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Tetrakis-[1-methylimidazoline-2(3H)-thione]-μ_2-[1-methylimidazoline-2(3H)-thione]-Di-Copper(I) Sulphate Trihydrate: Preparation, Thermal Analysis and Crystal Structure

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Abstract

1-methylimidazoline-2(3H)-thione (mimtH) reacts with copper(II) sulphate pentahydrate in aqueous acetone to produce the dinuclear complex, $Cu_2(mimtH)_5SO_4 \cdot 3H_2O$; the formula has been established by a combination of chemical and thermal analysis. The monoclinic crystals, (space group P_c, $Z = 2$), contain dinuclear cations, sulphate ions and water molecules. The dinuclear cation, $Cu_2(mimtH)_5^{2+}$, consists of two trigonal copper(I) atoms, four terminal, monodentate, S-donating mimtH molecules and one S-bridging (μ_2) mimtH molecule. Some average dimensions are: Cu–S, 2.258 Å and S–Cu–S, 120.0°; the Cu–S–Cu bridging angle is 94.8° and the Cu–Cu separation distance is 3.308 Å.

Introduction

Imidazole-thiones are known to reduce copper(II) salts with the production of monomeric complexes containing sulphur donating ligands and trigonal copper(I) [1–4]. Dimeric complexes are also reported with both trigonal and tetrahedral copper(I) [5] or tetrahedral copper(I) [6], together with a combination of terminal and bridging (μ_2) S-donating ligands [5, 6] and occasionally, relatively short metal-metal separation distances [6]. A polynuclear complex is reported to contain four copper(I) atoms tetrahedrally coordinated by a combination of monodentate and bridging (μ_2 and μ_4) sulphur donating ligands [7].

Prominent among the unsaturated imidazoline-thione molecules is 1-methylimidazoline-2(3H)-thione (mimtH) which forms a dimeric complex with copper(I) chloride, $Cu_2(mimtH)_4Cl_2$ [6] as well as the monomeric complex $Cu(mimtH)_3(NO_3)$ [4].

This series of complexes has been extended to include the title compound, $Cu_2(mimtH)_5SO_4 \cdot 3H_2O$, whose electronic spectrum and diamagnetic character are indicative of copper(I); the further characterisation of this complex is the subject of this report.

Experimental

Starting Materials

The ligand (mimtH) was used as received from the Aldrich Chemical Company Ltd; the remaining chemicals, which were of at least reagent grade, were obtained from BDH Ltd.

Preparation and Analysis of $Cu_2(mimtH)_5SO_4 \cdot 3H_2O$

The air stable complex, $Cu_2(mimtH)_5SO_4 \cdot 3H_2O$, is prepared by reacting the ligand and copper(II) sulphate pentahydrate in a 1:4 (metal:ligand) ratio in aqueous acetone. Copper(II) sulphate pentahydrate (0.2495 g; 1 mmol in 10 cm^3 of distilled water) is added dropwise to a refluxing solution of the ligand (mimtH; 4 mmol; 0.4560 g in 10 cm^3 of acetone). After cooling the reaction mixture slowly to room temperature followed by further slow evaporation of the solvent for several days a brown crystalline product was obtained. This was removed by filtration and dried over silica gel at reduced pressure. Chemical analysis for $Cu_2(mimtH)_5SO_4 \cdot$

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TABLE I. Crystallographic Data.

Compound	$Cu_2C_{20}H_{30}N_{10}S_5 \cdot 3H_2O \cdot SO_4$
M_r	847.36
a, Å	7.126(11)
b, Å	17.396(7)
c, Å	13.804(12)
β, deg.	99.95(18)
μ, Å^3	1685.5
Z	2
space group	Pc
$F(000)$	872
D_c, g cm^{-3}	1.67
μ, cm^{-1}	16.0
diffractometer	Enraf-Nonius CAD-4
scanning mode	$\omega-2\theta$
radiation, Å	monochromatised, Mo(Kα), 0.71069
2θ range, deg.	4.0–50.0
total data	3227
$F_o{}^2 > 1.5\sigma(F_o)^2$	2925
R	0.037
Rw	0.039
w	unit weights

$3H_2O$ gives: calculated (%) C 28.3; H 4.3; N 16.5; found (%) C 28.6; H 4.3; N 16.5.

