DALTON
FULL PAPER

Self-assembling copper(I) clusters involving electron-deficient, quadruply bridging thiolate ligands

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The structures of two new compounds containing the $Cu_{12}(\mu_4\text{-}S)_6$ Atlas-sphere cluster have been determined: $(CuBr)_{13}(SR)_6\cdot x H_2O$ (x = *ca.* 1.5) and $(CuCl)_{17}(SR')_6$ (SR = $CH_2CH_2NH_3$, SR′ = $CH_2CH_2NHMe_2$). The zwitterionic ligands are unique amongst simple thiolates in forming μ_4 bridges between four metal ions. The formation of these materials from solutions which contain an excess of the thiolate is discussed.

Somewhat serendipitously, we recently discovered a novel copper(I)–thiolate cluster unit in which the zwitterionic ligand $^{+}NH_3CH_2CH_2S^{-}$ bridges four copper atoms.[1] The basic "Atlas-sphere" core of this compound, $Cu_{12}S_6$, is shown in Fig. 1, and involves a regular octahedron of sulfur atoms with each edge bridged by a copper atom. The thiolate is a neutral ligand and charge balancing is achieved by each copper atom being bound also to a chlorine atom. In the crystal, the Atlas spheres are linked in two dimensions by bridging chlorine and copper atoms so that the overall formula is $[Cu_{13}Cl_{13}(SR)_6]$ (SR = $SCH_2CH_2NH_3$). Water molecules are accommodated, zeolite-like, in the cavities of this supramolecular structure.

Under slightly different conditions, we obtained a more complicated ionic chain-polymer of composition $[Cu_8Cl_8(SR)_6]$, in which the same zwitterionic thiolate ligand plays both μ_3 and μ_4 roles.[2] A related silver complex has recently been reported.[3]

At the time of publishing our previous papers we were unaware that another example of μ_4-SR bridging had just been reported by van Koten and co-workers:[4] $[Cu_8\{SC_6H_3(CH_2NMe_2)_2\text{-}2,6\}_3Br_5]$. We regret this omission, and apologise to these authors. However, they appeared to be unaware of its electron-deficient character, to which we drew attention.[1] Our systems are unique in involving a simple, non-chelating thiolate ligand.

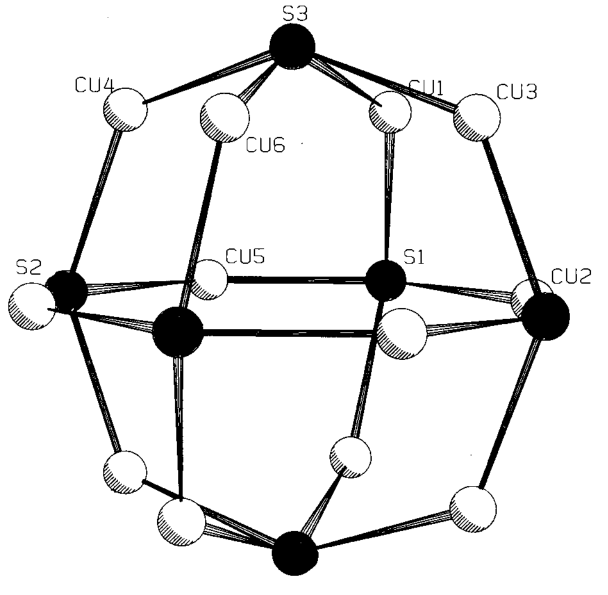

Fig. 1 The basic, centrosymmetric Atlas-sphere. Each sulfur atom (filled circles) carries a $CH_2CH_2NH_3^{+}$ group and each copper at least one halide ligand.

We now present two more derivatives which also involve the Atlas-sphere unit. Their structures are described and compared with the first structure; both similarities and differences are noted. Discussion is given of the possible mode of formation of these beautiful and intriguing clusters.

Experimental

Preparation of $[Cu_{13}Br_{13}(SR)_6]\cdot x H_2O$

Cysteamine (0.566 g, 7.3 mmol) was dissolved in water (100 cm^3) and the pH adjusted to approximately 4 by addition of dilute HBr. Solid copper(I) bromide (0.64 g, 4.5 mmol) was added in small portions, each being allowed to dissolve before the next was added. The final clear solution had a pH of 1.52. White solids were deposited after a few days, which rapidly became brown on contact with air. The filtrate was treated with ethanol and allowed to stand for 3 d, when air-stable white crystals were obtained.

Preparation of $[Cu_{17}Cl_{17}(SR')_6]$

Dimethyl(2-sulfanylethyl)amine hydrochloride (1.41 g, 10 mmol) was dissolved in water and solid copper(I) chloride (0.25 g, 2.5 mmol) added in small portions with continuous stirring. The resulting clear solution was allowed to stand for 5 d, during which white crystals formed.

Under other conditions we have also obtained an adduct of composition $[Cu_3Cl_3(SR)_2]\cdot H_2O$, but not yet been able to obtain crystals.

Crystallography

Both products were characterised by X-ray crystallography, using a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. Structures were solved by direct methods (SHELXS 86)[5a] and refined by full-matrix least squares on F^2 (SHELXL 93).[5b] Owing to the ready loss of water, crystal samples were not reproducible, and the partial occupancy of the water sites and the disorder in the bridging systems meant that the lighter atoms and those of the bridging systems had to be refined isotropically. Further details are recorded in Table 1.

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See http://www.rsc.org/suppdata/dt/1999/243/ for crystallographic files in .cif format.

Table 1 Crystal data and structure refinement details

	$[Cu_{13}Br_{13}(SR)_6]$	$[Cu_{17}Cl_{17}(SR')_6]$
Empirical formula	$C_{12}H_{42}Br_{13}Cu_{13}N_6O_{1.58}S_6$	$C_{24}H_{66}Cl_{17}Cu_{17}N_6S_6$
M	2359.73	2314.02
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1/n$
a/Å	22.074(4)	13.058(4)
b/Å	11.955(2)	36.961(6)
c/Å	21.039(4)	13.417(2)
β/°	115.20(2)	92.54(3)
V/Å^3	5023.7(16)	6469(2)
Z, D_c/Mg m^{-3}	4, 3.120	4, 2.376
μ/mm^{-1}	15.995	6.382
F(000)	4400	4520
Crystal size/mm	0.30 × 0.15 × 0.15	0.40 × 0.25 × 0.25
θ range for data collection/°	1.99 to 25.00	1.66 to 24.02
Index ranges	$-25 \leqslant h \leqslant 23, 0 \leqslant k \leqslant 14, 0 \leqslant l \leqslant 24$	$-10 \leqslant h \leqslant 0, 0 \leqslant k \leqslant 42, -15 \leqslant l \leqslant 15$
Reflections collected/unique	4263/4263 [R(int) = 0.0000]	8886/8886 [R(int) = 0.0000]
ψ-Scan absorption corrections	1.00, 0.63	1.00, 0.72
Maximum and minimum transmission	0.1977 and 0.0864	—
Data/restraints/parameters	4263/20/345	8886/0/631
Goodness of fit on F^2	2.276	1.263
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0867, 0.1908	0.1133, 0.1690
(all data)	0.1082, 0.1965	0.2445, 0.2086
Absolute structure parameter	0.03(7)	—
Largest difference peak and hole/e Å^{-3}	1.911 and −2.040	1.344 and −1.096

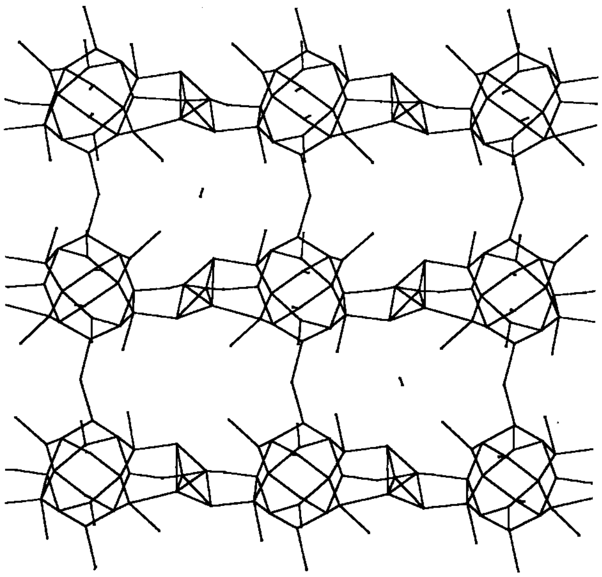

Fig. 2 The sheet structure in $[Cu_{13}Br_{13}(SR)_6]\cdot xH_2O$ (SR = $SCH_2CH_2NH_3$); hydrogen atoms are omitted for clarity. Water molecules occupy approximately half of the available cavities.

