$ ,  $wR2 = 0.112$  ( $a = 0.040$ ),  $S = 1.00$ .  $|\Delta\rho_{\max}| = 0.70 \text{ e } \text{\AA}^{-3}$ .

$[Cu(Me_5\text{tricosane}N_6)](OSO_2CF_3)(F_3CSO_3) \equiv C_{24}H_{48}CuF_6N_6O_6S_2$ ,  $M = 758.3$ . Monoclinic, space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14 (variant)),  $Z = 4$ . Specimen:  $0.25 \times 0.08 \times 0.01 \text{ mm}$ .

- (a)  $T$  ca. 300 K (CCD instrument).  $a = 13.238(1)$ ,  $b = 14.555(1)$ ,  $c = 18.696(2)$  \AA,  $\beta = 105.582(1)^\circ$ ,  $V = 3470 \text{ \AA}^3$ .  $D_c = 1.45_2 \text{ g cm}^{-3}$ .  $\mu_{Mo} = 0.83 \text{ mm}^{-1}$ ;  $T_{\min/\max} = 0.80$ .  $2\theta_{\max} = 60^\circ$ ;  $N_t = 38727$ ,  $N = 8888$  ( $R_{\text{int}} = 0.005$ ),  $N_o = 3694$ ;  $R1 = 0.052$ ,  $wR2 = 0.123$  ( $a = 0.045$ ),  $S = 1.00$ .  $|\Delta\rho_{\max}| = 0.51 \text{ e } \text{\AA}^{-3}$ .
- (b)  $T$  ca. 153 K (CCD instrument).  $a = 13.129(2)$ ,  $b = 14.410(2)$ ,  $c = 18.422(3)$  \AA,  $\beta = 105.002(3)^\circ$ ,  $V = 3366 \text{ \AA}^3$ .  $D_c = 1.49_6 \text{ g cm}^{-3}$ .  $\mu_{Mo} = 0.85 \text{ mm}^{-1}$ ;  $T_{\min/\max} = 0.80$ .  $2\theta_{\max} = 60^\circ$ ;  $N_t = 23030$ ,  $N = 8622$  ( $R_{\text{int}} = 0.081$ ),  $N_o = 4930$ ;  $R1 = 0.050$ ,  $wR2 = 0.110$  ( $a = 0.045$ ),  $S = 1.00$ .  $|\Delta\rho_{\max}| = 0.69 \text{ e } \text{\AA}^{-3}$ .

## Results and discussion

Structurally characterized copper(II) complexes of macrobicyclic sar and simple substituted derivatives, i.e., with no further fused rings, are relatively few in number. Most are complexes of the 1,8-diamino derivative ('diansar'), the majority of these being further substituted by pendants at the amine groups [1, 29, 32–36], one example only being substituted elsewhere ( $\text{CH}_2\text{COOH}$  at a coordinated nitrogen atom [34]). In all of these, although Cu–N distances are

understandably diverse, nevertheless, the copper atom may be considered to be contained within the cage, with significant bonding interactions with all six nitrogen atoms. There are, however, two examples of Cu(II) complexes of N-methylated forms of the parent sar ligand where, perhaps at least partly because of steric consequences of the methyl substituents or nitrogen quaternization (the  $\text{Me}_7$  complex), one of the strands of the ligand is detached from coordination to the copper atom, so that the environment of the latter becomes quasi-square-planar and free to interact with associated anions (perchlorate) [7]. In a further example, with expanded 'propylene' rather than 'ethylene' bridges within the ligand (but with the central carbon atoms of the  $\text{C}_3$  strings methylated, as also are the 1,9-sites), the copper atom again lies  $N_6$ -coordinated within the  $\text{Me}_5$ -tricosane $N_6$  cage [37]. In all examples except one [34], where a minor component of anion disorder was modelled as chloride, the counterions are oxyanions; diverse protonations are represented, but in no case is that associated with the macrocycle nitrogen atoms. With the exception of a reference to some bond length data from a preliminary structural study [4], there is no literature referring to the structure of a Cu(II) complex of the unfunctionalised sar ligand. Thus, the present work not only establishes that Cu(II) is bound as an essentially octahedral, six-coordinate species by the neutral ligand but also that acid may be used to induce partial stripping of the ligand down to a quadridentate form, allowing, for example, the intrusion of chloride ion into the coordination sphere and the formation (in the solid state) of binuclear chloro-bridged systems. Bridging of Cu(II) centres bound to multidentate N-donor ligands by simple anions is a common observation [38, 39], although examples in which four nitrogen atoms at each copper atom are equivalent are few, restricted to complexes with the ligands 2,2'-bipyridyl ('bpy') [40, 41] and monoprotonated 1,3,5-triaminocyclohexane [42]. More extended arrays are found with 1,10-phenanthroline ('phen') [43] and the ligand 'cyclam' (1,4,8,11-tetra-azacyclotetradecane) is known to form both trinuclear [44] and polymeric [45] species, in which the coordination number of the metal is increased to six; in such circumstances, a chloride component of a complex  $[\text{MCl}_4]^{2-}$  ( $=\text{ClMCl}_3^{2-}$ ) form may function as the bridging entity [46, 47].