The analysis was performed by Elemental Microanalysis Ltd., Beaworthy, Devon.

Physical Methods

Infrared spectra were recorded as caesium iodide discs in the range 4000–200 cm^{-1} from a Perkin-Elmer 577 grating spectrophotometer.

Thermal analysis measurements (TG and DTG) were obtained from a Stanton-Redcroft TG750 instrument using column dried flowing air or argon and platinum crucibles. Differential Thermal Analysis measurements were obtained from a Stanton-Redcroft DTA 673/4 instrument in flowing nitrogen with quartz crucibles. Sample masses were in the range 5–8 mg and heating rates were either 10 or 20 °C min^{-1}. Details of the quantitative method for the determination of reaction enthalpies from DTA endotherms have been published previously [8].

X-ray powder photographs of the complex and end products from the thermal dissociation in air were taken with a Guinier-Hägg parafocussing camera using CuKα monochromated radiation (λ = 1.5405 Å) and Kodirex single coated film.

A room temperature Gouy Balance was used to monitor the diamagnetic behaviour of the complex.

TABLE II. Final Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.s (in Parentheses) and B_{eq} Values.

Atom	x	y	z	B_{eq} (Å^2)
Cu(1)	0	1394(1)	10000	3.09(8)
Cu(2)	−412(2)	3279(1)	9718(1)	2.31(8)
S(21)	2683(4)	678(1)	10149(2)	2.95(10)
S(22)	−2678(4)	1152(1)	9005(2)	3.78(8)
S(23)	−3062(3)	3193(1)	8597(2)	2.79(8)
S(24)	1813(4)	4211(1)	9694(2)	3.01(8)
S(25)	−62(3)	2428(1)	10966(2)	2.12(8)
C(21)	2767(12)	311(5)	9013(6)	2.9(3)
N(31)	3122(11)	−418(4)	8808(6)	3.4(3)
C(41)	3197(15)	−497(6)	7832(8)	4.0(5)
C(51)	2879(13)	189(6)	7422(7)	3.7(5)
N(11)	2600(10)	696(4)	8146(5)	2.8(3)
C(11)	2292(15)	1526(5)	8003(7)	3.6(4)
C(22)	−2268(12)	374(5)	8307(6)	2.7(3)
N(32)	−2351(12)	369(5)	7333(6)	3.3(3)
C(42)	−2067(18)	−352(6)	7011(8)	4.3(5)
C(52)	−1814(15)	−814(5)	7801(8)	3.9(4)
N(12)	−1935(11)	−363(4)	8598(5)	3.0(3)
C(12)	−1801(17)	−650(6)	9594(7)	4.3(5)
C(23)	−3628(11)	4122(5)	8256(6)	2.4(3)
N(33)	−4308(11)	4358(4)	7329(5)	2.8(3)
C(43)	−4685(15)	5129(6)	7331(7)	3.6(4)
C(53)	−4269(13)	5379(5)	8238(8)	3.3(4)
N(13)	−3613(10)	4757(4)	8827(5)	2.6(3)
C(13)	−3090(15)	4783(6)	9887(6)	3.8(4)
C(24)	1187(11)	4618(4)	8542(6)	2.3(3)
N(34)	745(10)	5347(4)	8346(5)	2.9(3)
C(44)	348(15)	5447(7)	7356(8)	3.8(5)
C(54)	586(15)	4773(6)	6946(7)	3.5(4)
N(14)	1101(10)	4250(4)	7673(5)	2.6(3)
C(14)	1484(14)	3440(5)	7525(7)	3.6(3)
C(25)	2127(12)	2514(4)	11755(5)	2.2(3)
N(35)	2267(11)	2538(4)	12733(5)	2.7(3)
C(45)	4141(14)	2599(5)	13159(7)	3.5(4)
C(55)	5166(13)	2610(5)	12440(8)	3.7(4)
N(15)	3906(10)	2552(4)	11551(5)	2.6(3)
C(15)	4502(14)	2548(6)	10592(7)	3.7(4)
S(6)	−499(3)	2916(1)	4683(2)	2.3(1)
O(1)	−641(10)	2562(4)	3719(4)	4.1(3)
O(2)	129(12)	2349(4)	5462(5)	4.8(3)
O(3)	909(12)	3522(4)	4762(5)	5.3(3)
O(4)	−2322(12)	3225(6)	4798(6)	6.8(5)
O(11)	−2831(15)	1861(5)	6491(7)	4.6(4)
O(12)	−5271(15)	3463(7)	5727(7)	5.9(5)
O(13)	3445(12)	−1531(4)	10295(6)	5.7(4)

Crystal Structure Analysis

Relevant crystallographic data are listed in Table I. Unit cell dimensions, initially obtained photographically, were refined from the setting angles of 25 automatically centred high angle reflections. Three intensity controls measured every hour during data collection showed no reduction in diffracted intensity. Intensity data, recorded at room temperature as previously described [9], were corrected for Lorentz and polarisation effects.

