Inorganica Chimica Acta, 103 (1985) 195–205

Copper(I) Halide Complexes of Imidazole Thiones: Crystal Structure of Dimeric Monochloro bis(1-methylimidazoline-2-thione) Copper(I)

JAMES R. CREIGHTON, DEREK J. GARDINER, ANTHONY C. GORVIN*, CHRISTINE GUTTERIDGE,
ANDREW R. W. JACKSON**, ERIC S. RAPER† and PETER M. A. SHERWOOD††

School of Chemical and Life Sciences, Newcastle-upon-Tyne Polytechnic, Newcastle-upon-Tyne NE1 8ST, U.K.

Received December 20, 1984

Abstract

Copper(I) halides form complexes with imidazole-2-thione, $imtH_2$, 1-methylimidazoline-2-thione, mimtH and 1,3-dimethylimidazoline-2-thione, dmimt of formula: $Cu(imtH_2)X$ (X = Cl, Br, I) and CuL_2X (L = mimtH and dmimt; X = Cl, Br, I). These complexes have been characterised by a variety of physical and spectroscopic techniques.

The crystal structure of $Cu(mimtH)_2Cl$ consists of centrosymmetrically constrained dimers occupying a monoclinic unit cell of space group $P2_1/n$ with Z = 2. The dimers contain a pair of copper(I) atoms tetrahedrally coordinated by terminal chlorine and terminal S-bonded mimtH together with two S-bridging (μ_2) mimtH molecules. The Cu_2S_2 core of the dimer is lozenge shaped with Cu–S distances of 2.301(1) and 2.572(1) Å, a Cu–S–Cu angle of 73.2(1)° and separation distances of 2.914(1) and 3.916(1) Å between copper atoms and sulphur atoms, respectively. The final R index for 1937 counter reflections is 0.0308.

Introduction

Complexes of imidazole-thione molecules with copper have been known for some time [1] although previous research has concentrated largely on complexes formed by the saturated imidazolidine-2-thione, (ethylenethiourea) $imdtH_2$, molecule and its N-alkyl substituted derivatives [2–5].

The ability of many heterocyclic thiones to reduce copper(II) and the unpredictability of both the stoichiometry and the structure of the reaction products have stimulated much of the research effort. However, the biological importance of copper–sulphur interactions [6] and other applications of heterocyclic thioamides, notably in corrosion protection [7] have also been major factors.

Many of the complexes of $imdtH_2$ and its derivatives may be formulated relatively simply as: $M(LH_2)_nX$ n = 1 to 4; X = Cl, Br, I, NO_3, $1/2SO_4$, BF_4) [1–5]. The complexes may be discrete [8, 9] or dimeric [2, 3, 10]; polymeric compounds are also formed with other heterocyclic thiones [11]. Structural studies have shown that the metal adopts either trigonal or tetrahedral environments [8–10].

Unusual stoichiometries also occur, for example, the diamagnetic tetra nuclear cation, $[Cu_4(imdtH_2)_9]^{4+}$, [12] as well as the dodecanuclear cation, $[Cu_{12}(L)_{12}(MeCN)_4]^{2+}$ [13]. The latter complex is paramagnetic, has electronic and EPR spectra similar to those observed for copper blue (type 1) proteins and contains 1-methyl-imidazoline-2-thionate ions (L^-). Furthermore, in these compounds, the thione-sulphur atom occurs in both terminal and bridging environments ranging from one to four (μ_4) coordinate.

Complexes of imidazoline-2-thione, ($imtH_2$), [14] and 1-methylimidazoline-2(3H)-thione, (mimtH), [14, 16]; $Cu(L)_2X$ (X = Cl, Br), have been reported to contain sulphur donating ligands on the basis of infrared and ^{13}C NMR data; no other structural details have been reported.

We now report the preparation and spectroscoy of the copper(I) halo complexes of $imtH_2$, mimtH and dmimt, together with the crystal structure of the dimeric complex, $[Cu(mimtH)_2Cl]_2$.

Experimental

Starting Materials

The ligands, $imtH_2$ (Lancaster Synthesis Ltd.) and mimtH (Aldrich Chemical Company Ltd.) were used as supplied; dmimt was prepared by a previously published method [15]. The remaining materials were reagent quality.

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*Present address: Department of Chemistry, University of York, U.K.

**Present address: Department of Chemistry, UMIST, Manchester, U.K.

†Author to whom correspondence should be addressed.

††Department of Inorganic Chemistry, University of Newcastle-upon-Tyne, U.K.

0020-1693/85/$3.30

Chemical Analysis

C, H, N and copper analyses were performed by Elemental Micro Analysis Ltd., Beaworthy, Devon.