However, such is not the case in the structure of the present complex  $[\text{Cu}(\text{sar})][\text{ZnCl}_4]$ , determined at room and 'low' temperature, the two results being very similar. Here one formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the non-centrosymmetric but racemic structure, being ionic, with discrete cationic and anionic components. In the cation, the copper atom is encapsulated within the  $N_6$  coordination environment available from the 'sar' ligand, all nitrogen atoms within

the one cation being of the same chirality (all *S* for the  $\Lambda$ -, *R* the  $\Delta$ -form). As in other similar copper(II) cage complexes [8], the latter is quite unsymmetrical, being well removed from octahedral or even potential  $D_3$  symmetry, with Cu–N distances ranging over more than 0.4 Å, ‘equivalent bite’ angles of the ligand strings over  $\sim 6^\circ$ , and ‘*trans*’ angles over more than  $15^\circ$ ; indeed these angles may be regarded as having subsets of (1 + 2) members, the bite angle of the unique subset being the smallest ( $76.8(3)^\circ$ ) and associated with two of the three long Cu–N distances (Table 1, Fig. 1), which, in turn, are associated with the smaller pair of the (2 + 1) set of *trans* angles. Indeed, the three shortest Cu–N distances, all  $<2.11$  Å, are associated with one end of the cage, the three longest (all  $>2.21$  Å) with the other. One of the inter-string *cis* angles is outstandingly large ( $119.0(3)^\circ$ ), exceeding all others by more than ten degrees. Torsion angles in the ligand strings are similar and of the same sign, corresponding to a  $\Lambda(\delta\delta\delta)$  ( $lel_3$ ) conformation for the cation as set. The counterion, although ‘tetrahedral’, is appreciably distorted (Zn–Cl range ca. 0.035 Å, Cl–Zn–Cl  $8^\circ$ ), presumably in consequence of strong hydrogen-bonding interactions with neighbouring cations, in which all chlorine atoms and NH hydrogen atoms participate. Two of the interactions are of the ‘chelate’ type, a single chlorine atom being wedged between ‘upper’ and ‘lower’ hydrogen atoms from adjacent ligand strings, familiar in cases of complexes where the metal ion coordination sphere is close to octahedral, with NH pairs being relatively close, but uncommon in M(II) complexes where the coordination geometry is closer to trigonal prismatic [1]. Other chlorine atoms contribute to the formation of a three-dimensional array.

A similar coordination environment is found in  $[\text{Cu}(\text{NH}_3)_2\text{sar}]\text{Cl}_4 \cdot 6\text{H}_2\text{O}$  (Table 1, Fig. 2). Here, however, one-half of the formula unit comprises the asymmetric unit of the structure, the copper atom of the cation being disposed on a crystallographic 2-axis which also passes through the mid-point of the central C–C bond of one of the ligands (‘A’); the cation is again  $\Lambda(\delta\delta\delta)$  ( $lel_3$ ), with Cu–N spanning a similar range to the previous but the distribution of the core distortion descriptors is very different. The Cu–N distances may be classified as pairs of short (2.051(5)), intermediate (2.159(4)), and long (2.299(5) Å). The short pair again are *trans*, associated with the largest N–Cu–N angle, whereas the others are grouped as *cis* pairs, the largest angle ( $121.9(2)^\circ$ ) being associated with the intermediate pair of distances, and exceeding all other *cis* angles by more than ten degrees. One distance of each type is associated with each end of the cage. As in the case of the acetate salt of the Cu(II) complex of neutral  $(\text{NH}_2)_2\text{sar}$  [1], all bound NH hydrogen atoms are hydrogen-bonded to counterion or water

molecule oxygen atom components. Thus, it appears that 1,8-substitution on a sarcophagine cage can induce significant differences in the hydrogen-bonding capacity of M(II) complexes relative to that of complexes of the parent ligand. This may be, of course, because introduction of extra H-bonding centres in the substituents perturbs an array which is not localised on the complex but extends throughout the lattice.

