[Bis{bis(imidazolidine-2-thione)-μ_2-(imidazolidine-2-thione)copper(I)}] diperchlorate: synthesis and crystal structure

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Abstract

Imidazolidine-2-thione (imdtH_2) and copper perchlorate hexahydrate produced, from a refluxing mixture of ethanol and acetonitrile, a colourless, diamagnetic, homoleptic, dinuclear complex, $[Cu_2(imdtH_2)_6](ClO_4)_2$, which crystallised in a monoclinic cell ($a=8.0275(5)$, $b=26.2252(14)$, $c=8.5399(6)$ Å, $\beta=91.707(5)$°, space group $P2_1/n$, $Z=2$ (dimers), final $R=0.0404$ from 2699 observed reflections with $F>4\sigma_c(F)$). The structure is centrosymmetric with the copper(I) atoms pseudo-tetrahedrally coordinated by pairs of both terminal thione-S and asymmetric μ_2-S bridging, imdtH_2 ligands (Cu–S 2.284(1)–2.490(1) Å). Each ligand is *trans*-related to its partner across crystallographic symmetry centres consequently each copper(I) atom has an identical S_4 donor set with angles at the metal ranging from 95.9(1) to 120.5(1)°. The strictly planar, centrosymmetric Cu_2S_2 core is rhomboid with Cu–S_{br} distances of 2.362(1) and 2.490(1) Å and Cu–S_{br}–Cu = 67.2(1)° with Cu---Cu and S_{br}---S_{br} separation distances of 2.686(1) and 4.043(3) Å, respectively.

Introduction

Imidazolidine-2-thione (imdtH_2), widely known by its trivial name, ethylenethiourea, is an effective ligand towards both metals and non-metals [1, 2].

Towards copper(I), imdtH_2 and its N-alkyl derivatives are monodentate S-donating ligands which generate mononuclear complexes with trigonal [3–6] and tetrahedral [7] environments about the metal. Dinuclear complexes are less common but $[Cu_2(imdtH_2)_4Cl_2]$ has a combination of trigonal and tetrahedrally coordinated copper(I) with S_2Cl and S_3Cl donor sets, respectively, as well as terminal thione-S and μ_2-S bridging imdtH_2 [7]. In $[Cu_4(imdtH_2)_9](NO_3)_4$ the planar, tetranuclear Cu_4 aggregate is coordinated by a combination of monodentate thione-S as well as μ_2-S and μ_4-S bridging ligands [8].

In common with other heterocyclic thiones imdtH_2 reduces copper(II) salts producing the corresponding copper(I) complex with, presumably, concomitant ligand oxidation [2]. The course of such reactions is unpredictable, as the production of $[Cu(imdtH_2)_4]^+$ and $[Cu_4(imdtH_2)_9]^{4+}$ from imdtH_2 and copper(II) nitrate clearly demonstrate. We have extended this series of copper(II)–thione reactions by studying the reaction between copper(II) perchlorate and imdtH_2. The resultant diamagnetic, dinuclear complex is the subject of this report.

Experimental

Starting materials

The ligand, imdtH_2, as 2-imidazolidinethione, and $Cu(ClO_4)_2 \cdot 6H_2O$ were obtained from the Aldrich Chemical Co., and were used as supplied.

Preparation and analysis of $[Cu_2(imdtH_2)_6](ClO_4)_2$

All solvents were thoroughly degassed before use. $Cu(ClO_4)_2 \cdot 6H_2O$, (0.5420 g, 2 mmol), dissolved in the minimum quantity of distilled water (*c.* 10 ml), was added slowly and with continuous stirring to a preheated solution of imdtH_2, (0.8160 g, 8 mmol), in 50 ml of acetonitrile–ethanol (50:50, vol./vol.). The initial bright green colour of the reaction mixture gradually faded to give a colourless solution. The reaction vessel was covered with parafilm and set aside. After several weeks colourless crystals, some of which were of diffraction quality, were obtained and removed from the resultant solution by filtration, washed with cold ethanol (20 ml)

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and dried *in vacuo*. Yield 0.57 g (60.0%). *Anal.* Calc. for $Cu_2C_{18}H_{36}N_{12}O_8S_6Cl_2$: C, 23.02; H, 3.86; N, 17.91. Found: C, 23.68; H, 3.75; N, 18.60%.