Preparations

Complexes of imtH_2, mimtH and dmimt are readily prepared by reacting the ligand, in absolute ethanol, and the appropriate copper(I) halide in acetonitrile.

The complexes of mimtH have also been prepared by reacting the ligand in acetone and the appropriate metal salt in a 1:1 (V:V) acetone: hydrohalic acid mixture [16]. A combination of chemical analysis, infrared spectroscopy, as well as X-ray powder diffraction showed the complexes, $Cu(mimtH)_2X$ (X = Cl, Br, I), prepared from both methods to be identical.

$Cu(imtH_2)Cl$ (1)

0.6545 g of $imtH_2 \cdot 0.5H_2O$ (6 mmol) in absolute ethanol (*ca.* 75 cm^3) was added to 0.3000 g of CuCl (3 mmol) in acetonitrile (*ca.* 30 cm^3). A gelatinous cream precipitate appeared immediately the reactants were mixed. The product was isolated by suction filtration and air dried under reduced pressure over silica gel at room temperature. The air sensitive compound was stored under argon. Yield; 40.0%. *Anal.*: Calculated (%) C 18.09, H 2.01, N 14.07; Found (%) C 18.29, H 2.21, N 13.82.

$Cu(imtH_2)Br$ (2)

0.4516 g of $imtH_2 \cdot 0.5H_2O$ (*ca.* 4 mmol) in absolute ethanol (*ca.* 75 cm^3) at 60 ℃ was added to 0.3000 g CuBr (*ca.* 2 mmol) in acetonitrile (*ca.* 30 cm^3) at 60 ℃. A white precipitate appeared immediately upon mixing the reactants and further precipitation appeared after cooling to room temperature. The product was isolated and dried as in (**1**). Yield; 35.4%. *Anal.:* Calculated (%) C 14.78, H 1.64, N 11.50; Found (%) C 14.81, H 1.78, N 11.15.

$Cu(imtH_2)I \cdot 0.25C_2H_5OH$ (3)

0.3402 g of $imtH_2 \cdot 0.5H_2O$ (*ca.* 3 mmol) in absolute ethanol (*ca.* 45 cm^3) at 60 ℃ was added to 0.3000 g of CuI (*ca.* 1.5 mmol) in acetonitrile (*ca.* 30 cm^3) at 60 ℃. About 75.0% of the solvent was removed by vacuum distillation at about 40 ℃; the resultant white granular solid was isolated and dried as in (**1**). Yield; 32.9%. *Anal.*: Calculated (%) C 13.91, H 1.82, N 9.27; Found (%) C 13.82, H 1.69, N 9.35.

$Cu(mimtH)_2Cl$ (4)

0.5700 g of mimtH (5 mmol) in absolute ethanol (*ca.* 20 cm^3) was added to 0.2479 g of CuCl (2.5 mmol) in acetonitrile (*ca.* 20 cm^3) at room temperature. The initially green solution gradually changed to deep blue leaving a white microcrystalline solid. Precipitation occurred within 1 min of mixing the reactants. The product was isolated and dried as in (**1**). Yield; 68.5%. *Anal.*: Calculated (%) C 29.4, H 3.7, N 17.1; Found (%) C 29.4, H 3.6, N 17.0.

$Cu(mimtH)_2Br$ (5)

0.5700 g of mimtH (5 mmol) in absolute ethanol (*ca.* 20 cm^3) was added to 0.3594 g of CuBr (2.5 mmol) in acetonitrile (*ca.* 25 cm^3) at room temperature. A white microcrystalline solid precipitated from a light blue solution within 1 min of mixing the reactants. The product was isolated and dried as in (**1**). Yield; 78.3%. *Anal.*: Calculated (%) C 25.9, H 3.2, N 15.1; Found (%) C 25.7, H 3.1, N 15.0.

$Cu(mimtH)_2I$ (6)

0.2280 g of mimtH (2.0 mmol) in absolute ethanol (*ca.* 25 cm^3) was added to 0.1904 g of CuI (1 mmol) in acetonitrile (*ca.* 25 cm^3) at room temperature. A white product precipitated from a pale green solution within 2 h of mixing the reactants. The product was isolated and dried as in (**1**). Yield; 76.0%. *Anal.*: Calculated (%) C 22.9, H 2.9, N 13.4; Found (%) C 22.7, H 2.8, N 13.1.

$Cu(dmimt)_2Cl$ (7)

0.2560 g of dmimt (2 mmol) in absolute ethanol (*ca.* 45 cm^3) was added to 0.0990 g of CuCl (1 mmol) in acetonitrile (*ca.* 20 cm^3) at room temperature. This produced a pale lilac solution which largely decolourised within about 20 mins at room temperature. About 75% of the solvent was removed by distillation at atmospheric pressure; on cooling to room temperature a white solid was obtained. The product was isolated and dried as in (**1**). Yield; not recorded owing to instability in air. *Anal.*: Calculated (%) C 33.80, H 4.51, N 15.77; Found (%) C 33.56, H 4.50, N 15.53.

