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Discrete molecular and extended polymeric copper(I) halide complexes of tetradentate thioether macrocycles

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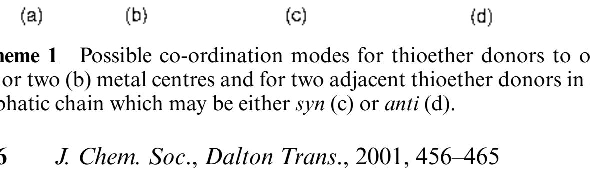
A series of complexes of copper(I) halides with either [12]aneS_4 (1,4,7,10-tetrathiacyclododecane) or [16]aneS_4 (1,5,9,13-tetrathiacyclohexadecane) have been synthesized, characterised and their crystal structures determined. Discrete molecular entities of formula [CuX([12]aneS_4)] (X = Cl, Br or I) were isolated from solutions containing a 1 : 1 metal : ligand stoichiometry. In [CuX([12]aneS_4)] (X = Br or I) the copper(I) centres adopt a rare square pyramidal geometry. Located on fourfold axes of symmetry, the copper(I) centres are co-ordinated by one halide ion [Cu–Br 2.4209(11) or Cu–I 2.573(5) Å] and four sulfur atoms [2.5386(12) (X = Br) and 2.521(5) Å (X = I)]. In contrast, the copper(I) centres in [CuCl([12]aneS_4)] adopt the more common tetrahedral co-ordination geometry, which is provided by one chloride ion [Cu–Cl 2.2666(13) Å] and three sulfur donors [Cu–S 2.3331(13), 2.3326(13), 2.4720(11) Å]. Polymeric materials, $[Cu_4Br_4([12]aneS_4)_2]_\infty$, $[Cu_4I_4([12]aneS_4)]_\infty$ and $[Cu_2I_2([16]aneS_4)]_\infty$, were obtained from reactions in which metal : ligand stoichiometries of 2 : 1 and 4 : 1 were used. $[Cu_4Br_4([12]aneS_4)_2]_\infty$ contains a previously uncharacterised copper(I) halide motif of formula Cu_4X_4 which is derived from the common Cu_4X_4 cubane tetramer and the Cu_4X_4 step-cubane tetramer. These Cu_4X_4 clusters are linked by [12]aneS_4 molecules to generate a two-dimensional framework [Cu–Br 2.410(2)–2.539(2); Cu–S 2.318(3)–2.385(3) Å]. In $[Cu_4I_4([12]aneS_4)]_\infty$, Cu_4I_4 cubane tetramers are linked by tetradentate [12]aneS_4 molecules to give a two-dimensional sheet structure [Cu–I 2.602(1)–3.021(1); Cu–S 2.285(1)]. In $[Cu_2I_2([16]aneS_4)]_\infty$ an infinite three-dimensional co-ordination polymer comprising Cu_2I_2 rhomboid dimers linked by tetradentate [16]aneS_4 molecules is formed [Cu–I 2.5972(9)–2.6702(9); Cu–S 2.292(2)–2.357(2) Å]. The Cu_2I_2 moiety acts as a pseudo-square planar linker while the bridging [16]aneS_4 units afford tetrahedral building blocks to give overall a PtS type structure for the polymer.

Introduction

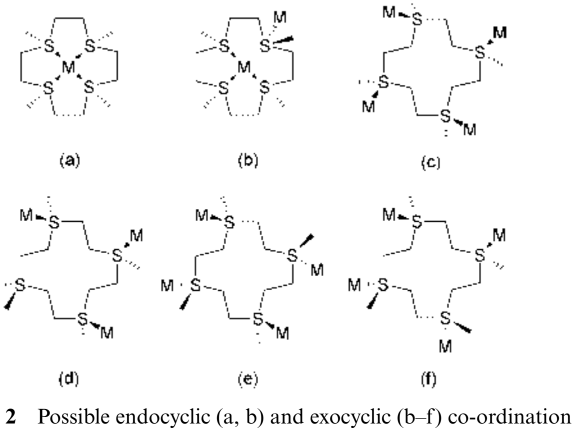
Many notable recent advances in the chemistry of co-ordination polymers have been achieved through the use of both linear and bent bridging bidentate[1–3] and multidentate ligands.[1,4] These complexes have demonstrated an extensive variety of structural motifs and novel topologies in one-, two- and three-dimensional co-ordination polymers.[1–4] Pyridyl nitrogen donors predominate[1–4] but other nitrogen donor ligands such as nitriles,[5] imidazoles [6] and aza macrocycles[7] are known, as are thioether sulfur donor ligands.[8,9]

Thioether ligands are potentially more versatile than *N*-donor ligands owing to the presence of two lone pairs on the sulfur atom. Thus, they can act not only as terminal ligands [Scheme 1(a)] but also as bridging ligands [Scheme 1(b)]. There is also the possibility of adjacent sulfur atoms co-ordinating metals on the same [Scheme 1(c)] or opposite sides [Scheme 1(d)] of the aliphatic chain creating *syn* and *anti* conformers.



Scheme 1 Possible co-ordination modes for thioether donors to one (a) or two (b) metal centres and for two adjacent thioether donors in an aliphatic chain which may be either *syn* (c) or *anti* (d).

Thioether macrocycles have the potential to bind metal ions in both endo- [Scheme 2(a), 2(b)] and exo-cyclic [Scheme 2(b)–2(f)] modes forming discrete molecular and extended network structures, respectively.[10–18] When binding metals in an exocyclic manner 1,4,7-trithiacyclononane ([9]aneS_3), 1,4,7,10-tetrathiacyclododecane ([12]aneS_4), 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS_5) and 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS_6) can be considered to be tri-, tetra-, penta- and



Scheme 2 Possible endocyclic (a, b) and exocyclic (b–f) co-ordination modes for a tetradentate thioether macrocycle (in this case [12]aneS_4).

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hexa-dentate connecting units, respectively. Ligand connecting junctions with such high denticity are relatively rare. For complexes of tetradentate macrocycles such as [12]aneS_4 and [16]aneS_4 four possible isomers can be envisaged depending on the disposition of the metal atoms. First, all four metal centres can be accommodated on one side of the macrocycle [Scheme 2(c)]; secondly three can be located on one side of the macrocycle and the other on the opposite side [Scheme 2(d)]; and finally two can be above the macrocycle and two below, either in an up, down, up, down arrangement [Scheme 2(e)] or in an up, up, down, down fashion [Scheme 2(f)].

Copper(I) halides were selected as the metal source due to their ability to form neutral arrays,[19,20] thus ensuring that channels/cavities contained within the structure would be anion free and available for guest inclusion. The strongly co-ordinating nature of the halide anion is such that it can bridge two or more copper centres giving neutral species of the form $(CuX)_n$ (X = Cl, Br or I; n = 1, 2, 3, 4 . . . ∞).[19,20] These species can have discrete molecular structures (*e.g.* rhomboid dimer or cubane tetramers),[21–24] one-dimensional structures (*e.g.* staircase chains, split staircase chains, zigzag chains or hexagonal columns)[20,21,23,25,26] or two-dimensional structures (*e.g.* corrugated sheets),[26] which can be connected to form co-ordination polymers using diverse bridging ligands. For example, when combined with the bridging bidentate ligands pyrimidine, pyrazine, 4,4′-bipyridine, 2,7-diazapyrene, quinoxaline and 4,7-phenanthroline, two-dimensional sheets comprising one-dimensional $(CuX)_\infty$ motifs linked by the bridging ligand are produced.[20–22,25] Similarly, 1,3,5-triazine in combination with copper(I) halides generates three-dimensional arrays consisting of either one-dimensional $(CuX)_\infty$ motifs linked by tridentate triazine or two-dimensional $(CuX)_\infty$ motifs joined by bidentate triazine.[26]

We report herein our studies of copper(I) halides with [12]aneS_4 and [16]aneS_4 to give both discrete and polymeric compounds. The complexes [CuX([12]aneS_4)] (X = Br **1** or I **2**) were found to contain discrete molecular units with very similar structures based on an unusual five-co-ordinate square-based pyramidal copper(I) geometry. [CuCl([12]aneS_4)] **3** was also found to contain discrete molecular units but with a more conventional tetrahedral copper(I) environment. Using a higher metal : ligand stoichiometry, polymeric species were obtained. Thus, $[Cu_4Br_4([12]aneS_4)_2]_\infty$ **4** and $[Cu_4I_4([12]aneS_4)]_\infty$ **5** both exist as two-dimensional sheets of (4,4) topology, although very different in construction, with the former containing a novel copper(I) halide motif. $[Cu_2I_2([16]aneS_4)]$ **6** was found to exist as a three-dimensional extended network with the PtS-type structure.