Results

Copper(I) chloride dissolves readily in aqueous solutions of cysteamine hydrochloride, $HSCH_2CH_2NH_3^+Cl^-$. The bromide dissolves less readily but the iodide is insoluble. Our previous pH and conductivity studies[2] showed that one proton is released for every copper atom dissolved, confirming that the ligand involved is the zwitterion $^-SCH_2CH_2NH_3^+$ (SR). However, as the addition continues, the ratio of H^+ released to CuCl added decreases, the limiting value being about 0.6. Solid materials can be obtained from these solutions, sometimes rapidly sometimes only after several days. Reproducible analytical data were difficult to obtain, partly due to variable water content, but the majority of products approximated to $[Cu_8X_8(SR)_6]$. In some cases other ratios were obtained, but the data were difficult to interpret, given the obviously polymeric nature of the products (once isolated, they could not be redissolved). Equally, NMR spectra of the solutions gave only single sets of resonances, indicating fast exchange, and solid-state investigations were complicated by loss of water as the samples became warm in the probe. In a few instances crystalline materials were formed, two of which we have reported.[1,2] Of the two new materials now presented one is the bromo-analogue of $[Cu_{13}Cl_{13}(SR)_6]\cdot H_2O$, and has a similar structure. The other is derived from dimethyl(2-sulfanylethyl)amine (the zwitterion $^+HMe_2NCH_2CH_2S^-$ is the ligand); it contains an augmented Atlas-sphere as the core cluster. Owing to the difficulties referred to above, these new compounds have been characterised only by crystallography.

$[Cu_{13}X_{13}(SR)_6]\cdot xH_2O$

The two compounds (X = Cl, x = 1.0; Br, x = *ca.* 1.5) have broadly similar structures, with sheets of Atlas-spheres linked in two dimensions. Both are hydrated: water molecules are loosely held in channels in the lattice and are weakly hydrogen bonded to the NH_3^+ group of the organic ligand and to terminal halogen atoms of the Atlas-spheres (Fig. 2). The bridging systems will be described later; they are similar but not identical.

The two $Cu_{12}S_6$ Atlas-sphere units are effectively identical. Each consists of three Cu_8S_8 rings which intersect gimbal-like at the sulfur atoms. Bond lengths and angles for the bromo compound are given in Tables 2 and 3; ranges and averages are given in Table 4, where they are compared with those of the chloro compound. The Cu–S bond lengths and the Cu–S–Cu and S–Cu–S bond angles have effectively identical ranges in both cases. Our previous analysis[2] shows that the Cu–S bonds for the μ_4-bridging sulfur atoms are marginally longer than those for conventional μ_3 and μ atoms.

Both compounds contain one simple ring, in which all copper atoms are three-co-ordinate (S_2CuX). For the chloride, each of the other two rings contains two copper atoms involved in bridging systems. One bridging system is formed by simple Cu–Cl–Cu links, *i.e.* two adjoining Atlas-spheres share a common chloride ligand [Fig. 3(a)]. The Cu–Cl bond [Cu(5)–Cl(5)] is slightly lengthened by comparison to the terminal Cu–Cl bonds. The other link is formed by inserting a copper atom between chlorine atoms of adjacent Atlas-spheres. This copper atom is disordered between two symmetry-equivalent positions. The Cu–Cl bonds to the Atlas-sphere copper atoms [Cu(4)–

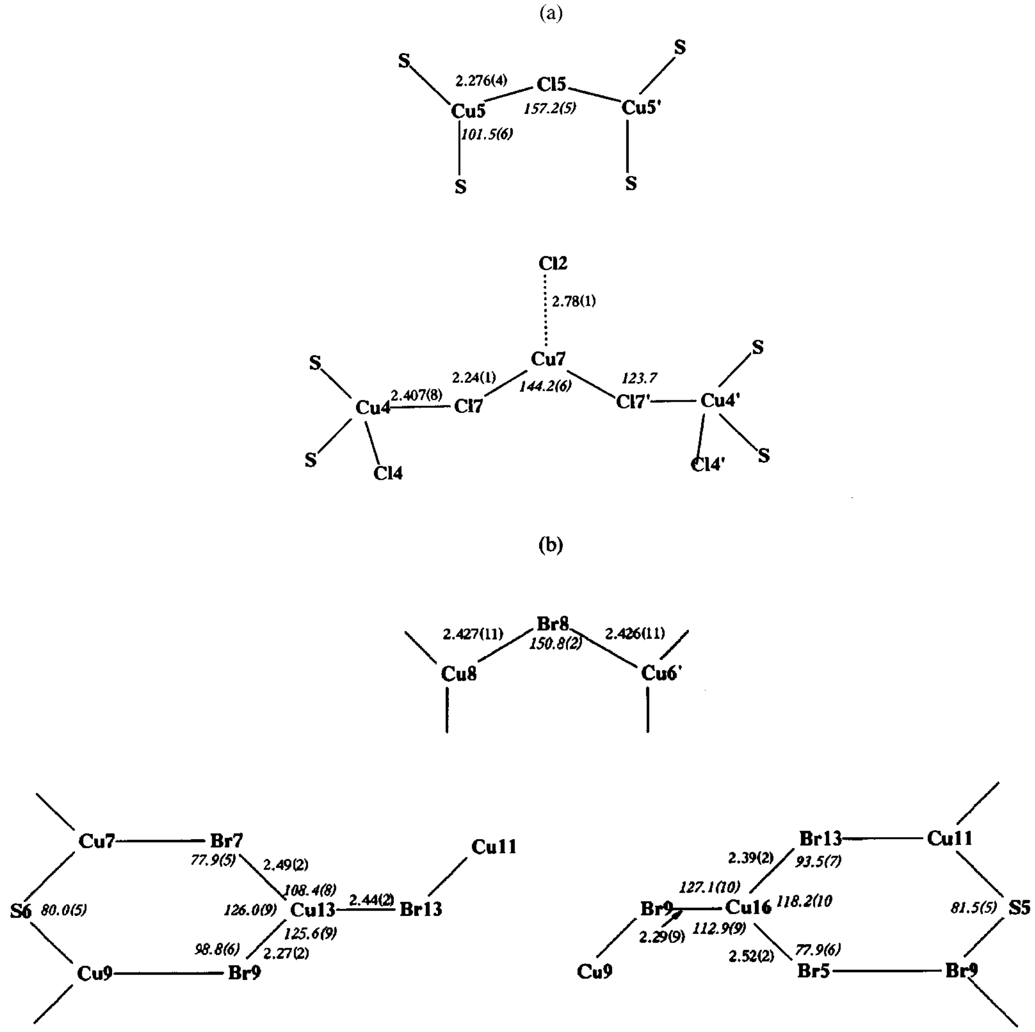

Fig. 3 The bridging systems in (a) $[Cu_{13}Cl_{13}(SR)_6]$, (b) $[Cu_{13}Br_{13}(SR)_6]$ (SR = $SCH_2CH_2NH_3$).

