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Tetrakis(1-methylimidazoline-2-thione)-μ_2-bis(1-methylimidazoline-2-thione)-dicopper(I) Tetrafluoroborate: Preparation, Thermal Analysis and Crystal Structure

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Abstract

Reaction between copper(II) tetrafluoroborate and 1-methylimidazoline-2-thione (mimtH) in acetone–acetonitrile solution and a dinitrogen atmosphere produced a compound of empirical formula, $Cu(mimtH)_3(BF_4)$, which has been characterised by a variety of physical techniques.

The crystal structure of the compound contains centrosymmetrically constrained dimeric cations, $[Cu_2(mimtH)_6]^{2+}$, in a monoclinic unit cell ($a = 14.499(1)$, $b = 16.195(2)$, $c = 8.433(1)$ Å, $\beta = 93.377(8)^\circ$, space group $P2_1/c$ and $Z = 2$), together with disordered tetrafluoroborate anions. The dimeric cations contain a pair of copper(I) atoms tetrahedrally coordinated by a pair of terminal S-bonded mimtH molecules (Cu–S (averaged) = 2.328 Å) and a pair of asymmetrically S-bridging (μ_2) mimtH molecules. The Cu_2S_2 core of the dimer is lozenge shaped with Cu–S distances of 2.358(1) and 2.459(1) Å, and a Cu–S–Cu angle of 77.2°. Distances of 3.003 and 3.766 Å separate the copper atoms and the sulphur atoms within the Cu_2S_2 core, respectively. The final *R* index for 3786 observed reflections is 0.0497.

Thermal decomposition of the complex in air (145–1000 °C), involves evolution of mimtH, desulphurisation of mimtH and copper(I, II) sulphide production followed by conversion of the mixed sulphides to copper(II) oxide.

Introduction

Reactions between heterocyclic-thiones and copper salts invariably produce complexes which are unpredictable with respect to stoichiometry, stereochemistry and metal oxidation state [1]. The pharmacologically active molecule, 1-methylimidazoline-2(3H)-thione (mimtH), also known as methimazole [2], is typical of many ligands in the above respect. With copper(I) halides mimtH forms complexes of empirical formulation, $Cu(mimtH)_2X$ (X = Cl, Br, I). The chloro complex, however, is a centrosymmetric dimer containing tetrahedral copper, terminal chlorine, terminal S-donating mimtH and doubly S-bridging mimtH [3]. With copper(II) sulphate pentahydrate the dinuclear cation, $[Cu_2(mimtH)_5]^{2+}$, is produced which contains trigonal copper(I), four terminal S-donating mimtH and one doubly S-bridging mimtH [4]. The trigonal, $[Cu(mimtH)_3]^+$ cation, produced from copper(II) nitrate trihydrate and mimtH, contains monodentate S-donating ligands [5].

Two structures have also been reported which involve an oxidised form of mimtH, namely, 1,1′-dimethyl-2,2′-dimidazolylmonosulphide (L–L′). Reduction of copper(II) salts by mimtH is accompanied by the *in situ* formation of L–L′ which over a period of several weeks generates $[Cu(L–L')_2(H_2O)_2](CH_3OSO_3)_2$, from copper(II) sulphate pentahydrate and mimtH in methanol [6]; $[Cu(L–L')_2Cl_4]$ is produced from copper(II) chloride dihydrate and mimtH in methanol [7]. This oxidised form of mimtH is N,N-chelating to copper(II). Reactions between copper(II) salts and thiazolidine-2-thione (tzdtH) also produce oxidised forms of tzdtH which coordinate to copper(II) centres [8].

Clearly, reaction between copper salts and mimtH is capable of producing a variety of products whose composition is dependent on the nature of the solvent, the coordinating properties of the counterion as well as the molar ratios of the reactants and the reaction times employed.

This series of complexes has been extended to include the title compound whose electronic spectrum and diamagnetic character are indicative of copper(I); the further characterisation of this complex is the subject of this report.

