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A polymeric cationic copper(I) complex involving a quadruply bridging, zwitterionic thiolate ligand: $\{[Cu_8Cl_6(SCH_2CH_2NH_3)_6]Cl_2\}_n$

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Solutions obtained by dissolving copper(I) chloride in an excess of aqueous cysteamine hydrochloride ($HSCH_2CH_2NH_3Cl$) deposited a white solid, for which X-ray diffraction revealed a unit cell of composition $Cu_8Cl_8(SCH_2CH_2NH_3)_6$. The material has a complex polymeric columnar structure containing three-co-ordinate copper(I) atoms linked in various ways to the zwitterionic ligand $^-SCH_2CH_2NH_3^+$; six chloride ions are bound to copper and two are ionic, so that the polymer chain is positively charged. The thiolate sulfur atoms bridge either three or four metal atoms, making the sulfur four- or five-co-ordinate. This is only the second reported example of the latter type of co-ordination, which is electron deficient. pH Measurements confirmed the release of one H^+ for each CuCl dissolved, and NMR data showed that the thiol undergoes copper-catalysed aerial oxidation in the time between making the solution and the appearance of the polymeric product. The oxidation reduces the copper : ligand ratio to levels allowing the formation of polymeric products.

Recently[1] we described the isolation of a novel cluster complex obtained by adding solid copper(I) chloride to an aqueous solution of cysteamine hydrochloride (2-sulfanylethylammonium chloride, $HSCH_2CH_2NH_3Cl$). This complex had the composition $Cu_{13}Cl_{13}L_6$, in which L was the zwitterionic thiolate $^-SCH_2CH_2NH_3^+$. X-Ray diffraction revealed a cluster involving six of these ligands linked by twelve Cu(Cl) units, giving a closed 'Atlas-sphere' unit (Fig. 1). A particularly novel feature of this cluster is the fact that each thiolate sulfur atom is five-co-ordinate, being bound to four copper atoms in addition to the ethylammonium group; the sulfur is therefore electron deficient but the Cu–S bond lengths are normal. Under similar conditions we have obtained other complexes containing the same 'Atlas-sphere' unit, and which will be described in a later communication.

These materials crystallise slowly from aqueous solutions containing a metal : ligand ratio of about 1 : 4. At ratios closer to 1 : 1 precipitation/crystallisation occurs more rapidly to give another product, which has the empirical composition $Cu_4Cl_4L_3$. A crystal structure determination has revealed this material to be a complicated ionic polymer, which contains some five-co-ordinate sulfur (μ_4) atoms in addition to more conventional triply bridging thiolates.

Experimental

The copper complex was synthesized by adding solid copper(I) chloride (248 mg, 2.50 mmol) in portions to a stirred solution of cysteamine hydrochloride (1.136 g, 10 mmol) in water (60 cm^3). The copper chloride dissolved readily to give a clear solution, which was allowed to stand for about 5 d. White crystals were formed, which were filtered off and washed with water, ethanol and diethyl ether.

Solution studies

The pH of a continuously stirred solution of cysteamine hydrochloride (1.54 g, 13.6 mmol) in water (300 cm^3) was monitored while small aliquots of copper(I) chloride were added, to a total of 0.67 g (6.6. mmol). The pH fell from an initial value of 4.78 to 1.93. The procedure was repeated, adding hydrochloric acid (0.10 mol dm^{-3}) in 0.5 cm^3 aliquots.

Crystallography

Data were collected using a Rigaku AFC6S diffractometer, using graphite-monochromated Mo-Kα radiation. Unit-cell dimensions were derived from the setting angles of 25 accurately centred reflections. Data were collected to an angle of $2\theta = 50°$ and corrected for Lorentz-polarisation and absorption effects (azimuthal scans; max., min. transmission 1.0, 0.76). The structure was solved by direct methods (SHELXS 86)[2a] and refined by full-matrix least-squares regression (SHELXL 93) with all non-hydrogen atoms being treated anisotropically and hydrogen atoms constrained to chemically reasonable positions.[2b] Details of data collection and processing are shown in Table 1.