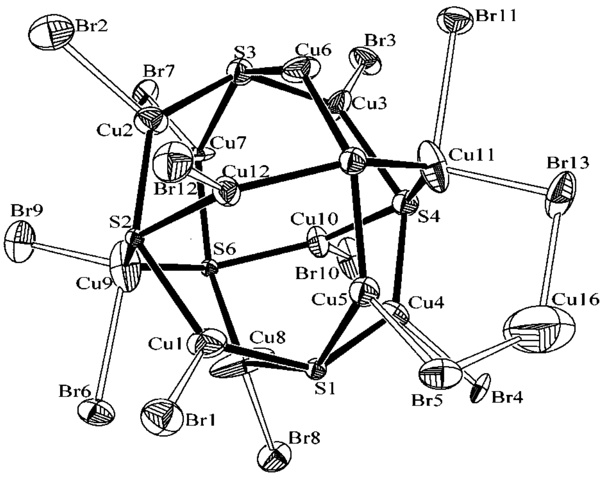

Fig. 4 The structure of $[Cu_{13}Br_{13}(SR)_6]$ (SR = $SCH_2CH_2NH_3$). Note that only one of the four possible bridging copper atoms is shown [Cu(16)].

Cl(7)] are appreciably lengthened (2.41 Å), while those to the bridging copper atom [Cu(7)] are normal (2.12, 2.23 Å). Thus, the bridge approximates to a $CuCl_2^-$ ion linking the two Atlas-spheres. Such an ion would normally be expected to be linear, but the present example has an angle at Cu(7) of only 144°. This may be due to packing constraints, but a long (2.78 Å) interaction with Cl(2) atoms in one of the Atlas-spheres appears to be significant. This chlorine atom lies in the Cu(7)Cl(7)Cl(7′) plane, so that Cu(7) could be regarded as three-co-ordinate.

The stoichiometry of the two bridging systems means that an additional chloride has to be accommodated, and it is bound to Cu(4) which is therefore four-co-ordinate; this is also the copper atom bound to the bridging $CuCl_2^-$. All the copper atoms not involved in bridging interactions are three-co-ordinate and accurately planar (sums of bond angles 359.6–360.0°), but for Cu(5) the sum is only 357.6°; a small distortion is imposed by the bridging.

The bromo compound also contains Atlas-sphere units (Fig. 4) with a slightly different linking system. The simple halide bridge is present, Cu(6)–Br(8′)–Cu(8′), with similar elongation of the Cu–Br bonds [Fig. 3(b)]. There is more twisting involved in these links, and Cu(8) deviates considerably from planarity (angle sum 347.3°). The second bridge is again formed by a single copper atom, this time disordered between four sites with unequal occupation [Cu(13), 0.34; Cu(14), 0.14; Cu(15), 0.17; Cu(16), 0.35; Fig. 5]. The two principal systems are shown in Fig. 3(b). The linking copper atoms [Cu(13),Cu(16)] are bonded to two bromide ligands of one Atlas-sphere and to one from the adjacent sphere, and are accurately planar. The Cu–Br bonds to the Atlas-spheres are somewhat lengthened (2.37–2.48 Å) but those to the linking copper atoms show considerable variation in length (2.27–2.52 Å). A further curiosity is that the angles at the bridging bromine atoms are very sharp (77.9–96.8°). The other two copper atom positions are considerably non-planar, and have larger bond distances to the neighbouring bromine atoms; these distortions are presumably caused by packing constraints.

As with the chloride, the configurations of two of the Atlas-sphere copper atoms [Cu(9),Cu(11)] are slightly distorted from planarity (351, 354°) by contact with an additional bromine atom [Br(11), Br(16) respectively]. The interatomic distance is very large (2.768, 2.766 Å), and would not normally be regarded as a bond; however, the geometry at copper suggests that a modest interaction occurs.

[$Cu_{17}Cl_{17}(SR')_6$] (SR′ = $CH_2CH_2NHMe_2$)

The use of a different zwitterionic ligand produces a modified structure, the bond-length and -angle data for which are given in Tables 5 and 6. A $Cu_{12}(SR')_6$ Atlas-sphere is still present (Fig. 6), with similar geometry and dimensions to those of the other compounds. However, four alternate faces of the S_6 octahedron are capped by an additional copper atom [Cu(16), Cu(27), Cu(35), Cu(48)], each of which is bonded to the chlorine atoms of three separate CuCl units in the Atlas-sphere (Figs. 6, 7). Four additional chlorine atoms [Cl(26), Cl(31), Cl(49), Cl(81)] are situated close to the remaining four faces of the S_6 octahedron. They are situated about 2.5 Å from one copper atom, 2.6–2.7 Å from another and further still from a third. This last distance is too great to have any effect

Table 2 Significant bond lengths (Å) of [$Cu_{13}Br_{13}(SR)_6$]

Br(1)–Cu(1)	2.385(9)	Cu(2)–S(3)	2.312(14)
Br(2)–Cu(2)	2.409(10)	Cu(3)–S(3)	2.212(15)
Br(3)–Cu(3)	2.365(9)	Cu(3)–S(4)	2.325(14)
Br(4)–Cu(4)	2.364(10)	Cu(4)–S(1)	2.199(12)
Br(5)–Cu(5)	2.402(9)	Cu(4)–S(4)	2.220(14)
Br(5)–Cu(16)	2.52(2)	Cu(5)–S(5)	2.239(15)
Br(6)–Cu(9)	2.766(12)	Cu(5)–S(1)	2.246(13)
Br(7)–Cu(7)	2.369(8)	Cu(6)–S(5)	2.228(14)
Br(7)–Cu(13^1)	2.49(2)	Cu(6)–S(3)	2.254(15)
Br(7)–Cu(15^1)	2.50(5)	Cu(7)–S(3)	2.280(15)
Br(8)–Cu(8)	2.427(11)	Cu(7)–S(6)	2.266(13)
Br(8)–Cu(6^2)	2.426(11)	Cu(8)–S(6)	2.259(13)
Br(9)–Cu(14^1)	2.24(4)	Cu(8)–S(1)	2.271(13)
Br(9)–Cu(13^1)	2.27(2)	Cu(9)–S(2)	2.244(14)
Br(9)–Cu(16^1)	2.29(2)	Cu(9)–S(6)	2.281(13)
Br(9)–Cu(9)	2.450(11)	Cu(10)–S(6)	2.215(13)
Br(9)–Cu(15^1)	2.61(6)	Cu(10)–S(4)	2.247(14)
Br(10)–Cu(10)	2.388(9)	Cu(11)–S(4)	2.252(14)
Br(11)–Cu(11)	2.768(12)	Cu(11)–S(5)	2.290(14)
Br(12)–Cu(12)	2.359(9)	Cu(12)–S(5)	2.233(14)
Br(13)–Cu(15)	2.32(5)	Cu(12)–S(2)	2.280(14)
Br(13)–Cu(16)	2.39(2)	S(1)–C(11)	1.828(19)
Br(13)–Cu(13)	2.44(2)	S(2)–C(21)	1.823(17)
Br(13)–Cu(11)	2.478(12)	S(3)–C(31)	1.833(18)
Br(13)–Cu(14)	2.65(4)	S(4)–C(41)	1.81(2)
Cu(1)–S(2)	2.257(14)	S(5)–C(51)	1.812(17)
Cu(1)–S(1)	2.301(12)	S(6)–C(61)	1.83(2)
Cu(2)–S(2)	2.249(14)		

Symmetry relations: (1) $x, y - 1, z$; (2) $x, -y + 1, z + \frac{1}{2}$; (3) $x, -y + 1, z - \frac{1}{2}$; (4) $x, y + 1, z$.