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Experimental

Starting Materials

The ligand, mimtH, was supplied by the Aldrich Chemical Co. as 2-mercapto-2-methylimidazole, and was used as supplied. Copper(II) tetrafluoroborate tetrahydrate was supplied by Ventron, GmbH, F.R.G. The remaining chemicals were of reagent quality.

Preparation and Analysis of $[Cu_2(mimtH)_6](BF_4)_2$

All solvents were thoroughly de-gassed with dinitrogen before use. A solution of the metal salt, $Cu(BF_4)_2 \cdot 4H_2O$, (2 mmol, 0.6200 g in 10 cm^3 of a mixture of acetone/acetonitrile (90:10, *v*/*v*)), was added dropwise to a refluxing solution of the ligand, (mimtH, 8 mmol, 0.803 g in 25 cm^3 of a mixture of acetone/acetonitrile (90:10, *v*/*v*)).

After refluxing for two hours the original green colour of the reaction mixture became virtually colourless. The volume of the reaction mixture was then reduced by approximately 50% and slowly cooled to room temperature under dinitrogen. Further slow evaporation over two weeks produced red–brown crystals of the product, some of which were of diffraction quality.

The product was removed by filtration and vacuum dried over silica gel. Yield 65%. *Anal.* Calc.: C, 29.22; H, 3.65; N, 17.04; Cu, 12.99. Found: C, 29.43; H, 3.75; N, 17.16; Cu, 12.98%. Elemental (C, H, N) analyses were performed by Butterworth Laboratories Ltd., 54–56 Waldegrave Road, Teddington, Middlesex.

Physical Methods

Infrared spectra were obtained as caesium iodide discs in the range 4000–200 cm^{-1} on a Perkin-Elmer 684 grating spectrophotometer.

The electrolytic conductivity of the complex was determined at room temperature (10^{-1} M in ethanol) by means of a Portland Electronics conductivity bridge and dip-type electrodes.

Thermogravimetric analyses (TG, DTG) were obtained with a Stanton-Redcroft TG750 instrument fitted with a ceramic furnace with column dried flowing air and platinum crucibles.

A Stanton-Redcroft DTA673/4 instrument was used for the DTA curves with flowing dinitrogen and quartz crucibles. Sample masses were in the region of 5 mg, heating rates in the range 10 to 50 °C min^{-1} were used for TG and DTG and 20 °C min^{-1} for DTA. Details of the quantitative DTA method for the determination of reaction enthalpies have been published previously [9]. The hot stage microscope consisted of a Stanton Redcroft HSM-5 unit with a Hitachi DK81 video camera and JVC TM/90 PSN colour monitor.

A room temperature Gouy balance was used to monitor the diamagnetic character of the complex.

X-ray powder photographs were obtained from a Guinier-Hägg parafocussing camera using Cu $K\alpha_1$, monochromatised radiation ($\lambda = 1.54051$ Å) and Kodirex single-coated X-ray film. Peak intensities of the X-ray powder lines were monitored with a Siemens microdensitometer.

Crystal Structure Determination

Crystal data

Colourless crystals of the title compound, $C_{24}H_{36}B_2N_{12}F_8S_6Cu_2$, $M_r = 985.68$, were grown by slow evaporation from the reaction mixture described above. A crystal of dimensions 0.70 × 0.45 × 0.38 mm was used for the X-ray analysis. Unit cell dimensions were obtained from diffractometer measurements by least-squares refinement of the 2θ values (range 20–35°) of 32 reflections centred on both sides of the direct beam. Monoclinic system, $a = 14.499(1)$, $b = 16.195(2)$, $c = 8.433(1)$ Å, $\beta = 93.377(8)°$, $V = 1976.7$ Å^3, space group $P2_1/c$, $Z = 2$, $D_c = 1.656$ g cm^{-3}, $F(000) = 1000$, $\mu = 4.92$ mm^{-1} for Cu $K\alpha$ radiation.

