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FULL PAPER

Synthesis and characterisation of pendant-arm alcohol derivatives of [9]aneN$_2$S and complexation with Cu^{II} ([9]aneN$_2$S = 1-thia-4,7-diazacyclononane) †

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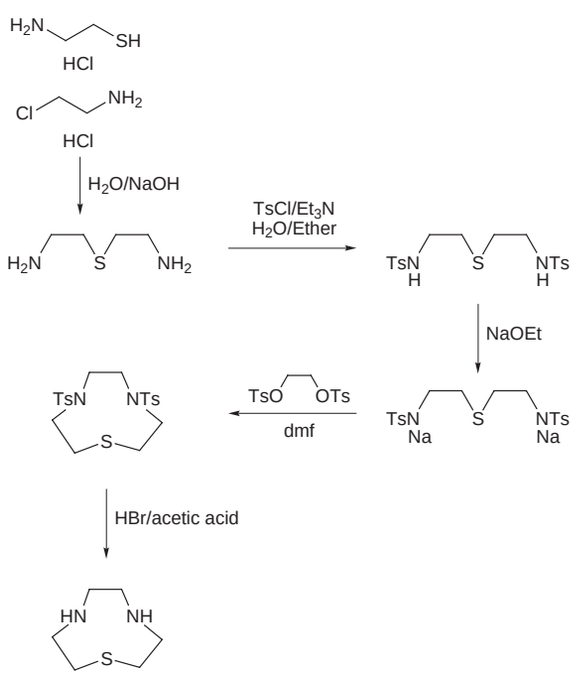
An improved detosylation of 4,7-bis(tolyl-*p*-sulfonyl)-1-thia-4,7-diazacyclononane to give the free amine [9]aneN$_2$S has been accomplished using Li/NH$_3$ or HBr/acetic acid. Reaction of [9]aneN$_2$S with ethylene oxide, 1,1-dimethylethylene oxide and methylenecyclohexane oxide in alcoholic solution affords the potentially pentadentate ligands 4,7-bis(hydroxyethyl)-1-thia-4,7-diazacyclononane (H$_2$L^1), 4,7-bis(2-hydroxy-2-methylpropyl)-1-thia-4,7-diazacyclononane (H$_2$L^2) and 4,7-bis(2-cyclohexyl-2-hydroxymethyl)-1-thia-4,7-diazacyclononane (H$_2$L^3) respectively. The copper(II) complexes of these ligands have been prepared and reveal that increasing the steric bulk on the pendant arm has a marked effect upon the resultant co-ordination chemistry. Thus, the complex of H$_2$L^1 shows a dimeric structure [Cu$_2$(HL^1)$_2$][PF$_6$]$_2$ **1** in which one of the hydroxy groups has been deprotonated. With H$_2$L^2 two complexes can be isolated: the dimer [Cu$_2$(HL^2)$_2$][PF$_6$]$_2$ **2** and the monomer [Cu(HL^2)][PF$_6$] **3**. In contrast, with H$_2$L^3 only the monomer [Cu(HL^3)][PF$_6$] **4** could be isolated. Single crystal structures of **1** and **3** have been determined. Magnetochemistry of **1** indicates that the two copper(II) centres are essentially non-coupled.

The co-ordination chemistry of the nine-membered ring crowns [9]aneN$_3$,[1,2] [9]aneN$_2$S,[3,4] [9]aneNS$_2$[3] and [9]aneS$_3$[5] has been investigated over recent years. The synthesis of pendant arm derivatives of [9]aneN$_3$ has led to the isolation of an enormous range of highly stable complexes.[6,7] However, the vast majority of these systems are based on trifunctionalisation of [9]aneN$_3$, leading to octahedral co-ordination to the metal centre. In contrast, there is relatively little published work on the synthesis of pendant arm derivatives of [9]aneN$_2$S leading to the formation of potential five-co-ordinate metal complexes.[8–10] Such complexes are of particular interest since they lead to the possibility of binding and activation of small molecules at the co-ordinatively unsaturated metal centre.[11] We report herein an alternative route to [9]aneN$_2$S and show that increasing the steric bulk of the ligating arms has a marked effect upon the co-ordination chemistry of the copper(II) complexes.