Physical methods

IR spectra were obtained from caesium iodide discs in the range 4000–200 cm^{-1} on a Perkin-Elmer grating spectrophotometer. The diamagnetic behaviour of $[Cu_2(imdtH_2)_6](ClO_4)_2$ was monitored with a Newport Instruments room temperature, magnetic balance. Elemental analysis was performed by the Chemistry Department, University of Leeds.

Crystal structure of [Cu$_2$(imdtH$_2$)$_6$](ClO$_4$)$_2$

Crystal data

A colourless crystal of $[Cu_2(C_3H_6N_2S)_6](ClO_4)_2$, $M = 938.9$, of dimensions 0.12 × 0.42 × 0.54 mm, was used for the data collection. Unit cell dimensions were obtained from the 2θ values (range 20–25°) of 32 reflections centred on either side of the direct beam. Monoclinic cell at 295 K: $a = 8.0275(5)$, $b = 26.2252(14)$, $c = 8.5399(6)$ Å, $\beta = 91.707(5)°$, $V = 1797.1$ Å^3, $Z = 2$ (dimers), $D_c = 1.735$ g cm^{-3}, $F(000) = 960$, $\mu = 1.73$ mm^{-1} (Mo radiation), space group $P2_1/n$.

Data collection and reduction

A Stoe-Siemens diffractometer was used for the data collection with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), ω/θ scanning mode with variable scanning range and time, on-line profile fitting [9], 2θ range 3–50°, index ranges: h −9 to 9; k 0 to 31; l 0 to 10 plus some equivalents with $k < 0$; no significant change was observed in the intensities of three standard reflections. A semi-empirical absorption, as well as the usual corrections, were applied to the data, range of transmission factors 0.358–0.491. Total unique data 3175, observed data 2699 with $F > 4\sigma_c(F)$ and σ_c from counting statistics only, $R_{int} = 0.033$.

Structure solution and refinement

The coordinates of the non-H atoms were obtained from direct methods and difference Fourier analyses and were refined by blocked-cascade least-squares methods to a minimum of $\Sigma w\Delta^2$, ($\Delta = |F_o| - |F_c|$), with anisotropic thermal parameters. Hydrogen atoms were allocated to ring angle external bisectors with C–H = 0.96, N–H = 0.87 Å and H–C–H = 109.5° and refined with isotropic thermal parameters, U(H) = 1.2eq (C) or (N). Final residual $R[=\Sigma|\Delta|/|F_o|] = 0.0404$, $R_w[=(\Sigma w\Delta^2/\Sigma F_o^2)^{1/2}] = 0.0385$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 6 + 87G - 51G^2 - 19H + 14H^2 - 99GH$, $G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$ [10]. Total parameters = 218, $\Delta/\sigma = 0.010$ (mean) and < 0.1 (max.), $\Delta/\rho = 0.83$(around the anion) and -0.45 e/Å^3, S = 1.12. Neutral atomic scattering factors were taken from ref. 11. SHELXTL [12] and local programs were used in the analysis.

Final refined atomic coordinates are listed in Table 1; bond lengths and angles are in Table 2. See also 'Supplementary material'.

Results and discussion

The IR spectrum of the complex revealed positive shifts to ν(NH) (3320 cm^{-1}), ν(CN) (1340, 1550 cm^{-1}) and negative shifts to ν(CS) (910, 495 cm^{-1}) and δ(CS) (370 cm^{-1}), ligand bands, coupled with ν(Cu–S) (245 cm^{-1}), which suggested ligand thione-S donation to the metal [13]. The ionic perchlorate group was confirmed by bands at 1090 and 600 cm^{-1} [14].

The structure consists of centrosymmetrically constrained dinuclear complex cations, $[Cu_2(imdtH_2)_6]^{2+}$, formed from two, edge-sharing, CuS_4 tetrahedra, as well as perchlorate anions.

There are two N···O distances which suggest weak hydrogen bonding between ligand amide groups and perchlorate oxygen atoms. These involve O(2) and N(12) at 2.962 Å and O(4) and N(13) at 2.978 Å (with O(2) transformed by $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$ and O(4) by $1+x$, y, z). In both cases the Cl–O···N angle is approximately trigonal (116.2 and 117.2°), with the angles at the hydrogen atoms signifying moderate divergence from linearity (150 and 152°). The range of Cl–O distances and O–Cl–O angles (Table 1), coupled with substantial thermal motion in the constituent atoms, suggest that the anion may be disordered.