Data collection and processing

Stoe-Siemens AED2 diffractometer, graphite monochromated Cu $K\alpha$ radiation ($\lambda = 1.54184$ Å). 7548 measured reflections, 3896 unique reflections ($3.0 < 2\theta < 150°$); h $-18 \rightarrow 18$, k $0 \rightarrow 20$, l $-10 \rightarrow 10$. No significant change in intensity was observed for three standard reflections. Empirical absorption correction, transmission factors 0.043–0.164. 3786 observed reflections with $F > 4\sigma(F)$, $R_{int} = 0.0396$.

Structure solution and refinement [10]

Multisolution direct methods followed by difference Fourier methods were used to locate the non-H atoms which were refined by blocked-cascade methods on F with anisotropic temperature factors. Hydrogen atoms were allocated to calculated positions with C–H = 0.96 Å, $U(H) = 1.2U_{iso}(C)$; methyl groups were refined as rigid groups with H–C–H = 109.5. Two-fold disorder in the tetrafluoroborate anion was accommodated by using two ideal tetrahedra, B–F = 1.42 Å, with site occupation factors refined to 0.64(1) and 0.36(1) respectively. Final conventional $R = 0.0497$, $R'[=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}] = 0.0868$ with $w^{-1} = \sigma^2(F) + 0.00053F^2$. The slope of the normal probability plot is 2.04; the largest peak in the final difference Fourier synthesis was 0.69 e Å^{-3} in the region of the disordered anions. Scattering factors for all atoms were taken from ref. 11. Final fractional atomic coordinates and U_{eq} values are in Table I, bond lengths and angles are in Table II, mean planes data are in Table III. See also 'Supplementary Material'.

TABLE I. Final Fractional Atomic Coordinates[a] ($\times 10^4$) for Non-H Atoms, Together with Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^4$)

Atom	*x*	*y*	*z*	U_{eq}
Cu	741(1)	5201(1)	3890(1)	551(1)
S(2A)	−813(1)	5635(1)	3672(1)	496(2)
C(2A)	−1420(2)	4974(1)	2411(3)	467(6)
N(3A)	−1072(1)	4401(1)	1470(3)	555(7)
C(4A)	−1780(2)	3988(2)	629(4)	650(9)
C(5A)	−2558(2)	4319(2)	1075(4)	608(8)
N(1A)	−2341(1)	4927(1)	2167(3)	508(6)
C(1A)	−3003(2)	5424(2)	3005(4)	643(9)
S(2B)	1213(1)	4330(1)	1870(1)	514(2)
C(2B)	1681(2)	3475(1)	2811(3)	493(7)
N(3B)	2582(2)	3320(1)	3021(3)	614(7)
C(4B)	2728(2)	2568(2)	3741(5)	721(10)
C(5B)	1904(2)	2255(2)	4016(4)	668(10)
N(1B)	1244(2)	2824(1)	3406(3)	550(6)
C(1B)	244(2)	2724(2)	3429(5)	770(12)
S(2C)	1554(1)	6416(1)	4315(1)	638(2)
C(2C)	2685(2)	6232(1)	4062(3)	496(7)
N(3C)	3054(2)	5690(1)	3080(3)	588(7)
C(4C)	3993(2)	5746(2)	3165(5)	748(11)
C(5C)	4226(2)	6321(2)	4237(5)	739(11)
N(1C)	3410(1)	6619(1)	4799(3)	545(6)
C(1C)	3354(2)	7261(2)	6013(5)	710(10)
B	4577(1)	3724(1)	1076(3)	678(11)
F(1)	3758	4205	1110	688(13)
F(2)	5335	4182	1760	1074(22)
F(3)	4743	3524	−521	1261(25)
F(4)	4469	2986	1955	1390(31)
F(1X)	4549	3418	2650	1791(63)
F(2X)	4755	3064	30	1895(75)
F(3X)	5288	4324	1015	1178(42)
F(4X)	3714	4092	609	674(23)

[a] e.s.d.s in parentheses.

Results and Discussion

The presence of a broad and intense absorption (1020–1100 cm^{-1}) in the IR spectrum of the complex indicated the presence of ionic tetrafluoroborate anions [12].

