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Preparation, Spectroscopy and Crystal Structure of a Novel Tetranuclear Copper(I) Benzimidazoline-2-thione Complex: *cyclo*-Hexakis-μ_2-(benzimidazoline-2-thione) Tetrakis[benzimidazoline-2-thione copper(I)] Perchlorate Quatrodeca Hydrate

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Abstract

Reaction between copper(II) perchlorate and benzimidazole-2-thione (bzimztH) in aqueous ethanol produced a pale green crystalline solid of empirical formula $[Cu_2(bzimztH)_5](ClO_4)_2 \cdot 7H_2O$. The compound is diamagnetic at room temperature and possesses no d–d absorption in its electronic spectrum.

The crystal structure of the compound contains centrosymmetrically constrained tetranuclear cations $[Cu_4(bzimztH)_{10}]^{4+}$, perchlorate anions and water molecules in a monoclinic unit cell [$a = 14.960(2)$, $b = 25.863(3)$, $c = 14.031(2)$ Å, $\beta = 110.331(8)°$, space group $P2_1/c$, $Z = 2$]. The tetranuclear cations contain a planar centrosymmetric array of copper(I) atoms, Cu_4, with edge dimensions of 2.681(2) and 4.216(3) Å and an internal angle of 85.8(1)°.

Each copper(I) atom is tetrahedrally coordinated by four S-donating ligands. The ten ligands in the cation consists of four terminal S-donating, one asymmetric μ_2-S bridging ligand along each of the long edges of the Cu_4 array and four asymmetric μ_2-S bridging ligands arranged in pairs along each of the short edges of the Cu_4 array. The latter generate pairs of Cu_2S_2 units with narrow angles at the bridging S atoms, 69.1(1)° and 66.8(1)°. The remaining bridging angle is much larger, 124.9(1)°. Cu–S distances are in the range 2.262(2) to 2.499(3) Å with the terminal distances somewhat shorter than the bridging ones. An alternating sequence of long and short Cu–S distances, created by the μ_2-S bzimztH ligands, links the copper atoms of the Cu_4 array. The final *R* index for 4672 observed reflections is 0.092.

Introduction

The current interest in copper–sulphur interactions owes much to the discovery of S-cysteinyl ligation of the metal in plastocyanin [1] as well as in other 'blue' copper proteins [2] and in copper–thionein proteins [3]. The proposed cubane structure for the $Cu_4(S\text{-}cys)_8$ core in yeast copper thionein [4], as well as the recently established $Cd_4(S\text{-}cys)_{11}$ core in Cd, Zn metallothionein [5], have been complemented by the synthesis of tetranuclear complexes for a variety of metals with S-donor ligands [6].

Among tetranuclear copper complexes the well established Cu_4S_6 cluster contains a tetrahedral arrangement of copper(I) atoms and a distorted octahedral distribution of doubly bridging sulphur atoms. Specific ligands involved in this arrangement include thiophenolate [7], orthoxylenyl-1,4-dithiolate [8] and thiourea [9].

With heterocyclic thione donors, however, the metal atoms in tetranuclear copper(I) clusters do not appear to adopt a tetrahedral configuration. In the $[Cu_4(imidazolidine\text{-}2\text{-}thione)_9]^{4+}$ ion the nine S-donating ligands consist of four terminal, four double bridging and one quadruple bridging species. A planar array is assumed for the Cu_4 unit in this structure although it is not described as such in the report [10].

A planar centrosymmetric array is reported for the metal atoms in $[Cu_4(1\text{-}methylpyrimidine\text{-}2\text{-}thione)_6]^{4+}$ together with a combination of terminal-S, μ_2-S bridging and μ_2-S,N bridging ligands. Each metal atom is trigonally coordinated [11].

We add to this interesting range of tetranuclear complexes of copper(I) involving S-donor ligands this report on the title compound.

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Experimental

Starting Materials

The ligand, benzimidazoline-2-thione, bzimztH, was supplied by the Aldrich Chemical Company as 2-mercaptobenzimidazole and was used as supplied. Copper(II) perchlorate hexahydrate was supplied by BDH Ltd. All solvents were thoroughly degassed before use.

