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trans-Bis[(thiocyanato-*S*)(1-methylimidazoline-2(3*H*)-thione)-μ_2-(1-methylimidazoline-2(3*H*)-thione)copper(I)]: preparation, thermal analysis and crystal structure

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Abstract

1-Methylimidazoline-2(3*H*)-thione (mimtH) and copper(I) thiocyanate in refluxing ethanol–acetonitrile produce a colourless, diamagnetic complex, $[Cu_2(mimtH)_4(SCN)_2]$, which crystallises in an orthorhombic cell ($a = 8.0724(3)$, $b = 15.9545(6)$, $c = 21.3357(8)$ Å), space group = *Pbca*, $Z = 4$, final $R = 0.0319$ from 2427 observed reflections $F > 4\sigma_c(F)$). In the dimeric complex the copper(I) atoms are pseudo-tetrahedrally coordinated by pairs of, respectively, asymmetrically μ_2-S bridging mimtH, terminal monodentate-S mimtH, (Cu–S = 2.290(1) Å), and terminal monodentate-S thiocyanate, (Cu–S = 2.332(1) Å). Each pair of ligands is *trans*-related to its partner across crystallographic centres of symmetry, consequently, each copper(I) atom has an identical S_4 donor set with angles at the metal ranging from 95.9(1)° to 121.8(1)°. The centro-symmetric Cu_2S_2 core is rhomboid with Cu–S = 2.377(1) and 2.457(1) Å, $Cu–S_{br}–Cu = 72.6(1)°$ and Cu---Cu, S_{br}---S_{br} separation distances of 2.861(1) and 3.897(2) Å, respectively. Thermal decomposition of the complex in flowing air, (133–1000 °C), involves de-sulfurisation of mimtH and thiocyanate with concomitant production of copper(II) sulfide followed by oxidation to copper(II) oxide.

Introduction

The bio-active molecule, 1-methylimidazoline-2(3*H*)-thione, (mimtH), commercially known as methimazole, is an effective ligand towards many metal and non-metal centres [1]. In common with many other thiones and thiols, mimtH, reduces copper(II) salts with the production of either the corresponding copper(I) complex [2–4] or, the generation of a complicated redox system from which copper(II) complexes of oxidised forms of mimtH, such as, 1,1-dimethyl-2,2′-diimidazolylmonosulfide, have been produced [5–7].

For reactions involving mimtH and copper(I) salts the solution chemistry is simpler but the products are unpredictable with respect to stoichiometry and structure. With copper(I) halides, in either ethanol/acetonitrile or molar acid (HCl) solution, mimtH produces complexes of formula $[Cu(mimtH)_2X]$ (X = Cl, Br, I) [8]. The chloro complex is a centro-symmetric dimer with a combination of terminal chlorine as well as terminal and bridging mimtH which generate pseudo-tetrahedrally coordinated copper(I) and a S_3Cl donor set [8]. In contrast, copper(I) cyanide and mimtH produce polymeric $[\{Cu(mimtH)CN\}_n]$, in which both ligands bridge metal centres in an extended two-dimensional polymeric array [9]. The metal has pseudo-tetrahedral coordination and a S_2CN donor set in this complex.

This series of complexes has now been extended by reacting mimtH with copper(I) thiocyanate. The resultant colourless, crystalline, diamagnetic complex appears to be stable to atmospheric oxidation at room temperature.

Experimental

Starting materials

Copper(I) thiocyanate and mimtH, as 2-mercapto-1-methylimidazole, were obtained from Aldrich and were used as supplied.

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Preparation and analysis of [$Cu_2(mimtH)_4(SCN)_2$]

Copper(I) thiocyanate, (0.2440 g; 2 mmol), and mimtH, (0.904 g; 8 mmol), in 50 ml of an ethanol/acetonitrile mixture, (25:75; vol./vol.), were refluxed until all the solid dissolved, *c.* 2 h. The reaction mixture was then left for several weeks, at room temperature, during which period colourless crystals slowly developed. The crystals, some of which were of diffraction quality, were removed by filtration, washed with cold absolute ethanol (10 ml) and stored *in vacuo*.

Yield, 0.16 g (65%). *Anal.* Calc. for $Cu_2C_{18}H_{24}N_{10}S_6$: C, 29.6; H, 3.3; N, 19.2; Cu, 18.17. Found: C, 29.90; H, 3.35; N, 19.25; Cu, 17.46%.