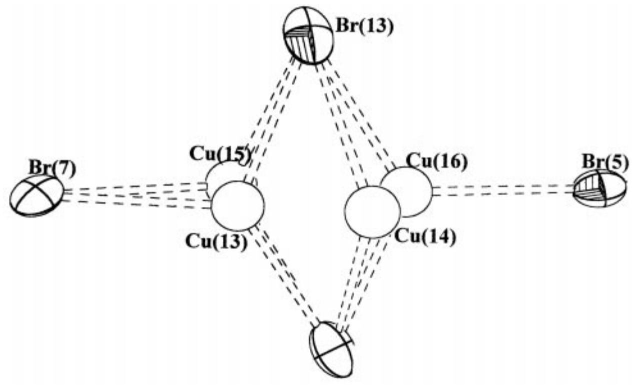

Fig. 5 The complex bridging system in [$Cu_{13}Br_{13}(SR)_6$], showing the four possible positions for the copper atoms.

Table 3 Selected bond angles (°) for [$Cu_{13}Br_{13}(SR)_6$]

S(2)–Cu(1)–S(1)	125.8(5)	S(6)–Cu(10)–Br(10)	115.4(4)	Cu(3)–S(3)–Cu(7)	80.2(5)	Cu(8)–S(6)–Cu(9)	78.9(5)
S(2)–Cu(1)–Br(1)	110.8(4)	S(4)–Cu(10)–Br(10)	112.1(4)	Cu(6)–S(3)–Cu(7)	137.4(6)	Cu(7)–S(6)–Cu(9)	80.0(5)
S(1)–Cu(1)–Br(1)	122.3(4)	S(4)–Cu(11)–S(5)	128.7(6)	C(31)–S(3)–Cu(2)	101.6(10)	Cu(5)–Br(5)–Cu(16)	77.9(6)
S(2)–Cu(1)–Cu(5)	107.4(4)	S(4)–Cu(11)–Br(13)	121.2(5)	Cu(3)–S(3)–Cu(2)	140.1(7)	Cu(7)–Br(7)–Cu(13^1)	77.9(5)
S(1)–Cu(1)–Cu(5)	50.0(3)	S(5)–Cu(11)–Br(13)	101.3(5)	Cu(6)–S(3)–Cu(2)	78.1(5)	Cu(7)–Br(7)–Cu(15^1)	71.1(13)
Br(1)–Cu(1)–Cu(5)	105.8(4)	S(4)–Cu(11)–Br(11)	96.5(5)	Cu(7)–S(3)–Cu(2)	81.9(5)	Cu(8)–Br(8)–Cu(6^2)	150.8(2)
S(2)–Cu(2)–S(3)	131.7(5)	S(5)–Cu(11)–Br(11)	104.6(5)	C(41)–S(4)–Cu(4)	112.1(17)	Cu(14^1)–Br(9)–Cu(13^1)	52.4(11)
S(2)–Cu(2)–Br(2)	112.9(4)	S(5)–Cu(12)–S(2)	132.3(5)	C(41)–S(4)–C(11)	110.5(15)	Cu(13^1)–Br(9)–Cu(16^1)	55.1(6)
S(3)–Cu(2)–Br(2)	115.4(5)	S(5)–Cu(12)–Br(12)	114.8(4)	Cu(4)–S(4)–Cu(11)	86.9(5)	Cu(14^1)–Br(9)–Cu(9)	147.1(10)
S(3)–Cu(3)–S(4)	124.5(5)	S(2)–Cu(12)–Br(12)	112.8(4)	C(41)–S(4)–Cu(10)	108.8(15)	Cu(13^1)–Br(9)–Cu(9)	98.8(6)
S(3)–Cu(3)–Br(3)	123.7(5)	C(11)–S(1)–Cu(4)	111.9(12)	Cu(4)–S(4)–Cu(10)	79.6(5)	Cu(16^1)–Br(9)–Cu(9)	126.3(7)
S(4)–Cu(3)–Br(3)	110.8(5)	C(11)–S(1)–Cu(5)	115.5(14)	Cu(11)–S(4)–Cu(10)	140.6(6)	Cu(14^1)–Br(9)–Cu(15^1)	60.5(15)
S(1)–Cu(4)–S(4)	133.7(6)	Cu(4)–S(1)–Cu(5)	83.9(4)	C(41)–S(4)–Cu(3)	106.9(16)	Cu(16^1)–Br(9)–Cu(15^1)	56.0(13)
S(1)–Cu(4)–Br(4)	113.9(4)	C(11)–S(1)–Cu(8)	105.4(13)	Cu(4)–S(4)–Cu(3)	139.1(6)	Cu(9)–Br(9)–Cu(15^1)	88.2(14)
S(4)–Cu(4)–Br(4)	112.4(4)	Cu(4)–S(1)–Cu(8)	86.0(5)	Cu(11)–S(4)–Cu(3)	91.0(6)	Br(13)–Cu(11)–Br(11)	98.6(3)
S(5)–Cu(5)–S(1)	133.7(5)	Cu(5)–S(1)–Cu(8)	138.7(6)	Cu(10)–S(4)–Cu(3)	76.5(5)	Br(9^4)–Cu(13)–Br(13)	125.6(9)
S(5)–Cu(5)–Br(5)	119.1(5)	C(11)–S(1)–Cu(1)	109.2(12)	C(51)–S(5)–Cu(5)	122.8(10)	Br(9^4)–Cu(13)–Br(7^4)	126.0(9)
S(1)–Cu(5)–Br(5)	107.1(4)	Cu(4)–S(1)–Cu(1)	138.9(6)	C(51)–S(5)–Cu(6)	101.7(10)	Br(13)–Cu(13)–Br(7^4)	108.4(8)
S(5)–Cu(6)–S(3)	133.8(6)	Cu(5)–S(1)–Cu(1)	78.2(4)	Cu(5)–S(5)–Cu(6)	135.5(6)	Br(9^4)–Cu(14)–Br(13)	117.9(15)
S(5)–Cu(6)–Br(8^3)	114.4(5)	Cu(8)–S(1)–Cu(1)	83.8(5)	C(51)–S(5)–Cu(12)	108.8(10)	Br(13)–Cu(15)–Br(7^4)	112(2)
S(3)–Cu(6)–Br(8^3)	109.4(4)	C(21)–S(2)–Cu(1)	110.7(11)	Cu(5)–S(5)–Cu(12)	82.9(5)	Br(13)–Cu(15)–Br(9^4)	116(2)
S(3)–Cu(7)–S(6)	130.4(5)	C(21)–S(2)–Cu(9)	117.1(11)	Cu(6)–S(5)–Cu(12)	82.7(5)	Br(7^4)–Cu(15)–Br(9^4)	112(2)
S(3)–Cu(7)–Br(7)	106.9(4)	Cu(1)–S(2)–Cu(9)	93.0(5)	C(51)–S(5)–Cu(11)	112.5(10)	Br(9^4)–Cu(16)–Br(13)	127.1(10)
S(6)–Cu(7)–Br(7)	122.3(4)	C(21)–S(2)–Cu(12)	102.0(10)	Cu(5)–S(5)–Cu(11)	81.5(5)	Br(9^4)–Cu(16)–Br(5)	112.9(9)
S(6)–Cu(8)–S(1)	128.2(5)	Cu(1)–S(2)–Cu(12)	77.1(5)	Cu(6)–S(5)–Cu(11)	81.7(5)	Cu(15)–Br(13)–Cu(16)	58.9(15)
S(6)–Cu(8)–Br(8)	112.1(4)	Cu(9)–S(2)–Cu(12)	140.6(6)	Cu(12)–S(5)–Cu(11)	138.0(6)	Cu(15)–Br(13)–Cu(13)	16.0(16)
S(1)–Cu(8)–Br(8)	107.0(4)	C(21)–S(2)–Cu(2)	106.5(12)	C(61)–S(6)–Cu(10)	112.4(16)	Cu(16)–Br(13)–Cu(13)	51.8(6)
S(2)–Cu(9)–S(6)	128.0(6)	Cu(1)–S(2)–Cu(2)	138.9(6)	C(61)–S(6)–Cu(8)	107.0(13)	Cu(15)–Br(13)–Cu(11)	139.0(19)
S(2)–Cu(9)–Br(9)	122.6(5)	Cu(9)–S(2)–Cu(2)	85.2(5)	Cu(10)–S(6)–Cu(8)	90.1(5)	Cu(16)–Br(13)–Cu(11)	98.5(7)
S(6)–Cu(9)–Br(9)	103.6(4)	Cu(12)–S(2)–Cu(2)	78.8(5)	C(61)–S(6)–Cu(7)	113.1(14)	Cu(13)–Br(13)–Cu(11)	123.1(7)
S(2)–Cu(9)–Br(6)	93.5(4)	C(31)–S(3)–Cu(3)	118.0(11)	Cu(10)–S(6)–Cu(7)	83.2(5)	Cu(15)–Br(13)–Cu(14)	59.0(17)
S(6)–Cu(9)–Br(6)	103.1(5)	C(31)–S(3)–Cu(6)	110.8(12)	Cu(8)–S(6)–Cu(7)	138.9(6)	Cu(13)–Br(13)–Cu(14)	45.8(10)
Br(9)–Cu(9)–Br(6)	97.9(4)	Cu(3)–S(3)–Cu(6)	91.7(6)	C(61)–S(6)–Cu(9)	108.6(16)	Cu(11)–Br(13)–Cu(14)	86.4(9)
S(6)–Cu(10)–S(4)	132.4(5)	C(31)–S(3)–Cu(7)	109.9(11)	Cu(10)–S(6)–Cu(9)	139.0(6)		