Results and discussion

Reaction of equimolar quantities of CuX (X = Cl, Br or I) with [12]aneS_4 in a 50 : 50 CH_2Cl_2–MeCN mixture afforded white precipitates of [CuX([12]aneS_4)] (X = Br **1**, I **2** or Cl **3**) which were characterised initially by elemental analysis and subsequently by single crystal X-ray diffraction. All were insoluble in common organic solvents. Single crystals of **1**–**3** were obtained by layered diffusion techniques from CH_2Cl_2–MeCN mixtures. Under identical conditions, but with increased metal halide : ligand molar ratios, different products were obtained. Reaction of copper(I) bromide with [12]aneS_4 in a 2 : 1 molar ratio afforded a white powder of composition $[(CuBr)_2([12]aneS_4)]$. Single crystals, grown by layered diffusion, were found by X-ray diffraction to have the polymeric structure $[Cu_4Br_4([12]aneS_4)_2]_\infty$ **4**. With even greater copper(I) bromide : ligand molar ratios (*e.g.* 3 : 1 and 4 : 1), white powders were obtained of non-integral stoichiometry and the single crystals obtained from layered diffusion experiments did not differ from those of **1** or **4**. It is assumed that these powders are mixtures of products of different stoichiometries. Layered diffusion experiments involving copper(I) iodide with [12]aneS_4 in a 4 : 1 molar ratio gave crystals which, by X-ray diffraction, were found to be $[Cu_4I_4([12]aneS_4)]_\infty$ **5**. Attempts to prepare a pure powder sample of this product proved to be impossible as it always contained an impurity of lower metal : ligand stoichiometry. We were not able to obtain single crystals of a copper(I) iodide and [12]aneS_4 product with 2 : 1 stoichiometry, and the products obtained from the corresponding powder experiments were always found to have non-integral stoichiometries. In experiments involving CuCl and CuBr every effort was made to exclude both O_2 and water.

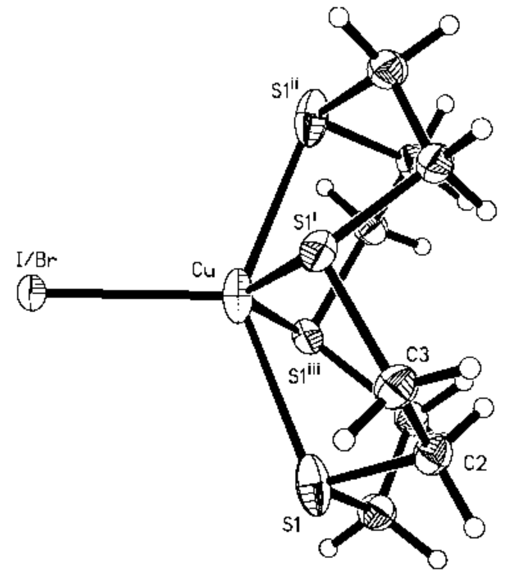


Fig. 1 View of the copper(I) centre in complexes **1** and **2**, illustrating its five-co-ordinate geometry. Displacement ellipsoids at the 50% probability level as in all cases shown. Symmetry codes i $-x, -y, z$; ii $-y, x, z$; iii $y, -x, z$.

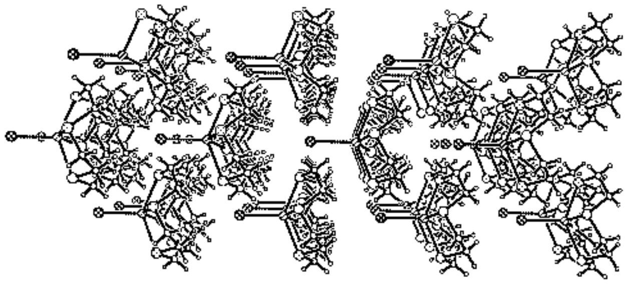


Fig. 2 A view of the packing in complexes **1** and **2**, showing the molecules aligned in a polar manner (Br/I, cross hatched; Cu, hatched; S, dotted; C, shaded; H, plain).

Reaction of two molar equivalents of CuI with [16]aneS_4 in a 50 : 50 CH_2Cl_2–MeCN mixture afforded a white precipitate of $[Cu_2I_2([16]aneS_4)]_\infty$ **6**. Attempts to prepare compounds with different stoichiometries always produced **6**. Crystals of **6** suitable for single crystal X-ray study were obtained by layering solutions of CuI in MeCN and [16]aneS_4 in CH_2Cl_2.

Molecular structure of [CuX([12]aneS_4)] (X = Br 1 or I 2)

The structure determination established a discrete mononuclear species of formula [CuX([12]aneS_4)] (X = Br **1** or I **2**) (Fig. 1). The [CuX([12]aneS_4)] moieties stack in a parallel fashion along the crystallographic c axis to give a polar crystal (Fig. 2). Pertinent structural data are given in Tables 1 and 2.

The copper(I) centre is ligated by four thioether donors and one halide anion. The Cu–X bond lies along a crystallographic C_4 axis. The asymmetric unit, therefore, consists of the copper(I) and halide centres and one quarter of the [12]aneS_4 moiety. The X^- anion occupies the apical position [for **1**, Cu–Br

Table 1 Selected bond lengths (Å) for [CuBr([12]aneS_4)] **1**, [CuI([12]aneS_4)] **2**, [CuCl([12]aneS_4)] **3**, [Cu_4Br_4([12]aneS_4)$_2$] **4**, [Cu_4I_4([12]aneS_4)] **5** and [Cu_2I_2([16]aneS_4)] **6**

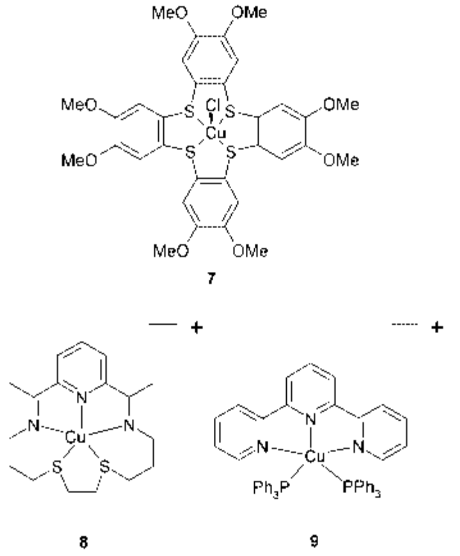
1		**2**		**3**		**4**		**5**		**6**	
Cu–Br	2.4209(11)	Cu–I	2.573(5)	Cu–Cl	2.2666(13)	Cu(1)–Br(1)	2.410(2)	Cu(1)–I(1)	2.6107(7)	Cu(1)–I(1)	2.6317(9)
				Cu(′)–Cl	2.266(7)	Cu(2)–Br(1)	2.429(2)	Cu(1^{i})–I(1)	2.6022(8)	Cu(1)–I(2)	2.6182(9)
						Cu(2)–Br(2)	2.516(2)	Cu(1^{ii})–I(1)	3.0212(8)	Cu(2)–I(1)	2.5972(9)
						Cu(2)–Br(2^{ii})	2.539(2)			Cu(2)–I(2)	2.6702(9)
										Cu(1)–Cu(2)	2.8079(12)
Cu–S(1)	2.5386(12)	Cu–S(1)	2.521(5)	Cu–S(1)	2.3331(13)	Cu(1)–S(1)	2.324(2)	Cu(1)–S(1)	2.2852(12)	Cu(1)–S(1)	2.357(2)
				Cu–S(4)	2.4720(11)	Cu(1)–S(4)	2.385(3)			Cu(1)–S(9^{i})	2.346(2)
				Cu–S(7)	2.3326(13)	Cu(1)–S(7)	2.319(2)			Cu(2)–S(5^{iii})	2.304(2)
				Cu(′)–S(1)	2.279(8)	Cu(2)–S(10^{i})	2.318(3)			Cu(2)–S(13^{ii})	2.292(2)
				Cu(′)–S(7)	2.320(8)						

Symmetry operators: **4**, i $x + 0.5, -y - 0.5, z + 0.5$; ii $-x, -y, -z$; **5**, i $1 - y, 0.5 + x, 2 - z$; ii $-x + 0.5, -y + 1.5, z$; **6**, i $-0.5 - x, 0.5 + y, -0.5 - z$; ii $-1 - x, -y, -z$; iii $0.5 + x, 0.5 - y, 0.5 + z$.