Results and Discussion

Ligand synthesis

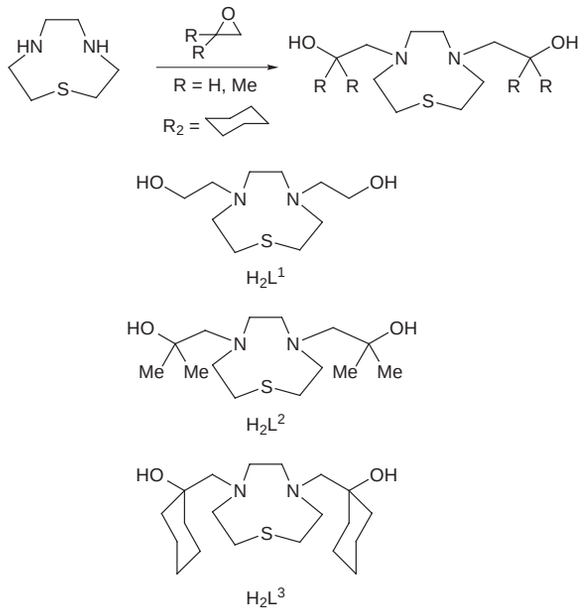
The compound [9]aneN$_2$S was first reported by Hancock and co-workers[12] and the synthesis of the ditosylated macrocycle has since been improved (Scheme 1).[12,13] The final step involves detosylation of the protected macrocycle using the procedure of Koyama and Yoshino.[14] This entails a lengthy (48–72 h) reflux with HBr/acetic acid and in our experience can result in appreciable decomposition and inconsistent yields of the desired material. We therefore decided to utilise a reductive detosylation with lithium and liquid ammonia.[15] The reaction is complete in minutes and the crude free base is purified by conversion into the HBr salt. The yields for this process are 60–70% providing a short reaction time is observed: reaction times of several hours lead to the isolation of a substantial quantity of a product which, although it remains unidentified, probably results from the degradation of the N$_2$S-donor macrocyclic ring.



Scheme 1 Ts = Toluene-*p*-sulfonyl (tosyl)

We subsequently returned to the question of the use of HBr/acetic acid for the deprotection of tosylated mixed N/S-substituted crowns. In our hands, this method can be successfully used for the preparation of [9]aneN$_2$S, although yields of detosylated product can vary enormously from 0 up to 75%. In parallel work, we have found this method of detosylation to be consistently successful for the preparation of [9]aneNS$_2$.[16] Therefore, over a period of many months we monitored a variety of commercially available batches of HBr/acetic acid and found that yields of detosylated product varied according to the source of HBr/acetic acid. In our hands, HBr/acetic acid from Fluka was invariably the most successful reagent, suggest-

† *Non-SI units employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.



Scheme 2

ing that the level of purity and/or the presence of trace contaminants critically influence the detosylation to [9]aneN$_2$S. Interestingly, detosylation to [9]aneNS$_2$ appears, in our hands, not to be so dependent on the HBr/acetic acid source.

The reaction of secondary amines with epoxides to give alcohols is well documented.[7,17] In the case of substituted epoxides nucleophilic attack occurs at the least hindered carbon of the three-membered ring and affords tertiary alcohols. The reaction of [9]aneN$_2$S with ethylene oxide, 1,1-dimethylethylene oxide and methylenecyclohexane oxide (prepared by the route of Corey and Chaykovsky[18]) in EtOH leads to the isolation of H_2L^1, H_2L^2 and H_2L^3 in good yields (Scheme 2). Increasing the steric bulk on the epoxides is known to decrease the rate of the ring-opening reaction.[19] Thus, reaction of [9]aneN$_2$S with ethylene oxide occurs in 20 h at room temperature, whereas with 1,1-dimethylethylene oxide the reaction takes 10 d. No reaction between [9]aneN$_2$S and methylenecyclohexane oxide was observed at room temperature but could be accomplished in 4 d under reflux.

Metal complexation

Reaction of H_2L^1 with $Cu(NO_3)_2{\cdot}3H_2O$ followed by counter-ion exchange with an excess of NH_4PF_4 afforded a green complex (**1**). With H_2L^2 the same procedure produced a black material, which on elution through a Sephadex column afforded a green (**2**) and a blue product (**3**). With H_2L^3 a single blue complex was obtained (**4**). Elemental analytical data for the four complexes indicate a stoichiometry [Cu(HL)][PF$_6$] (L = L^1, L^2 or L^3) in each case which suggests that deprotonation of one of the alcohol arms has occurred leading to an alkoxide interaction with Cu^{II}. The loss of a proton to form a co-ordinated alkoxide is unusual for a metal(II) cation, as a metal(III) cation is usually required to render the alcohol sufficiently acidic.[2,7,20] The FAB mass spectrum of complex **1** shows a peak at m/z = 592 assigned to $[Cu_2(HL^1)_2 + 1]^+$ indicating an overall binuclear structure, while the spectrum for the green complex **2** also indicates a dimeric structure. This evidence supports the formulation $[Cu_2(HL)_2][PF_6]_2$ for these complexes. The FAB mass spectra of the blue complexes **3** and **4** do not show peaks for a dimeric species, but molecular ions for monomeric 1:1 metal:ligand complexes.