A significant feature of the structures of the two complexes isolated from reaction mixtures involving  $[\text{Cu}(\text{sar})]^{2+}$  and acid after short periods sufficient for partial ligand stripping to have occurred [27, 28] is that the bound-N configurations in both correspond to that described as ‘cyclam *Trans-I*’ [48] or R,S,R,S. While an apparently monoprotonated species could be isolated very rapidly after dissolution of the complex in acid by precipitation with  $[\text{Co}(\text{CN})_6]^{3-}$ , unfortunately it was not obtained in a form suitable for a structure determination. Since in the reactant complex, all bound N-atoms are of one configuration, the presence of mixed configurations in the structurally characterised materials indicates that, despite the acid conditions [49], N-inversion occurs readily as part of the reaction [50]. This may be explained if there is an intramolecular exchange between the detached and one attached string of the macrobicycle. In the tetranitrate  $[\text{Cu}(\text{sarH}_2)(\text{ONO}_2)](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ , the consequences of protonation are clearcut with two strands of the ligand coordinating the metal atom about the base of a square-pyramidal array, the apical site being occupied by an anionic oxygen atom (Table 1, Fig. 3); the third ligand strand, being protonated, is uncoordinated and does not approach a sixth coordination site *trans* to the nitrate oxygen atom. The hydrogen atoms of the coordinated amine groups all lie to the one side of the coordination plane, away from the dissociated strand; the overall configurations of the four coordinated amines (‘cyclam *trans-I*’) are the same as are found in the structures of other partially coordinated N-methylated cage ligands [7, 8, 24]. The copper atom lies 0.533(8) Å out of the plane of the nitrate ion, and 0.168(2) Å out of the plane of the four coordinated nitrogen atoms; the N–Cu–N *trans* angles of the latter are  $169.0(1)$ ,  $171.5(1)^\circ$ , with Cu–N distances closely ranged. The central N–C–C–N torsion of the uncoordinated ligand string (‘B’) is of opposite chirality to those of the coordinated strings. All water molecule hydrogen atoms interact with nitrate ion oxygen atoms; the complex cation  $\text{NH}_{(2)}$  hydrogen atom interactions are distributed between nitrate and water molecule oxygen atoms. All oxygen atoms except that coordinated to the copper atom are involved in the hydrogen-bonded array.

In the other sar complex, modelled as a protonated mixed chloride-perchlorate salt, and formulated ad hoc as

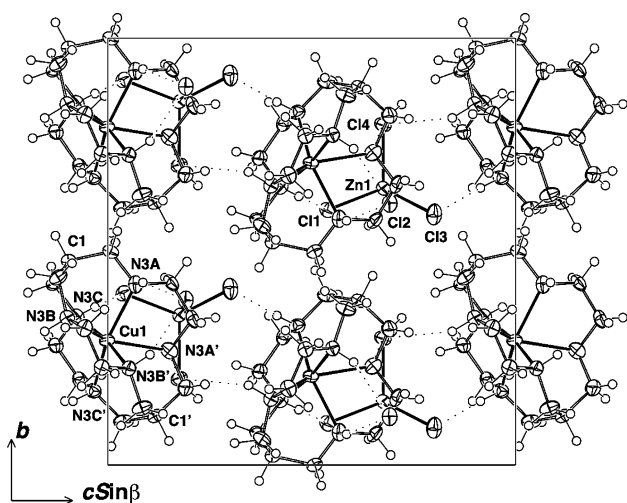
**Table 1** Copper atom environments in Cu(sar) species