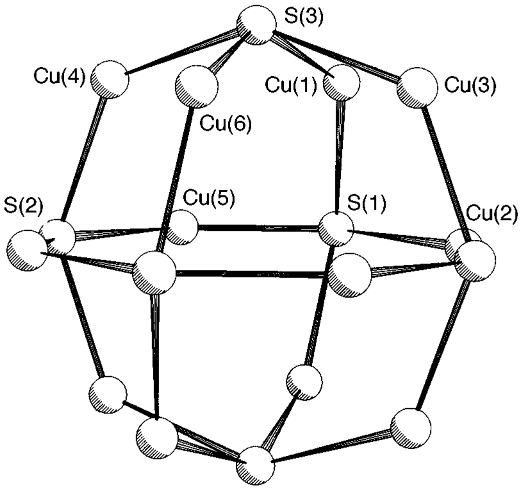

Fig. 1 The 'Atlas-sphere' cluster $Cu_{12}Cl_{12}L_6$; only the sulfur atoms of the ligand L (= $SCH_2CH_2NH_3$) are shown

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Results

Synthesis and solution studies

Aqueous mixtures of copper(I) halides and cysteamine hydrochloride gave a variety of solid products. The addition of the thiol to aqueous solutions of $[CuX_2]^-$ anions (X = Cl, Br or I; in KX or HX solution) produced immediate white precipitates. From microanalytical data, which gave ratios of Cu : S approximating to 2 : 1, we initially formulated these products as $\{[CuX(SR)][CuX_2]\}_n$ ($SR = SCH_2CH_2NH_3$). Mixing in the reverse order also gave white solids, but often after some delay, and

Table 1 Crystal data and structure refinement for compound **1**

Empirical formula	$C_{12}H_{42}Cl_8Cu_8N_6S_6$
M	1254.80
T/K	293(2)
λ/Å	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.932(3)
b/Å	11.590(2)
c/Å	11.647(2)
α/°	89.46(2)
β/°	67.67(2)
γ/°	103.38(2)
U/Å^3	1803.2(6)
Z	2
D_c/Mg m^{-3}	2.311
μ/mm^{-1}	5.583
F(000)	1240
Crystal size/mm	0.35 × 0.20 × 0.20
θ Range for data collection/°	2.48–24.98
hkl Ranges	0–16, −13 to 13, −12 to 13
Reflections collected	5137
Independent reflections (R_{int})	4870 (0.0695)
Refinement method	Full-matrix least squares on F^2
Data, restraints, parameters	4860, 0, 370
Goodness of fit on F^2	1.014
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0462, 0.1093 (2691 reflections)
(all data)	0.1263, 0.1444 (4870 reflections)
Largest difference peak, hole/e Å^3	1.575, −0.909