Physical methods

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

Thermogravimetric analysis (TG, DTG) were obtained with a Stanton-Redcroft TG770 thermal analyser using platinum crucibles, sample masses in the region of 6 mg and column dried flowing air.

A Stanton-Redcroft DTA 673/4 instrument was used for the differential thermal analysis (DTA) curves in flowing dinitrogen with quartz crucibles and sample masses in the region of 8 mg. Heating rates for both techniques were 20 °C min^{-1}.

A Stanton-Redcroft hot-stage microscope (HSM5) with a Hitachi DK81 video recorder and JVC TM/90 colour monitor were used for the hot-stage microscopy.

X-ray powder photographs and line intensities were obtained with a Guinier-Hagg parafocussing camera with Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å), Kodirex single-coated film and a Siemens microdensitometer.

The diamagnetic behaviour of [$Cu_2(mimtH)_4(SCN)_2$] was monitored with a Newport Instruments room temperature Gouy magnetic balance.

Crystal structure of [$Cu_2(mimtH)_4(SCN)_2$]

Crystal data

A colourless crystal of [$Cu_2(mimtH)_4(SCN)_2$, $C_{18}H_{24}N_{10}S_6Cu_2$, $M = 699.9$, of dimensions 0.16×0.44×0.56 mm, was used for the data collection. Unit cell dimensions were obtained from the 2θ values (range 20–25°) of 32 reflections centred on both sides of the direct beam. Orthorhombic cell at 22 °C, $a = 8.0724(3)$, $b = 15.9545(6)$, $c = 21.3357(8)$ Å, $V = 2747.9$ Å^3, $Z = 4$, space group $Pbca$, $D_c = 1.692$ g cm^{-3}, $F(000) = 1424$, $\mu = 2.02$ mm^{-1} for molybdenum radiation.

Data collection and reduction

A Stoe-Siemens diffractometer was used for the data collection with graphite monochromated Mo $K\alpha$ radiation (0.71073 Å), and ω/θ scanning mode with variable scanning range and time, on-line profile fitting [10], 2θ range 3–50°, index ranges: h, 0 to 9; k, 0 to 18; l, 0 to 25 together with some equivalents, no significant change was observed in the intensities of 3 standard reflections. A semi-empirical absorbtion, as well as the usual corrections, were applied to the data, maximum and minimum transmission factors were 0.280 and 0.434, respectively.

2427 unique data and 2100 observed data with $F > 4\sigma_c(F)$ and $\sigma_c(F)$ from counting statistics only, $R_{int} = 0.030$.

Structure solution and refinement

The coordinates of the non-H atoms were obtained by direct methods and difference Fourier analyses and refined by blocked-cascade least-squares methods to a minimum of $\Sigma w\Delta^2$, ($\Delta = |F_o| - |F_c|$), with anisotropic thermal parameters. H atoms were allocated to ring angle external bisectors with C–H and N–H = 0.96 Å and the methyl group was treated as a rigid group with H–C–H = 109.5°. All H atoms were refined isotropically with $U(H) = 1.2U_{eq}$ (C) or (N). An extinction correction was applied, $F_c^1 = F_c/(1 + xF_c^2/sin2\theta)^{1/4}$ with $x = 1.2(2) \times 10^{-6}$.

Final conventional $R[=\Sigma|\Delta|/\Sigma|F_o|] = 0.0319$, $R_w[=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}] = 0.0280$ with $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 49 - 347G + 872G^2 - 103S + 61S^2 + 212GS$ with $G = F_o/F_{max}$ and $S = \sin\theta/\sin\theta_{max}$ [11]. Total parameters = 170, shift/e.s.d. = 0.007(mean) and 0.023(max.), slope = 1.15, residual peaks in the final difference synthesis = +0.30 and −0.45 e/Å^3. Neutral atom scattering factors were taken from ref. 12. Final refined atomic coordinates are given in Table 1, bond lengths and angles in Table 2, SHELXTL [13] and local programs were used in the analysis. See also 'Supplementary material'.