	[Cu(sar)]ZnCl <sub>4</sub> <sup>a</sup>		[Cu(diamsarH <sub>2</sub> )Cl <sub>4</sub> ·6H <sub>2</sub> O] <sup>b</sup>		[Cu(sarH <sub>2</sub> )(ONO <sub>2</sub> )](NO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O		[Cu(Me <sub>5</sub> tricosaneN <sub>6</sub> )(O-tfs)](tfs) <sup>c</sup>		[Cu(sarH <sub>(1,2)</sub> ) <sub>2</sub> Cl](ClO <sub>4</sub> ) <sub>6</sub> ·2H <sub>2</sub> O	
	295 K	170 K	295 K	295 K	295 K	300 K	153 K	295 K	300 K	295 K
Distances (Å)										
Cu–N(3A)	2.211(8)	2.231(5)	2.299(5)	2.006(3)	2.012(2)	2.012(2)	2.017(2)	1.997(11)		
Cu–N(3A')	2.403(9)	2.422(6)	(2.299(5))	1.980(3)	2.031(2)	2.031(2)	2.033(2)	1.980(3)		
Cu–N(3B)	2.239(8)	2.238(5)	2.159(4)		2.036(2)	2.036(2)	2.042(2)	1.996(13)		
Cu–N(3B')	2.043(8)	2.035(5)	(2.159(4))		2.063(2)	2.063(2)	2.070(2)			
Cu–N(3C)	2.002(7)	2.003(5)	2.051(5)	1.979(3)	2.832(3)	2.832(3)	2.845(2)			
Cu–N(3C')	2.107(8)	2.093(5)	(2.051(5))	1.998(3)	2.586(3)(O)	2.586(3)(O)	2.534(2)(O)	2.470(2)(Cl)		
Cu–O/C(=X)				2.332(3)(O)						
Angles (°)										
N(3A)–Cu–N(3A')	76.8(3)	75.6(2)	76.4(2)	87.9(1)	96.33(10)	96.33(10)	96.29(9)	173.5(6)		
N(3A)–Cu–N(3B)	84.7(3)	84.9(2)	83.8(2)		88.19(9)	88.19(9)	88.10(9)	91.4(5)		
N(3A)–Cu–N(3B')	101.2(3)	100.8(2)	150.5(2)		165.33(10)	165.33(10)	166.07(9)	88.2(6)		
N(3A)–Cu–N(3C)	85.5(3)	85.3(2)	83.9(2)	91.4(1)	86.24(9)	86.24(9)	86.03(8)			
N(3A)–Cu–N(3C')	155.8(3)	154.1(2)	109.1(2)	171.5(1)						
N(3A')–Cu–N(3B)	154.0(3)	153.0(2)	(150.5(2))		164.35(10)	164.35(10)	163.60(9)			
N(3A')–Cu–N(3B')	83.8(3)	83.3(2)	(83.8(2))		90.69(9)	90.69(9)	90.83(9)			
N(3A')–Cu–N(3C)	105.5(3)	105.2(2)	(109.1(2))	169.0(1)	89.53(9)	89.53(9)	88.67(8)			
N(3A')–Cu–N(3C')	85.1(3)	84.4(2)	(83.9(4))	92.2(1)						
N(3B)–Cu–N(3B')	82.1(3)	82.3(2)	121.9(2)		88.46(19)	88.46(19)	88.40(9)	173.4(10)		
N(3B)–Cu–N(3C)	90.9(3)	91.3(2)	90.9(2)		75.78(9)	75.78(9)	75.84(8)			
N(3B)–Cu–N(3C')	117.2(3)	119.0(3)	82.2(2)		106.74(9)	106.74(9)	106.16(8)			
N(3B')–Cu–N(3C)	169.7(3)	170.7(2)	(82.2(2))							
N(3B')–Cu–N(3C')	92.5(3)	92.8(2)	(90.0(2))							
N(3C)–Cu–N(3C')	84.0(3)	84.4(2)	(163.8(2))	86.9(1)						
X–Cu–N(3A)				92.5(1)	81.94(9)	81.94(9)	82.07(8)	93.2(3)		
X–Cu–N(3A')				93.8(1)	85.45(10)	85.45(10)	84.18(8)			
X–Cu–N(3B)				97.1(1)(3C)	110.06(10)	110.06(10)	112.12(8)	93.3(5)		
X–Cu–N(3B')				95.9(1)(3C')	85.81(10)	85.81(10)	86.76(8)			
N–C–N/C torsion angles (°)										
String A	56.9(12)	56.3(7)	58.7(4)	–51.7(4)	–70.7(3), 67.5(4)	–70.7(3), 67.5(4)	–72.0(3), 68.7(3)	37(2)		
String B	55.6(11)	55.9(6)	56.7(4)	68.5(5)	–23.8(4), 72.5(4)	–23.8(4), 72.5(4)	–25.0(4), 74.4(3)	–37(2)		
String C	53.2(11)	53.8(6)	(56.7(4))	–50.8(4)	–54.0(4), –49.4(4)	–54.0(4), –49.4(4)	–54.8(3), –48.7(4)	–45(6)		