Diffusion of Et$_2$O vapour into a MeCN solution of the complex **1** afforded deep green crystals suitable for X-ray analysis. The single crystal determination confirms the dimeric structure for the product $[Cu_2(HL^1)_2][PF_6]_2$ (Fig. 1). Selected bond

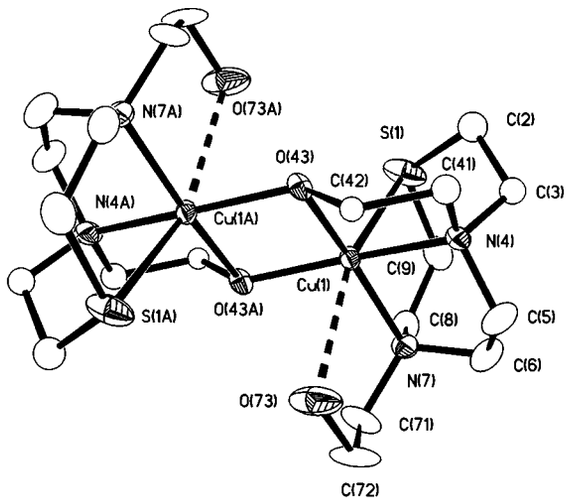


Fig. 1 Crystal structure of $[Cu_2(HL^1)_2][PF_6]_2$ **1** with numbering scheme adopted. Only one component of each disordered atom is shown. The suffix A indicates the symmetry operation $-x, -y, 1-z$

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Cu(1)···Cu(1A)	2.941(2)	Cu(1)–N(4)	2.003(6)
Cu(1)–O(43)	1.939(4)	Cu(1)–S(1)	2.648(2)
Cu(1)–O(43A)	1.931(4)	Cu(1)–O(73)	2.757(6)
Cu(1)–N(7)	2.043(6)		
Cu(1)–O(43A)–Cu(1A)	98.9(2)	O(43)–Cu(1)–N(7)	164.9(2)
Cu(1)–O(43)–Cu(1A)	98.9(2)	N(4)–Cu(1)–N(7)	86.9(2)
O(43)–Cu(1)–O(43A)	81.1(2)	O(43)–Cu(1)–S(1)	108.4(2)
O(43A)–Cu(1)–N(4)	162.1(2)	N(4)–Cu(1)–S(1)	85.7(2)
O(43)–Cu(1)–N(4)	86.5(2)	N(7)–Cu(1)–S(1)	84.6(2)
O(43A)–Cu(1)–N(7)	101.9(2)		

Symmetry operator: A $-x, -y, 1-z$.

lengths and bond angles are given in Table 1. The two copper(II) centres are separated by 2.941(2) Å and are bridged by two alkoxides which result from the deprotonation of an alcohol arm from each ligand. The Cu_2O_2 unit is planar. The geometry about each Cu^{II} is Jahn–Teller distorted octahedral, with two aza nitrogen and two alkoxide oxygens forming the close equatorial positions. The axial positions are occupied by the relatively poorly σ-donating sulfur and alcohol oxygen atoms.

Diffraction quality crystals were obtained for complex **3** by diffusion of Et$_2$O vapour into a solution of the complex in MeCN. The structure determination of the complex confirmed it to be the monomer $[Cu(HL^2)][PF_6]$ (Fig. 2). Selected bond lengths and bond angles for **3** are given in Table 2. The geometry around the Cu^{II} is a distorted square-based pyramid, with the two aza atoms and the two oxygen atoms forming the base of the square, and the sulfur atom of the macrocyclic ring at the apical site. One of the oxygen atoms is deprotonated and forms an alkoxide interaction with the copper centre. The alcohol and alkoxide donors lie at the same distance from the Cu^{II}, but this is ascribed to disorder which causes scrambling of the alkoxide and alcohol ligands. It was possible to locate the hydroxy hydrogen H(45) [on O(45)] from a circular Fourier-difference synthesis, while the position of H(75) [on O(75)] was not clear; H(45) is therefore included in the model to represent one component of the disorder, possibly the major one. Molecules interact through pairwise hydrogen bonds [O(45)–H(45)···O(75) $(-x, 2-y, -z)$] between centrosymmetrically related molecules.