$Cu(dmimt)_2Br$ (8)

0.1177 g of dmimt (1 mmol) in absolute ethanol (*ca.* 30 cm^3) was added to 0.0660 g of CuBr (0.5 mmol) in acetonitrile (*ca.* 20 cm^3) at room temperature. The resultant pale lilac solution decolourised on heating to 60 ℃. About 75% of the solvent was removed by distillation at atmospheric pressure. On cooling to room temperature a white granular solid was obtained from a pale lilac solution. The product was isolated and dried as in (**1**). Yield; 79.4%. *Anal.*: Calculated (%) C 30.04, H 4.00, N 14.02; Found (%) C 30.21, H 3.92, N 13.72.

$Cu(dmimt)_2I$ (9)

Attempts to prepare this complex by reaction of dmimt in absolute ethanol with CuI in acetonitrile were unsuccessful, however, fusion of approximately 2 g of a 2:1 (ligand:metal) molar ratio mixture of dmimt (0.2500 g) and CuI (0.1900 g) under argon and over boiling decalin at 188 ℃ for 2 mins resulted in a green 'glassy' solid. This product was refluxed with approximately 50 cm^3 of absolute ethanol for several hours. The reaction mixture was hot filtered and the clear colourless solution was allowed to stand for three months; the resultant colourless crystals were removed and dried as in (1). Yield; very low, *ca.* 5%. *Anal.*: Calculated (%) C 26.9, H 3.6, N 12.5; Found (%) C 26.8, H 3.5, N 12.6.

Spectroscopy

Infrared spectra were recorded to a precision of ±4 cm^{-1} as caesium iodide discs on a Perkin-Elmer 577 grating spectrophotometer in the range 4000 to 200 cm^{-1}. All the spectra were calibrated by means of a 0.5 mm polystyrene film.

Raman spectra were recorded on a Spex 1403 0.85 m double monochromator spectrometer with a multi alkali Hamamatsu R928 photomultiplier tube. A Spex datamate control and data acquisition system and a Spectra Physics 164-07 argon laser operating at 514.5 nm was used to excite the Raman spectra. Laser sensitive samples were supported in spinning caesium iodide discs, the remainder were contained in glass capillary tubes.

X-ray photoelectronic spectra (X-ray P.E.S.) were recorded using an AEI ES200B spectrometer which was calibrated by a carbon (1s) hydrocarbon peak (284.6 eV). All spectra were obtained at $\leqslant 10^{-1}$ torr from samples held on double sided Sellotape and X-rays of energy 1253.6 eV. Curve fitting was achieved by means of an Apple microcomputer and the NUMAC IBM 370/168 mainframe computer at the University of Newcastle upon Tyne. The software was prepared by Dr. P. M. A. Sherwood.

Magnetic Measurements

A room temperature Gouy (Newport Instruments Ltd.) magnetic balance was used to monitor the diamagnetic complexes.

Conductivity Measurements

A Portland Electronics P310 conductivity meter and a dip-type electrode were used. All measurements were carried out with the complexes in 10^{-3} M concentration in nitromethane.

Crystal Structure Analysis

Diffraction quality crystals were obtained by recrystallising the complex from n-butyronitrile. Relevant crystal data are listed in Table I; intensity data were corrected for Lorentz, polarisation and absorption effects.

Non-hydrogen atoms were located by a combination of direct methods and difference Fourier syntheses and their coordinates refined by full-matrix least squares methods with anisotropic temperature factors. Positional parameters for the hydrogen atoms were included in the calculations but were not refined; the imido (NH) hydrogen atoms were located by difference Fourier methods whereas the remainder were fixed by the program (C–H = 1.08 Å). Common isotropic temperature factors were also applied to the imido, olefinic and methyl hydrogen atoms and refined to final U values (Å^2) of 0.047(7), 0.059(7) and 0.150(12) respectively. Scattering factors for all atoms were calculated from an analytical approximation [17]. Final atomic coordinates and Beq values [18] are in Table II.

TABLE I. Crystallographic Data.