TABLE III. Bond Distances (Å) and Angles (°) with e.s.d.s in Parentheses.

Bond	(Å)	Angle	(°)
(a) the coordination sphere			
		Cu(1)–S(25)–Cu(2)	94.8(2)
Cu(1)–Cu(2)	3.308(4)	S(21)–Cu(1)–Cu(2)	127.8(2)
Cu(1)–S(21)	2.262(5)	S(22)–Cu(1)–Cu(2)	93.8(2)
Cu(1)–S(22)	2.191(5)	S(25)–Cu(1)–Cu(2)	42.7(1)
Cu(1)–S(25)	2.243(4)	S(23)–Cu(2)–Cu(1)	93.6(1)
Cu(2)–S(25)	2.151(4)	S(24)–Cu(2)–Cu(1)	131.4(1)
Cu(2)–S(23)	2.230(4)	S(25)–Cu(2)–Cu(1)	42.5(1)
Cu(2)–S(24)	2.272(4)	S(21)–Cu(1)–S(22)	125.6(2)
		S(21)–Cu(1)–S(25)	119.4(2)
		S(22)–Cu(1)–S(25)	115.0(2)
		S(23)–Cu(2)–S(24)	123.1(2)
		S(23)–Cu(2)–S(25)	117.1(2)
		S(24)–Cu(2)–S(25)	119.7(2)
		Cu(1)–S(21)–C(21)	106.4(4)
		Cu(1)–S(22)–C(22)	106.8(4)
		Cu(1)–S(25)–C(25)	109.4(4)
		Cu(2)–S(23)–C(23)	105.0(4)
		Cu(2)–S(24)–C(24)	103.7(4)
		Cu(2)–S(25)–C(25)	112.9(4)
(b) the sulphate ions			
S(6)–O(1)	1.454(7)	O(1)–S(6)–O(2)	110.4(5)
S(6)–O(2)	1.471(8)	O(1)–S(6)–O(3)	108.4(5)
S(6)–O(3)	1.447(8)	O(1)–S(6)–O(4)	109.7(6)
S(6)–O(4)	1.439(9)	O(2)–S(6)–O(3)	108.3(5)
		O(2)–S(6)–O(4)	109.6(6)
		O(3)–S(6)–O(4)	110.3(7)

(c) the heterocyclic molecules

(A = 1 to 5)	Molecule 1	Molecule 2	Molecule 3	Molecule 4	Molecule 5	Average
bond lengths (Å)						
S2(A)–C2(A)	1.703(11)	1.715(11)	1.711(10)	1.727(10)	1.748(10)	1.721
C2(A)–N1(A)	1.359(12)	1.352(11)	1.356(11)	1.352(11)	1.348(11)	1.353
N1(A)–C1(A)	1.468(12)	1.451(12)	1.447(11)	1.456(12)	1.458(12)	1.456
C2(A)–N3(A)	1.333(11)	1.336(12)	1.351(11)	1.324(11)	1.337(11)	1.336
N3(A)–C4(A)	1.364(14)	1.357(14)	1.368(13)	1.358(13)	1.366(13)	1.363
C4(A)–C5(A)	1.323(15)	1.343(16)	1.308(15)	1.326(15)	1.331(15)	1.326
C5(A)–N1(A)	1.373(12)	1.357(14)	1.368(13)	1.356(12)	1.393(12)	1.369
bond angles (°)						
S2(A)–C2(A)–N1(A)	128.0(7)	128.3(7)	129.1(7)	126.5(7)	130.1(6)	128.4
S2(A)–C2(A)–N3(A)	126.1(8)	126.0(7)	125.2(8)	126.1(7)	122.4(7)	125.2
N1(A)–C2(A)–N3(A)	105.8(8)	105.5(8)	105.5(8)	107.4(8)	107.5(8)	106.3
C2(A)–N1(A)–C1(A)	126.3(8)	126.0(9)	126.1(8)	126.9(8)	128.5(8)	126.8
C1(A)–N1(A)–C5(A)	124.8(9)	124.2(9)	124.8(9)	125.3(9)	123.8(9)	124.6
C2(A)–N1(A)–C5(A)	108.8(8)	109.8(8)	109.0(8)	107.8(8)	107.8(8)	108.6
C2(A)–N3(A)–H3(A)	119.2(50)	116.5(51)	102.8(74)	138.1(60)	136.7(76)	122.7
C4(A)–N3(A)–H3(A)	130.3(49)	132.8(50)	143.9(73)	109.9(61)	113.7(76)	126.1
C2(A)–N3(A)–C4(A)	110.3(9)	110.7(9)	109.6(9)	109.2(9)	109.5(9)	109.9
N3(A)–C4(A)–C5(A)	107.4(10)	107.1(9)	108.4(9)	107.2(10)	107.6(9)	107.5
C4(A)–C5(A)–N1(A)	107.7(10)	107.0(9)	107.5(9)	108.4(9)	107.6(9)	107.6