Temperature-dependent susceptibility measurements on a sample of the complex were carried out in the range 4–300 K using a SQUID magnetometer. Fig. 3 shows plots of effective moment (μ_{eff}) *vs.* temperature T and of susceptibility (χ_m) *versus* T for $[Cu_2(HL^1)_2][PF_6]_2$ **1**. The effective moment (μ_{eff}) was

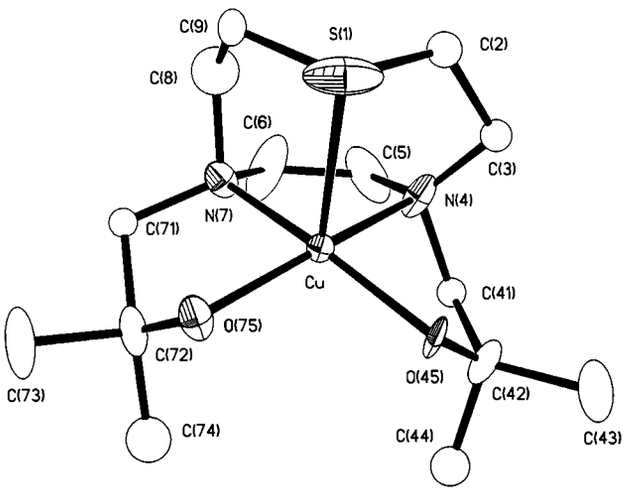


Fig. 2 Crystal structure of $[Cu(HL^2)][PF_6]$ **3** with numbering scheme adopted. Only one component of each disordered atom is shown

Table 2 Selected bond lengths (Å) and angles (°) for compound **3**

Cu–S(1)	2.502(4)	Cu–N(4)	2.037(9)
Cu–N(7)	2.031(10)	Cu–O(45)	1.938(10)
Cu–O(75)	1.948(9)		
S(1)–Cu–N(4)	88.1(3)	S(1)–Cu–N(7)	89.3(3)
S(1)–Cu–O(45)	105.1(3)	S(1)–Cu–O(75)	106.4(3)
N(4)–Cu–N(7)	84.9(4)	N(4)–Cu–O(45)	83.5(4)
N(4)–Cu–O(75)	160.9(4)	N(7)–Cu–O(45)	161.1(4)
O(45)–Cu–O(75)	83.1(3)	O(45)–Cu–O(75)	103.9(3)

Table 3 Electronic spectrophotometric data

Complex	Colour	λ_{max}/nm	ε_{max}/M^{-1} cm^{-1}
1	Green	683	85
2	Green	668	81
3	Blue	630	56
4	Blue	639	70

measured to be 1.65 μ_B per Cu at 300 K. This is reasonably close to the theoretical spin only (μ_{SO}) moment of 1.73 μ_B for a mononuclear species, though due to orbital contributions the effective magnetic moment is normally in the range 1.9–2.2 μ_B.[22] The magnetic susceptibility χ_m decreases rapidly with increasing temperature and fitting the data by the Bleaney–Bowers equation[21] gives a value for $2J$ of -0.001 cm^{-1} ($R = 0.999937$), indicating that the two copper(II) centres are essentially non-interacting. This is confirmed by EPR spectroscopy which shows a signal consistent with a single paramagnetic d^9 centre with $g_{\|} = 2.15$, $g_{\perp} = 2.07$. The size and sign of $2J$ has been demonstrated previously to be directly dependent upon the Cu–O–Cu angle (Φ) for hydroxo-bridged dimers, assuming planarity of the Cu_2O_2 fragment.[23] An angle below 97.5° or so results in ferromagnetic coupling and a positive value for $2J$, while for Cu–O–Cu angles above 97.5° antiferromagnetic coupling is observed. At angles approaching 97.5° there is little or no exchange between the copper(II) centres. More recently, Thompson *et al.*[24] have shown that the crossover between ferromagnetic and antiferromagnetic exchange in phenoxo-bridged binuclear copper(II) centres occurs at an angle well below 90°. Binuclear copper(II) centres with alkoxide bridges also exhibit a general dependence of $2J$ upon Φ.[25] The value of Φ in **1** is 98.9(2)° suggesting that alkoxy-bridged binuclear Cu^{II} species of this type show a crossover close to this angle. This is generally consistent with experimental and theoretical studies on alkoxo-bridged systems.[24,25]

The UV/VIS spectrophotometric data are summarised in Table 3. The spectrum of the dimeric complex **1** is typical for a