Preparation and Analysis of $[Cu_4(bzimztH)_{10}]$-$(ClO_4)\cdot 14H_2O$

Copper(II) perchlorate hexahydrate (0.7420 g, 2 mmol) was dissolved in the minimum quantity (10 ml) of distilled water. The ligand, bzimztH (1.200 g, 8 mmol) was added to 100 ml of an aqueous ethanol mixture (50/50; *v*:*v*) and the mixture was refluxed until the ligand dissolved. Dropwise addition of the metal salt solution to the cooled solution of bzimztH, at room temperature, produced a transient green colouration which was quickly dispersed by stirring the reaction mixture. When all of the metal salt solution had been added the reaction solution was straw-coloured.

The reaction mixture was thoroughly degassed with dinitrogen and the reaction vessel was sealed with parafilm. During the following two days the reaction mixture adopted an apple-green colouration of progressively increasing intensity. This solution was allowed to stand for several weeks during which pale green crystals of the complex formed which were recovered by filtration, washed with cold distilled water, vacuum dried and stored at room temperature under dinitrogen. Yield, 0.65 g, 64%.

Anal. Found: C, 34.68; H, 3.34; N, 11.13; S, 13.65; Cu, 10.00. Calc. for $C_{70}H_{88}N_{20}O_{30}S_{10}Cl_4Cu_4$: C, 34.91; H, 3.65; N, 11.63; S, 13.30; Cu, 10.04%.

Physical Methods

Infrared spectra were obtained from caesium iodide discs in the range 4000–200 cm^{-1} on a Perkin-Elmer 684 grating spectrophotometer. A Shimadzu 160 spectrophotometer was used to record the electronic spectra (10^{-3} M in dimethylformamide) in the range 200–1100 nm. A room temperature Gouy balance was used to monitor the diamagnetic character of the complex.

Crystal Structure Determination

Crystal data

$C_{70}H_{88}N_{20}O_{30}S_{10}Cl_4Cu_4$, $M = 2406.2$, pale green crystal, 0.15 X0.29 X0.38 mm, monoclinic, space group $P2_1/c$, $a = 14.960(2)$, $b = 25.863(3)$, $c = 14.031(2)$ Å, $\beta = 110.331(8)^\circ$, $V = 5090.6$ Å^3, $Z = 2$, $F(000)$ 2464, $D_c = 1.570$ g cm^{-3}, cell dimensions determined from 32 centred reflections ($30^\circ < 2\theta < 40^\circ$), $\mu = 4.51$ mm^{-1} for Cu Kα radiation ($\lambda = 1.54184$ Å).

Data collection and processing

Siemens AED2 diffractometer, 2θ range 3–115°; range of indices h $-16 \rightarrow 16$, k $0 \rightarrow 28$, l $-15 \rightarrow 3$; 3 standard reflections with a decay in the region of 4% corrected in the data reduction; semi-empirical absorption correction; transmission factors, 0.233–0.425; 8897 intensities measured, 6956 unique reflections [4672 observed reflections, $F > 4\sigma_c(F)$, σ_c based on counting statistics]. $R_{int} = 0.068$.

Structure solution [12]

Direct methods and difference Fourier methods were used to locate the non-H atoms which were refined by blocked-cascade least-squares on F, to a minimum of $\Sigma w\Delta^2$, with anisotropic temperature factors. Perchlorate ions were refined as rigid tetrahedral groups with Cl–O = 1.43 Å. Hydrogen atoms, except those from the water molecules, were allocated calculated positions with NH = CH = 0.96 Å and $U(H) = 1.2U_{iso}$ (C or N). Final conventional $R = \Sigma|\Delta|/\Sigma|F_o| = 0.092$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2} = 0.064$ with $w^{-1} = \sigma^2_c(F) + 117 - 477G + 2230G^2 - 207S + 123S^2 - 110GS$, obtained empirically from an analysis of variance [13]; $G = F_o/F_{max}$, $S = \sin\theta/\sin\theta_{max}$. The maximum shift/e.s.d. ratio is 0.09 and mean is 0.02. The largest peak in the final difference Fourier synthesis is +1.79 e Å^{-3} and the largest hole is -1.53 e Å^{-3}, both are close to the anions. Slope of normal probability plot is 0.99. Scattering-factors for neutral atoms were taken from ref. 14.