A perspective view of the cation, with the atoms labelled, is in Fig. 1; unit cell contents are in Fig. 2.

The copper(I) atoms in the dinuclear cation are coordinated by a combination of terminal, monodentate thione-S and μ_2-S bridging ligands, Fig. 1. Because of the imposed centrosymmetry in the cation the metal atoms have identical S_4 coordination with distorted tetrahedral geometry and angles ranging from 95.9(1) to 120.5(1)°.

Terminal, Cu–S$_t$ distances (Tables 2 and 3) are in the range normally observed for tetrahedral CuS_4 systems, (2.262(2)–2.358(1) Å), involving σ-donating imidazole-thione donors [7, 15–17] and are typically shorter than the bridging Cu–S$_{br}$ distances (Table 3). Terminal ligands form typical Cu–S–C angles (105.0(1)–110(1)°) [15–17]; they also 'tilt' about the Cu_2S_2 core (75.6 and 100.1°) and 'twist' about their respective Cu–S–C planes (18.2 and 17.0°).

Both terminal and bridging ligands are effectively planar, maximum deviations from the least-squares mean planes being +0.080 and +0.064 for C(43) and C(53), respectively. Changes to ligand dimensions on coordination involve, on average, a modest lengthening

TABLE 1. Atomic coordinates (×10⁴)

Atom	*x*	*y*	*z*
Cu(1)	6285(1)	4850(1)	4140(1)
C(21)	5433(4)	4075(1)	7145(3)
S(21)	6218(1)	4675(1)	6850(1)
N(11)	5307(5)	3866(1)	8545(3)
N(31)	4882(4)	3756(1)	6063(3)
C(41)	4331(6)	3273(1)	6718(4)
C(51)	4638(5)	3348(1)	8473(4)
S(22)	5958(1)	4163(1)	2460(1)
C(22)	7586(4)	3760(1)	2909(3)
N(12)	7643(4)	3277(1)	2473(4)
N(32)	8955(4)	3885(1)	3689(4)
C(52)	9137(6)	3024(1)	3086(5)
C(42)	10127(5)	3459(1)	3853(5)
S(23)	8552(1)	5372(1)	3991(1)
C(23)	8741(4)	5555(1)	2116(4)
N(13)	9621(5)	5954(1)	1663(4)
N(33)	8097(5)	5321(1)	854(4)
C(53)	9716(7)	5985(2)	−13(5)
C(43)	8437(6)	5593(2)	−585(5)
Cl(1)	870(1)	7332(1)	2129(1)
O(1)	−521(7)	7245(2)	1075(8)
O(2)	289(16)	7631(4)	3320(7)
O(3)	2088(9)	7550(4)	1218(15)
O(4)	1516(5)	6866(1)	2782(5)

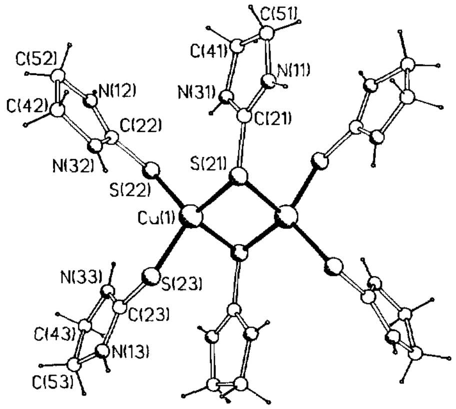

Fig. 1. Perspective view of the $[Cu_2(imdtH_2)_6]^{2+}$ cation with the independent atoms labelled.

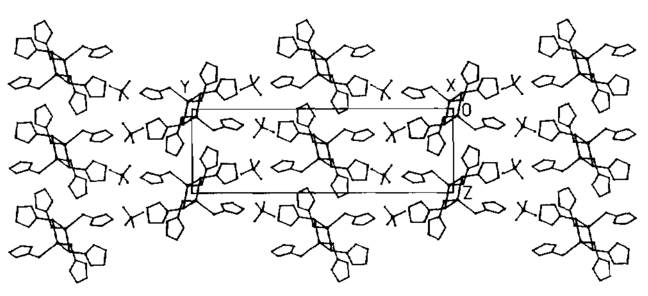

Fig. 2. Unit cell contents in parallel projection along the *a* axis showing alternating layers of cations and anions.