Changes to the ligand spectrum upon coordination involve a slight perturbation to the thioamide II band (1270 cm^{-1}) and major perturbation to thioamide IV (770, 740 cm^{-1}) which is converted from its clearly resolved components in the uncoordinated molecule [13] into a peak (730 cm^{-1}) with associated shoulders (720–740 cm^{-1}) in the complex. Modest shifts (±10 cm^{-1}) together with band-splitting also occur with δ(C–S) (670 cm^{-1}) and π(C–S) (530 cm^{-1}). The general indication is one of significant perturbation in the thione region (800–500 cm^{-1}) which usually signifies sulphur donation by the ligand [14]. This observation is supported by the presence of a weak ν(Cu–S) absorption at 290 cm^{-1} [3] although somewhat higher energies (322, 342 cm^{-1}) have been reported for the corresponding absorptions among some copper–thiolate complexes [15].

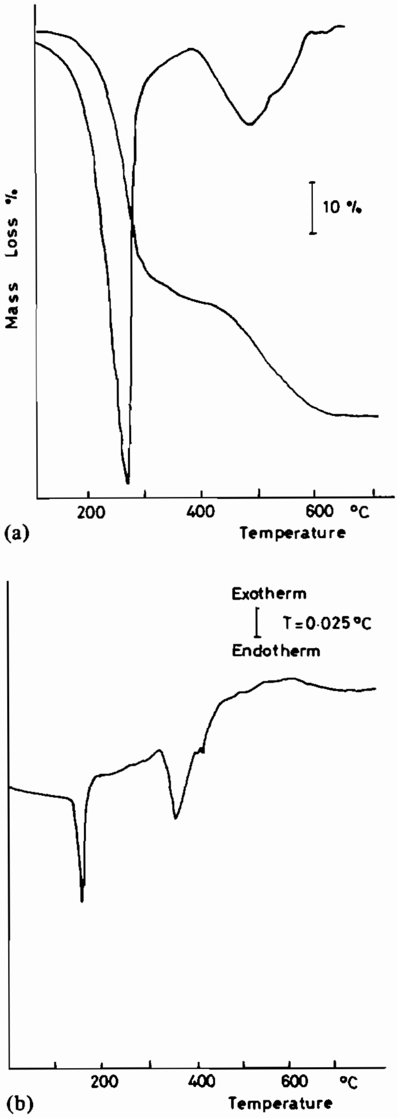

Fig. 1. Thermal analysis curves: (a) TG/DTG in flowing air, heating rate 50 °C min^{-1}; (b) DTA in flowing heating rate 20 °C min^{-1}.

Thermal analysis in flowing air (Fig. 1a) shows that the complex decomposes over the temperature range 145–1000 °C to copper(II) oxide. The agreement between experimental (83.0%) and theoretical mass loss (83.77%) for the above process is within experimental error (±2.0%) and confirms the formula of the complex. Both TG and DTG curves show the thermal decomposition to be a three-stage process. The first stage (145–331 °C), about 48.0% mass loss, involves a combination of mimtH evolution and thermal degradation of the tetrafluoroborate anion. The mass loss at this stage is dependent on the heating

TABLE II. Bond Distances (Å) and Angles (°)[a]