Results and discussion

Changes to the infrared spectrum of mimtH upon coordination are restricted, essentially, to the 'thione' region (800–500 cm^{-1}). The thioamide IV band is particularly affected with the bands in the free ligand (770, 740 cm^{-1}) [14] replaced with a sharp but split band (735, 725 cm^{-1}) in the complex. Modest shifts (±10 cm^{-1}) and band splitting also characterise δ(CS) at 670 cm^{-1} and π(CS) at 530 cm^{-1}. A weak ν(Cu–S) absorbtion at 290 cm^{-1} further supports S-donating mimtH in the complex [9]. Vibrational activity of the thiocyanate ion is characterised by a strong, sharp ($\Delta\nu_{1/2} = 10$ cm^{-1}) ν_{CN} band at 2095

TABLE 1. Atomic coordinates ($\times 10^4$)

Atom	x	y	z
Cu	410(1)	45(1)	4349(1)
S(21)	675(1)	1388(1)	3983(1)
C(21)	−741(3)	1565(1)	3408(1)
N(31)	−1405(3)	1007(1)	3010(1)
N(11)	−1340(3)	2319(1)	3242(1)
C(11)	−969(5)	3113(2)	3550(2)
C(51)	−2390(4)	2222(2)	2732(1)
C(41)	−2424(4)	1413(2)	2588(1)
S(22)	−2333(1)	−192(1)	4815(1)
C(22)	−3265(3)	752(1)	4679(1)
N(12)	−4295(3)	933(1)	4205(1)
C(12)	−4934(4)	328(2)	3751(1)
N(32)	−3092(3)	1467(1)	5008(1)
C(42)	−4005(4)	2091(2)	4736(1)
C(52)	−4765(4)	1766(2)	4239(1)
S(23)	629(1)	−1112(1)	3686(1)
C(23)	1798(4)	−779(2)	3099(1)
N(23)	2591(4)	−553(2)	2679(1)

cm^{-1}, a weak ν_{CS} band at 720 cm^{-1} on the low-energy side of the thioamide IV band, and δ_{NCS} at 415 cm^{-1}. Raising of the ν_{CN} band above the free ion value, 2053 cm^{-1}, coupled with the presence of ν_{CS} near 700 cm^{-1} and δ_{NCS} near 420 cm^{-1} are consistent with thiocyanato-S coordination [15].

The complex decomposes in the temperature range 153–1000 °C to copper(II) oxide in flowing air. The agreement between experimental (77.0%) and theoretical mass losses (77.0%) is within experimental error (±2.0%) and confirms the empirical formula of the complex. Both TG and DTG curves, Fig. 1, show a two-stage decomposition to copper(II) sulfide (70.0% mass loss, 593 °C) with a discontinuity at 390 °C (40.0% mass loss). The two contiguous stages represent progressive de-sulfurisation of mimtH and thiocyanate with concomitant production of copper(II) sulfide together with some copper(I) sulfide and residual sulfur. Room temperature X-ray powder diffraction studies of the cooled melt, initially obtained at about 650 °C, as well as hot-stage microscopic studies of the decomposing complex, confirmed the presence of copper(II) and copper(I) sulfides in the residues. The final decomposition stage (7%) accounts for the conversion of the sulfide residues to copper(II) oxide with some initial, and superficial, oxidation (*c.* 2%) to copper(II) sulfate. The final end-product was also identified by X-ray powder diffraction.

The DTA curve in dinitrogen, Fig. 1, involves two well separated thermal events which consist of melting (T=140–160 °C, ΔH=60.0±6 kJ mol^{-1}) and decomposition (T=360–490 °C, ΔH=105±8 kJ mol^{-1}) endotherms. The energy values are more consistent

TABLE 2. Bond lengths (Å) and angles (°)