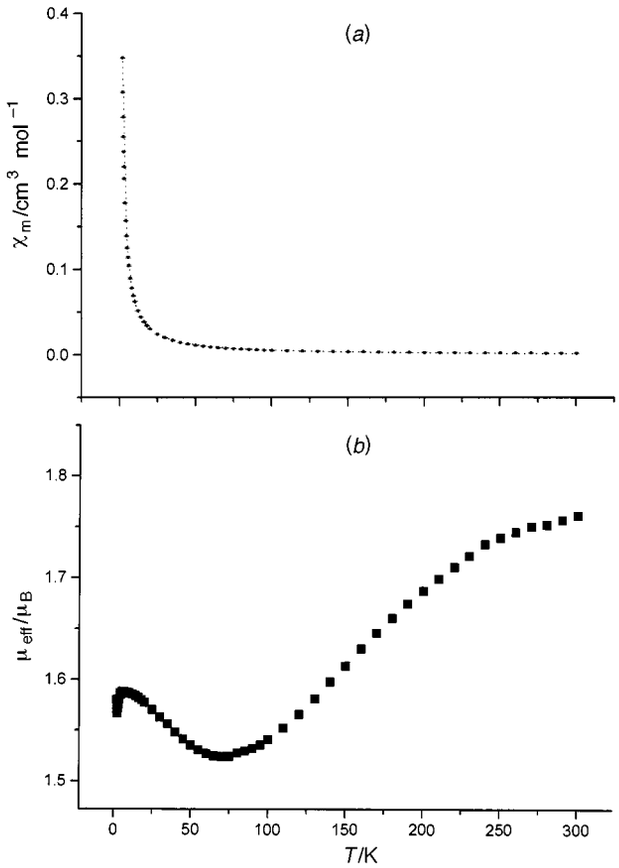


Fig. 3 Plots of (*a*) χ_m *vs.* temperature (··· obtained by modelled Bleaney–Bowers expression[21] for $S_1 = S_2 = \frac{1}{2}$; points are experimental data) and (*b*) of μ_{eff} *vs.* temperature for $[Cu_2(HL^1)_2][PF_6]_2$ **1**

tetragonally distorted octahedral copper complex, with a λ_{max} at 683 nm, and is similar to that of **2**, implying that **1** and **2** have similar geometries. The spectrum of the monomeric blue complex **3** by contrast has a λ_{max} at 630 nm, which is very similar to that of **4** suggesting that the latter is also monomeric (Fig. 4).

Current work is aimed at developing this chemistry further and to investigate further redox and magnetochemical properties of these and related systems.

Experimental

Unless otherwise stated, commercial grade chemicals were used without further purification. Ethylene oxide and 1,1-dimethylethylene oxide were purchased from Lancaster Synthesis.

Instrumental methods

All elemental analyses were carried out by the University of Edinburgh and the University of Nottingham analytical services (Perkin-Elmer 240B analyser). Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer, NMR spectra (^{1}H and ^{13}C) on Bruker DPX300 and AC250 instruments, fast atom bombardment (FAB) and electron impact (EI) mass spectra on VG Autospec VG7070E and Kratos MS 50TC spectrometers and X-band EPR spectra on a Bruker ER-2000 spectrometer employing 100 kHz modulation, as frozen glasses at 77 K under a nitrogen atmosphere. Magnetic measurements were carried out at the University of Edinburgh using an $MPMS_2$ SQUID magnetometer (Quantum Design) operating with a magnetic field of 1000G. Diamagnetic corrections were calculated using Pascal's constants.

Preparations

1-Thia-4,7-diazacyclononane dihydrobromide, [9]aneN_2S·2HBr. To a three-necked round-bottomed flask (2 l) was added