Bond	(Å)	Angle	(°)
(a) The coordination sphere[b]			
Cu–S(2A)	2.358(1)	S(2A)–Cu–S(2B)	116.2(1)
Cu–S(2B)	2.345(1)	S(2B)–Cu–S(2C)	117.2(1)
Cu–S(2C)	2.310(1)	S(2B)–Cu–S(2A′)	106.0(1)
Cu–S(2A′)	2.459(1)	S(2A)–Cu–S(2C)	103.6(1)
Cu–Cu(′)	3.007(1)	S(2A)–Cu–S(2A′)	102.8(1)
S(2A)–S(2A′)	3.766(1)	S(2C)–Cu–S(2A′)	110.1(1)
		Cu–S(2A)–Cu(′)	77.2(1)
		Cu–S(2A)–C(2A)	108.4(1)
		Cu–S(2B)–C(2B)	105.9(1)
		Cu–S(2C)–C(2C)	108.6(1)
		Cu(′)–S(2A)–C(2A)	99.8(1)
(X = A, B or C)	Molecule A	Molecule B	Molecule C
(b) Heterocyclic molecules			
C(2X)–S(2X)	1.714(3)	1.716(3)	1.693(3)
C(2X)–N(1X)	1.342(3)	1.342(3)	1.345(3)
N(1X)–C(1X)	1.460(4)	1.460(4)	1.464(4)
C(2X)–N(3X)	1.328(3)	1.332(3)	1.339(4)
N(3X)–C(4X)	1.385(4)	1.371(4)	1.362(4)
C(4X)–C(5X)	1.324(4)	1.331(5)	1.327(5)
C(5X)–N(1X)	1.372(4)	1.403(4)	1.387(4)
S(2X)–C(2X)–N(1X)	126.9(2)	128.7(2)	126.6(2)
S(2X)–C(2X)–N(3X)	127.1(2)	124.8(2)	128.2(2)
N(1X)–C(2X)–N(3X)	106.1(3)	106.4(2)	105.1(2)
C(2X)–N(1X)–C(1X)	124.7(2)	125.6(2)	125.5(2)
C(1X)–N(1X)–C(5X)	125.9(2)	125.3(3)	124.7(3)
C(2X)–N(1X)–C(5X)	109.3(2)	109.1(2)	119.8(2)
C(2X)–N(3X)–C(4X)	110.2(2)	110.6(2)	110.0(3)
N(3X)–C(4X)–C(5X)	106.1(3)	107.4(3)	107.2(3)
C(4X)–C(5X)–N(1X)	108.4(3)	106.6(3)	106.8(3)

[a] e.s.d.s in parentheses. [b] Symmetry code: (′) $-x, 1 - y, 1 - z$.

TABLE III. Mean Planes in the Form $aX + bY + cZ + d$ (Crystal Coordinates)

Plane	Atoms	a (Å)	b (Å)	c (Å)	d	Maximum deviation (Å)	
1	ligand A	−0.9820	−10.9532	6.2083	3.8133	N(1A)	0.057
2	ligand B	−0.5418	7.4801	7.4785	−4.589	C(4B)	0.018
3	ligand C	−0.2177	−11.3021	6.0355	4.661	N(3C)	0.023
4	Cu(1)S(2A)C(2A)	−3.5629	−9.4167	6.6512	2.574		
5	Cu(1)S(2B)C(2B)	13.011	7.099	−0.621	−4.648		
6	Cu(1)S(2C)C(2C)	1.223	−3.661	8.128	−1.348		
7	Cu(1)S(2A)Cu(1′)S(2A′)	3.064	13.201	4.436	−8.818		

Planes	Angle (°)	Planes	Angle (°)	Planes	Angle (°)
Dihedral angles (°)					
1/2	70.1	1/7	99.8	2/7	32.2
1/3	3.4	2/3	71.8	3/6	31.6
1/4	11.83	2/5	77.7	3/7	100.7

rate employed and at 50 °C min^{-1} about 62.0% mass loss occurs which accounts for the loss of the counter-ion and two-thirds of the mimtH molecules.

In the second stage (331–600 °C), which is contiguous with the first, the remaining ligands are desulphurised. This process is accompanied by the formation of a mixture of copper(I & II) sulphides, in the melt, and by the evolution of 1-methylimidazole. Confirmation of these processes has been achieved by room temperature X-ray powder diffraction studies of the cooled melt, initially obtained at about 450 °C, by collection and IR analysis of the evolved heterocycles and by visual observation of the decomposition by means of hot-stage microscopy. The final decomposition (600–1000 °C) accounts for the conversion of copper(II) sulphide to copper(II) oxide.