2.4209(11) Å; for **2**, Cu–I 2.573(5) Å] and the four sulfur atoms of the macrocycle occupy the basal positions [for **1**, Cu–S 2.5386(12) Å; for **2**, Cu–S 2.521(5) Å] of a distorted square-based pyramidal copper(I) centre (Table 1). The Cu–X bond lengths in **1** and **2** are not significantly different from those in other copper(I) halide systems. The Cu–S bond lengths in both compounds are significantly longer than those in four-co-ordinate copper(I) systems (typically ≈2.3 Å) and longer than those found in the copper(II) complex [Cu([12]aneS_4)(H_2O)][ClO_4]$_2$ (av. 2.33 Å).[27]

The copper cation sits above the plane comprising the four sulfur atoms of the macrocycle, the torsion angles of which (Table 3) correspond to a [3333]$_4$ conformation, as observed in the structure of the "free" ligand.[28] The small ring size of the [12]aneS_4 macrocycle forces the metal centre to be displaced from the plane containing the sulfur atoms (**1** 0.95 Å; **2** 0.93 Å). Similar but smaller displacements are also seen in the four-co-ordinate platinum(II) complexes [Pt([12]aneS_4)][PF_6]$_2$ (0.28 Å)[12a] and [Pt([12]aneS_4)]Cl_2 (0.33 Å)[12b] and the five-co-ordinate copper(II) complex [Cu^{II}([12]aneS_4)(H_2O)][ClO_4]$_2$ (0.53 Å).[27]

Five-co-ordinate copper(I) cations are rare[29] and only two examples are known with *S*-donor ligands.[30,31] Three relevant examples, **7**–**9**, including the two with *S*-donor ligands (**7**, **8**), are shown in Scheme 3. Compound **7** has an S_4Cl donor set and is most closely related to **1** and **2**. It should be noted that the average Cu–S bond length (2.568 Å) in **7** does not differ considerably from those in **1** and **2**. There is, however, a wide range of Cu–S bond lengths in **7** [2.395(5), 2.511(5), 2.644(7), 2.722(7) Å]. Compound **8** has an N_3S_2 donor set with Cu–S bond lengths [2.324(8), 2.328(7) Å] considerably shorter than those in **1**, **2** and **7**. In **8**, however, the bonds to the imine nitrogens [Cu–N 2.28(2), 2.52(3) Å] are longer than expected for a typical Cu^I–N bond (1.9–2.1 Å). Compound **9** consists of an acyclic ligand system and also shows long Cu^I–N bonds [2.386(3), 2.535(4) Å]. Ainscough *et al.*[31b] postulated that these bonds, which are longer than expected for five-co-ordinate copper(I) compounds,[30,31c,e] were due to the stereo-electronic demands of the cation. More recent work[31a,d] and compounds **1** and **2**, which also have unusually long bonds, are consistent with this argument.



Scheme 3 Representations of five-co-ordinate copper(I) complexes; {chloro(2,3,7,8,12,13,17,18-octamethoxy-10,15,20-trihydro-5*H*-5,10,15,20-tetrathiatetrabenzo[*a*,*d*,*g*,*j*]cyclododecane)copper(I)} **7**;[24] (2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene)copper(I) **8**;[25] and [Cu(PPh_3)$_2$(terpy)]$^+$ **9**.[26]

Molecular structure of [CuCl([12]aneS_4)] 3

The structure determination established the formation of a discrete mononuclear species for [CuCl([12]aneS_4)] **3** (Fig. 3). The packing differs from that observed in complexes **1** and **2** in that the [CuCl([12]aneS_4)] moieties stack in an anti-parallel fashion along the crystallographic *c* axis to give a non-polar crystal (Fig. 4). Pertinent structural data are given in Tables 1 and 2. As there is lower crystallographic symmetry in **3** than in **1** or **2**, the asymmetric unit of the former consists of an entire macrocycle as well as the copper(I) and chloride ions (Fig. 3a). Despite the lower symmetry, the macrocycle retains a [3333] conformation as confirmed by the torsion angle data (Table 3).

Although neither the macrocycle nor the Cl^- anion exhibits disorder, the copper(I) centre is disordered over two positions in a ratio of approximately 7 : 1. In the major component the copper(I) centre is ligated by three sulfur atoms of the macrocycle [Cu–S 2.3326(13), 2.3331(13), 2.4720(11) Å] and a Cl^- anion [Cu–Cl 2.2666(13) Å] to give a distorted tetrahedral arrangement (Fig. 3a). The fourth sulfur atom cannot be considered to be involved in direct co-ordination [Cu···S 3.3940(12) Å].

The structural parameters of the major component of complex **3** are typical of a tetrahedral copper(I) compound. The variation in the Cu–S bond lengths [Cu–S 2.3326(13)–2.4720(11) Å] is ascribed to the spatial constraints of the macrocycle. [CuI([9]aneS_3)], which forms a discrete four-co-ordinate species with an *S_3I*-donor set,[16] shows similar Cu–S distances [2.329(1), 2.331(1), 2.343(1) Å] and a tetrahedral co-ordination environment. A tetrahedral *S_3Cl* donor set with similar geometrical parameters to those of the major component of **3** is also found in chloro(2,5,8-trithia[9]-*o*-benzenophane)copper(I) [Cu–Cl 2.252(2); Cu–S 2.303(2), 2.311(2), 2.398(2) Å].[14c]

In the minor component the copper(I) centre is more centrally located within the macrocycle (Fig. 3b) and has a

Table 2 Selected angles (°) for complexes **1**–**6**

1		**2**		**3**		**4**		**5**		**6**	
Br–Cu–S(1)	111.98(3)	I–Cu–S(1)	111.6(2)	Cl–Cu–S(1)	115.47(5)	S(7)–Cu(1)–S(1)	128.78(8)	S(1)–Cu(1)–I(1)	110.60(4)	I(1)–Cu(1)–I(2)	115.55(3)
S(1)–Cu–S(1^{i})	81.94(2)	S(1)–Cu–S(1^{i})	82.19(11)	Cl–Cu–S(4)	124.58(4)	S(7)–Cu(1)–S(4)	89.60(9)	S(1)–Cu(1)–I(1^{ii})	87.40(3)	I(1)–Cu(2)–I(2)	114.94(3)
S(1)–Cu–S(1^{ii})	136.03(6)	S(1)–Cu–S(1^{ii})	136.7(3)	Cl–Cu–S(7)	111.80(5)	S(1)–Cu(1)–S(4)	92.77(9)	S(1)–Cu(1)–I(1^{iii})	116.63(3)	S(1)–Cu(1)–I(1)	108.30(4)
				S(1)–Cu–S(4)	89.27(4)	S(7)–Cu(1)–Br(1)	113.09(7)	I(1)–Cu(1)–I(1^{ii})	122.65(2)	S(9^{i})–Cu(1)–I(1)	107.84(4)
				S(1)–Cu–S(7)	125.10(5)	S(1)–Cu(1)–Br(1)	111.75(7)	I(1)–Cu(1)–I(1^{iii})	114.67(3)	S(1)–Cu(1)–I(2)	104.56(4)
				S(4)–Cu–S(7)	85.99(4)	S(4)–Cu(1)–Br(1)	115.35(8)	I(1^{ii})–Cu(1)–I(1^{iii})	102.34(2)	S(9^{i})–Cu(1)–I(2)	117.91(4)
				Cl–Cu(′)–S(1)	117.7(3)	S(10^{i})–Cu(2)–Br(1)	123.52(8)	Cu(1)–I(1)–Cu(1^{i})	62.73(3)	S(1)–Cu(1)–S(9^{i})	101.26(5)
				Cl–Cu(′)–S(7)	112.3(3)	S(10^{i})–Cu(2)–Br(2)	101.54(8)	Cu(1)–I(1)–Cu(1^{ii})	55.32(2)	S(5^{ii})–Cu(2)–I(1)	111.94(4)
				S(1)–Cu(′)–S(7)	128.4(3)	Br(1)–Cu(2)–Br(2)	113.57(7)	Cu(1^{i})–I(1)–Cu(1^{ii})	57.11(2)	S(13^{iii})–Cu(2)–I(1)	108.64(4)
						S(10^{i})–Cu(2)–Br(2^{ii})	102.29(9)	Cu(1)–S(1)–C(2)	109.0(2)	S(5^{ii})–Cu(2)–I(2)	96.60(4)
						Br(1)–Cu(2)–Br(2^{ii})	107.89(5)	Cu(1)–S(1)–C(3^{iv})	105.4(2)	S(13^{iii})–Cu(2)–I(2)	111.59(4)
						Br(2)–Cu(2)–Br(2^{ii})	106.47(5)			S(5^{ii})–Cu(2)–S(13^{iii})	112.84(5)
						S(10^{i})–Cu(2)–Cu(2^{ii})	110.18(7)			Cu(1)–I(1)–Cu(2)	64.96(3)
						Br(1)–Cu(2)–Cu(2^{ii})	126.17(6)			Cu(1)–I(2)–Cu(2)	64.13(3)
						Br(2)–Cu(2)–Cu(2^{ii})	53.58(4)				
						Br(2^{ii})–Cu(2)–Cu(2^{ii})	52.88(4)				
						Cu(1)–Br(1)–Cu(2)	111.49(7)				
						Cu(2)–Br(2)–Cu(2^{ii})	73.53(5)				