Symmetry relations: (1) $x, y - 1, z$; (2) $x, -y + 1, z + \frac{1}{2}$; (3) $x, -y + 1, z - \frac{1}{2}$; (4) $x, y + 1, z$.

on the copper atoms [Cu(1,3,7,10)], which have planar three-co-ordination, but the other copper atoms are all effectively four-co-ordinate. Atom Cl(31) is bonded more closely (2.20 Å) to the seventeenth CuCl unit [Cu(30)Cl(32)] forming a $CuCl_2^-$ anion which is weakly (2.56 Å) connected to Cl(12) (Fig. 6).

The $Cu_{17}Cl_{17}(SR')_6$ units are effectively independent, but are weakly linked into zigzag chains (across a glide plane) by pairs of long bonds between two of the capping copper atoms [Cu(35), Cu(48′)] and chlorine atoms of adjacent Atlas-spheres [Cl(4) and Cl(3′), Figs. 7(b), 8]. These two copper atoms are pulled slightly out of their Cl_3 planes (0.223 and 0.365 Å respectively).

The single hydrogen atoms of the ammonium groups are involved in hydrogen bonding with the terminal chlorine atoms of their own Atlas-sphere or with the "external" chloride ions.

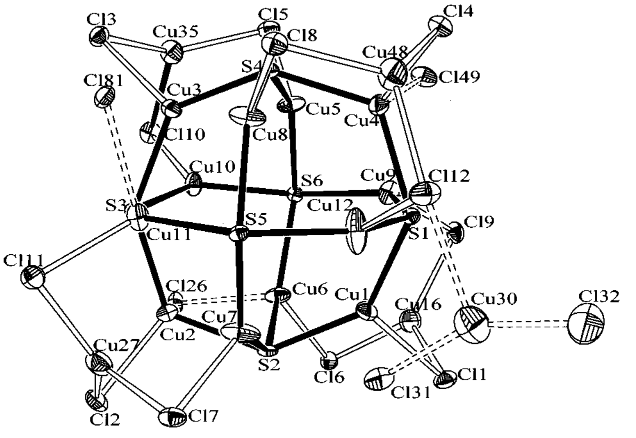

Fig. 6 The structure of $[Cu_{17}Cl_{17}(SR')_6]$ (SR′ = $SCH_2CH_2NHMe_2$).

Discussion

Several features of these systems are of interest. First, they are unusual among complexes of simple thiolates in having SR : metal ratios less than 1 : 1.[6] Secondly, they were obtained from solutions apparently containing an excess of the thiolate. Thirdly, the structures appear to be unnecessarily complicated [we have been unable to isolate the neutral $Cu_{12}X_{12}(SR)_6$ units]. Finally, the μ_4-SR unit is electron deficient, since there are only three lone pairs on the thiolate sulfur atom. Each of these matters is addressed below.

(*a*) Stoichiometry

In many thiolate complexes the thiolate is the only anionic

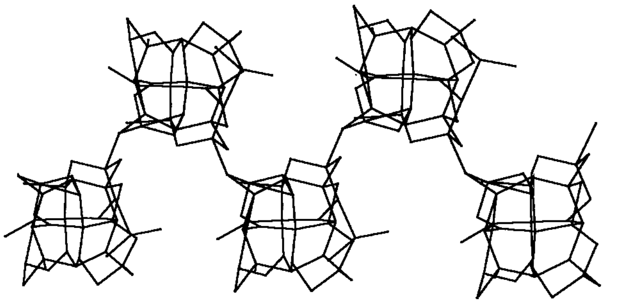

Fig. 8 The chain structure of $[Cu_{17}Cl_{17}(SR')_6]$ (SR′ = $SCH_2CH_2NHMe_2$).

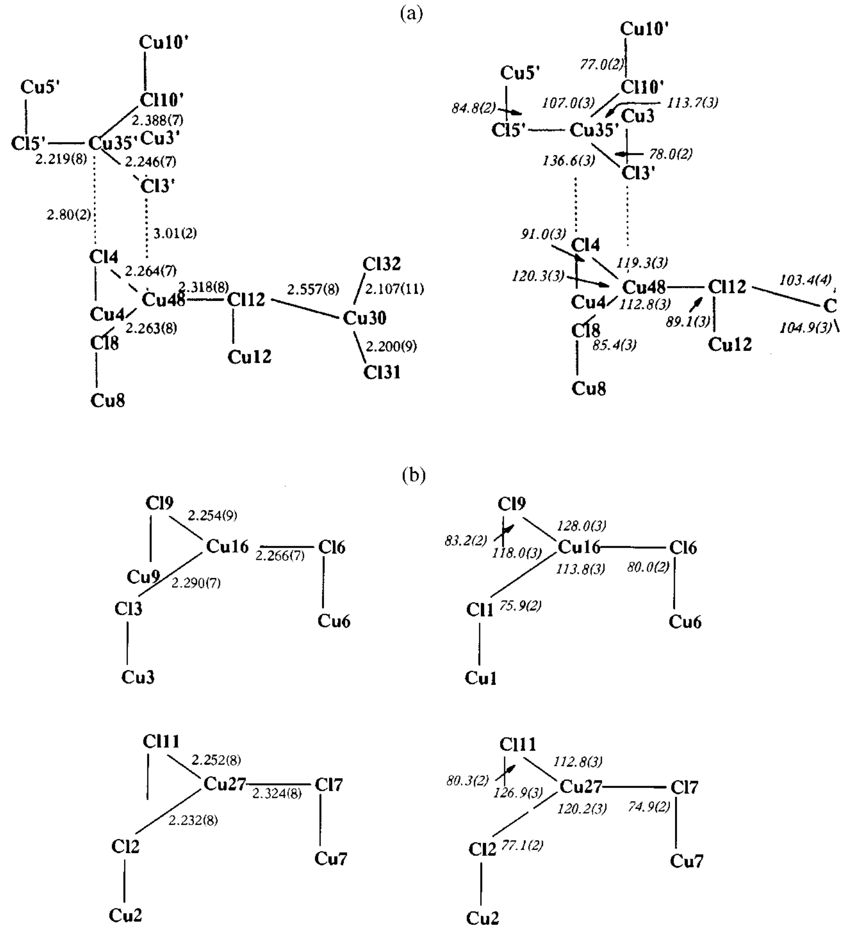

Fig. 7 The geometry of the capping copper atoms in $[Cu_{17}Cl_{17}(SR')_6]$ (SR′ = $SCH_2CH_2NHMe_2$). (a) The non-bridging copper atoms, (b) the bridging system [the angle Cu(48)–Cl(12)–Cu(30) is 159.6(4)°].