TABLE IV. Least Squares Planes, in the Form $ax + by + cz$ X d (Crystal Coordinates).

Plane	Atoms	*a*, Å	*b*, Å	*c*, Å	*d*, Å	max. dev. (Å)
1	Ligand 1	6.911	3.051	−0.001	2.037	C(21), 0.030
2	Ligand 2	6.927	3.178	−0.316	−1.749	C(22), 0.034
3	Ligand 3	6.951	3.266	−3.901	−4.425	C(23), 0.029
4	Ligand 4	6.961	3.731	−2.354	0.547	C(24), −0.008
5	Ligand 5	−0.479	17.340	−0.423	3.753	C(25), 0.007
6	Cu(1), S(21), C(21)	3.964	13.974	−4.22	−2.274	–
7	Cu(1), S(22), C(22)	2.835	10.669	−10.226	−8.739	–
8	Cu(1), S(25), C(25)	3.338	9.855	−10.335	−8.961	–
9	Cu(2), S(23), C(23)	−4.894	1.230	11.475	11.756	–
10	Cu(2), S(24), C(24)	−4.702	11.395	6.581	10.325	–
11	Cu(2), S(25), C(25)	−3.620	11.415	8.799	12.443	–
12	Cu(1), S(25), Cu(2)	7.069	1.390	−1.035	−0.841	–
13	Cu(1), S(21), S(22), S(25)	3.121	9.826	−10.554	−9.202	Cu(1), 0.017
14	Cu(2), S(23), S(24), S(25)	−4.166	10.584	8.692	12.118	Cu(2), −0.029
15	Cu(1), S(21), S(22), S(25), Cu(2), S(23), S(24)	−3.687	1.088	12.839	12.840	S(25), 1.526

Dihedral Angles

Planes	Angle (°)
1/6	49.9
2/7	66.5
3/9	137.8
4/10	120.3
5/8	55.8
5/11	48.4
5/12	89.5
1/13	66.1
2/13	64.8
3/14	121.2
4/14	116.2
13/14	106.7
5/15	86.5

(e.s.d.s in the range 1–2.0°)

The systematically absent reflections ($h0l$ absent when l is odd) do not distinguish between the centric ($P2/c$) and non-centric (P_c) monoclinic space groups. The latter was confirmed by solution and refinement of the structure.

The heavy atom method was used to solve the structure [10(a)] after having obtained the positions of the two copper and six sulphur atoms by Patterson-search techniques [10(b)]. After isotropic refinement of all non-hydrogen atoms the DIFABS method of absorption correction [11] was applied. Following refinement using anisotropic thermal parameters for all atoms difference Fourier maps revealed the location of all hydrogen atoms on the mimtH molecules as well as those on two of the three water molecules. All hydrogen atom positions were refined freely, with individual isotropic temperature factors, except those of the methyl group which were refined with rigid constraints in order to maintain the tetrahedral geometry.

The refinement was completed by full-matrix, least-squares methods; the correct absolute configuration of the structure was determined since the inverted structure produced R = 0.045 and R_w = 0.049 (*cf.* Table I).