Cu–S(21)	2.290(1)	Cu–S(22)	2.457(1)
Cu–S(23)	2.332(1)	Cu–S(22′)	2.377(1)
S(21)–C(21)	1.699(2)	C(21)–N(31)	1.342(3)
C(21)–N(11)	1.345(3)	N(31)–C(41)	1.382(4)
N(11)–C(11)	1.459(4)	N(11)–C(51)	1.387(4)
C(51)–C(41)	1.328(4)	S(22)–C(22)	1.709(3)
C(22)–N(12)	1.342(3)	C(22)–N(32)	1.346(3)
N(12)–C(12)	1.461(3)	N(12)–C(52)	1.385(3)
N(32)–C(42)	1.368(4)	C(42)–C(52)	1.331(4)
S(23)–C(23)	1.655(3)	C(23)–N(23)	1.158(4)
S(21)–Cu–S(22)	111.5(1)	S(21)–Cu–S(23)	121.8(1)
S(22)–Cu–S(23)	101.1(1)	S(21)–Cu–S(22′)	95.9(1)
S(22)–Cu–S(22′)	107.4(1)	S(23)–Cu–S(22′)	119.0(1)
Cu–S(21)–C(21)	109.8(1)	S(21)–C(21)–N(31)	127.9(2)
S(21)–C(21)–N(11)	125.5(2)	N(31)–C(21)–N(11)	106.4(2)
C(21)–N(31)–C(41)	109.8(2)	C(21)–N(11)–C(11)	125.8(2)
C(21)–N(11)–C(51)	109.1(2)	C(11)–N(11)–C(51)	125.2(2)
N(11)–C(51)–C(41)	107.7(3)	N(31)–C(41)–C(51)	107.0(3)
Cu–S(22)–C(22)	101.1(1)	Cu–S(22)–Cu′	72.6(1)
C(22)–S(22)–Cu′	109.1(1)	S(22)–C(22)–N(12)	126.2(2)
S(22)–C(22)–N(32)	127.8(2)	N(12)–C(22)–N(32)	106.0(2)
C(22)–N(12)–C(12)	125.2(2)	C(22)–N(12)–C(52)	109.7(2)
C(12)–N(12)–C(52)	124.9(2)	C(22)–N(32)–C(42)	109.9(2)
N(32)–C(42)–C(52)	107.6(2)	N(12)–C(52)–C(42)	106.8(2)
Cu–S(23)–C(23)	104.4(1)	S(23)–C(23)–N(23)	178.5(3)

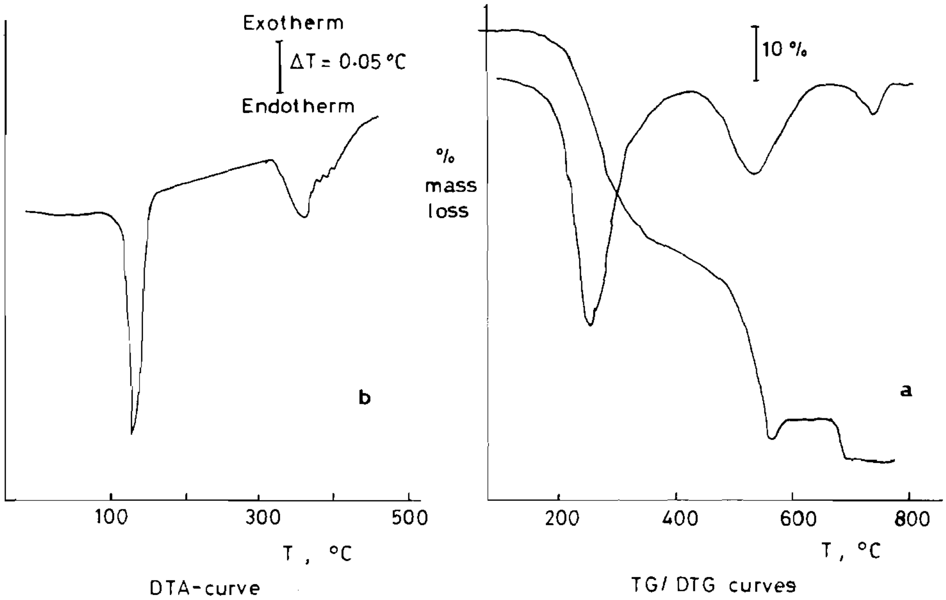


Fig. 1. Thermal analysis curves: (a) thermogravimetric (TG) and derivative thermogravimetric (DTG) curves in flowing air; (b) differential thermal analysis (DTA) curve in flowing nitrogen. Heating rates 20 °C min^{-1}.

with ligand decomposition and copper(II) sulfide formation than the alternative scheme which involves the evolution of unchanged mimtH from the complex [16].

A perspective diagram of the dimeric complex with the independent atoms labelled is shown in Fig. 2. The unit cell contents are in Fig. 3.

Coordination of the copper(I) atoms in the centrosymmetric dimer involves two asymmetrically bridging, μ_2-S donating, mimtH, as well as pairs of *trans*-terminal, monodentate-S donating mimtH and thiocyanate ligands, respectively. Each copper(I) atom has an identical S_4 donor set and pseudo-tetrahedral geometry with angles, at the metal, ranging from 95.9(1)–121.8(1)°.