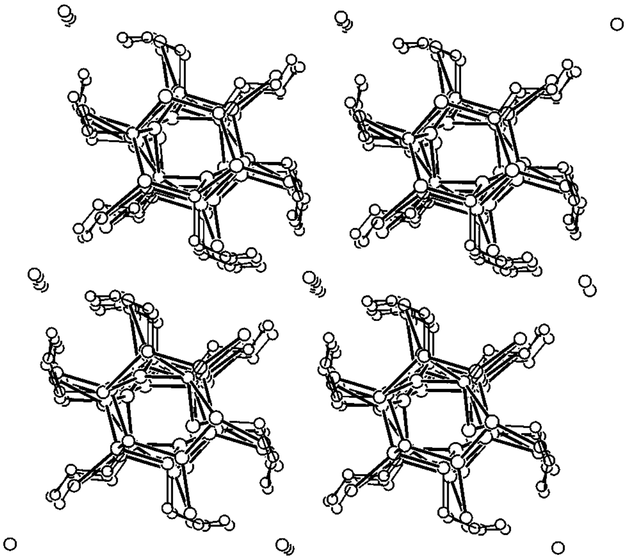

Fig. 2 A view of the crystal structure along the columnar axis

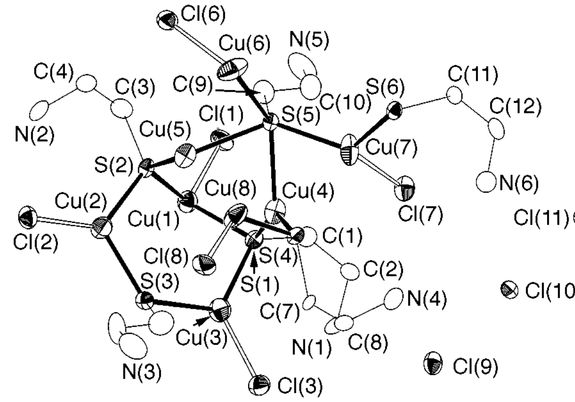

Fig. 3 The simplest repeating unit of the structure: $Cu_8Cl_8L_6$; the hydrogen atoms are omitted for clarity

consistent analytical data could not be obtained. Solid copper(I) chloride or bromide dissolved readily in solutions of the thiol, and addition could be continued up to about a 1 : 1 ratio of copper to thiol; relatively concentrated solutions began to deposit a product at the same time as the last aliquots of copper(I) halide were added. There was again little consistency of microanalytical data between different samples. The only constant factors were a precise 1 : 1 mole ratio for Cu : X, and the presence of less ligand than copper.

The best synthetic method was found to be to dissolve copper(I) chloride in an aqueous solution of cysteamine hydrochloride up to a ratio between 1 : 2 and 1 : 1 (Cu : thiol), and to leave the solution to stand. Depending on the total concentration, precipitation or crystallisation began in a few hours to a few days. This gave more consistency: several samples showed identical X-ray powder diffraction patterns, and some crystals were obtained. Their examination is detailed below. None of the materials obtained could be recrystallised.

The solutions became acidic as the copper halide was added, and attempts to control or buffer the pH were frustrated by spontaneous oxidation of the copper, giving purple colourations similar to those reported for mixed-valence systems.[3] The addition of each portion of CuCl produced a decrease in pH, from the initial 4.7 to finally about 1.9. Continuous measurements during the addition show that one proton was liberated for every atom of copper added, and the pH *vs.* [Cu] curve was identical to the pH *vs.* [H$^+$] curve obtained by adding dilute (0.1 mol dm^{-3}) hydrochloric acid to the cysteamine hydrochloride solution. Thus, the thiolate group is being deprotonated, giving the zwitterion which presumably binds to copper in some type of polymeric 1 : 1 complex, $[\{CuCl(L)\}_n]$.

In the very early stages of the addition up to a Cu : L ratio of about 1 : 20, the slope of the curve indicates that between three and four protons are liberated per copper atom, indicating the formation of polythiolatocopper(I) complexes, $[CuL_n]^{(n-1)+}$ (n = 3 or 4). Similar observations have been made previously for acetonitrile solutions.[4]

Some reactions were performed in D_2O, to enable NMR spectra to be obtained. The ^1H spectra showed two triplets due to the two CH_2 groups of cysteamine [δ 2.82 (CH_2N), 3.12 (CH_2S)]; all other proton signals (residual water in the D_2O, HS, HN) fell under a single sharp peak at δ 4.80. When this solution was allowed to stand two additional triplets appeared (δ 3.02, 3.20), presumably due to oxidation of some of the cysteamine to the corresponding disulfide (these signals were also seen, at low intensity, for old samples of cysteamine hydrochloride). The addition of CuCl to a fresh solution produced no discernible change, except that the oxidation occurred more rapidly. A solution which had produced a considerable amount of solid deposit was filtered and its spectrum showed only the disulfide. The disulfide still involves the quaternised nitrogen, and would not be expected to complex to copper(I). The occurrence of only one set of signals for the cysteamine show that rapid exchange occurs between the free thiol and the bound zwitterion.

Similar results were obtained from the ^{13}C-{^1H} NMR spectra (δ 22.48, 43.21 for cysteamine hydrochloride, 34.54, 38.99 for the disulfide), except that, in the presence of CuCl, the δ 22.48 peak (CS) became very broad.