Compound	$Cu_2C_{16}H_{24}N_8S_4Cl_2$
Mr	654.91
a (Å)	10.2974 (21)
b (Å)	14.7433 (63)
c (Å)	8.4459 (17)
β (deg.)	100.498 (16)
U (Å^3)	1260.8 Å
Z	2
space group	$P2_1/n$
Dc (g × cm^{-3})	1.73
F(000)	712
μ (cm^{-1})	21.56
diffractometer	Enraf-Nonius CAD-4
radiation (Å)	0.71069
max. 2θ (deg.)	55.0
total data	2218
$F_o^2 > 3\sigma(F_o)^2$	1937
R	0.0308
R_w	0.0435
w	$1.0000/[(\sigma^2)F_o + 0.003103F_o^2]$

TABLE II. Final Fractional Atomic Coordinates (× 10^4) with e.s.d.s in Parentheses for non-H Atoms and Beq [18].

Atom	x	y	z	B_{eq} (Å^2)
(a) non-H atoms				
Cu	−583(0)	4115(0)	5185(1)	3.59(3)
Cl	−2864(1)	3858(1)	4321(1)	3.19(3)
S(21)	−42(1)	5111(0)	7300(1)	2.48(3)
C(21)	−1437(3)	5740(2)	7340(3)	2.5(1)
N(11)	−1495(3)	6492(2)	8245(3)	3.0(1)
N(31)	−2646(3)	5610(2)	6475(3)	2.9(1)
C(41)	−3476(3)	6278(2)	6803(4)	3.5(1)
C(51)	−2784(3)	6820(2)	7900(4)	3.6(1)
C(11)	−389(3)	6865(3)	9392(4)	4.1(1)
S(22)	691(1)	2849(1)	5597(1)	3.25(3)
C(22)	−21(3)	2017(2)	4367(3)	2.7(1)
N(12)	542(3)	1226(2)	4079(3)	3.4(1)
N(32)	−1284(2)	1978(2)	3526(3)	3.0(1)
C(42)	−1493(4)	1161(3)	2730(5)	3.9(1)
C(52)	−381(4)	687(3)	3083(5)	4.5(2)
C(12)	1930(4)	991(3)	4695(6)	4.6(2)
(b) H-atoms				
H(31)	−2825	5142	5753	
H(32)	−1841	2557	3424	

All calculations were performed on the NUMAC, IBM 370/168 computer at the University of Newcastle upon Tyne. SHELX [19] and related programs were used in the solution.*

Results and Discussion

Formulation and General Properties of the Complexes

Chemical (C, H, N) analysis confirms two types of stoichiometry: $Cu(imtH_2)X$ (X = Cl, Br, I) and $Cu(L)_2X$ (X = Cl, Br, I; L = mimtH and dmimt). The complexes are white, moderately air-stable with generally low solubility in organic solvents. Molar conductivities in nitromethane (10^{-3} M) show the $imtH_2$ and mimtH complexes to be non-conducting (Λ_m range 5.9–22.1 Ω^{-1} cm^2 mol^{-1}). The dmimt complexes, on the other hand, show anomalously high values which suggest that the complexes decompose in nitromethane and possibly other organic solvents as well.

Spectroscopy

The infrared and Raman spectra of the ligands and their complexes are listed in Tables III and IV respectively, together with proposed assignments for the major bands. In addition, several of the complexes showed evidence of hydration.

In general, thioamide band activity [20] is more pronounced in the infrared than in the Raman spectra of the ligands and their complexes. We note, in particular, the relative lack of thioamide IV band activity in the Raman spectra of complexes **2**, **4**, and **6** as well as the absence of the band formally related to the thioamide II band among dmimt and its complexes (**7**, **8** and **9**).

The absence of any ν(SH) activity (*ca.* 2500 cm^{-1}) confirms the presence of the thione tautomer for both $imtH_2$ and mimtH as well as their complexes in the solid; similar observations have been reported for other metals with these ligands [21].

The salient feature of the infrared spectra of the complexes is the major perturbation of the thioamide IV, and related bands, in the region, 800–500 cm^{-1}. This activity is indicative of thione sulphur donation to the metal and has been previously established for the complex tris (methylimidazoline-2(3H)-thione) copper(I) nitrate [22] by a combination of infrared and X-ray methods. Rather surprisingly no corresponding ν(Cu–S) activity occurs in the infrared spectra of the complexes.

Changes to the Raman spectra of the ligands upon coordination are limited to perturbation of the π(C–S) band (522 and 531 cm^{-1}) for $imtH_2$ and mimtH and to the δ(C–S) band (646 cm^{-1}) for dmimt. However, the presence of ν(Cu–S) activity (266–298 cm^{-1}) among the complexes of mimtH (**4**–**6**) and dmimt (**7**, **8**) provides unequivocal evidence for thione–sulphur donation. In addition, ν(Cu–X) activity, (167–278 cm^{-1}), confirms the presence of terminal halide [2, 3] for complexes **1**, **2**, **3**, **4**, **5** and **8**.