All computations were made using SHELX [10(a,b)] procedures on a DEC VAX-11/750 computer at Queen Mary College, University of London.

Final fractional coordinates and Beq [12] values are listed in Table II; bond distances and angles are in Table III; some least squares planes are in Table IV. [Anisotropic temperature factors, hydrogen atom coordinates and structure factor Tables have been deposited with the editor].

Results and Discussion

Thermal analysis in flowing air, (Fig. 1(a)), gives an initial mass loss (6.6%; 30–150 °C) which corre-

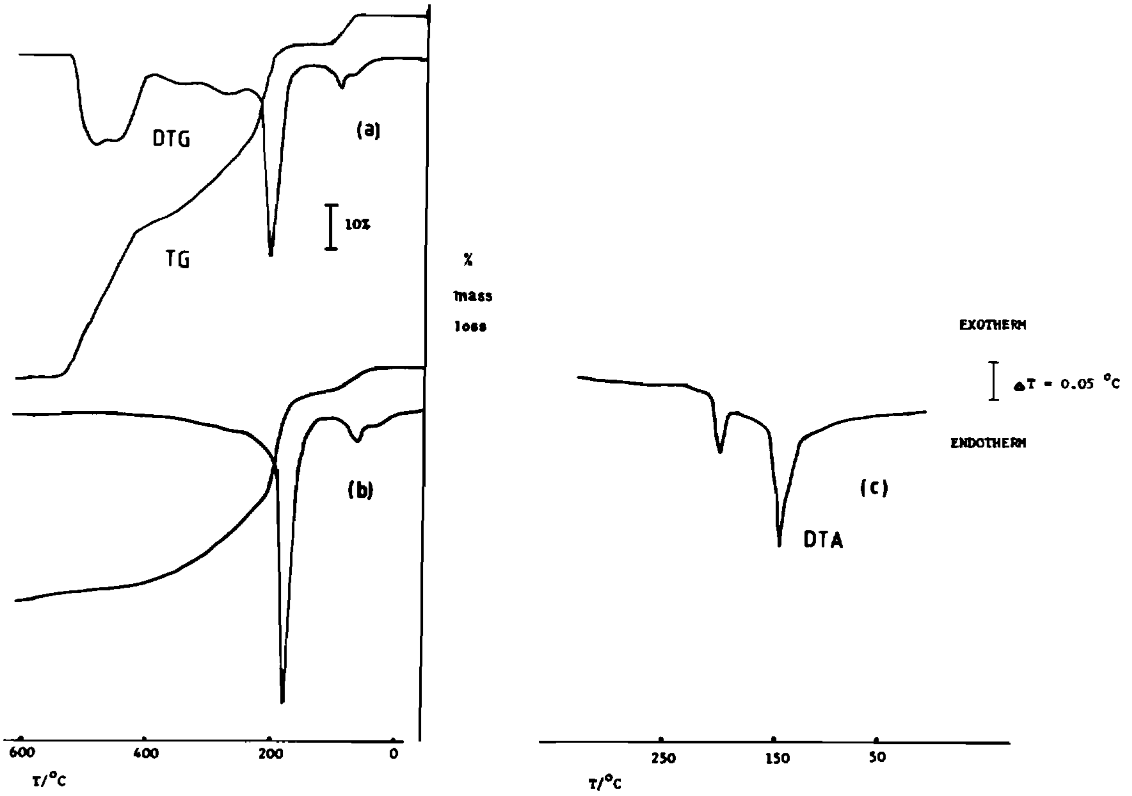

Fig. 1. Thermal analysis Curves for the complex.

sponds with the loss of three water molecules (theor. mass loss, 6.38%). Splitting of the DTG curve (Fig. 1(a)) suggests sequential rather than simultaneous dehydration of the complex.

A total mass loss in flowing air, (83.0%, 30–535 °C), with the end-product [Cu(II)O], identified by X-ray powder diffraction, is within experimental error (±2.0%) of the theoretical value (81.2%) for the decomposition of the complex to the oxide and confirms the unusual stoichiometry of the complex.