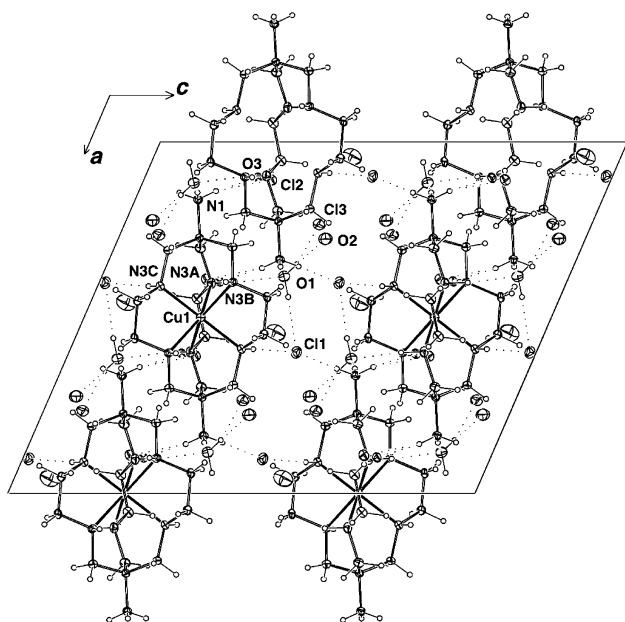
<sup>a</sup> In the anion, at room, low temperature, Zn–Cl are 2.236(3)–2.274(3), 2.247(2)–2.282(2) Å, Cl–Zn–Cl 105.25(12)–114.80(12), 105.16(6)–114.74(6)°

<sup>b</sup> The cation is located with the copper atom on a 2-axis; primed components are related by that axis; in the ligand strings, the central connectivities are N(3A)–C(4A)–C(4A')–N(3A'), N(3B)–C(4B)–C(4C')–N(3C') and image

<sup>c</sup> For N(3X') read N(7X)

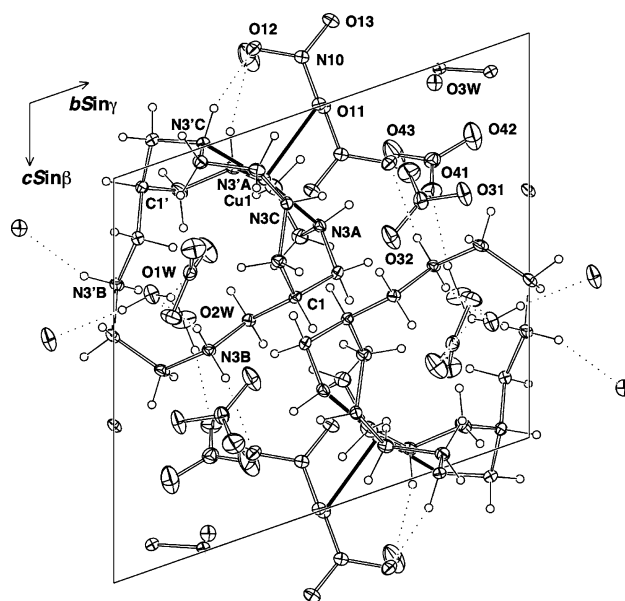


**Fig. 1** Unit cell contents of  $[\text{Cu}(\text{sar})][\text{ZnCl}_4]$ , (170 K), projected down  $a$



**Fig. 2** Unit cell contents of  $[\text{Cu}(\text{diamsarH}_2)]\text{Cl}_4 \cdot 6\text{H}_2\text{O}$ , projected down  $b$