The DTA curve in dinitrogen clearly shows two well separated thermal events (Fig. 1b). The first of these is a melting endotherm (145–157 °C; $\Delta H_M = 66.8 \pm 5$ kJ mol^{-1}) and the second, broader endotherm, corresponds to the decomposition of the complex (340–420 °C; $\Delta H_D = 101.1 \pm 5$ kJ mol^{-1}). Between these events the complex exists as a mobile but highly viscous phase. The melting endotherm is similar to the value observed for the mononuclear [Cu(mimtH)$_3$](NO$_3$) complex (65.5 kJ mol^{-1}) [5].

The enthalpy requirement for the sublimation of three uncoordinated mimtH molecules amounts to 210 kJ mol^{-1} [9]. Consequently, the decomposition endotherm appears to be a combination of endothermic mimtH removal and de-sulphurisation as well as exothermic sulphide formation.

The structure of the complex consists of dinuclear Cu$_2$(mimtH)$_6$$^{2+}$ cations and disordered tetrafluoroborate anions. A perspective view of the cation, with atomic labelling is given in Fig. 2. Unit cell contents are in Fig. 3. The dinuclear cation contains two copper(I) atoms which are coordinated by four terminal monodentate S-donating mimtH ligands and two S-bridging (μ_2) mimtH ligands. Consequently both copper(I) atoms have an S$_4$-donor set and distorted tetrahedral environments with angles at the metal ranging from 102.8° to 117.2°.

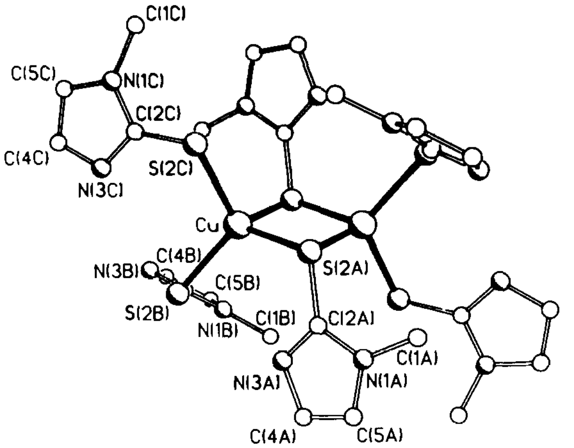

Fig. 2. Structure of the cation, with the atom numbering scheme.

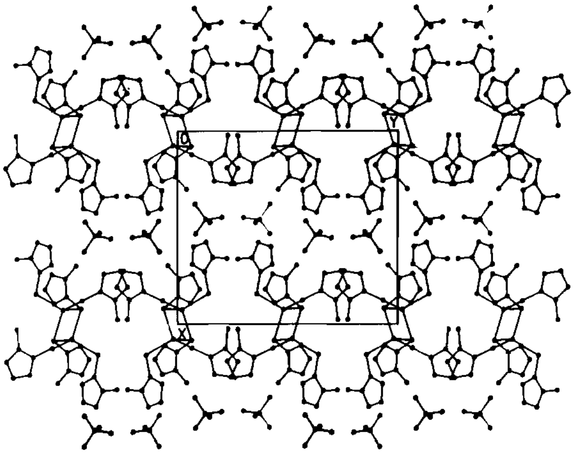

Fig. 3. Unit cell contents showing centrosymmetric cations and the major component of the disordered anions.

The centre of each dimer occupies a crystallographic centre of symmetry, Fig. 3, consequently, the copper and bridging sulphur atoms form a planar, lozenge shaped Cu$_2$S$_2$ core. The Cu$_2$S$_2$ core dimensions have the typical combination of alternating short and long Cu–S distances, a narrow angle at the bridging sulphur atom, a larger angle at the copper atom and relatively long and short separation distances between the sulphur and copper atoms respectively. Table IV lists the above parameters for the Cu$_2$(mimtH)$_6$$^{2+}$ complex and for other systems [3, 16, 17].