Table 4 Ranges and means of bond lengths (Å) and angles (°) for $[Cu_{13}X_{13}(RS)_6]$

	X = Cl		X = Br	
	Range	Mean	Range	Mean
Cu–S (all)	2.221(7)–2.307(7)	2.248(23)	2.199(12)–2.325(14)	2.255(32)
Cu–X (term)	2.248(6)–2.267(6)	2.255(8)	2.359(11)–2.409(10)	2.378(17)
Cu–S–Cu	137.2(2)–142.0(3)	139.6(15)	135.5(6)–140.6(6)	138.8(13)
S–Cu–S[a]	125.7(2)–139.9(2)	131.6(48)	124.5(5)–133.8(6)	130.6(32)
S–Cu–S[b]	127.9(3)[c]		128.0(6), 128.7(6)[d]	
Cu···Cu[e]	2.786(3)–3.046(3)	2.915(80)	2.827(5)–3.068(5)	2.934(76)

[a] Three-co-ordinate copper. [b] Four-co-ordinate copper. [c] One angle only. [d] Two angles only. [e] For $[Cu_{17}Cl_{17}(SR')_6]$: 2.778–3.058; 2.931(96) Å.

Table 5 Bond lengths (Å) for $[Cu_{17}Cl_{17}(SR')_6]$

Cu(1)–S(2)	2.202(7)	Cu(10)–S(3)	2.262(7)
Cu(1)–S(1)	2.240(7)	Cu(10)–Cl(10)	2.328(7)
Cu(1)–Cl(1)	2.331(7)	Cu(11)–S(3)	2.322(6)
Cu(2)–S(3)	2.293(7)	Cu(11)–S(5)	2.329(7)
Cu(2)–S(2)	2.314(7)	Cu(11)–Cl(11)	2.364(8)
Cu(2)–Cl(2)	2.326(7)	Cu(11)–Cl(81)	2.548(7)
Cu(2)–Cl(26)	2.624(7)	Cu(12)–S(1)	2.212(7)
Cu(3)–S(4)	2.252(7)	Cu(12)–S(5)	2.251(7)
Cu(3)–S(3)	2.299(7)	Cu(12)–Cl(12)	2.385(8)
Cu(3)–Cl(3)	2.347(7)	Cu(16)–Cl(9)	2.254(7)
Cu(4)–S(4)	2.298(7)	Cu(16)–Cl(6)	2.266(7)
Cu(4)–S(1)	2.342(7)	Cu(16)–Cl(1)	2.290(7)
Cu(4)–Cl(4)	2.380(7)	Cu(27)–Cl(2)	2.232(8)
Cu(4)–Cl(49)	2.463(7)	Cu(27)–Cl(11)	2.252(8)
Cu(5)–S(4)	2.262(6)	Cu(27)–Cl(7)	2.324(8)
Cu(5)–S(6)	2.273(7)	Cu(30)–Cl(32)	2.107(11)
Cu(5)–Cl(5)	2.320(7)	Cu(30)–Cl(31)	2.200(9)
Cu(6)–S(6)	2.276(6)	Cu(30)–Cl(12)	2.557(8)
Cu(6)–S(2)	2.340(6)	Cu(35)–Cl(5)	2.219(8)
Cu(6)–Cl(6)	2.353(7)	Cu(35)–Cl(3)	2.246(7)
Cu(6)–Cl(26)	2.567(7)	Cu(35)–Cl(10)	2.388(7)
Cu(7)–S(2)	2.198(6)	Cu(48)–Cl(8)	2.263(8)
Cu(7)–S(5)	2.233(7)	Cu(48)–Cl(4)	2.264(7)
Cu(7)–Cl(7)	2.343(7)	Cu(48)–Cl(12)	2.318(8)
Cu(8)–S(4)	2.227(6)	S(1)–C(11)	1.80(2)
Cu(8)–S(5)	2.253(7)	S(2)–C(21)	1.84(2)
Cu(8)–Cl(8)	2.286(7)	S(3)–C(31)	1.78(2)
Cu(8)–Cl(81)	2.727(8)	S(4)–C(41)	1.89(2)
Cu(9)–S(6)	2.310(7)	S(5)–C(51)	1.85(2)
Cu(9)–S(1)	2.313(6)	S(6)–C(61)	1.86(2)
Cu(9)–Cl(9)	2.348(7)		
Cu(9)–Cl(49)	2.574(7)		
Cu(10)–S(6)	2.239(7)		

ligand. The thiolate : metal ratio is therefore constrained to be at least equal to the oxidation state of the metal. In the present case the thiolate is a zwitterion, a neutral ligand, and there is no constraint on the stoichiometry. In mononuclear complexes the ligand : metal ratio has to be at least unity. This not always the case in polynuclear materials, where the stoichiometry depends on the nature of the bridging; nevertheless, it is usually the anionic ligands which form the bridges (chelates apart). A major exception is cluster compounds, in which the average oxidation state of the metal is very low. The present clusters contain stoichiometrically exact copper(I).

(*b*) Solution chemistry

Solid copper(I) halides dissolve readily in aqueous solutions of HSR. The pH of the solution drops rapidly and the conductivity increases.[2] In the very early stages of the addition, at CuX : HSR ratios up to about 20 : 1, more H^+ is liberated than CuX added. With continued addition, the ratio of H^+ to CuX becomes unity and then decreases. Similar behaviour has been noted for acetonitrile solutions.[7] This suggests the early formation of conventional complexes of the type $[Cu(SR)_n]^+$ (n = 2–4) or $[CuX(SR)_n]$ (n = 1–3) which rapidly give way to 1 : 1 complexes $[CuX(SR)]_n$; the latter are probably cyclic trimers or tetramers, containing μ-SR.[6] However, at CuX : HSR of about 4 : 1 (the precise ratios vary with dilution, pH, *etc.*), less H^+ is liberated, showing that CuX is associating with the simple polymers to form more condensed structures.

The self-assembling, closed three-ring Atlas-sphere structure can only be obtained by μ_4 bridging. This novel feature appears to be characteristic of the zwitterionic ligands employed; possible factors involved in forming the closed Atlas-sphere structure may be the repulsion between the positive charges or the high degree of solvation. If all thiolate groups are to be equivalent it is not possible to achieve a closed structure based on the more usual μ_3-bridging thiolate. The only possibilities are rings (μ) or the present structure involving the μ_4 system. Its formation may also be encouraged by the large number of Cu···Cu contacts which span (Table 1) the range of those recently reported for unsupported "cuprophilic" interactions,[8] but we do not believe this to be of great importance.

Although there is no direct evidence, it is tempting to suppose that the Cu_{12} units are formed in appreciable concentration in the solutions. A pair of six-membered $(CuX)_3(SR)_3$ rings could be joined together by progressive insertion of six CuX units, a process which would become more probable as it proceeded (because the original rings would be getting closer), leading to a type of co-operativity of binding. Perhaps more probable is the addition of CuX(SR) and CuCl units to one three- or four-membered ring polymer.