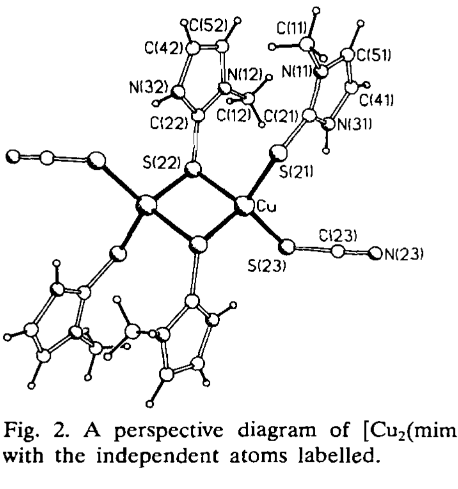


Fig. 2. A perspective diagram of $[Cu_2(mimtH)_4(SCN)_2]$ with the independent atoms labelled.

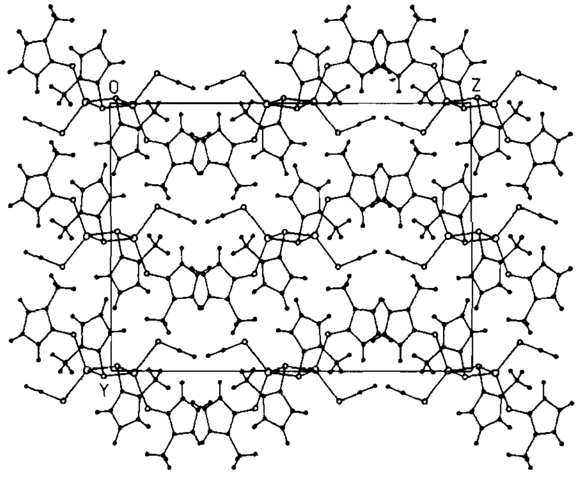


Fig. 3. Unit cell contents in *a* axis projection showing the distribution of the centrosymmetric dimers.

Because of the crystallographic symmetry centre the copper(I) atoms and the bridging thione-S atoms form a strictly planar, rhomboid, Cu_2S_2 core, with the ligands in the 2-*anti*, rather than the 2-*syn*, arrangement [17]. The 2-*anti* arrangement is common to all the mimtH generated Cu_2S_2 cores listed in Table 3 with the exception of $[\{Cu(mimtH)CN\}_n]$ which is non-centrosymmetric. Asymmetry in the Cu_2S_2 cores is reflected in the Cu–S_{br} distances (Table 3) and the Cu–S_{br}–C angles (Table 2). The bridging angle Cu–S_{br}–Cu (72.6(1)°) is the smallest in the series and is only slightly larger than the value required for regular, edge-sharing, tetrahedra (70.5°)

TABLE 3. Cu_2S_2 core dimensions in copper(I)–mimtH complexes

Compound	Reference	Cu–S_{br} (Å)	Cu–S_{br}–Cu (°)	S–Cu–S (°)	$S_{br}\cdots S_{br}$ (Å)	Cu···Cu (Å)
$Cu_2(mimtH)_4Cl_2$	8	2.301(1); 2.572(1)	73.2(1)	105.5(1)	3.916(1)	2.914(1)
$Cu_2(mimtH)_6](BF_4)_2$	4	2.358(1); 2.459(1)	77.2(1)	110.1(1)	3.766(1)	3.007(1)
$[\{Cu(mimtH)(CN)\}_n]^a$	9	2.344(1); 2.565(1) 2.366(1); 2.556(1)	79.1(1) 79.7(1)	98.4(1) 98.7(1)	3.729(2)	3.145(1)
$[Cu_2(mimtH)_4(SCN)_2]$	this work	2.377(1); 2.457(1)	72.6(1)	107.4(1)	3.897(2)	2.861(1)

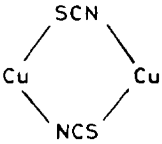
[a] Non-centrosymmetric structure.