Symmetry operators: **1** and **2**, i $-x, -y, z$; ii $x, -y, z$; **4**, i $x + 0.5, -y - 0.5, z + 0.5$; ii $-x, -y, -z$; **5**, i $-y - 1, x + 0.5, -z - 2$; ii $-x + 0.5, -y + 1.5, z$; iii $y - 0.5, -x + 1, -z - 2$; iv $-y + 1.5, x + 1, z$; **6**, i $-0.5 - x, 0.5 + y, -0.5 - z$; ii $-1 - x, -y, -z$; iii $0.5 + x, 0.5 - y, 0.5 + z$.

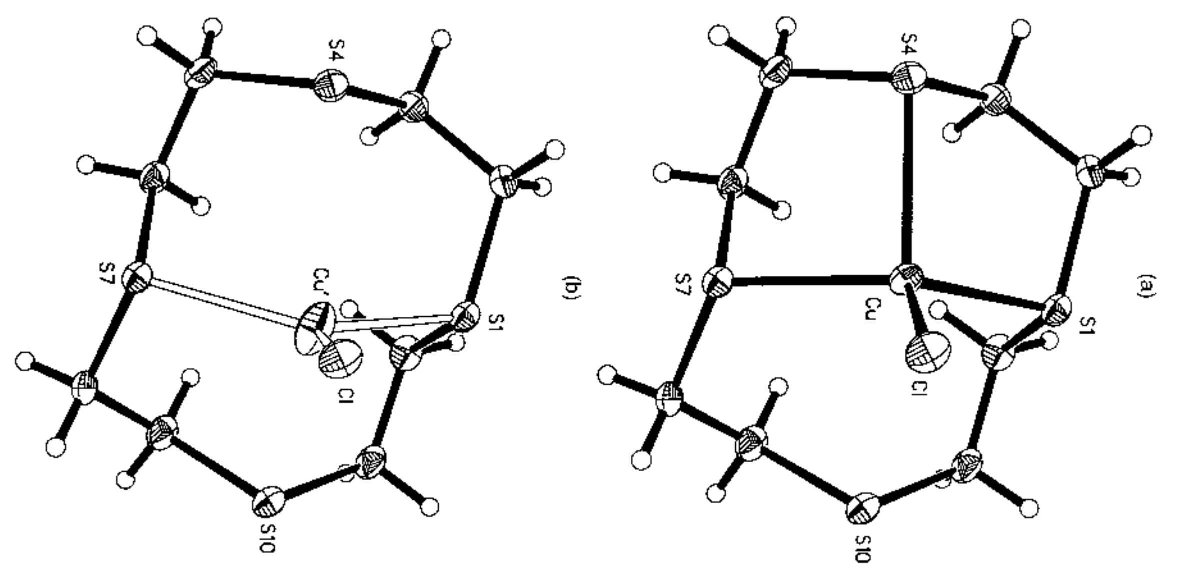


Fig. 3 View of the copper(I) co-ordination environments in the major (a; tetrahedral) and minor (b; trigonal planar) components of complex **3**. Bonds to major component and common bonds are filled and those to minor component only are open.

distorted trigonal planar co-ordination geometry Σ(angles) = 359.5° with two contacts to sulfur atoms [Cu–S 2.279(8), 2.320(8) Å] and one to a Cl^- anion [Cu–Cl 2.266(7) Å]. The other two sulfur centres cannot be considered to be co-ordinated [Cu · · · S 2.896(6), 2.957(6) Å].

Molecular structure of [Cu_4Br_4([12]aneS_4)$_2$]$_\infty$ 4

The structure determination revealed a two-dimensional polymeric network for [Cu_4Br_4([12]aneS_4)$_2$]$_\infty$ **4**. The structure is related to that of **3**. It contains the fragment [CuBr([12]aneS_4)] (Fig. 5), the copper(I) centre of which has a similar tetrahedral co-ordination environment to that of the copper(I) centre found in the major component of **3** [Fig. 3(a)]. That is, the copper(I) cation is co-ordinated to the Br^- anion [Cu–Br 2.410(2) Å] and to three of the four sulfur donors of the [12]aneS_4 macrocycle in an endocyclic manner [Cu–S 2.324(2), 2.385(3), 2.319(2) Å] giving a tetrahedral co-ordination sphere. The macrocycle adopts a [3333] conformation (Table 3).

Whereas in complex **3** the [CuX([12]aneS_4)] units remain discrete, in **4** two units are linked through a centrosymmetric Cu_2Br_2 rhomboid dimer [Cu–Br 2.516(2), 2.539(2) Å; Fig. 6]. Furthermore, the fourth sulfur centres of the macrocycles co-ordinate in an exocyclic manner to two other Cu_2Br_2 rhomboid

Table 3 Selected torsion angles (°) for complexes **1**–**6**

1		**2**		**3**	
S(1)–C(2)–C(3)–S(1^{i})	58.4(4)	S(1)–C(2)–C(3)–S(1^{i})	−58.9(12)	C(12)–S(1)–C(2)–C(3)	69.9(2)
C(2)–C(3)–S(1^{iii})–C(2^{iii})	−164.2(3)	C(2)–C(3)–S(1^{iii})–C(2^{iii})	−75.5(13)	S(1)–C(2)–C(3)–C(4)	59.8(2)
C(3^{iii})–S(1)–C(2)–C(3)	76.2(4)	C(3^{iii})–S(1)–C(2)–C(3)	162.4(7)	C(2)–C(3)–S(4)–C(5)	−146.2(2)
				C(3)–S(4)–C(5)–C(6)	77.1(2)
				S(4)–C(5)–C(6)–S(7)	54.8(2)
				C(5)–C(6)–S(7)–C(8)	−178.8(2)
				C(6)–S(7)–C(8)–C(9)	69.7(2)
				S(7)–C(8)–C(9)–S(10)	65.8(3)
				C(8)–C(9)–S(10)–C(11)	−141.0(2)
				C(9)–S(10)–C(11)–C(12)	71.5(2)
				S(10)–C(11)–C(12)–S(1)	60.3(3)
				C(11)–C(12)–S(1)–C(2)	177.1(2)
5		**6**		**4**	
C(16)–S(1)–C(2)–C(3)	176.5(3)	C(12)–S(1)–C(2)–C(3)	−73.2(7)	C(3^{iv})–S(1)–C(2)–C(3)	−69.8(4)
S(1)–C(2)–C(3)–C(4)	−48.9(5)	S(1)–C(2)–C(3)–S(4)	−63.8(8)	S(1)–C(2)–C(3)–S(1^{v})	172.6(2)
C(2)–C(3)–C(4)–S(5)	−48.3(5)	C(2)–C(3)–S(4)–C(5)	150.7(6)	C(2)–C(3)–S(1^{v})–C(2^{v})	−74.0(4)
C(3)–C(4)–S(5)–C(6)	−74.8(4)	C(3)–S(4)–C(5)–C(6)	−74.6(7)		
C(4)–S(5)–C(6)–C(7)	102.5(4)	S(4)–C(5)–C(6)–S(7)	−52.0(8)		
S(5)–C(6)–C(7)–C(8)	64.9(5)	C(5)–C(6)–S(7)–C(8)	170.6(6)		
C(6)–C(7)–C(8)–S(9)	−175.9(3)	C(6)–S(7)–C(8)–C(9)	−73.6(6)		
C(7)–C(8)–S(9)–C(10)	−179.9(3)	S(7)–C(8)–C(9)–S(10)	−75.3(7)		
C(8)–S(9)–C(10)–C(11)	−71.5(4)	C(8)–C(9)–S(10)–C(11)	148.4(6)		
S(9)–C(10)–C(11)–C(12)	−62.9(5)	C(9)–S(10)–C(11)–C(12)	−59.8(8)		
C(10)–C(11)–C(12)–S(13)	178.7(3)	S(10)–C(11)–C(12)–S(1)	−63.3(8)		
C(11)–C(12)–S(13)–C(14)	−118.8(4)	C(2)–S(1)–C(12)–C(11)	179.3(6)		
C(12)–S(13)–C(14)–C(15)	72.9(4)				
S(13)–C(14)–C(15)–C(16)	174.8(3)				
C(14)–C(15)–C(16)–S(1)	172.6(3)				
C(2)–S(1)–C(16)–C(15)	−77.9(4)				