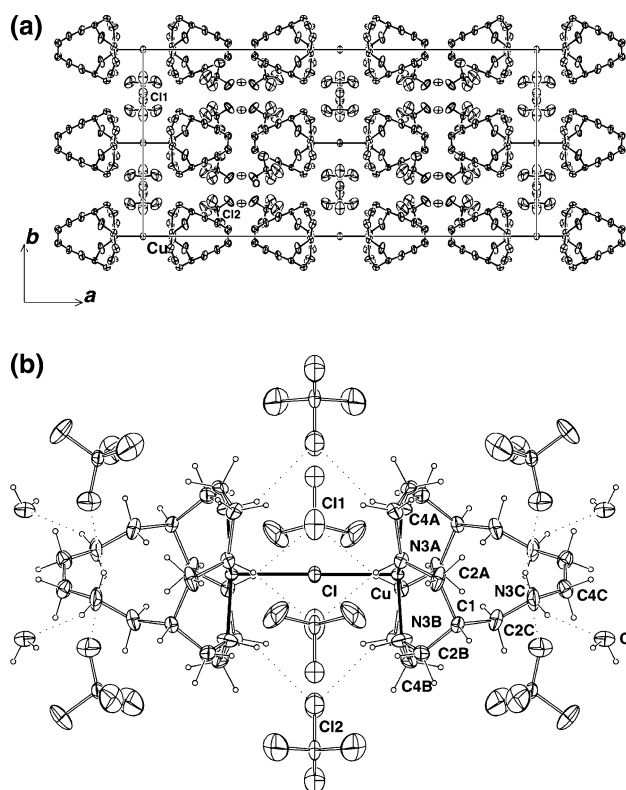
$[(\text{sarH})\text{CuClCu}(\text{sarH}_2)](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ , one-quarter of the formula unit comprises the asymmetric unit of the structure; this comprises one full anion and a half anion, the latter with the chlorine and two oxygen atoms disposed in a crystallographic mirror plane of space group  $Cmca$  (Table 1, Fig. 4). The complex cation is disposed with the central chlorine atom located on a site of  $2/m$  symmetry with the associated symmetry related pair of copper atoms lying on two-fold axes, as does a residue assigned as a water molecule oxygen atom; although protonic hydrogen atoms were not located in the refinement, it appears reasonable to assign those associated with the putative water



**Fig. 3** Unit cell contents of  $[\text{Cu}(\text{sarH}_2)(\text{ONO}_2)](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  projected down  $a$

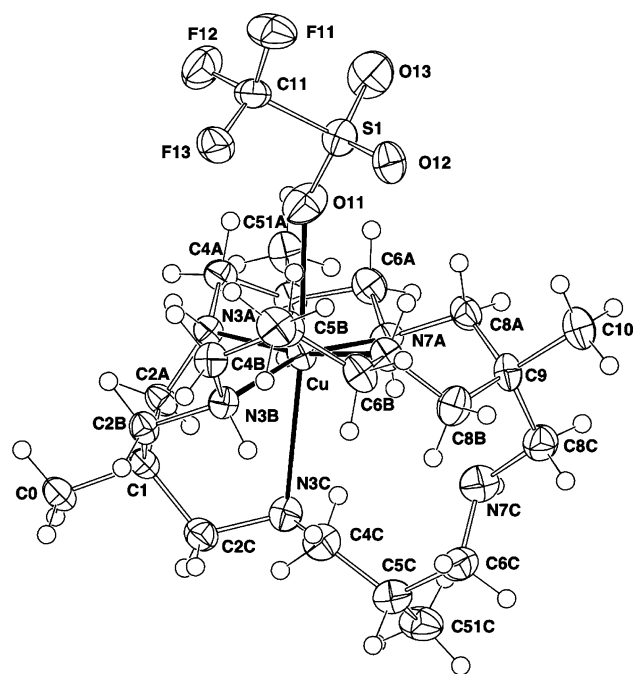
molecule as being hydrogen-bonded to symmetry-related perchlorate oxygen atoms ( $\text{O}_1\text{H}\cdots\text{O}(21)$  ( $x,y,z$ ;  $\bar{x},y,z$ ) 3.02(2), 2.05; 3.07(2), 2.4 Å). In the cation, Cu–Cl are 2.470(2) Å, the chlorine atom lying at the apex of a square-pyramidal array, the basal nitrogen atoms deriving from a pair of ligand strings, each acting as a chelate, the third string being uncoordinated; the amine coordination (RSRS) is the same as that in the preceding compound. Cu–N are 1.997(11), 1.996(13) Å, the ‘bite’ angle within the ligand strings being 88.23(6)°, and between 91.4(5)°; N–Cu–N (*trans*) are 173.5(1), 173.4(10)°, with Cl–Cu–N 93.2(3), 93.3(5)°. The diminution in coordination of the sar ligand is presumably to be ascribed to the facility of chloride coordination, coupled with the acidity of the crystallisation solution; the location of the presumed protonic hydrogen atoms (one and a half per ligand) required for charge balance may be accommodated within the proximity of the nitrogen atoms of the third strand to water molecule oxygen atoms, at 2.94(2) Å, while a further N $\cdots$ O interaction may be postulated to a perchlorate oxygen atom at 3.05(2) Å (see above) accommodating the remaining disordered protonic component. A tidy supramolecular aggregate (equal to the full binuclear unit) results (Fig. 4b).