Final fractional atomic coordinates are given in Table I, bond lengths and angles in Table II, see also 'Supplementary Material'. A perspective view of the complex cation with atomic numbering is shown in Fig. 1; unit cell contents are shown in Fig. 2.

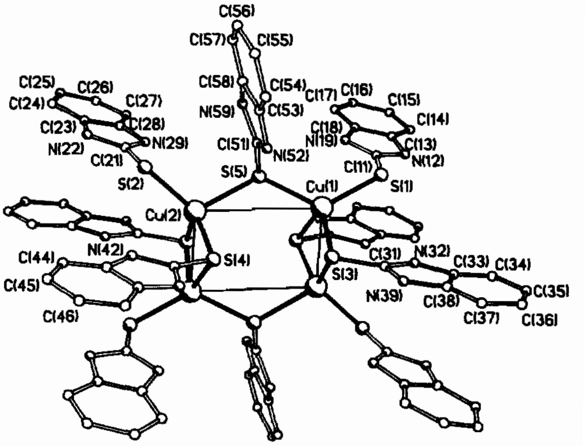

Fig. 1. Perspective view of the $[Cu_4(bzimztH)_{10}]^{4+}$ cation with atomic numbering. H atoms are omitted. Ligand 4, incompletely labelled, follows the same numbering scheme as the other ligands.

TABLE I. Atomic Coordinates (×10^4)

	x	*y*	*z*
Cu(1)	3681(1)	4634(1)	3422(1)
Cu(2)	6051(1)	5619(1)	4645(1)
S(1)	2442(2)	4307(1)	2125(1)
C(11)	1586(6)	4760(3)	1771(5)
N(12)	632(5)	4665(3)	1497(5)
C(13)	117(6)	5125(3)	1239(5)
C(14)	−858(7)	5214(4)	926(7)
C(15)	−1151(8)	5732(5)	741(7)
C(16)	−459(9)	6127(4)	871(7)
C(17)	496(8)	6031(4)	1198(8)
C(18)	785(7)	5517(3)	1390(6)
N(19)	1675(5)	5279(2)	1742(5)
S(2)	7000(2)	6101(1)	4035(2)
C(21)	6567(7)	6710(3)	3884(5)
N(22)	7076(5)	7148(2)	3958(5)
C(23)	6491(7)	7572(3)	3774(6)
C(24)	6692(11)	8104(3)	3734(7)
C(25)	5922(9)	8426(4)	3503(6)
C(26)	5002(10)	8250(4)	3401(9)
C(27)	4819(8)	7732(4)	3401(7)
C(28)	5582(7)	7403(3)	3605(5)
N(29)	5660(5)	6859(3)	3675(5)
S(3)	4657(1)	3949(1)	4304(1)
C(31)	4053(7)	3372(3)	3987(5)
N(32)	3130(6)	3282(2)	3711(5)
C(33)	2936(6)	2755(3)	3545(5)
C(34)	2119(7)	2474(3)	3255(6)
C(35)	2190(7)	1944(3)	3192(7)
C(36)	3060(9)	1713(3)	3423(7)
C(37)	3893(8)	1988(3)	3706(6)
C(38)	3818(6)	2513(3)	3755(5)
N(39)	4493(5)	2905(2)	4020(5)
S(4)	6816(2)	4836(1)	5358(2)
C(41)	8019(7)	4860(3)	5693(6)
N(42)	8585(5)	5281(3)	5854(5)
C(43)	9545(6)	5147(4)	6137(6)
C(44)	10372(8)	5416(5)	6360(7)
C(45)	11192(9)	5149(7)	6610(8)
C(46)	11208(10)	4604(7)	6648(8)
C(47)	10396(10)	4323(6)	6435(7)
C(48)	9547(7)	4597(4)	6163(6)
N(49)	8596(6)	4448(3)	5891(5)
S(5)	4634(1)	5327(1)	3296(1)
C(51)	5183(6)	5199(3)	2449(5)
N(52)	5709(5)	4790(3)	2384(5)
C(53)	6051(6)	4854(4)	1597(6)
C(54)	6609(7)	4535(4)	1194(8)
C(55)	6786(8)	4721(6)	378(8)
C(56)	6455(8)	5202(5)	−43(7)
C(57)	5905(8)	5513(4)	324(6)
C(58)	5718(6)	5336(3)	1152(5)
N(59)	5199(5)	5533(2)	1702(4)
Cl(1)	163(3)	2669(1)	5100(3)
O(11)	−626	2805	5403
O(12)	−172	2555	4037
O(13)	818	3092	5302
O(14)	633	2225	5660
Cl(2)	3258(2)	6562(1)	1609(4)
O(21)	3468	6662	2667
O(22)	4128	6501	1413
O(23)	2705	6100	1329
O(24)	2731	6986	1026
O(1)	1232(5)	3640(2)	3624(5)
O(2)	3499(7)	7102(4)	5552(10)
O(3)	3316(8)	6060(3)	6449(7)
O(4)	−42(9)	3630(3)	1581(7)
O(5)	2109(16)	6584(5)	3940(12)
O(6)	1866(22)	6632(14)	−1372(35)
O(7)	8608(47)	2697(14)	7302(30)