Symmetry operators: **1**, i $x, -y, z$; iii $-x, y, z$; **2**, i $-x, y, z$; iii $x, -y, z$; **5**, iv $-y + 1.5, x + 1, z$; v $y - 1, -x + 1.5, z$.

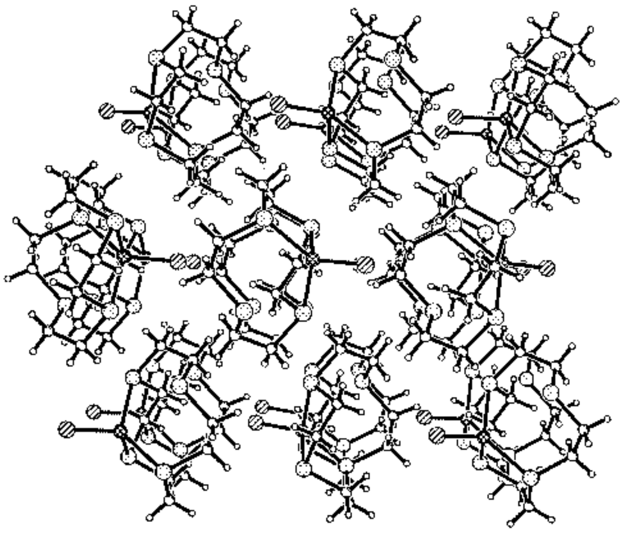


Fig. 4 View of the packing in complex **3**, showing the molecules arranged into sheets in an anti-parallel fashion giving overall a non-polar arrangement (Cu, cross hatched; Cl, hatched; S, dotted; C, shaded; H, plain).

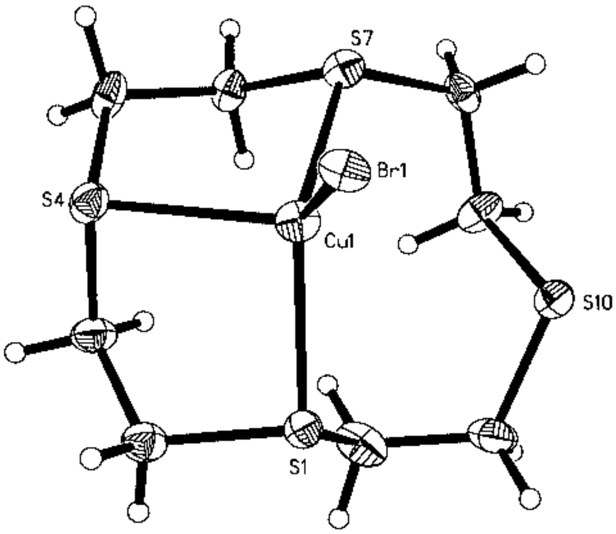


Fig. 5 The [CuBr([12]aneS$_4$)] moiety contained within complex **4**.

dimers to create a polymeric structure (Fig. 7). The Cu$_2$Br$_2$ rhomboid dimer connecting unit has four available co-ordination sites, which are occupied by four [CuBr([12]aneS$_4$)] moieties, two of which co-ordinate through Br$^-$ anions [Cu–Br 2.429(2) Å] and two through S atoms [Cu–S 2.318(3) Å]. Consequently each macrocycle has one endocyclically co-ordinated copper(I) ion and one exocyclically co-ordinated copper(I) ion, a configuration previously seen in [Cu([14]aneS$_4$)(ClO$_4$)]$_\infty$.[14a] The overall two-dimensional polymeric structure in **4** has a (4,4) topology (Fig. 7).

An alternative description of the binuclear unit shown in Fig. 6 is that of two [12]aneS$_4$ macrocycles connected by a Cu$_4$Br$_4$ moiety, which adopts a novel structural type, for which we propose the term open-cubane tetramer [Scheme 4(c)]. Previously, two types of Cu$_4$X$_4$ (X = halide) moiety have been described: the cubane tetramer[20,23,24] [Scheme 4(a)] and the step-cubane tetramer[24a,32] [Scheme 4(b)]. The step-cubane tetramer is derived from the cubane tetramer by the breaking of two Cu–X bonds *trans* located in the same face of the tetramer. The tetrahedral co-ordination of the two copper centres is completed by addition of an extra donor atom giving two in total. The open-cubane tetramer is derived from the step-cubane tetramer by breaking one of the two Cu–X bonds associated with each of the terminal copper centres and completing the tetrahedral co-ordination sphere of the terminal copper centres by the addition of a further donor atom giving three in total

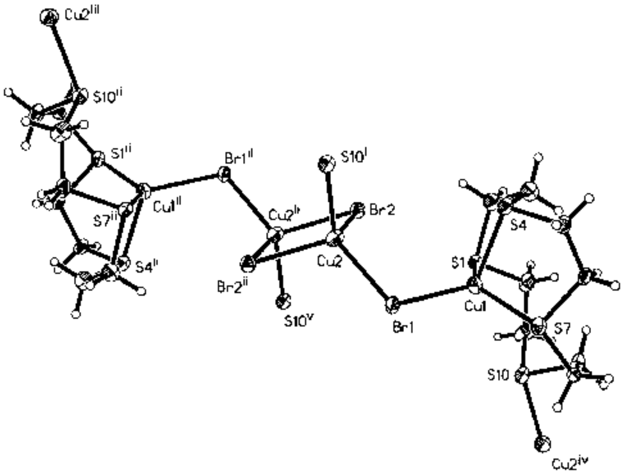


Fig. 6 View of the connectivities of Cu_4Br_4 open cubane tetramers and [12]aneS_4 macrocycles in complex **4**. Symmetry codes: i $-x, -y, -z$; ii $-0.5 + x, -0.5 - y, -0.5 + z$; iii $0.5 - x, 0.5 + y, 0.5 - z$; iv $0.5 + x, -0.5 - y, 0.5 + z$; v $-0.5 - x, 0.5 + y, -0.5 - z$.

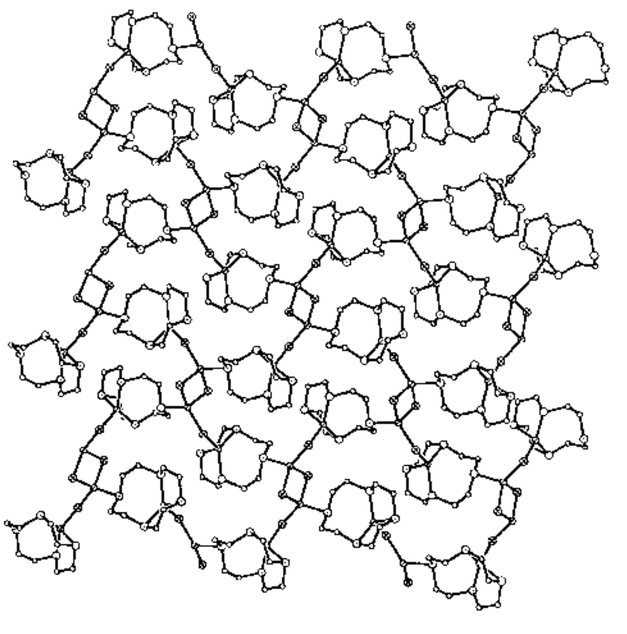


Fig. 7 View of the two-dimensional framework in complex **4** (Br, cross hatched; Cu, hatched; S, dotted; C, shaded).