Surprisingly, a similar coordination environment is found in  $[\text{Cu}(\text{Me}_5\text{tricosaneN}_6)(\text{O-tfs})](\text{tfs})$ , in which expansion of the cage by the introduction of a further methylene group at each bridge is accompanied by introduced substituent hindrance at that group; the structure complements that of the previously determined perchlorate salt [37]. Determinations at room and low-temperatures yield very similar results for a structure in which one



**Fig. 4** **a** Unit cell contents of  $[(\text{Hsar})\text{CuClCu}(\text{sarH}_2)](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ , projected down  $c$ ; **b** the aggregate of that stoichiometry, without the disordered protonic component

formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. Here one would expect the quasi-square-pyramidal environment of the cation (Table 1, Fig. 5) to be more nearly square planar with the  $O$ -triflate anion coordinating less emphatically than the chloride in the sar complex. However, in this complex, presumably because of that or the greater ligand flexibility, one of the nitrogen atoms of the third ligand string occupies the coordination site opposite the oxygen atom, perhaps weakening that interaction. The  $\text{CuN}_4$  coordination plane is appreciably wrinkled, with the pair of  $\text{N}-\text{Cu}-\text{N}$  *trans* angles bowed in opposite directions. In all other known structures of complexes of this ligand [10–13, 37], it behaves as a sexidentate species, though the structure of its complex with  $\text{Cu}(\text{ClO}_4)_2$  [37] is complicated by dynamic distortions and disorder involving diastereomeric forms. In the  $\text{Co}(\text{III})$  [10] and  $\text{Pt}(\text{II})$  [11] complexes, the three central six-membered chelate rings (corresponding to the five-membered rings in sarcophagines) adopt chair conformations, with equatorial methyl substituents but of the two such rings retained in the present complex, one has a chair conformation while the other has a skew form, albeit that both have equatorial methyl groups. The complex is chiral and of the five bound  $\text{N}$ -centres, four are of one configuration and one of the other. The initial



**Fig. 5** The cation of  $[\text{Cu}(\text{Me}_5\text{tricosaneN}_6)(\text{OSO}_2\text{CF}_3)](\text{F}_3\text{CSO}_3)$  (153 K)

expectation [37] that  $\text{Me}_5\text{tricosaneN}_6$  should be a less effective ligand for  $\text{Cu}(\text{II})$  than those of the sarcophagine type is perhaps justified by the present results, although it is worthy of note that the  $\text{Cu}(\text{II})$  complex of a trithia-triaza ligand of the sarcophagine type has recently been shown to undergo particularly facile interconversion between forms in which it is sexidentate and quadridentate [51].

## Conclusions

The ready adoption of four-, five- and six-coordination by copper(II) appears to have various consequences in terms of its binding to macrocyclic hexamines. With the small cages provided by sarcophagines, it is clear that although six-coordination of the neutral ligand is favourable, in solution at least there must be a process involving rapid partial release of the ligand which allows the  $\text{N}$ -donor atoms of one strand to be captured by  $\text{H}^+$ . The detached arm, presumably when monoprotonated, appears to be able to become involved in a transfer of  $\text{Cu}(\text{II})$  from another arm and so allow inversion of the donor atoms to occur. With the larger ligand  $\text{Me}_5\text{tricosaneN}_6$ , even as weak a ligand as triflate appears to be capable of displacing one  $\text{N}$ -donor of the cage in the solid state. It is conceivable that this could have useful consequences in terms of catalysis of the reactions of a bound sixth ligand by the unbound  $\text{N}$ -atom, though this hypothesis is yet to be tested.



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