Crystal structure

The structure is formed of parallel tubular ribbons (Fig. 2) in which the simplest repeating unit is $[Cu_8Cl_8L_6]^{2+}$ (Fig. 3). The charge-balancing chloride ions lie between the tubular columns and are hydrogen bonded to NH_3^+ groups. Within the columns most of the sulfur donor atoms are bonded to three copper atoms, but one in every six has four close copper neighbours. Five out of every eight copper atoms are three-co-ordinate, $CuClS_2$: two more are also three-co-ordinate but bound only to sulfur donor atoms, CuS_3: the remaining copper atom is four-

Table 2 Bond angles (°) about sulfur atoms

	Neighbours	Bond angle	Average Cu–S–Cu	Neighbours	Bond angle (°)	Average C–S–Cu
μ_3-Sulfur						
S(1)	Cu(3), Cu(4)	94.91(13)		C(1), Cu(3)	124.4(4)	
	Cu(3), Cu(1)	102.33(14)		C(1), Cu(4)	112.1(4)	
	Cu(4), Cu(1)	118.7(2)	105.32	C(1), Cu(1)	105.1(4)	113.8
S(2)	Cu(5), Cu(2)	87.56(13)		C(3), Cu(2)	124.8(5)	
	Cu(2), Cu(1)	109.91(14)		C(3), Cu(5)	108.1(5)	
	Cu(5), Cu(1)	122.2(2)	106.53	C(3), Cu(1)	105.1(5)	112.7
S(3)	Cu(2), Cu(1′)	101.75(14)		C(5), Cu(1′)	113.0(5)	
	Cu(3), Cu(1′)	105.37(14)		C(5), Cu(2)	112.9(5)	
	Cu(2), Cu(3)	123.6(2)	110.26	C(5), Cu(3)	99.8(5)	108.8
S(4)	Cu(8), Cu(6′)	83.30(13)		C(7), Cu(4)	115.5(5)	
	Cu(8), Cu(4)	110.2(2)		C(7), Cu(8)	108.2(5)	
	Cu(4), Cu(6′)	127.8(2)	107.1	C(7), Cu(6′)	106.3(4)	110.0
S(6)	Cu(5′), Cu(8′)	103.59(14)		C(11), Cu(5′)	115.8(5)	
	Cu(5′), Cu(7)	136.8(2)		C(11), Cu(8′)	105.6(4)	
	Cu(7), Cu(8′)	79.52(12)		C(11), Cu(7)	104.2(5)	108.5
	Overall average Cu-μ_3–S–Cu		107(16)	Overall average C-μ_3–S–Cu		111(7)
μ_4-Sulfur						
S(5)	Cu(7), Cu(4)	71.45(11)		C(9), Cu(7)	116.5(4)	
	Cu(4), Cu(5)	72.96(10)		C(9), Cu(6)	106.7(5)	
	Cu(6), Cu(5)	75.48(11)		C(9), Cu(4)	105.6(5)	
	Cu(7), Cu(6)	116.03(14)	83.98	C(9), Cu(5)	98.5(4)	106.8

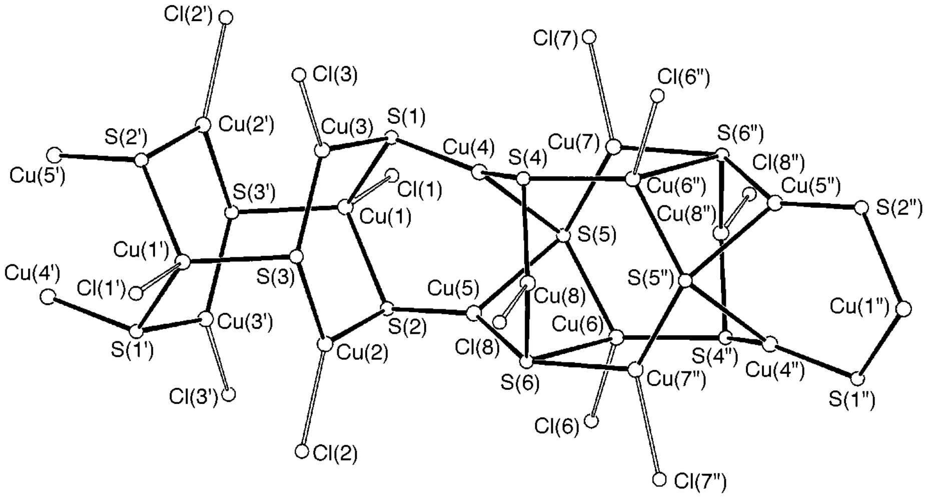

Fig. 4 The repeating unit of the chains, $Cu_{16}Cl_{16}L_{12}$; the ethylammonium side chains of the ligand are omitted for clarity

co-ordinate, $CuClS_3$. None of the chloride ligands is bridging. The structure contains several local centres of symmetry, giving the repeating chain unit shown in Fig. 4.