Electron core binding energies (eV), derived from the X-ray photoelectron spectra of mimtH and $Cu(mimtH)_2Br$, together with relevant data for benzimidazoline-2-thione ($bzimtH_2$, LH_2) and some of its copper(I) complexes, as well as values for copper(II) salts are listed in Table V. In addition to the values listed, mimtH and $Cu(mimtH)_2Br$ both show C(1s) binding energies in the range 284.6 to 287.3 eV.

The N(1s) and $S(2p_{3/2})$ binding energies for mimtH are consistent with imido (NH) and thione sulphur groups, respectively, in the molecule [29, 30].

The binding energies for $Cu(mimtH)_2Br$ show some significant changes relative to the ligand values. Both the N(1s) and the $S(2p_{3/2})$ bands consist of two peaks which suggest two types of ligand environment in the complex. The positive chemical shifts to the $S(2p_{3/2})$ binding energies indicate sulphur thione donation to the metal; the binding energies are within the range reported for copper complexes of $bzimtH_2$ (Table V). The negative chemical shifts to the N(1s) binding energies are substantial and the fact that the binding energies are themselves so disparate also suggests different environments for the two ligands involved.

The binding energy for the metal in $Cu(mimtH)_2Br$ is clearly closer to the values for the copper(I) complexes rather than the copper(II) salts, listed in Table V, and confirms the oxidation state of the metal.

Crystal Structure of $Cu_2(mimtH)_4Cl_2$

Bond lengths and angles are in Table VI; mean planes data are in Table VII; selected dimensions from relevant structures are in Table VIII. Figure 1

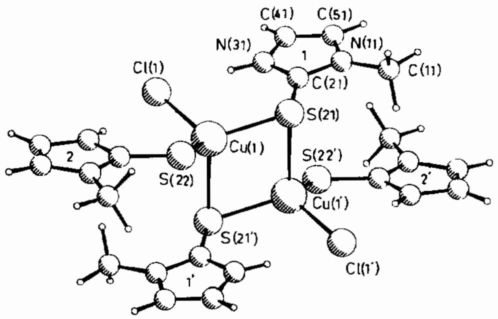

Fig. 1. Perspective diagram of $Cu_2(mimtH)_4Cl_2$ with atomic numbering.

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*Structurally insignificant H-atom coordinates, anisotropic temperature factors, observed and calculated structure factors have been deposited with the Editor-in-Chief.

TABLE III. Major Infrared Band Assignments for Ligands and Complexes (cm^{-1}).

imtH$_2$(LH$_2$)	Cu(LH$_2$)Cl	Cu(LH$_2$)Br	Cu(LH$_2$)I	mimtH(LH)	Cu(LH)$_2$Cl	Cu(LH)$_2$Br	Cu(LH)$_2$I	[a]dmimt(L)	Cu(L)$_2$Cl	Cu(L)$_2$Br	Cu(L)$_2$I	Assignments
3600 (vs) 3020 (vs)	3320 (vs) 3000 (vs)	3350 (vs) 3040 (vs)	3400 (vs) 3040 (vs)	3120 (s)	3230 (s) 3120 (s)	3230 (s) 3120 (s)	3240 (vs) 3160 (s) 3140 (s)	–	–	–	–	ν(NH)
1585 (vs)	1580 (vs)	1575 (vs)	1580 (vs)	1575 (s)	1575 (s)	1575 (s)	1575 (s)	1575 (m) 1560 (sh)	1565 (m)	1570 (m)	1565 (vs) 1560 (sh)	ν(C=C) + ν(C=N)
1480 (s) 1420 (sh)	1470 (vs) 1410 (m)	1470 (s) 1400 (w)	1470 (vs) 1390 (w)	1460 (vs)	1460 (vs)	1460 (vs)	1460 (s) 1470 (s)	1510 (sh) 1500 (sh) 1490 (s)	1480 (vs)	1480 (vs)	1470 (vs)	Thioamide I ν(C–N) + δ(C–H)[a]
–	–	–	–	1335 (m)	1345 (m)	1340 (w)	1330- 1350 (w)	1410 (s) 1385 (vs)	1410 (sh) 1395 (vs)	1390 (vs)	1390 (vs)	ν(N–Me)
1265 (m) 1225 (vs)	1285 (w) 1230 (m)	1275 (w) 1225 (w)	1265 (w) 1210 (w)	1275 (s)	1265 (m) 1270 (s) 1285 (s)	1260 (m) 1270 (s) 1285 (s)	1275 (s) 1285 (m)	1240 (vs)	1240 (vs) 1230 (vs)	1240 (s) 1230 (sh)	1225 (vs)	Thioamide II ν(C–N) + δ(C–H) + ν(C=S)[a]
1070 (s)	1070 (m)	1065 (m)	1060 (m) 1040 (w)	1090 (m)	1090 (m)	1090 (m)	1090 (m)	1085 (m)	1090 (m)	1090 (m)	1085 (s)	Thioamide III ν(C–N) + ν(C=S)[a]
785 (br, m) 735 (vs)	790 700 (vs)	810 710 (vs)	740 (s) 700 (m)	770 (sh) 740 (s)	790 (m) 750 (s) 730 (s) 720 (s)	770 (m) 740 (s) 730 (s) 720 (s)	750 (sh) 740 (s) 730 (s) 720 (s)	750 (vs) 730 (vs)	760 (s) 750 (s) 735 (s) 730 (s)	755 (s) 745 (s) 735 (s) 730 (s)	740 (vs) 720 (vs)	Thioamide IV ν_s(C=S) + ν_{as}(C=S)[a]
675 (vs)	665 (m)	665 (m)	660 (m) 635 (sh)	675 (m)	670 (m)	670 (m)	665 (m)	660 (vs)	670 (s) 630 (w)	670 (s) 630 (w)	670 (s) 625 (vw)	δ(C–S)
520 (vs)	480 (m)	490 (m)	495 (m)	530 (m)	515 (m) 530 (m)	510 (m) 525 (m)	515 (w) 530 (w)	515 (vs)	505 (m)	500 (m) 480 (w)	500 (m) 480 (w)	π(C–S)