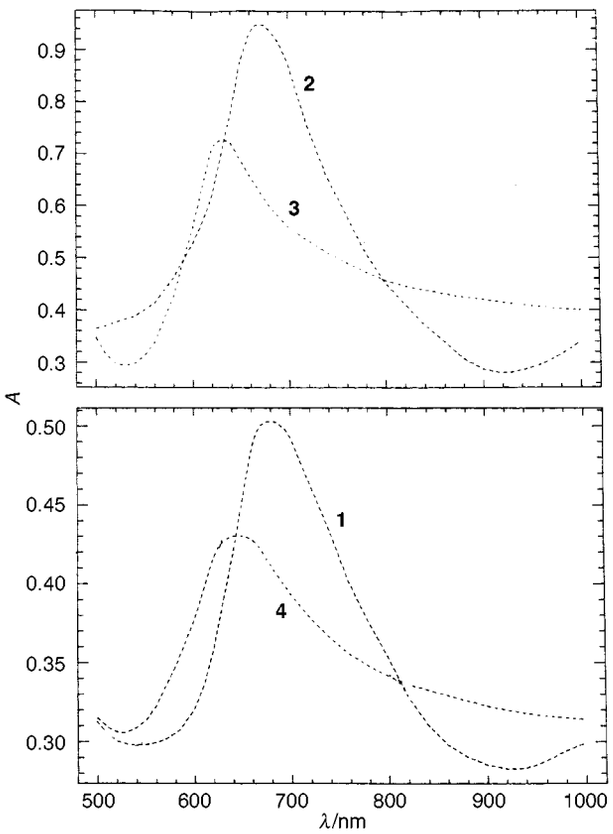


Fig. 4 Electronic spectra for complexes **1**, **2**, **3** and **4**

N,*N*′-bis(tolyl-*p*-sulfonyl)-1-thia-4,7-diazacyclononane[12,13] (10 g, 22 mmol). The flask was fitted with a mechanical stirrer, an inlet for ammonia and an ammonia condenser. The whole system was flushed with N_2. Dry thf (250 cm^3) and dry ethanol (30 cm^3) were added and the suspension was cooled in a solid CO_2–acetone bath. Liquid ammonia (1.2 l) was condensed into the system and lithium metal (4.2 g, 0.61 mol) added over 30 min. The resulting deep blue colouration only persisted for a few minutes. After stirring the resultant bright yellow solution for 15 min the bath was removed and the ammonia distilled off (**CARE**). Water (100 cm^3) was added to the remaining solution and solvent removed *in vacuo* to yield an off-white residue. The solid was dissolved in hydrochloric acid (6 M, 220 cm^3, 1.32 mol), and washed with Et_2O (2 × 100 cm^3). The aqueous layer was reduced *in vacuo*, redissolved in KOH solution (6 M, 220 cm^3, 1.32 mol) and extracted with CH_2Cl_2 (5 × 100 cm^3). The combined organic layers were dried over magnesium sulfate, filtered, then reduced *in vacuo* to give the crude product as a yellow oil. The oil was dissolved in EtOH–Et_2O (2:1, 100 cm^3) and HBr (48% v/v) was added until no further precipitate formed. The precipitate was filtered off and washed with EtOH–Et_2O (2:1) followed by Et_2O to yield the product as the HBr salt (3.21 g, 68.7%), m.p. 221–222 °C. NMR Spectra: $\delta_H(D_2O)$ 2.58 (4 H, t, J = 6.5, NCH_2CH_2S), 3.03 (4 H, t, J = 6.5 Hz, NCH_2CH_2S) and 3.33 (4 H, s, NCH_2CH_2N); $\delta_C(D_2O)$ 25.11 (NCH_2CH_2S), 39.96 (NCH_2CH_2S) and 41.96 (NCH_2CH_2N).

1-Thia-4,7-diazacyclononane. 1-Thia-4,7-diazacyclononane dihydrobromide (1.8 g, 5.8 mmol) and sodium hydroxide (2.3 g, 58 mmol) were dissolved in water (20 cm^3). Toluene (50 cm^3) was added and the resulting solution azeotroped using a Dean and Stark apparatus until all the water was removed. The toluene was decanted off and a further portion of toluene (50 cm^3) added to the flask and the resulting solution refluxed for 1 h. The combined organic fractions were reduced *in vacuo* to yield the free base as a very pale oil (800 mg, 94%). NMR Spectra: $\delta_H(CDCl_3)$ 2.50–2.59 (8 H, m, NCH_2CH_2S and NCH_2CH_2N) and 2.73 (4 H, t, NCH_2CH_2S); δ_C 32.75 (NCH_2CH_2S), 46.08 (NCH_2CH_2S) and 46.84 (NCH_2CH_2N). EI Mass spectrum: m/z = 147 ($[M + 1]^+$).

Methylenecyclohexane oxide. Sodium hydride (8.8 g, 0.22 mol, 60% dispersion in oil) was added to a dry three-necked round-bottomed flask (500 cm^3) equipped with a condenser, dropping funnel and a nitrogen inlet. The NaH was washed with pentane (3 × 100 cm^3) to remove the oil and after the final washing the last traces of pentane were removed from the flask under reduced pressure. Trimethylsulfonium iodide (50.6 g, 0.23 mol) was added to the NaH and the flask placed under a positive nitrogen pressure. Dry dmso (120 cm^3) was added *via* the dropping funnel at such a rate as to keep the temperature below 50 °C (**CAUTION**: H_2 is evolved). After the effervescence had ceased, cyclohexanone (19.6 g, 20.7 cm^3, 0.2 mol) was added *via* the dropping funnel in one portion and the solution was stirred at 50 °C for 1 h, then at room temperature for 12 h. Water (300 cm^3) was added and the mixture extracted with Et_2O (5 × 100 cm^3). The combined extracts were dried over magnesium sulfate and their volume reduced *in vacuo* to yield a very pale yellow liquid. The crude oxirane was distilled under reduced pressure to give a colourless liquid (14 g, 62%). NMR Spectra: $\delta_H(CDCl_3)$ 1.33 to 1.67 (10 H, m, cyclohexyl CH_2) and 2.46 [2 H, s, $(CH_2)_2CCH_2O$]; $\delta_C(CDCl_3)$ 24.52, 24.90, 33.29 (cyclohexyl CH_2), 54.02 [$(CH_2)_2CCH_2O$] and 58.53 (quaternary C). EI Mass spectrum: m/z = 112 (M^+).