As with many metal–thiolate complexes,[5] the structure is composed of rings of alternating metal and sulfur atoms. The difference here is that the negative charge on the thiolate sulfur is balanced by the positive charge of the ethylammonium group, so that most of the metal atoms carry a halide ion in order to achieve neutrality. Both six- and eight-membered –Cu–S– rings can be discerned, but nearly all have sides in common with other rings. A six-membered ring –S(1)–Cu(3)–S(3)–Cu(2)–S(2)–Cu(1)– is bridged at S(1) and S(2) by Cu(4)–S(5)–Cu(5), thus forming another six-membered ring; an alternative description would be as an eight-membered ring, –S(5)–Cu(4)–S(1)–Cu(3)–S(3)–Cu(2)–S(2)–Cu(5)–, in which S(1) and S(2) are cross-linked by Cu(1).

As shown in Fig. 4, two of these sub-units are linked at Cu(1) and S(3), to S(3′) and Cu(1′) respectively. At the other end of each sub-unit S(5) is bonded to two more copper atoms, Cu(6) and Cu(7), which link to S(4″) and S(6″) and thence to Cu(4″) and Cu(5″) of the next sub-unit. Complementary, symmetry-required binding of S(5″) to Cu(6″)–S(4)–Cu(4) and to Cu(7″)–S(6)–Cu(5) gives further sets of eight-membered rings. The repeating unit is completed by Cu(8) [and Cu(8′)] which bridge between S(4) and S(6) [S(4″), S(6″)].

Bond angles. The majority of the sulfur atoms are triply bridging, and have approximately tetrahedral geometry (Table 2). However, the constraints of forming the rings leads to wide variations in bond angle: C–S–Cu 99.8–124.8 [average 111(7)], Cu–S–Cu 83.3–127.8 [average 107(6)°]. The Cu–S–Cu angles about the quadruply bridging sulfur are also irregular: three between 71.4 and 75.5, the fourth 116°. Only the last is comparable to those in the 'Atlas sphere'.[1] The smallest of the angles might imply a degree of copper–copper bonding, but we do not believe this to be important [Cu–Cu 2.773(3) Å]. Other Cu–Cu distances range up to 2.996(3) Å.

The copper atoms fall into three groups (Table 3). One, Cu(1), is four-co-ordinate and has bond angles which vary from 97.9 to 116.5°. There appear to be no systematic variations. The remaining copper atoms are all three-co-ordinate, with a range of bond angles from 95.8 to 149.9°, although most are reasonably close to the trigonal angle. The sum of the three angles at any given atom is close to 360°, showing good planarity,

Table 3 Bond angles (°) at copper

		Sum
S(1)–Cu(1)–S(2)	97.94(12)	
S(1)–Cu(1)–Cl(1)	106.73(13)	
S(2)–Cu(1)–Cl(1)	113.17(13)	
S(3′)–Cu(1)–S(1)	116.55(13)	
S(3′)–Cu(1)–Cl(1)	112.54(13)	
S(3′)–Cu(1)–S(2)	109.19(13)	
S(1)–Cu(4)–S(4)	143.29(14)	
S(1)–Cu(4)–S(5)	119.44(13)	
S(4)–Cu(4)–S(5)	97.04(12)	359.8
S(2)–Cu(5)–S(5)	114.01(12)	
S(2)–Cu(5)–S(6′)	149.88(14)	
S(5)–Cu(5)–S(6′)	95.89(12)	359.8
S(2)–Cu(2)–S(3)	109.49(13)	
S(2)–Cu(2)–Cl(2)	126.49(14)	
S(3)–Cu(2)–Cl(2)	123.75(14)	359.7
S(1)–Cu(3)–S(3)	115.02(14)	
S(1)–Cu(3)–Cl(3)	127.42(14)	
S(3)–Cu(3)–Cl(3)	114.80(14)	357.2
S(5)–Cu(6)–S(4′)	118.21(14)	
S(5)–Cu(6)–Cl(6)	118.61(14)	
S(4′)–Cu(6)–Cl(6)	111.59(14)	348.4
S(5)–Cu(7)–S(6)	119.97(13)	
S(5)–Cu(7)–Cl(7)	126.41(14)	
S(6)–Cu(7)–Cl(7)	108.61(13)	355.0
S(4)–Cu(8)–S(6′)	117.34(13)	
S(4)–Cu(8)–Cl(8)	126.32(14)	
S(6′)–Cu(8)–Cl(8)	112.99(14)	356.7