[a] Equivalent to Thioamide bands.

TABLE IV. Major Raman Band Assignments for Ligands and Complexes (cm^{-1}).

$imtH_2(LH)$	$Cu(LH_2)Cl$	$Cu(LH_2)Br$	$Cu(LH_2)I$	mimtH(LH)	$Cu(LH)_2Cl$	$Cu(LH)_2Br$	$Cu(LH)_2I$	[a]dmimt(L)	$Cu(L)_2Cl$	$Cu(L)_2Br$	$Cu(L)_2I$	Assignments
3123 (s) 3155 (m) 3183 (w)				3108 (s) 3131 (s) 3164 (s)	3119 3175 (s, m)	3119 3170 (s, m)	3118 3166 (s, m)					ν(NH)
1590 (w)	1582 (w)	–	1582 (vw)	1574 (s)	1566 (m)	1570 (m)	1574 (w)	1574 (m)	1574 (w)	1570 (w)	1574 (m)	$\nu(C{=}C) + \nu(C{=}N)$
1486 (s)	1478 (vs) 1418 (vw)	1470 (s)	1470 (vs)	1465 (m) 1450 (sh)	1478 (vs) 1458 (sh)	1478 (vs)	1466 (vs)	1490 (m) 1446 (s)	1482 (m) 1438 (s)	1478 (m) 1434 (s)	1482 (w) 1446 (m) 1426 (w)	Thioamide I $\nu(C{-}N) + \delta(C{-}H)^a$
–	–	–	–	1339 (m)	1342 (m)	1346 (s)	1350 (m)	1398 (vs) 1350 (s)	1398 (vs) 1346 (s)	1398 (vs) 1346 (s)	1398 (vs) 1345 (s)	$\nu(N{-}Me)$
1230 (vs)	1230 (vs)	–	1214 (s)	1277 (w)	1278 (m)	1286 (s) 1262 (m)	1286 (m)					Thioamide II
1118 (m)	1118 (m)	1106 (m)	1118 (w) 1098 (m)	1094 (m)	1082 (w)	1094 (w)	1094 (m)	1090 (w) 1034 (w) 1018 (w)	1030 (w)	1030 (w)	1090 (w) 1018 (w)	Thioamide III $\nu(C{-}N) + \nu(C{-}S)^a$
734 (vw)	682 (vw)	–	754 (vw) 670 (vw)	737 (vw)	–	738 (vw)	–	754 (m) 726 (w)	752 (m)	750 (m)	754 (m) 730 (w)	Thioamide IV $\nu_s(C{=}S) + \nu_{as}(C{=}S)^a$
–	–	–	–	693 (vs) 680 (w)	690 (sh) 666 (m)	694 (s) 674 (m)	694 (m) 674 (m)	646 (s)	634 (s)	638 (s)	650 (s) 634 (m)	$\delta(C{-}S)$
522 (w)	502 (w)	–	502 (w)	531 (s)	528 (m)	525 (m)	529 (m)	578 (w)	502 (vw)	–	–	$\pi(C{-}S)$
–	–	–	–	–	294 (s)	298 (s)	296 (s)	–	266 (w)	266 (w)		$\nu(Cu{-}S)$
–	278 (w)	266 (w)	210 (vs)	–	253 (w)	167 (w) 213 (w)	–	–	–	218 (w) 178 (w)	–	$\nu(Cu{-}X)$

[a] Equivalent to Thioamide bands.