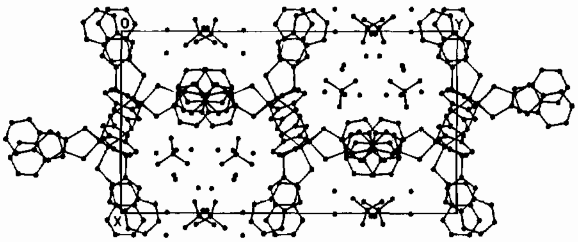

Fig. 2. Unit cell contents, seen in parallel projection along the *c* axis.

Results and Discussion

The UV–Vis spectrum of the complex in DMF at ambient temperature consists of a peak (λ_{max} = 300 nm, $\epsilon \sim 1.9 \times 10^4$ mol^{-1} l cm^{-1}) with a prominent shoulder (λ_{max} = 291.8 nm, $\epsilon \sim 1.7 \times 10^4$ mol^{-1} l cm^{-1}). These transitions are suggested to involve substantial π–π^* character since bzimztH in DMF has a similar UV spectral profile. The pale green colour of the complex is presumed to arise from the 'tailing' of the band at 300 nm into the visible region since the complex shows no d–d spectral bands in the range 400–1100 nm and is diamagnetic at room temperature.

The IR spectrum of the complex indicated the presence of ionic perchlorate (1090br and 600m cm^{-1}) [15] and water molecules (3530br and 1620m cm^{-1}) [16].

Changes in the IR spectrum of bzimztH upon coordination involve broadening and splitting of ν(C=C + C=N) (1510 cm^{-1}), thioamide(I) (1470 cm^{-1}) and thioamide(II) (1360 cm^{-1}). Thioamide(III) (1180 cm^{-1}) undergoes a modest shift of 10 cm^{-1} (1170 cm^{-1}) and thioamide(IV) is converted from its clearly resolved components in bzimztH (710, 745 cm^{-1}) into a single broad peak (740 cm^{-1}) of moderate intensity in the complex. The absorption at 660 cm^{-1} in bzimztH, δ(C–S), occurs at 615 cm^{-1} in the complex.