[18]. Furthermore, the Cu---Cu and the S_{br}---S_{br} separation distances are, respectively, the smallest and the second largest in the series (Table 3). Narrowing of the bridging angle is inevitably accompanied by a reduction in the metal separation distance and an increase in the S_{br}---S_{br} distance. The reason for the wide variation in S_{br}---S_{br} distances in Table 3 as well as the asymmetry in the Cu–S_{br} distances is not at all clear. The need to minimise repulsion between the electron-rich, bridging, thione-S atoms by generating asymmetric Cu–S_{br} distances as well as S_{br}---S_{br} distances in the region of the van der Waals value (3.550(1) Å) [19] is manifest. However, the S_{br}---S_{br} distances in copper(I)–mimtH complexes (Table 3) range from 3.729(1)–3.916(1) Å, clearly in excess of simple van der Waals requirements, and the differences between pairs of asymmetric, Cu–S_{br} distances range from 0.08 Å in $[Cu_2(mimtH)_4(SCN)_2]$ to 0.271 Å in $[Cu_2(mimtH)_4Cl_2]$. These data suggest an inherent flexibility for the thione-S bridging atoms of mimtH in these copper(I) complexes and that the Cu_2S_2 core dimensions are not exclusively due to the bonding requirements of the ligand. Other factors which probably influence Cu_2S_2 core dimensions include intramolecular NH---Cl bond formation in $[Cu_2(mimtH)_4Cl_2]$ [8], packing considerations for the ionic components in $[Cu_2(mimtH)_6](BF_4)_2$ [4], the need to accommodate the Cu_2S_2 cores in a two-dimensional polymeric array in $[\{Cu(mimtH)CN\}_n]$ [9] as well as the steric requirements of the N-methyl group. Furthermore, in both $[Cu_4(\text{benzimidazoline-2-thione})_{10}]^{4+}$ [20] and $[Cu_4(\text{imidazolidine-2-thione})_9]^{4+}$ [21], planar, rhomboid, Cu_4 cores are asymmetrically bridged by Cu–S_{br} bonds along short (<3.0 Å) as well as long (>4.0 Å) Cu---Cu distances. The resultant generation of alternating long and short Cu–S_{br} distances along the periphery of the Cu_4 core appears to be more electronic than steric in origin and adds another factor to the list of those which determine Cu_2S_2 core dimensions.

The Cu–S(21) distance (2.290(1) Å) and Cu–S–C angle (109.8(1)°) are typical of terminal, monodentate-S, σ-donating mimtH with tetrahedrally coordinated Cu(1) [4, 8]. The essentially planar ligand also 'twists' (27.2°) about the corresponding Cu–S–C plane and 'tilts' (89.6°) about the Cu_2S_2 plane. In common with other complexes in this series (Table 3), slight lengthening of the C(21)–S(21) and C(22)–S(22) distances (1.699(2), 1.709(3) Å) occurs, relative to the mean free ligand distance (1.685 Å) [22], otherwise, the ligand dimensions are essentially unchanged upon coordination.

The bridging mimtH ligand 'twists' (100.3°) about the corresponding Cu–S–C plane, is virtually normal (83.4°) ('tilted') to the Cu_2S_2 plane, has a narrow Cu–S_{br}–Cu bridging angle, dissimilar Cu–S_{br} distances and Cu–S–C angles; the ligand virtually adopts an 'end-on' or longitudinal attachment to the bridging copper(I) atoms. Conventional thione-S, σ-donation coupled with involvement of the thioamide π-MO group of the heterocycle have been used to rationalise coordination of bridging mimtH in this series of complexes (Table 3). In spite of the relatively short Cu---Cu distance (2.861(1) Å), no significant metal–metal interactions are expected in this complex [18, 23].

The Cu–S distance (2.332(1) Å) and Cu–S–C angle (104.4(1)°) of the terminal thiocyanate group are in the range (2.290(4)–2.380(4) Å; 100.3(5)–105.4(6)°) reported for a series of complexes formed from copper(I) thiocyanate and a number of nitrogen containing heterocyclic bases [24]. In addition, and in common with terminal and bridging mimtH, the thiocyanate group is 'tilted' about the Cu_2S_2 core (114.6°). Monodentate thiocyanate appears to be quite rare, especially in the presence of competing heterocyclic ligands, and at the limit of a series of possibilities which include the formation of eight- and four-membered cyclic units (see below) as well as single-stranded Cu–SCN–Cu polymers [24–27].



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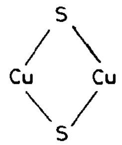

The formation of monomeric [Cu(imidazolidine-2-thione)$_2$NCS] [25] and dimeric [Cu$_2$(mimtH)$_4$(SCN)$_2$] with terminal N- and S-donating thiocyanate, respectively, reflect the stabilising effect of intramolecular (ligand)NH---N(thiocanate) H-bonding in the former and the superior, relative to thiocyanate, μ_2-S donating behaviour of mimtH in the latter.

Supplementary material

Anisotropic thermal parameters for the non-H atoms, H atom coordinates and isotropic thermal parameters and mean planes data with dihedral angles are available from the authors on request.

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