(Scheme 4). The co-ordination requirements of the open-cubane moiety are best satisfied by a tridentate donor and a monodentate donor, a combination the [12]aneS_4 macrocycle can provide. A copper halide motif with a similar connectivity has been reported by Busch and co-workers.[33] It consists of two copper(II) cations bridged by a $[Cu_2Cl_4]^{2-}$ anion creating a $[Cu_4Cl_4]^{2+}$ unit. The principal difference between this and the Cu_4Br_4 open cubane tetramer is that the copper centres of the central Cu_2Cl_2 fragment of the Cu_4Cl_4 moiety described by Busch do not have a co-ordinated donor atom.

Molecular structure of $[Cu_4I_4([12]aneS_4)]_\infty$ 5

The structure determination revealed a two-dimensional polymeric network for $[Cu_4I_4([12]aneS_4)]_\infty$ **5**. The asymmetric unit consists of a copper(I) ion, one iodide ion and one quarter of a [12]aneS_4 macrocycle [Cu–I 2.6022(8), 2.6107(7), 3.0212(8) Å; Cu–S 2.2852(12) Å]. The elaboration of the structure corresponds to a Cu_4I_4 cubane tetramer species linked through each Cu atom to four separate [12]aneS_4 macrocycles, all of which adopt a $[3333]_4$ conformation (Fig. 8). The disposition of the four metal atoms co-ordinated to each macrocycle is such that all four are on the same side as shown in Scheme 2(c).

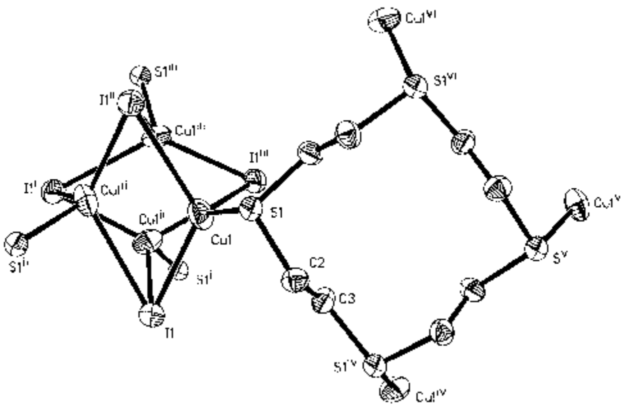
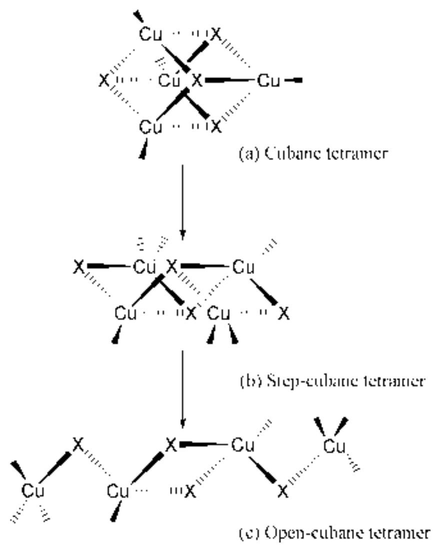


Fig. 8 The connectivities of the Cu_4I_4 cubane tetramer and [12]aneS_4 macrocycle in complex **5**. Symmetry codes: i $0.5 - x, 1.5 - y, z$; ii $-0.5 + y, 1 - x, 2 - z$; iii $1 - y, 0.5 + x, 2 - z$; iv $-1 - y, 1.5 - x, z$; v $0.5 - x, 2.5 - y, z$; vi $1.5 - y, 1 + x, z$.



Scheme 4 The relationship between Cu_4X_4 (X = halide) moieties: (a) cubane tetramer, (b) step-cubane tetramer and (c) open-cubane tetramer. (a) is derived from (b) and (c) is derived from (b) each through cleavage of two Cu–X bonds resulting in the need for two new Cu–donor atom bonds in each transformation.

Since both the Cu_4I_4 moieties and the [12]aneS_4 macrocycles have connectivities of four, the structure contains an equal number of each arranged to give a two-dimensional sheet of (4,4) topology (Fig. 9). The constituent 14-membered metallocycles comprise two edges of separate [12]aneS_4 macrocycles and two faces of separate Cu_4I_4 cubane tetramers. Sheets are stacked in a front to back fashion such that each sheet overlaps exactly with adjacent sheets (Fig. 9). This packing method is not totally efficient with cavities, centred at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{6})$ and at $(\frac{3}{4}, \frac{3}{4}, \frac{5}{6})$, between stacked macrocycles.[34] The cavities (volume 17.6 Å^3) are not sufficiently large to accommodate guest molecules.

Although discrete molecular compounds involving Cu_4X_4 cubane tetramers are commonplace, polymeric species are rare. $[Cu_4I_4(Et_2S)_3]_\infty$ exists as one-dimensional chains comprising alternating Cu_4I_4 cubane units and bridging Et_2S ligands, with terminal Et_2S ligands occupying the other copper co-ordination sites in the Cu_4I_4 moiety.[35] $[Cu_4I_4(Me_6[12]aneSe_3)]_\infty$ exists as a three-dimensional architecture with Cu_4I_4 cubane tetramers linked through μ-Me_6[12]aneSe_3 macrocycles to create doubly interpenetrated diamondoid arrays.[36]

Molecular structure of $[Cu_2I_2([16]aneS_4)]_\infty$ 6

The structure determination reveals a three-dimensional extended architecture for $[Cu_2I_2([16]aneS_4)]_\infty$ **6**. The asymmetric

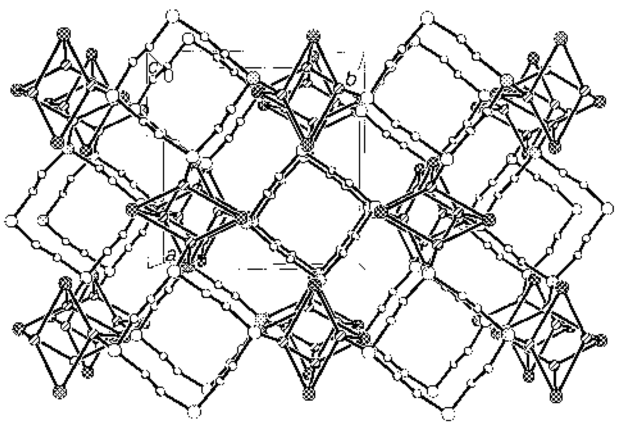


Fig. 9 View of the stacking of two sheets comprising Cu_4I_4 cubane tetramers and [12]aneS_4 macrocycles in complex **5** (I, cross hatched; Cu, hatched; S, dotted; C, shaded).