TABLE II. Bond Lengths (Å) and Angles (°)^a

Cu(1)–S(1)	2.262(2)	Cu(1)–S(3)	2.356(2)
Cu(1)–S(5)	2.335(3)	Cu(1)–S(4′)	2.499(3)
Cu(2)–S(2)	2.269(3)	Cu(2)–S(4)	2.369(2)
Cu(2)–S(5)	2.420(2)	Cu(2)–S(3′)	2.373(3)
S(1)–C(11)	1.679(9)	C(11)–N(12)	1.364(12)
C(11)–N(19)	1.350(10)	N(12)–C(13)	1.396(11)
C(13)–C(14)	1.389(13)	C(13)–C(18)	1.387(12)
C(14)–C(15)	1.405(16)	C(15)–C(16)	1.422(17)
C(16)–C(17)	1.364(17)	C(17)–C(18)	1.392(13)
C(18)–N(19)	1.394(11)	S(2)–C(21)	1.688(8)
C(21)–N(22)	1.347(11)	C(21)–N(29)	1.341(13)
N(22)–C(23)	1.370(11)	C(23)–C(24)	1.414(13)
C(23)–C(28)	1.369(14)	C(24)–C(25)	1.367(18)
C(25)–C(26)	1.409(20)	C(26)–C(27)	1.369(16)
C(27)–C(28)	1.372(15)	C(28)–N(29)	1.413(10)
S(3)–C(31)	1.720(8)	C(31)–N(32)	1.319(13)
C(31)–N(39)	1.368(10)	N(32)–C(33)	1.395(9)
C(33)–C(34)	1.358(13)	C(33)–C(38)	1.396(13)
C(34)–C(35)	1.381(12)	C(35)–C(36)	1.364(16)
C(36)–C(37)	1.370(16)	C(37)–C(38)	1.365(10)
C(38)–N(39)	1.388(10)	S(4)–C(41)	1.696(10)
C(41)–N(42)	1.347(11)	C(41)–N(49)	1.339(12)
N(42)–C(43)	1.395(12)	C(43)–C(44)	1.356(15)
C(43)–C(48)	1.423(14)	C(44)–C(45)	1.343(19)
C(45)–C(46)	1.412(26)	C(46)–C(47)	1.357(21)
C(47)–C(48)	1.386(18)	C(48)–N(49)	1.392(14)
S(5)–C(51)	1.696(9)	C(51)–N(52)	1.341(11)
C(51)–N(59)	1.363(10)	N(52)–C(53)	1.378(13)
C(53)–C(54)	1.422(16)	C(53)–C(58)	1.406(12)
C(54)–C(55)	1.351(17)	C(55)–C(56)	1.393(20)
C(56)–C(57)	1.373(18)	C(57)–C(58)	1.366(14)
C(58)–N(59)	1.369(12)		
S(1)–Cu(1)–S(3)	109.1(1)	S(1)–Cu(1)–S(5)	125.3(1)
S(3)–Cu(1)–S(5)	109.5(1)	S(1)–Cu(1)–S(4′)	113.6(1)
S(3)–Cu(1)–S(4′)	109.3(1)	S(5)–Cu(1)–S(4′)	88.0(1)
S(2)–Cu(2)–S(4)	110.8(1)	S(2)–Cu(2)–S(5)	111.7(1)
S(4)–Cu(2)–S(5)	103.2(1)	S(2)–Cu(2)–S(3′)	116.6(1)
S(4)–Cu(2)–S(3′)	113.3(1)	S(5)–Cu(2)–S(3′)	100.0(1)
Cu(1)–S(1)–C(11)	107.7(3)	S(1)–C(11)–N(12)	125.0(6)
S(1)–C(11)–N(19)	129.0(7)	N(12)–C(11)–N(19)	106.0(7)
C(11)–N(12)–C(13)	110.5(7)	N(12)–C(13)–C(14)	130.4(8)
N(12)–C(13)–C(18)	106.2(7)	C(14)–C(13)–C(18)	123.3(8)
C(13)–C(14)–C(15)	116.2(9)	C(14)–C(15)–C(16)	119.7(11)
C(15)–C(16)–C(17)	122.9(11)	C(16)–C(17)–C(18)	117.3(10)
C(13)–C(18)–C(17)	120.6(9)	C(13)–C(18)–N(19)	106.2(6)
C(17)–C(18)–N(19)	133.2(9)	C(11)–N(19)–C(18)	111.0(7)
Cu(2)–S(2)–C(21)	107.4(4)	S(2)–C(21)–N(22)	126.4(8)
S(2)–C(21)–N(29)	127.5(7)	N(22)–C(21)–N(29)	106.1(7)
C(21)–N(22)–C(23)	110.6(8)	N(22)–C(23)–C(24)	131.0(10)
N(22)–C(23)–C(28)	108.0(8)	C(24)–C(23)–C(28)	121.1(10)
C(23)–C(24)–C(25)	115.4(12)	C(24)–C(25)–C(26)	122.8(10)
C(25)–C(26)–C(27)	120.3(12)	C(26)–C(27)–C(28)	117.1(11)
C(23)–C(28)–C(27)	122.9(8)	C(23)–C(28)–N(29)	104.6(8)
C(27)–C(28)–N(29)	132.5(9)	C(21)–N(29)–C(28)	110.7(7)
Cu(1)–S(3)–C(31)	110.0(3)	Cu(1)–S(3)–Cu(2′)	69.1(1)
C(31)–S(3)–Cu(2′)	105.2(4)	S(3)–C(31)–N(32)	129.2(6)
S(3)–C(31)–N(39)	123.6(7)	N(32)–C(31)–N(39)	107.1(7)
C(31)–N(32)–C(33)	111.0(7)	N(32)–C(33)–C(34)	133.3(8)
N(32)–C(33)–C(38)	106.0(7)	C(34)–C(33)–C(38)	120.7(7)