TABLE V. Electron Core Binding Energies (eV).

Compound	Binding Energy			Reference
	N(1s)	S(2p$_{3/2}$)	Cu(2p$_{3/2}$)	
mimtH	404.5	161.6	–	this work
Cu(mimtH)$_2$Br	400.5; 398.6	163.8; 162.4	931.6	this work
BzimtH$_2$(LH$_2$)	400.6	162.4	–	[29]
Cu(LH$_2$)Cl	400.7	163.1	933.2	[29]
Cu(LH)	400.4; 399.0	162.8	933.5	[29]
CuCl$_2$	–	–	935.8	[30]
[Cu(CH$_3$COO)$_2$·2H$_2$O]$_2$	–	–	935.2	[30]

TABLE VI. Bond Distances (Å) and Angles (°) with e.s.d.s in Parentheses[a].

(a) The coordination sphere

Bond	(Å)	Angle	(°)
Cu–S(21)	2.301(1)	S(21)–Cu–Cl	115.4(1)
Cu–S(22)	2.271(1)	Cl–Cu–S(22)	115.5(1)
Cu–S(21′)	2.572(1)	S(22)–Cu–S(21′)	105.5(1)
Cu–Cl	2.360(1)	S(21′)–Cu–S(21)	106.8(1)
Cu–Cu(′)	2.914(1)	S(22)–Cu–S(21)	110.7(1)
S(21)–S(21′)	3.916(1)	Cl–Cu–S(21′)	101.7(1)
		Cu–S(21)–C(21)	106.0(1)
		Cu–S(22)–C(22)	109.2(1)
		Cu–S(21)–Cu(′)	73.2(1)
		Cu(′)–S(21)–C(21)	96.3(1)

(b) Heterocyclic molecules

A = 1 or 2	Molecule 1	Molecule 2
C(2A)–S(2A)	1.715(3)	1.686(3)
C(2A)–N(1A)	1.354(4)	1.345(4)
N(1A)–C(1A)	1.461(4)	1.470(4)
C(2A)–N(3A)	1.338(4)	1.365(4)
N(3A)–C(4A)	1.365(4)	1.376(5)
C(4A)–C(5A)	1.328(5)	1.328(6)
C(5A)–N(1A)	1.353(4)	1.396(5)
S(2A)–C(2A)–N(1A)	125.3(2)	126.1(3)
S(2A)–C(2A)–N(3A)	127.7(2)	128.2(2)
N(1A)–C(2A)–N(3A)	107.0(3)	105.7(3)
C(2A)–N(1A)–C(1A)	125.0(3)	124.3(3)
C(1A)–N(1A)–C(5A)	127.3(3)	126.2(3)
C(2A)–N(1A)–C(5A)	107.8(3)	109.5(3)
C(2A)–N(3A)–H(3A)	121.7(3)	118.3(3)
H(3A)–N(3A)–C(4A)	128.3(3)	130.8(3)
C(2A)–N(3A)–C(4A)	109.9(3)	109.9(3)
N(3A)–C(4A)–C(5A)	107.4(3)	107.5(3)
C(4A)–C(5A)–N(1A)	107.8(3)	107.4(3)

(c) Hydrogen bonding

Bond	Lengths			Angle
A····H–D	A····D	A····H	H–D	A····H–D
Cl····H(31)–N(31)	3.144	2.243	0.917	167.3
Cl····H(32)–N(32)	3.343	2.377	1.023	157.1

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[a] Symmetry code, superscript; none, x, y, z; (′), $-x, 1-y, 1-z$.

TABLE VII. Least Squares Mean Planes (Crystal Coordinates) and Dihedral Angles.

(a) Planes

No.	Plane	Equation	Maximum displacement (Å)
1	Ligand 1	$0.2367X + 0.5754Y - 0.7829Z + 0.5249 = 0.0$	S(21), 0.018
2	Ligand 2	$-0.2900X - 0.4222Y + 0.8589Z - 1.9403 = 0.0$	S(22), 0.031
3	CuS(21)C(21)	$0.2980X + 0.6696Y - 0.6803Z - 0.8331 = 0.0$	–
4	CuS(22)C(22)	$-0.5037X - 0.3009Y + 0.8098Z - 2.1061 = 0.0$	–
5	CuS(21)Cu(')S(21')	$0.9138X - 0.4025Y + 0.0537Z + 2.7403 = 0.0$	–
6	CuS(22)Cl	$-0.1249X - 0.0284Y + 0.9918Z - 4.3528 = 0.0$	–

(b) Dihedral Angles

Plane	Angle (°)[a]
1/2	12.1
1/3	8.7
2/4	153.2
1/5	93.3
2/5	90.5
1/6	34.7
2/6	134.0
4/6	29.0
5/6	92.8

[a] E.s.d. s are in the range 1.0–2.0°.