Average S–Cu–S 116.0(36). S–Cu–Cl 119.7(68)

Table 4 Bond lengths (Å) involving sulfur atoms

S(1)–Cu(1)	2.345(4)
S(1)–Cu(3)	2.212(4)
S(1)–Cu(4)	2.217(4)
S(1)–C(1)	1.832(13)
S(2)–Cu(1)	2.374(4)
S(2)–Cu(2)	2.243(4)
S(2)–Cu(5)	2.221(4)
S(2)–C(3)	1.814(13)
S(3)–Cu(1′)	2.314(4)
S(3)–Cu(2)	2.265(4)
S(3)–Cu(3)	2.275(4)
S(3)–C(5)	1.846(13)
S(4)–Cu(4)	2.245(3)
S(4)–Cu(6′)	2.289(4)
S(4)–Cu(8)	2.218(4)
S(4)–C(7)	1.824(12)
S(5)–Cu(4)	2.439(4)
S(5)–Cu(5)	2.478(4)
S(5)–Cu(6)	2.335(4)
S(5)–Cu(7)	2.307(4)
S(5)–C(9)	1.819(11)
S(6)–Cu(5′)	2.217(3)
S(6)–Cu(7)	2.326(4)
S(6)–Cu(8′)	2.251(4)
S(6)–C(11)	1.835(11)

Average μ_3-S–Cu 2.268(50), μ_3-S–C 1.830(12), μ_3-S–CuY$_2$ = 2.248(34), μ_3-S–CuY$_3$ = 2.345(25), μ_4-S–Cu 2.389(70), μ_4-S–C 1.819 (Y = S or Cl).

Table 5 Additional bond lengths (Å) and averages

	Bond length		Average length/Å
Cu(1)–Cl(1)	2.350(3)[a]	μ_3-S–Cu	2.268(50)
Cu(2)–Cl(2)	2.269(4)	μ_4-S–Cu	2.389(70)
Cu(6)–Cl(6)	2.288(4)	μ_4-S–CuS$_2$	2.457(17)
Cu(7)–Cl(7)	2.288(4)	μ_4-S–CuSCl	2.321(13)
Cu(8)–Cl(8)	2.237(4)	μ_3-S–CuS$_2$	2.225(12)
Average[b]	2.271(21)	μ_3-S–CuSCl	2.260(35)

[a] Four-co-ordinate copper. [b] Average for three-co-ordinate copper atoms.

although it is noticeable that the CuS$_3$ units deviate less from planarity than do the CuS$_2$Cl units, in spite of the fact that each CuS$_3$ set has one very large bond angle (>140°). For the CuS$_2$Cl units the S–Cu–S angles appear to be generally smaller than the S–Cu–Cl angles, although the difference is not statistically significant. The difference could be due to the constraints of ring formation; the chloride ligands are terminal.

Bond lengths. The electron-deficient, quadruply bridging S(5) might be expected to form longer bonds than the other, triply bridging sulfur atoms. For the S–C bonds such a difference is not discernible (Table 4). For S–Cu bonds there is a difference of 0.121 Å between the average bond lengths, which is on the limit of statistical significance ($\sigma_1 + \sigma_2$, Table 4). Closer inspection suggests that the S–Cu bond length may also depend on the other ligands bonded to copper: for S(5) the bonds to a copper bound to three thiolates are significantly longer than those to copper bound to thiolate and chloride, by 0.136 Å. The latter Cu–S distance, 2.321(13) Å, is close to that of the only other recorded example of (μ_4-S)$_2$CuCl units, in the 'Atlassphere' cluster,[1] 2.249(24) Å. However, any similar trend for the triply bridging sulfur atoms is obscured by the wide range of the μ_3-S–Cu(μ_3-S)Cl bond lengths (2.212–2.325 Å). The average, 2.268(50) Å (Table 5), is effectively identical to the average of similar bonds in the literature, 2.265(19) Å (Table 6).