(continued)

TABLE II. *(continued)*

C(33)–C(34)–C(35)	117.9(9)	C(34)–C(35)–C(36)	120.5(9)
C(35)–C(36)–C(37)	122.6(8)	C(36)–C(37)–C(38)	116.6(10)
C(33)–C(38)–C(37)	121.6(8)	C(33)–C(38)–N(39)	105.9(6)
C(37)–C(38)–N(39)	132.5(9)	C(31)–N(39)–C(38)	109.9(7)
Cu(2)–S(4)–C(41)	113.3(3)	Cu(2)–S(4)–Cu(1′)	66.8(1)
C(41)–S(4)–Cu(1′)	109.3(3)	S(4)–C(41)–N(42)	128.3(7)
S(4)–C(41)–N(49)	125.0(7)	N(42)–C(41)–N(49)	106.6(8)
C(41)–N(42)–C(43)	111.9(7)	N(42)–C(43)–C(44)	134.8(10)
N(42)–C(43)–C(48)	104.3(8)	C(44)–C(43)–C(48)	120.9(10)
C(43)–C(44)–C(45)	118.3(14)	C(44)–C(45)–C(46)	121.6(14)
C(45)–C(46)–C(47)	121.6(14)	C(46)–C(47)–C(48)	116.9(14)
C(43)–C(48)–C(47)	120.7(10)	C(43)–C(48)–N(49)	106.1(8)
C(47)–C(48)–N(49)	133.2(10)	C(41)–N(49)–C(48)	111.1(8)
Cu(1)–S(5)–Cu(2)	124.9(1)	Cu(1)–S(5)–C(51)	111.2(3)
Cu(2)–S(5)–C(51)	95.9(3)	S(5)–C(51)–N(52)	129.8(6)
S(5)–C(51)–N(59)	124.0(6)	N(52)–C(51)–N(59)	106.2(8)
C(51)–N(52)–C(53)	110.5(7)	N(52)–C(53)–C(54)	133.0(9)
N(52)–C(53)–C(58)	106.7(8)	C(54)–C(53)–C(58)	120.2(9)
C(53)–C(54)–C(55)	116.5(10)	C(54)–C(55)–C(56)	122.1(12)
C(55)–C(56)–C(57)	122.4(11)	C(56)–C(57)–C(58)	116.6(10)
C(53)–C(58)–C(57)	122.1(9)	C(53)–C(58)–N(59)	105.2(8)
C(57)–C(58)–N(59)	132.7(9)	C(51)–N(59)–C(58)	111.3(7)

^{a}Symmetry operator (′): $1 - x, 1 - y, 1 - z$.

Changes in the IR spectra of bzimztH in the range 745 to 600 cm^{-1} are due to coordination by the thione sulphur atom and changes between 1510 and 1400 cm^{-1} are probably due to hydrogen bonding between the ligands' (NH) imido groups, water molecules and perchlorate oxygen atoms (Fig. 2). This is further supported by the conversion of ν(NH) from a broad, strong absorption (3130 cm^{-1}) in bzimztH into a broader absorption of moderate intensity (3280 cm^{-1}) in the complex.

The complex cation contains a planar centrosymmetric array of four copper atoms with edge dimensions of 2.681(2) Å (Cu(1)–Cu(2′)) and 4.216(3) Å (Cu(1)–Cu(2)) with an internal angle of 85.8(1)° (Fig. 1). Edge dimensions for tetrahedral Cu$_4$ clusters are typically 2.76 Å [7] and 2.726 Å [8]. Of the ten bzimztH ligands in this complex four are terminal S-bonded and the remainder are μ_2-S bridging. Each copper atom has a distorted tetrahedral configuration with angles about the metal ranging from 88.0(1)° to 125.3(1)° and an S$_4$-donor set. In addition the ligands are significantly inclined ('tilted') to the mean plane of the Cu$_4$ cluster (planes 1–6, Table III).