A discontinuity occurs in the TG curve in air at 410 °C; the mass loss at this temperature (41.9%) is consistent with the removal of three mimtH molecules (theor. mass 40.4%). The DTG curve suggests that the bulk of the ligand loss occurs in the region of 210 °C, (Fig. 1(a)). The final stage of the decomposition in air (31.1%, 450–535 °C) accounts for the remaining ligands and the degradation of the sulphate.

A low temperature mass loss (6.5%; 75–130 °C) is also consistent with dehydration of the complex in flowing argon, (Fig. 1(b)). The TG and DTG curves both indicate an essentially one stage decomposition (43.3%; 190–600 °C) for the complex in flowing argon with the bulk of the mass loss occurring between 190 and 400 °C. The production of amorphous deposits in argon however inhibits the interpretation of mass losses in terms of specific decomposition schemes. Although the overall mass loss appears to correspond with the loss of approximately three ligand molecules at 600 °C there is evidence from the DTA curve that the sulphate ion also decomposes within the above temperature range.

The DTA curve in flowing nitrogen, (Fig. 1(c)) consists of an endotherm (T_R 134 °C; ΔH_R 244 ± 15 kJ mol^{-1}) whose reaction enthalpy suggests a combination of dehydration and melting of the complex. The decomposition endotherm (T_R 260 °C; ΔH_R 43.0 ± 2.0 kJ mol^{-1}) has a relatively small reaction enthalpy which could well be the net result of endothermic ligand removal and exothermic ligand decomposition; the latter is probably due to the simultaneous decomposition of the ligands and the sulphate ion.

The infrared spectrum shows a broad and strong absorption in the range 3000 to 3400 cm^{-1} which contains contributions from ν(OH) (3220 cm^{-1}), ν(NH) (3120 cm^{-1}) and ν(CH) (3160 cm^{-1}). Additional infrared bands due to the water molecules occur at 1655 cm^{-1} (ν_2) and 510 cm^{-1} (ρ_w) [13(a)].

The 'thioamide' bands of the uncoordinated molecule (I, II, III, IV) occur at 1460, 1275, 1090 and 770, 740 cm^{-1} respectively [14]. In this complex

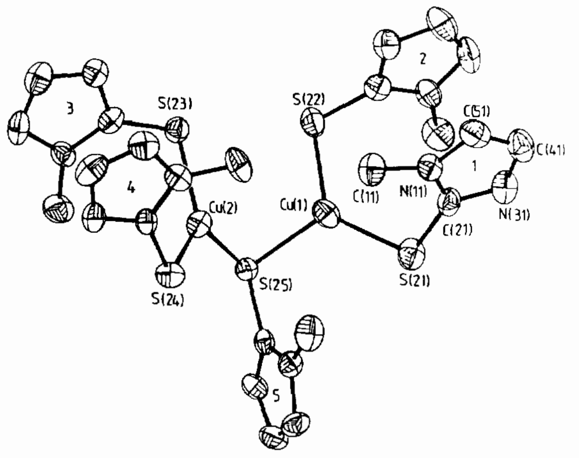

Fig. 2. Perspective diagram of the Cu $(\text{mimtH})_5{}^{2+}$ cation with hydrogen atoms omitted for clarity. The thermal ellipsoids are drawn to include 50% probability [20].

the 1460 cm^{-1} and 1090 cm^{-1} bands are unchanged upon coordination, band (II) is split (1282, 1270 cm^{-1}), and band (IV) consists of three components (740, 727 and 719 cm^{-1}). In the low frequency region the δ(C–S) (670 cm^{-1}) and π(C–S) (530 cm^{-1}) bands show slight (±5 cm^{-1}) shifts in band position. Rather surprisingly, and in contrast with other complexes of mimtH, no ν(M–S) activity occurs in the 250–350 cm^{-1} region [15]. The indications are however that the ligand uses its thione sulphur atom to coordinate to copper(I) in this complex.

Bands due to ionic sulphate occur at 1104 cm^{-1} (ν_3) and 613 cm^{-1} (ν_4) [13(b)].

The structure consists of dinuclear cations, water molecules and sulphate ions held together by an extensive hydrogen bonded network. This involves the imido (NH) group of each ligand and either the water oxygen atoms [N(31,32,33)·····O(11,12,13): 2.695 to 2.840 Å] or sulphate oxygen atoms [N(34, 35)·····O(3,1): 2.761 and 2.669 Å]; together with the sulphate oxygen atoms and the water oxygen atoms [O(2,3,4)·····O(11,12,13); 2.677 to 2.868 Å].