Table 6 also shows that bond lengths depend more on the co-ordination number of copper than of sulfur, and this extends to the Cu–Cl bonds: that to the four-co-ordinate copper is 0.08 Å longer than the average for the three-co-ordinate copper atoms.

Discussion

The aqueous copper(I)–cysteamine hydrochloride system is curious. First, only at very high thiol : Cu ratios is there any evidence for complexes containing more than one thiolate. The pH studies show that 1 : 1 complexes are being formed under most conditions. On the other hand, the only solids we have been able to isolate contain more copper than thiolate; in the present case the ratio is 4 : 3; in the previously reported complex[1] it was 13 : 6.

The solutions are very likely to contain thiolate-bridged polymers, presumably cyclic with six- or eight-membered rings,[5] [{CuCl(μ-SR)}$_n$] (n = 3 or 4, R = CH$_2$CH$_2$NH$_3$). It has to be presumed that these polymers are very water soluble which, given their highly polar nature, is very plausible; they would be expected to form strong hydrogen bonds with water molecules. We have not been able to extract any copper-containing species into other solvents. The NMR spectra showed that the polymers are very labile, there being rapid exchange between bound thiolate and free thiol. This could occur readily by an associative mechanism, since the ring copper atoms are only three-co-ordinate and could easily bind a second thiolate.

Solid products were obtained rapidly only from concentrated solutions in which the Cu : thiol ratio was close to 1 : 1. X-Ray powder diffraction showed that these usually contained the material reported here. In more dilute solutions and with ratios closer to 1 : 2, precipitation/crystallisation occurred only after some time. The NMR spectra showed that oxidation of the thiol to disulfide is occurring, and that it is catalysed by the copper complexes in solution. Thus, during this gestation period, the copper : thiol ratio is slowly increasing, giving the opportunity for more complicated polymers to form. The lability of the system means that all equilibria are very facile, and the polymer which is least soluble under the prevailing conditions will be deposited.

In the present case, the insoluble polymeric material has a very complex structure, certainly one which could not be predicted. Although the atomic arrangement has considerable symmetry, it is not possible to explain the mixture of types of co-ordination involved. Nevertheless, it is a structure which assembles itself readily, since this is the product we have most frequently obtained under a range of conditions, including

Table 6 Reported Cu^I–S distances (excluding chelates)