The S(5) and S(5′) atoms asymmetrically bridge pairs of copper atoms along the long edges of the Cu$_4$ cluster, S(3) and S(4) generate asymmetric bridges along the short edges of the Cu$_4$ cluster. Furthermore, since S(3) and S(4) are displaced above the plane of the Cu$_4$ cluster they combine with their symmetry related partners, S(3′) and S(4′) and the copper atoms to generate Cu$_2$S$_2$ cores.

A major consequence of asymmetric μ_2-S bridging is the production of an alternating sequence of short and long Cu–S distances between the metal atoms. A similar sequence of Cu–S distances also bridges the metal atoms in the [Cu$_4$(imidazolidine-2-thione)$_9$]$^{4+}$ ion [10].

The remarkably open appearance of the structure (Fig. 1) results from the *syn-exo* configuration of the terminal and bridging ligands along the short edges of the Cu$_4$ cluster.

Terminal Cu–S distances (2.262(2) and 2.269(3) Å; Table II) are typically significantly shorter than the corresponding bridging distances (2.335–2.499 Å; Table II) [17, 10]. All Cu–S distances however are within the range (2.196–2.631 Å) known for dinuclear [18–20] and tetranuclear [10, 11] copper complexes with heterocyclic thione donors [21].

Angles (Cu–S–C) at the sulphur atoms, are similar to one another for the terminal ligands (S(1) 107.7(3)°; S(2) 107.4(4)°; Table II). Such angles are typical of terminal sulphur donors including imidazole-thiones [21], alkylthiolates [22], phenylthiolate [7] and cysteinylthiolate [23]. While the angular range for such systems is relatively wide [21] average values are generally in the region of the tetrahedral angle.

Both of the terminal ligands 'tilt' with respect to the mean plane of the Cu$_4$ cluster (planes 1, 2 and 3; Table III) and 'twist' about their respective Cu–S–C planes (planes 2, 3, 7 and 8; Table III). Such ligands orientations are typical of other terminal S-donating imidazole-thione donors [17–19] and,

TABLE III. Least-squares Mean Planes (Orthogonal Coordinates) and Dihedral Angles

Plane no.	Atoms	Equation	Major atomic displacements (Å)
(a) Planes			
1	Cu(1), Cu(2), Cu(1′), Cu(2′)	$0.6093XO - 0.7428YO - 0.2776ZO + 6.5576 = 0.0$	S(1), 0.1034; S(2), 0.2502; S(3), 1.9475; S(4), 1.9899; S(5), −0.3304.
2	Ligand 1	$0.0517XO + 0.0968YO + 0.9940ZO - 2.9693 = 0.0$	N(19), 0.0369
3	Ligand 2	$0.1661XO + 0.0670YO + 0.9838ZO - 4.6971 = 0.0$	C(25), 0.0513
4	Ligand 3	$0.0746XO + 0.0973YO + 0.9925ZO - 3.0487 = 0.0$	N(39), −0.0302
5	Ligand 4	$0.0781XO + 0.0293YO + 0.9965ZO - 5.0689 = 0.0$	C(41), 0.0155
6	Ligand 5	$0.8279XO + 0.4376YO + 0.3509ZO - 12.1858 = 0.0$	C(58), 0.0175
7	Cu(1), S(1), C(11)	$0.3929XO + 0.3661YO - 0.8436ZO - 3.9796 = 0.0$	
8	Cu(2), S(2), C(21)	$0.5854XO + 0.2192YO + 0.7806ZO - 10.7868 = 0.0$	
9	Cu(1), Cu(2′), S(3), C(31)	$0.9740XO + 0.2163YO + 0.0678ZO - 7.6042 = 0.0$	
10	Cu(1′), Cu(2), S(4), C(41)	$0.6230XO + 0.7777YO + 0.0840ZO - 16.7028 = 0.0$	
11	Cu(1), Cu(2), S(5), C(51)	$0.5563XO + 0.6215YO + 0.5510ZO - 6.1694 = 0.0$	
12	Cu(1), S(3), Cu(2′), S(4′)	$0.8383XO + 0.5451YO + 0.0129ZO - 10.9913 = 0.0$	
13	Cu(2), S(4), Cu(1′), S(3′)	$0.8383XO + 0.5451YO + 0.0129ZO - 14.9797 = 0.0$	