The Atlas-sphere structure resembles a surfactant micelle, in that its outer surface consists of NH_3^+ groups, and the organic/metal halide constituents are in the interior. Such a system must be heavily hydrated, and its high solubility is not surprising. We have never been able to isolate or extract such clusters; they appear to crystallise only by incorporation of additional CuX units. The role of these units may be to allow the positive surfaces to be kept at acceptable distances or, more probably, to create spaces for the water molecules which form hydrogen bonds to the cationic ends of the thiolate ligands. This also implies the presence of a (probably small) equilibrium concentration of free $[CuX_2]^-$ ions, which would be facilitated by the increasing concentration of halide ion and the decreasing pH produced as addition continues. It also suggests that the concentration of the thiolate ligand has somehow been reduced. The halide CuX is usually added only up to a Cu : SR ratio of about 2 : 1 and even at 1 : 1 (the maximum possible before spontaneous precipitation occurs) the product obtained is $(CuX)_8(SR)_6$. We have given evidence that the thiolate is undergoing aerial oxidation during the long crystallisation process.[2] In one case, cystamine $[(H_2NCH_2CH_2S)_2]$ was isolated, in others it was detected by NMR; we have also shown by NMR that the oxidation is more rapid in the presence of copper(I).[2] The oxidation reduces the concentration of free thiolate and encourages equilibria involving sub-stoichiometric complexes.

(*c*) Structural aspects

(i) The bridging systems. The solid compounds all contain

Table 6 Bond angles (°) for [$Cu_{17}Cl_{17}(SR')_6$]

S(2)–Cu(1)–S(1)	136.0(3)	Cl(8)–Cu(8)–Cl(81)	97.3(3)	Cu(48)–Cl(4)–Cu(4)	91.0(3)	C(31)–S(3)–Cu(3)	104.6(8)
S(2)–Cu(1)–Cl(1)	112.9(3)	S(6)–Cu(9)–S(1)	126.4(3)	Cu(35)–Cl(5)–Cu(5)	84.8(2)	Cu(10)–S(3)–Cu(3)	78.1(2)
S(1)–Cu(1)–Cl(1)	111.0(3)	S(6)–Cu(9)–Cl(9)	104.8(2)	Cu(16)–Cl(6)–Cu(6)	80.0(2)	Cu(2)–S(3)–Cu(3)	141.3(3)
S(3)–Cu(2)–S(2)	122.9(3)	S(1)–Cu(9)–Cl(9)	117.0(3)	Cu(27)–Cl(7)–Cu(7)	74.9(2)	C(31)–S(3)–Cu(11)	102.6(8)
S(3)–Cu(2)–Cl(2)	121.6(3)	S(6)–Cu(9)–Cl(49)	106.8(2)	Cu(48)–Cl(8)–Cu(8)	85.4(3)	Cu(10)–S(3)–Cu(11)	140.6(3)
S(2)–Cu(2)–Cl(2)	105.0(3)	S(1)–Cu(9)–Cl(49)	96.3(2)	Cu(16)–Cl(9)–Cu(9)	83.2(2)	Cu(2)–S(3)–Cu(11)	92.1(2)
S(3)–Cu(2)–Cl(26)	96.1(2)	Cl(9)–Cu(9)–Cl(49)	101.7(3)	Cu(10)–Cl(10)–Cu(35)	77.0(2)	Cu(3)–S(3)–Cu(11)	76.9(2)
S(2)–Cu(2)–Cl(26)	104.7(2)	S(6)–Cu(10)–S(3)	125.8(3)	Cu(27)–Cl(11)–Cu(11)	80.3(2)	C(41)–S(4)–Cu(8)	113.3(8)
Cl(2)–Cu(2)–Cl(26)	102.5(3)	S(6)–Cu(10)–Cl(10)	114.3(2)	Cu(48)–Cl(12)–Cu(12)	89.1(3)	C(41)–S(4)–Cu(3)	111.8(8)
S(4)–Cu(3)–S(3)	132.9(3)	S(3)–Cu(10)–Cl(10)	119.2(3)	Cu(48)–Cl(12)–Cu(30)	159.6(4)	Cu(8)–S(4)–Cu(3)	87.0(3)
S(4)–Cu(3)–Cl(3)	119.4(3)	S(3)–Cu(11)–S(5)	126.4(3)	Cu(12)–Cl(12)–Cu(30)	77.9(2)	C(41)–S(4)–Cu(5)	107.8(8)
S(3)–Cu(3)–Cl(3)	106.1(3)	S(3)–Cu(11)–Cl(11)	103.1(3)	Cu(6)–Cl(26)–Cu(2)	64.70(18)	Cu(8)–S(4)–Cu(5)	138.9(3)
S(4)–Cu(4)–S(1)	123.7(3)	S(5)–Cu(11)–Cl(11)	119.8(3)	Cu(4)–Cl(49)–Cu(9)	69.37(19)	Cu(3)–S(4)–Cu(5)	79.1(2)
S(4)–Cu(4)–Cl(4)	105.4(2)	S(3)–Cu(11)–Cl(81)	107.6(2)	Cu(11)–Cl(81)–Cu(8)	69.58(19)	C(41)–S(4)–Cu(4)	105.5(8)
S(1)–Cu(4)–Cl(4)	116.3(2)	S(5)–Cu(11)–Cl(81)	96.7(2)	C(11)–S(1)–Cu(12)	112.9(8)	Cu(8)–S(4)–Cu(4)	92.3(3)
S(4)–Cu(4)–Cl(49)	109.3(3)	Cl(11)–Cu(11)–Cl(81)	98.6(2)	C(11)–S(1)–Cu(1)	102.1(7)	Cu(3)–S(4)–Cu(4)	139.6(3)
S(1)–Cu(4)–Cl(49)	98.7(2)	S(1)–Cu(12)–S(5)	132.1(3)	Cu(12)–S(1)–Cu(1)	86.4(3)	Cu(5)–S(4)–Cu(4)	75.2(2)
Cl(4)–Cu(4)–Cl(49)	100.6(2)	S(1)–Cu(12)–Cl(12)	112.8(3)	C(11)–S(1)–Cu(9)	107.4(8)	C(51)–S(5)–Cu(7)	104.1(8)
S(4)–Cu(5)–S(6)	136.7(2)	S(5)–Cu(12)–Cl(12)	110.3(3)	Cu(12)–S(1)–Cu(9)	139.5(3)	C(51)–S(5)–Cu(12)	102.1(8)
S(4)–Cu(5)–Cl(5)	111.9(2)	Cl(9)–Cu(16)–Cl(6)	128.0(3)	Cu(1)–S(1)–Cu(9)	80.8(2)	Cu(7)–S(5)–Cu(12)	86.0(3)
S(6)–Cu(5)–Cl(5)	107.2(2)	Cl(9)–Cu(16)–Cl(1)	118.0(3)	C(11)–S(1)–Cu(4)	119.5(7)	C(51)–S(5)–Cu(8)	112.0(8)
S(6)–Cu(6)–S(2)	125.9(2)	Cl(6)–Cu(16)–Cl(1)	113.8(3)	Cu(12)–S(1)–Cu(4)	88.0(3)	Cu(7)–S(5)–Cu(8)	143.8(3)
S(6)–Cu(6)–Cl(6)	117.8(2)	Cl(2)–Cu(27)–Cl(11)	126.9(3)	Cu(1)–S(1)–Cu(4)	136.7(3)	Cu(12)–S(5)–Cu(8)	84.4(3)
S(2)–Cu(6)–Cl(6)	105.5(2)	Cl(2)–Cu(27)–Cl(7)	120.2(3)	Cu(9)–S(1)–Cu(4)	76.1(2)	C(51)–S(5)–Cu(11)	117.9(8)
S(6)–Cu(6)–Cl(26)	99.3(2)	Cl(11)–Cu(27)–Cl(7)	112.8(3)	C(21)–S(2)–Cu(7)	117.0(7)	Cu(7)–S(5)–Cu(11)	83.1(2)
S(2)–Cu(6)–Cl(26)	105.7(3)	Cl(32)–Cu(30)–Cl(31)	151.8(4)	C(21)–S(2)–Cu(1)	107.4(8)	Cu(12)–S(5)–Cu(11)	140.0(3)
Cl(6)–Cu(6)–Cl(26)	97.6(2)	Cl(32)–Cu(30)–Cl(12)	103.3(4)	Cu(7)–S(2)–Cu(1)	91.0(3)	Cu(8)–S(5)–Cu(11)	82.2(2)
S(2)–Cu(7)–S(5)	131.6(3)	Cl(31)–Cu(30)–Cl(12)	104.9(3)	C(21)–S(2)–Cu(2)	110.6(8)	C(61)–S(6)–Cu(10)	108.4(9)
S(2)–Cu(7)–Cl(7)	120.3(3)	Cl(5)–Cu(35)–Cl(3)	136.3(3)	Cu(7)–S(2)–Cu(2)	87.0(3)	C(61)–S(6)–Cu(5)	103.6(7)
S(5)–Cu(7)–Cl(7)	106.4(3)	Cl(5)–Cu(35)–Cl(10)	107.0(3)	Cu(1)–S(2)–Cu(2)	138.2(3)	Cu(10)–S(6)–Cu(5)	79.2(2)
S(2)–Cu(7)–Cu(27)	96.2(2)	Cl(3)–Cu(35)–Cl(10)	113.7(3)	C(21)–S(2)–Cu(6)	103.4(7)	C(61)–S(6)–Cu(6)	119.7(7)
S(5)–Cu(7)–Cu(27)	102.9(2)	Cl(8)–Cu(48)–Cl(4)	120.3(3)	Cu(7)–S(2)–Cu(6)	139.2(3)	Cu(10)–S(6)–Cu(6)	85.2(2)
S(4)–Cu(8)–S(5)	124.6(2)	Cl(8)–Cu(48)–Cl(12)	112.8(3)	Cu(1)–S(2)–Cu(6)	81.6(2)	Cu(5)–S(6)–Cu(6)	136.6(3)
S(4)–Cu(8)–Cl(8)	115.6(3)	Cl(4)–Cu(48)–Cl(12)	119.3(3)	Cu(2)–S(2)–Cu(6)	73.3(2)	C(61)–S(6)–Cu(9)	104.4(9)
S(5)–Cu(8)–Cl(8)	115.8(3)	Cu(16)–Cl(1)–Cu(1)	75.9(2)	C(31)–S(3)–Cu(10)	112.9(8)	Cu(10)–S(6)–Cu(9)	142.5(3)
S(4)–Cu(8)–Cl(81)	99.2(2)	Cu(27)–Cl(2)–Cu(2)	77.1(2)	C(31)–S(3)–Cu(2)	114.0(8)	Cu(5)–S(6)–Cu(9)	75.9(2)
S(5)–Cu(8)–Cl(81)	93.7(2)	Cu(35)–Cl(3)–Cu(3)	78.0(2)	Cu(10)–S(3)–Cu(2)	88.7(2)	Cu(6)–S(6)–Cu(9)	94.1(2)