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

Cu(1)–S(21)	2.362(1)	Cu(1)–S(22)	2.312(1)
Cu(1)–S(23)	2.284(1)	Cu(1)–Cu(1′)	2.686(1)
Cu(1)–S(21′)	2.490(1)	C(21)–S(21)	1.716(3)
C(21)–N(11)	1.322(4)	C(21)–N(31)	1.314(4)
N(11)–C(51)	1.461(5)	N(31)–C(41)	1.458(5)
C(41)–C(51)	1.525(5)	S(22)–C(22)	1.715(3)
C(22)–N(12)	1.322(4)	C(22)–N(32)	1.309(4)
N(12)–C(52)	1.455(6)	N(32)–C(42)	1.463(5)
C(52)–C(42)	1.528(6)	S(23)–C(23)	1.683(4)
C(23)–N(13)	1.326(5)	C(23)–N(33)	1.332(5)
N(13)–C(53)	1.438(6)	N(33)–C(43)	1.454(6)
C(53)–C(43)	1.524(7)	Cl(1)–O(1)	1.432(6)
Cl(1)–O(2)	1.377(8)	Cl(1)–O(3)	1.390(10)
Cl(1)–O(4)	1.433(4)		
S(21)–Cu(1)–S(22)	116.8(1)	S(21)–Cu(1)–S(23)	102.3(1)
S(22)–Cu(1)–S(23)	120.5(1)	S(21)–Cu(1)–Cu(1′)	58.7(1)
S(22)–Cu(1)–Cu(1′)	119.5(1)	S(23)–Cu(1)–Cu(1′)	118.8(1)
S(21)–Cu(1)–S(21′)	112.8(1)	S(22)–Cu(1)–S(21′)	95.9(1)
S(23)–Cu(1)–S(21′)	108.5(1)	Cu(1′)–Cu(1)–S(21′)	54.1(1)
S(21)–C(21)–N(11)	123.5(2)	S(21)–C(21)–N(31)	126.7(2)
N(11)–C(21)–N(31)	109.8(3)	Cu(1)–S(21)–C(21)	110.0(1)
Cu(1)–S(21)–Cu(1′)	67.2(1)	C(21)–S(21)–Cu(1′)	102.3(1)
C(21)–N(11)–C(51)	112.7(3)	C(21)–N(31)–C(41)	112.6(3)
N(31)–C(41)–C(51)	102.8(3)	N(11)–C(51)–C(41)	102.1(3)
Cu(1)–S(22)–C(22)	105.6(1)	S(22)–C(22)–N(12)	124.1(3)
S(22)–C(22)–N(32)	125.7(2)	N(12)–C(22)–N(32)	110.2(3)
C(22)–N(12)–C(52)	111.8(3)	C(22)–N(32)–C(42)	112.7(3)
N(12)–C(52)–C(42)	103.0(3)	N(32)–C(42)–C(52)	101.8(3)
Cu(1)–S(23)–C(23)	108.6(1)	S(23)–C(23)–N(13)	124.5(3)
S(23)–C(23)–N(33)	126.5(3)	N(13)–C(23)–N(33)	109.0(3)
C(23)–N(13)–C(53)	112.3(4)	C(23)–N(33)–C(43)	112.3(3)
N(13)–C(53)–C(43)	103.0(4)	N(33)–C(43)–C(53)	101.6(3)
O(1)–Cl(1)–O(2)	106.3(5)	O(1)–Cl(1)–O(3)	105.2(5)
O(2)–Cl(1)–O(3)	116.0(7)	O(1)–Cl(1)–O(4)	112.0(3)
O(2)–Cl(1)–O(4)	108.9(4)	O(3)–Cl(1)–O(4)	108.4(4)

of the $C–S_{thione}$ distance from 1.694(4) to 1.704(3) Å [1] and an average shortening of the C(2)–N(1, 3) distances from 1.394(3) to 1.321(4) Å [1].

Coordination has clearly resulted in some redistribution of electron density within the thioamido portion of $imdtH_2$; similar changes have been observed in $[Cu(imdtH_2)_2(NCS)]$ [4].