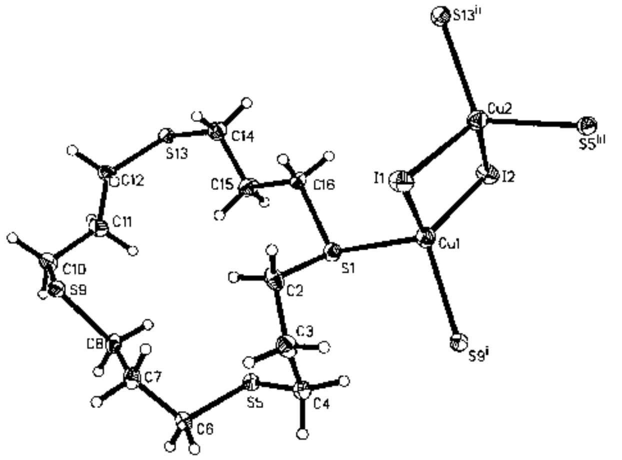


Fig. 10 View of the asymmetric unit of complex **6**. Symmetry codes: i $-0.5 - x, 0.5 + y, -0.5 - z$; ii $0.5 + x, 0.5 - y, 0.5 + z$; iii $-1 - x, -y, -z$.

unit consists of two copper(I) and two iodide ions, which form a rhomboid dimer [Cu–I = 2.5972(9), 2.6182(9), 2.6317(9), 2.6702(9) Å], and one complete [16]aneS_4 macrocycle (Fig. 10). Selected molecular geometry parameters are given in Tables 1 and 2. The Cu_2I_2 moiety is co-ordinated by four crystallographically distinct sulfur atoms, from separate macrocycles, in a pseudo square planar arrangement [Cu–S 2.292(2), 2.304(2), 2.346(2), 2.357(2) Å] (Fig. 11). The [16]aneS_4 molecule has an unusual distorted conformation with eight torsion angles less than 90° (Table 3) which allows it to bind four copper atoms from separate Cu_2I_2 dimers in a pseudo tetrahedral geometry (Fig. 11).

The Cu_2I_2 dimers are linked by [16]aneS_4 macrocycles, which use adjacent sulfur atoms to act as exocyclic bidentate bridges, in two distinct arrangements. Firstly, an alternating sequence of two macrocycles and two dimers link to form a 16-membered metallocycle, and secondly an alternating sequence of macrocycles and dimers link to form a spiral structure which propagates the 3-D network structure. Whereas both copper atoms of the dimers are involved in the metallocycles only one is involved in the spiral structure. A precedence exists for the former arrangement in the honeycomb structure of $[Cu_2I_2(4,4'\text{-bipy})]_\infty$,[21,22] first described by Yaghi and Li[22a] and in $[Cu_4I_4(Me_6[12]aneSe_3)]_\infty$, first described by Adams *et al.*[36] The 16-membered metallocycles are similar to 14-membered metallocycles found in **5**, the only difference being due to the C_3 and C_2 linkers of [16]aneS_4 and [12]aneS_4, respectively.

Since there are equal numbers of Cu_2I_2 dimers and [16]aneS_4 units in complex **6** the overall architecture is similar to the structure of PtS (Fig. 11).[37] The correspondence is shown in Fig. 12 which includes a view of the structure of **6** down the *c* axis, a schematic of this view and a schematic of the corresponding view in the PtS structure. PtS-like networks are rare in metal organic frameworks. Previously, they have been produced using either a mixture of square planar and tetrahedral metal centres linked through linear rods[38] (for example in $\{[Cu^IPt(CN)_4]^-\}_\infty$)[39] or using tetrahedral metal centres and either metalloporphyrins[40] or pseudo-D_{4h} organic moieties[5a,41] (for example in $\{[Cu(TCNB)]^+\}_\infty$ [TCNB = 1,2,4,5-tetracyanobenzene][5a]). Complex **6** is, to our knowledge, the first example in which a tetrahedral organic ligand and a pseudo square planar metal fragment have been employed in the construction of a PtS-like co-ordination polymer.

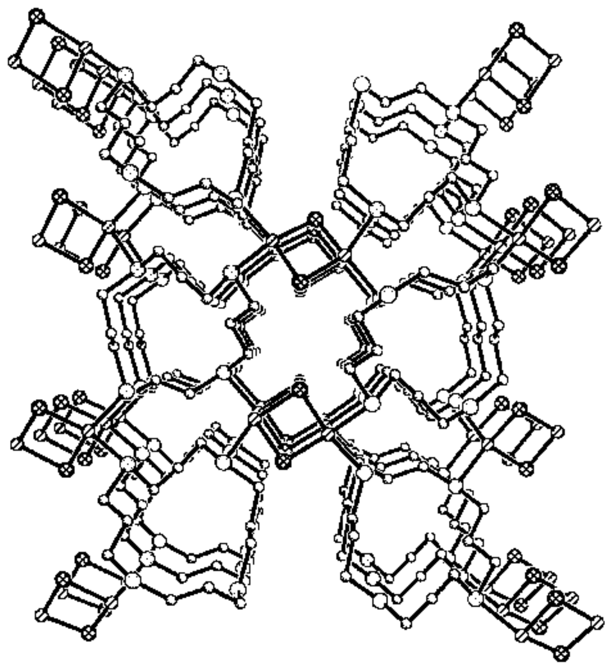


Fig. 11 The extended architecture of complex **6**, viewed perpendicular to the (1,0,0) plane, showing the pseudo square planar Cu_2I_2 dimers and pseudo tetrahedral [16]aneS_4 macrocycles (I, cross hatched; Cu, hatched; S, dotted; C, shaded).

Conclusion

Reaction stoichiometry is of paramount importance in copper(I) halide–cyclic thioether systems. As the proportion of copper(I) halide in the CuX : [12]aneS_4 system is increased the molar ratio in the products increases from 1 : 1 through 2 : 1 to 4 : 1. Whereas the 1 : 1 products (**1**–**3**) are discrete molecules the 2 : 1 (**4**) and 4 : 1 (**5**) products are two-dimensional co-ordination polymers. The building block in the 4 : 1 product, $[Cu_4I_4([12]aneS_4)]_\infty$, is the well known Cu_4I_4 cubane tetramer (Scheme 4a). That in the 2 : 1 product, $[Cu_4Br_4([12]aneS_4)_2]_\infty$, is the novel Cu_4Br_4 open-cubane tetramer (Scheme 4c). The self-assembly of the latter, rather than the anticipated Cu_2Br_2 rhomboid dimer, is attributed to the molecular recognition properties of the [12]aneS_4 macrocycle, which acts as a tridentate chelate towards one copper centre and as a monodentate ligand towards a second copper centre.

The [12]aneS_4 macrocycle also acts as a tridentate chelate in complex **3**. In **1** and **2** however it acts as a tetradentate chelate. We are uncertain of the reason for this difference in behaviour but postulate that the increase in co-ordination number may be attributed to the decreasing ligating ability of the halides as the group is descended.

In the discrete molecular products, **1**–**3**, the thioether donors co-ordinate the copper centres in an endocyclic manner (Scheme 2a). In **4** three thioether donors ligate in an endocyclic

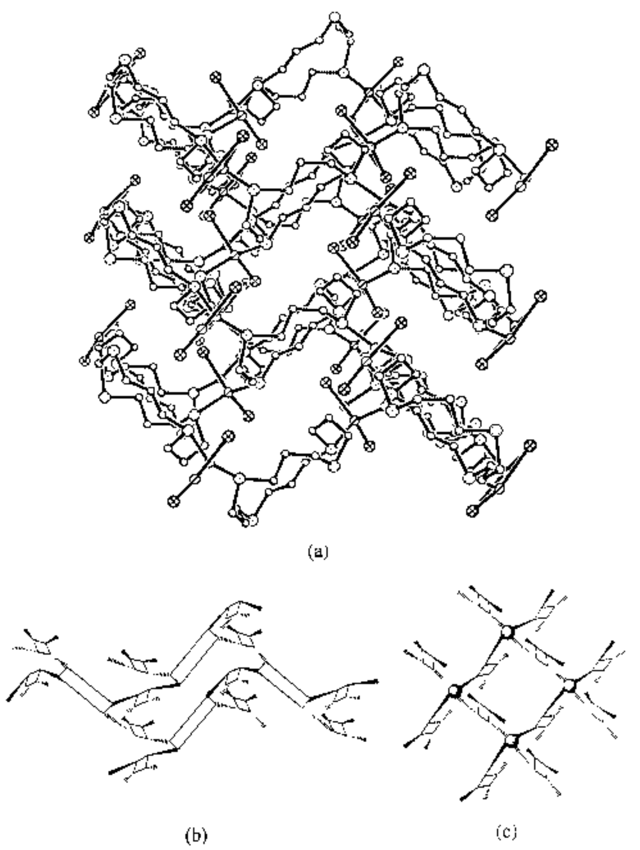


Fig. 12 (a) The extended architecture of complex **6**, viewed perpendicular to the (0,0,1) plane I, cross hatched; Cu, hatched; S, dotted; C, shaded), (b) a schematic of this view pseudo square planar Cu_2I_2 rhomboid dimers are shown as diamonds and pseudo tetrahedral [16]aneS_4 macrocycles as rectangles) and (c) a schematic of the PtS structure viewed perpendicular to the (0,0,1) plane square planar platinum(II) cations are shown as diamonds and tetrahedral sulfide anions as shaded circles) showing the correspondence between the two structures.

and one in an exocyclic manner (Scheme 2b). In **5** all four thioether donors adopt exocyclic co-ordination geometries (Scheme 2c). The macrocycles in **1**–**5** all adopt a [3333] conformation but they differ in the siting of the corners, which are at carbon atoms when ligating in an endocyclic manner (**1**–**4**) and at sulfur atoms when ligating in an exocyclic manner (**5**).