additional CuX units involved in the linking of the Atlas-spheres. There is an interesting trend in the way in which they are incorporated. In [$Cu_{13}Cl_{13}(SR)_6$] one copper atom is bonded to two chlorine atoms from different Atlas-spheres, with a weak link to a second chlorine in one of them. In the bromide the corresponding copper atom is linked to two bromine atoms of one Atlas-sphere and forms a short bond to one bromine on the adjacent one. Finally, in [$Cu_{17}Cl_{17}(SR')_6$] the external copper atoms are bonded to three chlorine atoms from the same Atlas-sphere. There is no obvious explanation for this trend unless the included water molecules are playing a templating role in the Cu_{13} systems. They are involved in multiple hydrogen bonds to halogen atoms and to the organic ammonium groups. In the Cu_{17} system there is much less scope for hydrogen bonding, and the compound is anhydrous.

We have found the μ_4 bridge also in [$Cu_8Cl_8(SR)_6$],[2] and in the silver analogue[3] all SR units form μ_4 bridges. In these cases the ethylammonium groups are hydrogen bonded to chloride ions, and it may be this factor which stabilises these structures.

(ii) Co-ordination of copper. In considering the configuration of individual copper atoms, it is often difficult to distinguish between packing constraints and "genuine" bonds. In the present compounds many examples are seen in which the co-ordination of the copper appears to be distorted. Usually this involves an atom which, on the basis of normally accepted bond lengths, would be regarded as two- or three-co-ordinate; deviation from non-planarity is nearly always towards another halogen atom, even though the distances are quite large (2.5–2.9 Å). It is hard to resist the conclusion that there are electronically significant interactions here.

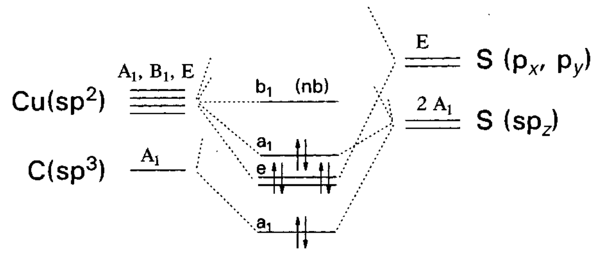

Fig. 9 Partial molecular-orbital diagram for the μ_4-SRCu$_4$ unit. The symmetry labels correspond to idealised C_{4v} symmetry.

(*d*) Bonding

The μ_4-thiolate bridges are forced by the need to form a closed structure. Technically, they are electron-deficient, since the sulfur atom has only three lone pairs (plus a bond pair in the S–C bond). On the assumption that only the s and p orbitals of the sulfur are involved, a simple bonding scheme has been proposed (Fig. 9)[1] which shows that three bonding molecular orbitals are available for the Cu–S bonds and to accommodate the six available electrons. The observed bond lengths show that these bonds are similar in strength to conventional Cu–S bonds,[2] presumably because overlap between the sulfur p orbitals and the copper orbitals is favoured by the square-pyramidal stereochemistry at sulfur.

Conclusion

The unique features of the present structures appear to be due to the use of the zwitterionic thiolate ligands, and these have been rationalised above. It would be of interest to see if similar structures could be obtained with other metals.

References

1 R. V. Parish, Z. Salehi and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 251.

2 Z. Salehi, R. V. Parish and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1997, 4241.

3 W. Su, R. Cao, M. Hong, J. Chen and J. Lu, *Chem. Commun.*, 1998, 1389.

4 M. D. Janssen, A. L. Spek, D. M. Grove and G. van Koten, *J. Am. Chem. Soc.*, 1996, **35**, 4078.

5 G. M. Sheldrick, (*a*) SHELXS 86, University of Göttingen, 1986; (*b*) SHELXL 93, Program for Structure Refinement, University of Göttingen, 1993.

6 I. G. Dance, *Polyhedron*, 1986, **5**, 1037.

7 V. Vorsich, P. Kronek and P. Hemmerick, *J. Am. Chem. Soc.*, 1976, **98**, 2821.

8 U. Siemeling, U. Vorfeld, B. Neumann and H.-G. Stammler, *Chem. Commun.*, 1997, 1723; see also J.-M. Poblet and M. Bénard, *ibid.*, 1998, 1179.

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