Compound	Ref.	Co-ordination of Cu	d(Cu–S)/Å		Average of means/Å
			Range	Mean[a]	
Two-co-ordinate Cu, μ-SR					
$[\{Cu[SSi(OBu)_3]\}_4]$	6	S_2	2.161–2.175	2.169(6)	
$[\{Cu[SC_6H_4(SiMe_3\text{-}2)]\}_{12}]$	7	S_2	2.142–2.169	2.160(9)	
$[\{Cu[SC_6H_3(SiMe_3)_2\text{-}2,6]\}_4]$	9	S_2	2.134–2.164	2.151(8)	
$[Cu_4(SBu^t)_4(PPh_3)_2]$	10	S_2	2.145–2.167	2.156(9)	
$[\{Cu(SC_6H_2Pr^i_3\text{-}2,4,6)\}_8]$	16	S_2		2.162	
$[NEt_4][Cu_5(SBu^t)_6]$	17	S_2		2.17(1)	
$[NMe_4]_2[Cu_5(SPh)_7]$	18	S_2	2.159–2.161	2.160(3)	2.161(6)
Two-co-ordinate Cu, μ_3-SR					
$[\{Cu[SC_6H_4(SiMe_3\text{-}2)]\}_{12}]$	7	S_2	2.189–2.212	2.200(9)	
$[NMe_4]_2[Cu_5(SPh)_7]$	18	S_2	2.159–2.161	2.160(1)	2.180(20)
Three-co-ordinate Cu, η^1-SR					
$[PPh_4]_2[Cu(SPh)_3]$	11	S_3	2.274–2.335	2.295(28)	
$[NEt_4]_2[Cu(SPh)_3]$	20	S_3	2.239–2.258(2)	2.250(8)	
$[NEt_4]_2[Cu\{SC_6H_4NHC(O)Bu^t\}_3]$	19	S_3	2.217–2.232(8)	2.227(7)	2.257(28)
Three-co-ordinate Cu, μ-SR					
$[PPh_4][Cu_6In_3(SEt)_{16}]$	12	S_3	2.24	2.24	
$[PPh_4][Cu_7(SEt)_8]$	13	S_3	2.206–2.247	2.238	
$[\{Cu[SC_6H_4(SiMe_3\text{-}2)]\}_{12}]$	7	S_3	2.198–2.220	2.210(8)	
$[PPh_4]_2[Cu_4(SPh)_6]$	8	S_3	2.252–2.315	2.281	
$[\{Cu(SCF_3)\}_{10}]\cdot 8MeCN$	14	S_2N, S_3	2.21–2.2	2.21_5	
$[Cu_4(SBu^t)_4(PPh_3)_2]$	15	S_2P	2.245–2.263	2.254(8)	
$[\{Cu_2(SPh)_3(PPh_4)\}_n]$ solvated? (see ref. 7)	11	S_3	2.242–2.338	2.29(3)	
$[NEt_4][Cu_5(SBu^t)_6]$	17	S_3		2.27(2)	
$[NMe_4]_2[Cu_5(SPh)_7]$	18	S_3	2.230–2.330	2.270(27)	
$[PPh_4]_2[Cu_4(SEt)_6]$	13	S_3	2.248–2.309(3)	2.281	2.255(27)
Three-co-ordinate Cu, μ_3-SR					
$[PPh_4][Cu_7(SEt)_8]$	13	S_3	2.246–2.359(4)	2.287	
$[\{Cu[SC_6H_4(SiMe_3\text{-}2)\}_{12}]$	7	S_3	2.243–2.263 2.301–2.315	2.252(8)[b] 2.309(6)[b]	
$[\{Cu(SCF_3)\}_{10}]\cdot 8MeCN$	14	S_3	2.19–2.29	$2.25_4(4)$	
$[PPh_4][Cu_6In_3(SEt)_{16}]$	12	S_3	2.21–2.26	2.24(3)	2.265(19)
Three-co-ordinate Cu, μ_4-SR					
$[Cu_{12}Cl_{12}(SCH_2CH_2NH_3)_6(\mu\text{-}Cl)]\mu\text{-}[CuCl_2]$	1	S_2Cl	2.221–2.301	2.248[c]	2.248
Four-co-ordinate Cu, μ_3-SR					
$[Cu_{10}(SCF_3)_{10}(MeCN)_8]$	14	N_2, $(\mu_3\text{-}S)_2$, N, $(\mu_3\text{-}S)_3$	2.31(1) 2.35–2.36(1)	2.31 2.35_3	
$[Cu_6In_3(SEt)_{16}]$	12	S_3	2.28–2.37	2.31(3)	2.315(5)
Four-co-ordinate Cu, μ_4-SR					
$[Cu_{12}Cl_{12}(SCH_2CH_2NH_3)_6(\mu\text{-}Cl)]\mu\text{-}[CuCl_2]$	1	S_2Cl_2	2.251–2.262	2.256	2.256

[a] Figures in parentheses are the standard deviation on the mean. [b] Alternating around a six-membered ring [overall average 2.281(29) Å]. [c] Range only quoted.

some under which precipitation appears to be almost instantaneous.

The electron-deficient, quadruply bridging thiolate groups are seen only in the present compound and in the 'Atlas-sphere' clusters. Here they play a vital role in the structure, being at one point the only link which continues the chain. We have previously given[1] an orbital description of the bonding, which probably applies approximately here although the geometry at the sulfur atoms is less regular. These distortions may account for the slight lengthening of the Cu–S bonds.

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