Because of the crystallographic inversion centre at the mid-point of the complex cation the bridging ligands are constrained to adopt the 2-*anti* configuration [20], they are also virtually orthogonal (85.1°) to the Cu_2S_2 plane and 'twist' slightly about the Cu–S–C plane (2.6°). Dimensions in the Cu_2S_2 core are typical of others in the series, Table 3. There is a direct correlation between $Cu–S_{br}–Cu$ bridging angles and Cu---Cu separation distances with the smallest combination of values in $[Cu_2(imdtH_2)_6]^{2+}$. The ideal bridging angle for two edge-sharing tetrahedra is 70.5° with a S–Cu–S angle of 109.5° [21]; the metal separation distance in the parent metal is 2.550 Å [22].

TABLE 3. Selected dimensions in $[Cu_2(LH)_6]^{2+}$ complexes

LH[a]	Cu–S$_t$	Cu–S$_{br}$	Cu–S$_{br}$–Cu	S$_{br}$–Cu–S$_{br}$	Cu···Cu	S$_{br}$···S$_{br}$
tu	2.313(3) 2.295(3)	2.429(3) 2.367(3)	72.6(1)	107.4(1)	2.840(3)	3.865(2)
dmtu	2.325(3) 2.301(3)	2.461(3) 2.328(3)	72.3(3)	107.7(1)	2.828(3)	3.868(2)
mimth	2.358(1) 2.345(1)	2.419(1) 2.358(1)	77.2(1)	110.1(1)	3.007(1)	3.766(1)
pytH	2.284(2) 2.318(3)	2.308(2) 2.498(3)	74.3(1)	105.7(1)	2.907(2)	
	2.298(3) 2.326(3)	2.320(3) 2.538(4)	74.6(1)	105.4(1)	2.950(2)	
	2.274(3) 2.278(3)	2.297(3) 2.534(3)	73.8(1)	106.2(1)	2.907(2)	
imdtH$_2$	2.284(1) 2.312(1)	2.362(1) 2.490(1)	67.2(1)	112.8(1)	2.686(1)	4.043(3)

[a] Ligand abbreviation and references: tu = thiourea [18]; dmtu = *S*-dimethylthiourea [18]; mimtH = 1-methylimidazoline-2(3*H*)-thione [16]; pytH = pyridine-2-thione [19]; imdtH$_2$ = this work.

Ligand orientation and metal–ligand bonding, for the bridging ligands in similar Cu_2S_2 cores, have been rationalised in terms of electron donation by a combination of thione-S sp^2 hybridised and thioamido π-molecular orbitals [20, 18], Table 3.

Rhomboid Cu_2S_2 cores are also a feature of copper–aryl thiolate chemistry [23–25]. In $[\{Cu(SC_6H_4CH_3\text{-}o)(1,10\text{-phenanthroline})\}_2]$ the non-centrosymmetric, non-planar Cu_2S_2 core has a mean Cu–S$_{br}$–Cu angle of 68.0(1)° and a Cu---Cu separation distance of 2.613(3) Å; metal–metal bonding is proposed for this structure [23]. In the wider context of metal–sulfur systems, phenylthiolate complexes $[M_2(PhS)_6]^{2-}$ (M = Zn and Cd) generate M_2S_2 cores which tend to be regular rather than rhomboid in character with M–S$_{br}$–M angles within 2° of 90° and metal separation distances, (3.421(1) (Zn) and 3.692(1) (Cd) Å), clearly in excess of those expected for metal–metal bonding [20, 26].

The reasons for the variations in Cu_2S_2 core dimensions (Table 3) are not immediately evident. The need to generate effective separation distances between electron rich thione-S atoms is one factor responsible for the asymmetric bridging but the known S---S separation distances invariably exceed van der Waals requirements [22], Table 3. The possibility that smaller Cu–S$_{br}$–Cu bridging angles enables more effective metal–metal overlap, as a result of shorter metal separation distances, is tempting but dubious. The most probable cause for the observed dimensional variations is a combination of the steric requirements of ligand geometry and crystal packing.

Supplementary material

Structure factor tables, anisotropic thermal parameters, H-atom coordinates with isotropic thermal parameters, least-squares, mean-planes data and dihedral angles are available from the authors on request.

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