The bridging and terminal mimtH ligands (planes 1, 2, 3; Table III) are attached to the copper atoms with a characteristic 'twist' about their respective Cu–S–C planes (planes 4, 5, 6; Table III) and also tilt' with respect to the Cu$_2$S$_2$ core (plane 7, Table III). Heterocyclic molecules normally twist about the coordination sphere in order to minimize nonbonding interactions [18] but tilting of mimtH about the Cu$_2$S$_2$ core is part of the bonding process for this ligand.

Three of the Cu–S–C angles (105.9, 108.4, 108.6(1)°) are close to the average value (107°) for mimtH complexes [1]; the fourth angle, 99.8(1)°, is radically different from the others but it does involve the long Cu–S bond and the bridging ligand.

The major effect of coordination on the bond lengths and angles of the mimtH ligand [2] is to increase C–S distances significantly in two instances (ligands A & B, Table II) and modestly in ligand C. The resultant C–S distances show a reduction in the π-character of the bond [19] from 52.0% in uncoordinated mimtH [2] to 48.9% (ligand C) and

TABLE IV. Cu_2S_2 Core Dimensions

Compound	Reference	Cu–S (Å)	Cu–S–Cu (°)	S–Cu–S (°)	S····S (Å)	Cu····Cu (Å)
$[Cu_2(thiourea)_6]^{2+}$	16	2.367(3); 2.429(3)	72.6(1)	107.4(1)	3.865(1)	2.840(3)
$[Cu_2(S\text{-dimethylthiourea})_6]^{2+}$	16	2.325(3); 2.461(3)	72.3(1)	107.7(1)	3.868(1)	2.828(3)
$[Cu(purinium\text{-}6\text{-}thione)Cl_2]_2$	17	2.244(5); 2.741(6)	87.5(2)	–	3.629(9)	3.456(3)
$[Cu_2(mimtH)_4Cl_2]$	3	2.301(1); 2.572(1)	73.2(1)	105.5(1)	3.916(1)	2.914(1)
$[Cu_2(mimtH)_6]^{2+}$	this work	2.358(1); 2.459(1)	77.2(1)	110.1(1)	3.766(1)	3.007(1)

40.4% (ligands A & B). Lengthening of C–S distances in coordinated mimtH is not unexpected in view of the S-donor character of the ligand but a wide range of such distances occur among copper complexes of mimtH (1.683–1.748 Å) with significant variations occurring in individual cases [3–5].

Terminal Cu–S distances for a variety of S-donors, range from 2.190 to 2.480 Å with those from trigonal environments generally smaller than those from tetrahedral environments [4, 20, 21]. For heterocyclic-thione donors the cross-over value occurs in the region of 2.270 Å [3, 21].

The terminal Cu–S bonds in the $Cu_2(mimtH)_6{}^{2+}$ complex cation are consistent with normal tetrahedral values and arise from conventional electron-pair donation from the ligand S-atom to the metal [5]. The disparate Cu–S distances generated by the bridging ligand point to a dual role for that molecule. In one respect the production of a typical Cu–S distance (2.358(1) Å) and Cu–S–C angle (108.4(1)°) are indicative of conventional coordination to the metal. However, the combination of a narrow angle at the bridging S-atom (77.2(1)°), a relatively long Cu–S distance (2.459(1) Å) and atypical Cu–S–C angle (99.8(1)°) coupled with the fact that the planar bridging ligand is virtually normal to the Cu_2S_2 core (99.8°, Table III) all suggest that an electron pair and a $p\pi$-MO concentrated in the C–S portion of the molecule are used in the completion of the bridging role of the ligand [3, 16].

The complex retains its character in absolute ethanol in which it behaves as a (2:1) electrolyte with a molar conductivity (Λ_M) of 93 S cm^2 mol^{-1} [22]. In other solvents, notably, nitromethane, dimethylformamide and acetonitrile the complex is gradually solvolysed.

Supplementary Material

Anisotropic temperature factors, H-atom coordinates and isotropic temperature factors, and F_{obs}/F_{calc} are available from the authors on request.

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