(b) Dihedral angles (°)
1/2, 108.4; 1/3, 102.8; 1/4, 99.1; 1/5, 104.5; 1/6, 85.3; 2/3, 6.8; 2/4, 11.2; 3/4, 10.8; 2/5, 4.2; 3/5, 5.5; 2/7, 141.5; 3/8, 28.4; 4/9, 90.9; 5/10, 81.1; 6/11, 90.3; 1/12, 88.7; 5/12, 84.6; 4/13, 88.7; 5/13, 84.6; 4/5, 7.3

in conjunction with the corresponding Cu–S distances (Table II), are consistent with conventional electron pair donation by the donor atoms.

Asymmetric bridging is reflected by the angles (Cu–S–C) at the donor atoms as well as by the corresponding Cu–S distances (Table II) [17, 18]. In this structure Cu–S–C angles are in the range 95.9(3)° to 113.3(3)°, with the greatest differences occurring in the case of S(5) and S(5′) (Cu(1)–S(5)–C(51), 111.2(3)°; Cu(2)–S(5)–C(51), 95.9(3)°). Invariably, the larger bridging angles (110.0(3)°–113.3(3)°; Table II) are aligned with the shorter Cu–S distances (2.335(3)–2.369(2) Å; Table II) and the smaller bridging angles (95.9(3)°–109.3(3)°, Table II) are aligned with the longer Cu–S distances (2.373(3)–2.499(3) Å; Table II). Each bridging ligand forms a 'normal' contact, with distances and angles consistent with CuS_4 tetrahedral environments and an 'abnormal' contact in which the Cu–S distance is longer and the Cu–S–C angle is smaller than in the 'normal' case. The 'normal' contacts are consistent with conventional electron pair donation by the bridging sulphur atom.

Within the Cu_2S_2 cores the narrow Cu–S–Cu angles (66.8(1)° and 69.1(1)°) bridge distances between the copper atoms (2.681(2) Å) which are among the smallest reported for such systems [17]. The bridging ligands (planes 4 and 5; Table III) are virtually normal to the plane of the Cu_2S_2 cores (planes 12 and 13; Table III); they also 'twist' about their Cu(1) Cu(2) S(3 or 4) C(31 or 41) planes (planes 9 and 10); Table III). Consequently, the bridging ligands are virtually parallel with the terminal ligands (planes 2, 3, 4 and 5; Table III).

Dimensions within the Cu_2S_2 cores, as well as ligand orientations, are similar to those of other copper(I) complexes in which thiourea [24] and 1-methylimidazoline-2-thione [17, 18] are reported to complete their bridging function by means of thioamide pπ molecular orbitals. Similar arguments have been used to rationalise asymmetric μ_2-S bridging in the $[Cu_4(\text{imidazolidine-2-thione})_9]^{4+}$ and $[Cu_4(\text{1-methylpyrimidine-2-thione})_6]^{4+}$ ions [10, 11]. They may also be used to rationalise similar behaviour by the remaining bridging ligands S(5), S(5′) in this structure.

The 'normal' and 'abnormal' contacts, previously mentioned, are clearly the result of radically different bonding functions by the bridging ligands.

The relatively large angle (Cu(1)–S(5)–Cu(2), 124.9(1)°), is clearly a consequence of the separation distance between the copper atoms (4.216(3) Å). Asymmetric bridging across such a large distance is not a steric requirement of the ligand but it does extend the pattern of long and short Cu–S distances, created within the Cu_2S_2 cores, to the rest of the cluster. It also suggests that asymmetric μ_2-S bridging may have an electronic, as well as a steric, basis. A similar combination of large bridging angle (137.3(3)°) and asymmetric μ_2-S bridging also occurs in $[Cu_2(\text{imidazolidine-2-thione})_4Cl_2]$ [20].

Significant differences among the metal atom separation distances within the Cu_4 cluster suggests that metal–metal interactions are limited to the metal atoms within the Cu_2S_2 cores. Soft attractive Cu(1)....Cu(1) coupling [25, 26] has been proposed for other Cu_2S_2 cores [17, 18] but the dominant stabilising influence in this structure must be the bridging ligands.

Supplementary Material

H atom coordinates, thermal parameters and structure factors are available from the authors on request.

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