4,7-Bis(2-hydroxyethyl)-1-thia-4,7-diazacyclononane, H_2L^1. 1-Thia-4,7-diazacyclononane (300 mg, 2.0 mmol) was dissolved in EtOH (10 cm^3). To this was added ethylene oxide (300 mg, 6.8 mmol; **CARE**, toxic) and the resulting solution sealed and left to stand for 20 h. Removal of the solvent *in vacuo* led to the isolation of the product as a pale yellow oil (460 mg, 96%). NMR Spectra: $\delta_H(CDCl_3)$ 2.58–2.85 (16 H, m, NCH_2CH_2N, SCH_2CH_2N, NCH_2CH_2OH) and 3.60 (4 H, t, NCH_2CH_2OH); $\delta_C(CDCl_3)$ 34.13 (SCH_2), 53.97 (NCH_2CH_2N), 56.26 (SCH_2CH_2N) and 59.30 (NCH_2CH_2OH). EI Mass spectrum: m/z = 235 ($[M + 1]^+$).

4,7-Bis(2-hydroxy-2-methylpropyl)-1-thia-4,7-diazacyclononane, H_2L^2. This was prepared in the same way as H_2L^1 except that the reaction time was 10 d. Yield 386 mg, 81%. NMR Spectra: $\delta_H(CDCl_3)$ 2.37, 2.43 [8 H, NCH_2CH_2N, $NCH_2C(CH_3)_2OH$], 2.47 (12 H, CH_3), 2.79 (4 H, SCH_2CH_2N) and 2.86 (4 H, SCH_2CH_2N); $\delta_C(CDCl_3)$ 27.68 (CH_3), 34.81 (NCH_2CH_2S), 52.07 (NCH_2CH_2S), 56.59 (NCH_2CH_2N), 66.54 [$NCH_2C(CH_3)_2OH$] and 70.34 [$C(CH_3)_2OH$]. EI Mass spectrum: m/z = 291 ($[M + 1]^+$).

4,7-Bis(2-cyclohexyl-2-hydroxyethyl)-1-thia-4,7-diazacyclononane, H_2L^3. 1-Thia-4,7-diazacyclononane (500 mg, 3.43 mmol) and methylenecyclohexane oxide (1.6 g, 14.3 mmol) were dissolved in EtOH (30 cm^3) and the mixture refluxed for 4 d. The cooled solution was reduced *in vacuo* to give an oil which was dissolved in CH_2Cl_2 (50 cm^3) and washed with water (5 × 50 cm^3). The organic layer was dried over $MgSO_4$ and solvent removed to give a pale yellow oil (257 mg, 26%). NMR Spectra: $\delta_H(CDCl_3)$ 1.12–1.70 (20 H, s, cyclohexyl CH_2), 2.49 (4 H, s, SCH_2) 2.57–2.88 [12 H, m, NCH_2CH_2S, NCH_2CH_2N and $NCH_2C(CH_2)_2OH$] and 3.39 (2 H, s, OH); $\delta_C(CDCl_3)$ 21.81, 25.80, 34.33 (cyclohexyl CH_2), 36.53 (NCH_2CH_2S), 57.95 (NCH_2CH_2S), 58.85 (NCH_2CH_2N), 70.18 [$NCH_2C(CH_2)_2OH$] and 70.47 [$C(CH_2)_2OH$]. EI Mass spectrum: m/z = 372 ($[M + 1]^+$).

$[Cu_2(HL^1)_2][PF_6]_2$ 1. The compound H_2L^1 (50 mg, 0.2 mmol) was dissolved in EtOH (2 cm^3) and an equimolar solution of $Cu(NO_3)_2 \cdot 3H_2O$ (62 mg, 0.2 mmol) in EtOH (2 cm^3) was added to yield immediately a deep green solution. After refrigeration

for 24 h green crystals of the product were isolated. There were dissolved in water and were converted into the PF_6^- salt by the addition of an excess of NH_4PF_6. A green solid was isolated and dried *in vacuo* (70%) (Found: C, 27.2; H, 5.0; N, 6.2. $C_{10}H_{21}CuF_6N_2O_2PS$ requires C, 27.2; H, 4.8; N, 6.3%). IR spectrum (KBr disc): $\tilde{\nu}_{max}/cm^{-1}$ 3438s (OH), 2926m (CH), 836s and 558m (PF_6^-). FAB mass spectrum: $m/z = 592$ ($[M - 2PF_6 + 1]^+$).