Among the water molecules the O–H distances are in the range: 0.602(115) to 1.010(117) Å with H–O–H angles of 99.4(135) and 111.4(114)° for those molecules whose hydrogen atoms were located.

The dinuclear cation contains two trigonally coordinated copper(I) atoms, four terminal monodentate sulphur donating mimtH molecules and one sulphur bridging (μ_2) mimtH molecule (Fig. 2).

Pronounced deviations from ideal trigonal symmetry are evident from the Cu–S bond lengths (2.191 to 2.272 Å), the S–Cu–S angles (115.0 to 125.6°) (Table III) and the deviations of the copper atoms from the copper-sulphur coordination sphere (Table IV). The bridging sulphur atom, [S(25)], is also significantly displaced from the Cu_2S_5 coordination sphere, (plane 15, Table IV); furthermore, the dihedral angle (106.7°, Table IV) between the two separate CuS_3 planes of the cation (planes 13, 14: Table IV) shows a distinct butterfly distortion or 'folding' of the molecule about the bridging sulphur [S(25)] atom. In addition, the bridging ligand (plane 5, Table IV) virtually bisects (89.5°) the Cu(1)–S(25)–Cu(2) angle (plane 12, Table IV).

The copper-sulphur bond lengths (2.191 to 2.272 Å) are within the range of values (2.916 to 2.282 Å) previously reported for trigonal copper(I) and imidazole-thione sulphur donors [1–4].

All the ligand carbon-sulphur distances are longer than the corresponding distance in the uncoordinated mimtH molecule (1.685 Å) [16]. On average, the increase in length corresponds to a reduction in π-character, [17], of about 14.0% in the carbon-sulphur bonds of the coordinated ligands. The remaining bond lengths and angles in the ligands have values which are largely unaffected by coordination.

Angles, (Cu–S–C; 103.7–112.9°), at the thione sulphur atoms are in the range previously observed for coordinated mimtH molecules with the average (107.4°) close to the tetrahedral value [16]. These angles probably reflect a combination of factors including the electron distribution at the coordinated sulphur as well as the steric requirements of the ligands.

Characteristically, the ligands, (planes 1–5), 'twist' about their respective Cu–S–C planes, (planes 6–11), and 'tilt' towards their respective CuS_3 planes (planes 13 and 14); relevant dihedral angles are in Table IV.

Virtually equivalent distances to the copper atoms [2.243(4), Cu(1); 2.251(4) Å, Cu(2)] suggest that the bridging sulphur, [S(25)], uses both of its non-bonding sp^2 lone pairs in the formation of the bridging copper-sulphur bonds. The orientation of the bridging molecule, so that it's mean plane virtually bisects the Cu–S(25)–Cu angle as well as the previously mentioned 'folding' of the molecule and the Cu–S(25)–Cu angle all appear to contradict the use of non-bonding sp^2 orbitals by the bridging, S(25), atom. However, the orientation of the bridging molecule probably arises as a result of its ability to 'twist' about the C(25)–S(25) bond in order to achieve a favourable orientation of the sterically cumbersome methyl group (Fig. 2). Furthermore, the 'folding' of the molecule and the relatively narrow Cu–S(25)–Cu angle (94.8°) combined to produce an acceptable, non-bonding, Cu(1)–Cu(2) separation distance, (3.308 Å). When the bridging angle approaches the ideal, trigonal, (120°) value, the separation distance between the copper atoms increases to 3.89 Å which is very much longer than the values (2.264–3.356 Å) normally observed for polynuclear copper(I) complexes [7, 18]. However, on the basis of a study of the factors governing 'folding' among square planar dimers it appears that those which dominate are steric and crystal packing in character rather than electronic [19]. We suggest that the same combination of factors predominate in this complex, particularly, since the metal–metal separation distance is so large.

Production of the $Cu_2(mimtH)_5^{2+}$ cation may arise from the oligomerisation of the trigonal $Cu(mimtH)_3^+$ ion:

$$nCu(LH)_3^+ \longrightarrow Cun(LH)_{3n-x} + xLH$$

Further oligomerisation is clearly feasible and with the retention of trigonal copper(I), species such as $Cu_3L_6^{3+}$ and $Cu_4L_8^{4+}$ are possible.

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