In the only product to have been crystallised from CuX : [16]aneS_4 systems, **6**, the Cu_2I_2 rhomboid dimers act as square planar connecting units and the [16]aneS_4 macrocycles as tetrahedral connecting units. These building blocks link to generate a three-dimensional architecture with the PtS structure. We believe this is the first such co-ordination polymer: in all previous examples of co-ordination polymers with the PtS structure the geometries of the two building blocks are reversed, with tetrahedral metal centres and square planar organic connecting units.

Experimental

All reagents (Aldrich) were used as received. When using CuBr and CuCl all procedures were carried out under argon and all solvents freshly distilled, degassed and dried by literature procedures.[42] Elemental analysis (C, H, N) was performed by the Nottingham University School of Chemistry Microanalytical Service using a Perkin-Elmer 240B instrument. Infrared spectra were obtained (as KBr pressed pellets) using a Nicolet Avatar 360 FTIR spectrometer.

Preparations

[CuBr([12]aneS_4)]. All six compounds were prepared using a similar procedure. That for [CuBr([12]aneS_4)] is typical. CuBr (10.0 mg, 0.070 mmol) in MeCN (10 cm^3) was added to a well stirred solution of [12]aneS_4 (16.8 mg, 0.070 mmol) in CH_2Cl_2 (20 cm^3). The mixture was stirred at room temperature overnight, and the resulting white precipitate filtered off, washed with CH_2Cl_2 and dried *in vacuo* (yield: 16.8 mg, 63%). Found (calc. for $C_8H_{16}BrCuS_4$) (%): C, 23.53 (25.03); H, 3.73 (4.21). IR (KBr disc), $\tilde{\nu}$/cm^{-1}: 2940w, 2904w, 1434m, 1393s, 1260s, 1240w, 917s, 856m and 835m. Crystals suitable for X-ray diffraction studies were grown by layered diffusion of solutions of CuBr in MeCN and [12]aneS_4 in CH_2Cl_2 in the appropriate stoichiometries.

[CuI([12]aneS_4)]. Treatment of CuI (9.0 mg, 0.047 mmol) with [12]aneS_4 (11.4 mg, 0.047 mmol) gave a yield of 13.0 mg, 64%. Found (calc. for $C_8H_{16}CuIS_4$) (%): C, 22.01 (22.14); H, 3.53 (3.72). IR (KBr disc), $\tilde{\nu}$/cm^{-1}: 2939w, 2903w, 1435w, 1421w, 1405s, 1260m, 1245w, 1120w, 913m, 853m and 827w.

[CuCl([12]aneS_4)]. Treatment of CuCl (8.2 mg, 0.083 mmol) with [12]aneS_4 (20.0 mg, 0.083 mmol) gave a yield of 19.1 mg, 68%. Found (calc. for $C_8H_{16}ClCuS_4$) (%): C, 28.10 (28.27); H, 4.50 (4.76). IR (KBr disc), $\tilde{\nu}$/cm^{-1}: 2960w, 2935w, 2914w, 1440m, 1414s, 1399s, 1261s, 1168w, 1127w, 923m, 897w, 840s, 677w and 446w.

[Cu_4Br_4([12]aneS_4)$_2$]$_\infty$. Treatment of CuBr (17.9 mg, 0.12 mmol) with [12]aneS_4 (15 mg, 0.062 mmol) gave a yield of 7.1 mg, 22%. Found (calc. for $C_8H_{16}Br_2Cu_2S_4$) (%): C, 20.33 (18.22); H, 3.07 (3.06). IR (KBr disc), $\tilde{\nu}$/cm^{-1}: 2905w, 1429m, 1405s, 1259s, 1240m, 1117w, 915s, 855m, 835w and 666w.

[Cu_4I_4([12]aneS_4)]$_\infty$. Treatment of CuI (20 mg, 0.11 mmol) with [12]aneS_4 (6.3 mg, 0.026 mmol) gave a yield of 16.0 mg, 61%. Found (calc. for $C_8H_{16}Cu_4I_4S_4$) (%): C, 10.35 (9.59); H, 1.48 (1.61). IR (KBr disc), $\tilde{\nu}$/cm^{-1}: 2945w, 2918m, 1424s, 1384s, 1283m, 1260w, 1183m, 1127m, 927w, 753w and 671s.

[Cu_2I_2([16]aneS_4)]$_\infty$. Treatment of CuI (10 mg, 0.053 mmol) with [16]aneS_4 (7.8 mg, 0.026 mmol) gave a yield of 14.2 mg, 80%. Found (calc. for $C_{12}H_{24}Cu_2I_2S_4$) (%): C, 20.72 (21.09); H, 3.29 (3.55). IR (KBr disc), $\tilde{\nu}$/cm^{-1}: 2950w, 2919s, 1433s, 1414s, 1334w, 1285m, 1252s, 1199w, 1035w, 729m and 695m.

Crystallography

Single crystal X-ray experiments for compounds **1**, **3**, **4** and **6** were performed on a Stoë Stadi-4 four circle diffractometer equipped with an Oxford Cryosystems open flow cryostat[43] [graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å)]. For **2** and **5** data collection was undertaken on a Bruker SMART diffractometer equipped with an Oxford Cryosystems open flow cryostat.[43] Other details of crystal data, data collection and processing are given in Table 4. The structures of all compounds were solved by direct methods using SHELXS 97[44] and full-matrix least squares refinement employed SHELXL 97.[45] All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Structure **2** was found to be merohedrally twinned so as to resemble the higher (4/*mmm*) Laue symmetry and this was modelled with the twin law (010 100 00-1) and a parameter to determine the proportions of the twin components which converged to values of 78.4(3) and 21.6(3)%. Structure **3** has the copper atom disordered over two sites with the major component comprising 87% of the total.

CCDC reference number 186/2275.

Table 4 Crystallographic data for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_8H_{16}BrCuS_4$	$C_8H_{16}CuIS_4$	$C_8H_{16}ClCuS_4$	$C_8H_{16}Br_2Cu_2S_4$	$C_8H_{16}Cu_4I_4S_4$	$C_{12}H_{24}Cu_2I_2S_4$
M	383.90	430.89	339.44	527.35	250.55	677.43
Crystal system	Tetragonal	Tetragonal	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group	$I4$	$I4$	$P2_1/c$	$P2_1/n$	$P4/n$	$P2_1/n$
a/Å	8.7331(12)	8.8510(13)	13.469(3)	7.295(7)	11.2982(9)	7.456(2)
b/Å	—	—	7.6268(15)	13.464(3)	—	14.804(3)
c/Å	8.251(2)	8.332(2)	13.578(3)	15.200(3)	8.2530(10)	18.470(5)
β/°	—	—	115.65(3)	98.68(3)	—	98.33(3)
U/Å^3	629.3(2)	652.7(2)	1257.3(4)	1476(2)	1053.5(2)	2017.2(9)
Z	2	2	4	4	2	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
μ(Mo-Kα)/mm^{-1}	5.533	4.639	2.573	8.83	10.23	5.572
Reflections collected	2052	705	2216	2876	6486	3540
Unique reflections, R_{int}	563, 0.142	434, 0.077	2214, 0.101	2876, 0.070	1257, 0.055	3540, —
Observed [$F > 4\sigma(F)$]	561	430	2009	2261	1036	3265
$R1$ [$F > 4\sigma(F)$]	0.0243	0.0552	0.0328	0.0511	0.0305	0.0304
$wR2$ (all data)	0.0469	0.1329	0.1215	0.1293	0.0864	0.0748

See http://www.rsc.org/suppdata/dt/b0/b008202n/ for crystallographic files in .cif format.

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