$[Cu_2(HL^2)_2][PF_6]_2$ 2 and $[Cu(HL^2)][PF_6]$ 3. These complexes were prepared using the same procedure as for **1**, except that after isolation of the PF_6^- salt the black solid was passed down a Sephadex (LH-20) column with MeCN and two fractions **2** and **3** were isolated. $[Cu_2(HL^2)_2][PF_6]_2$ **2** (Found: C, 35.9; H, 6.2; N, 6.1. $C_{19}H_{29}CuF_6N_2O_2PS$ + MeCN + $0.3Et_2O$ requires C, 35.8; H, 6.2; N, 6.5%): IR spectrum (KBr disc) $\tilde{\nu}_{max}/cm^{-1}$ 3441s (OH), 2930m, 2839w (CH), 836s and 561m (PF_6^-); FAB mass spectrum $m/z = 705$ ($[M - 2PF_6]^+$). $[Cu(HL^2)][PF_6]$ **3** (Found: C, 34.2; H, 5.8; N, 6.4. $C_{14}H_{29}CuF_6N_2O_2PS{\cdot}0.25MeCN$ requires C, 34.3; H, 5.9; N, 6.2%): IR spectrum (KBr disc) $\tilde{\nu}_{max}/cm^{-1}$ 3430s (OH), 2921m, 2831w (CH), 841s and 558m (PF_6^-); mass spectrum $m/z = 353$ ($[M - PF_6 + 1]^+$).

$[Cu(HL^3)][PF_6]$ 4. This was prepared using the same procedure as for compound **1** and the product was isolated as a blue solid (Found: C, 41.7; H, 6.96; N, 4.3. $C_{20}H_{38}CuF_6N_2O_2PS$ requires C, 41.7; H, 6.4; N, 4.8%). IR spectrum (KBr disc): $\tilde{\nu}_{max}/cm^{-1}$ 3425s (OH), 2928m, 2804w (CH), 840s and 564m (PF_6^-). FAB Mass spectrum: $m/z = 433$ ($[M - PF_6]^+$).

Crystallography

Single-crystal X-ray data were collected on a Stoë STADI-4 four circle diffractometer, fitted with an Oxford Cryosystems low temperature device.[26]

Crystal data. $C_{20}H_{42}Cu_2F_{12}N_4O_4P_2S_2$ **1**, $M = 883.72$, orthorhombic, space group *Pnam*, $a = 20.566(3)$, $b = 8.7516(10)$, $c = 17.013(2)$ Å, $U = 3062.0(6)$ Å^3, $T = 150(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.741 mm^{-1}, 2788 unique reflections measured and used in all calculations. The final $wR(F^2)$ was 0.1813, $R1 = 0.0670$. Atoms C(2), C(3), C(4) and C(42) were each equally disordered over two sites. Disorder in the PF_6^- anion was treated by restraining U_{ij} components. The final ΔF extrema of 1.55 and −1.66 e Å^{-3} lie near the disordered PF_6^- and represent the residual electron densities after disorder modelling.

$C_{14}H_{29}CuF_6N_2O_2PS$ **3**, $M = 498.0$ monoclinic, space group $P2_1/c$, $a = 7.799(3)$, $b = 13.563(3)$, $c = 19.060(3)$ Å, $\beta = 97.35(3)°$, $U = 1999.6(10)$ Å^3, $T = 150(2)$ K, $Z = 4$, μ(Mo-Kα) = 1.343 mm^{-1}, 4597 reflections measured, 3517 unique ($R_{int} = 0.101$). The final $wR(F^2)$ was 0.241, $R1 = 0.1103$. It was possible to locate the hydroxy hydrogen H(45) [on O(45)] from a circular ΔF synthesis, while the position of H(75) [on O(75)] was not clear; H(45) is therefore included in the model to represent one component of the disorder, possibly the major one. Disorder throughout the ligand required modelling and the following restraints were employed, S–C 1.82, C–C 1.52 Å within the macrocyclic ring and C–C 1.54 Å elsewhere. Further disorder, in the PF_6^- anion, was treated by the use of restraints to distances, angles and U_{ij} components.

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