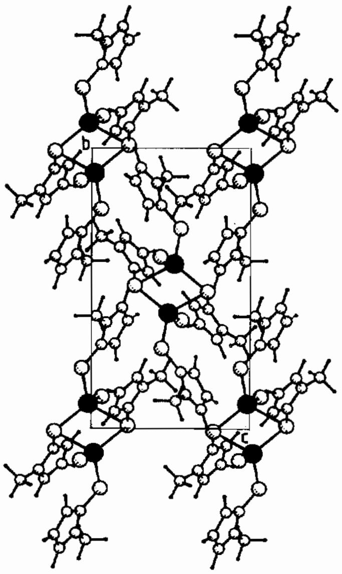

Fig. 2. Unit cell contents viewed down a^*, ● = Cu.

contains a perspective view of the complex with atomic numbering and Fig. 2 shows the unit cell contents.

The dimeric complex is crystallographically constrained to occupy centres of symmetry in the unit cell (Fig. 2). Consequently, both of the copper(I) atoms in the dimer have identically distorted tetrahedral environments with angles, at the metal, ranging from 101.7 to 115.5°. The tetrahedral coordination consists of one chlorine atom (2.360(1) Å), one terminally sulphur bonded mimtH molecule (2.271(1) Å) and two sulphur bridging (μ_2) mimtH molecules (2.301 and 2.572(1) Å).

The bridging sulphur atom, (S(21)), generates a strictly planar Cu_2S_2 core, (plane 5, Table VII), which contains alternating short and long Cu–S bonds. The core also contains a relatively short distance between the two copper atoms (2.914(1) Å), a narrow Cu–S(21)–Cu angle (73.2(1)°) and a separation distance of 3.916(1) Å between the bridging sulphur atoms (Table IX).

The ligands, (planes 1 and 2, Table VII), which are only slightly inclined to one another, are virtually normal to the Cu_2S_2 core, (plane 5, Table VII), and 'twist' about their respective Cu–S–C planes, (planes 3 and 4, Table VII); relevant dihedral angles are in Table VII.

Two of the Cu–S–C angles (106.0, 109.2(1)°) are normal for coordinated mimtH molecules [23]; the third value (96.3(1)°) is radically different and involves the 'long' Cu–S contact.

The terminal ligand has a C–S distance (1.686(3) Å) which is essentially the same as the value in the uncoordinated molecule (1.685 av. Å) [24] while the bridging ligand has a significantly longer C–S distance (1.715(3) Å). Differences also occur between the C(2A)–N(3A) and the C(5A)–N(1A) distances of the coordinated ligands. For both bonds it is the bridging ligand which has the shorter distances.

TABLE VIII. Copper (Thione) Chloro Complexes: Selected Dimensions (Å).

Complex	Metal Stereochemistry	Cu–Cl	Cu–S		C–S	Reference
			terminal	bridging		
Cu(thiouracil)$_2$Cl	trigonal	2.260(1)	2.227(av)	–	1.69(av)	[31]
[Cu(imidazolidine-2-thione)$_2$Cl]$_2$	tetrahedral	2.319(3)	2.256(4)	2.631(3)	1.694(av) (terminal-S)	[10]
			2.282(3)	–	–	
	trigonal	2.277(3)	2.196(3)	2.204(3)	1.717(7) (bridging-S)	[10]
[Cu(purinium-8-thione)Cl$_2$]$_n$ ^{a}	tetrahedral	2.423(2)	–	2.375(2)	1.683(6)	[11]
		2.276(2)	–	2.289(2)	–	
[Cu(purinium-6-thione)Cl$_2$]$_2$ ^{a}	tetrahedral	2.242(av)	–	2.253(av)	1.69(3)	[32, 33]
		2.364(av)	–	2.736(av)	–	
Cu(tetrahydropyrimidine-2-thione)$_2$Cl	trigonal	2.317(3)	2.206(2)	–	1.727(2)	[34]
Cu(1,3-dimethylimidazolidine-2-thione)$_2$Cl	trigonal	2.233(3)	2.229(3)	–	1.698(4)	[8]
Cu(1-ethylimidazolidine-2-thione)$_2$Cl	trigonal	2.258(2)	2.216(av)	–	1.702(av)	[9]
Cu(thiourea)$_2$Cl	trigonal	–	2.244(5)	2.280(av)	1.68(av) (terminal-S)	[35]
	tetrahedral	–	2.229(5)	2.287(av)	1.73(av) (bridging-S)	

^{a}Protonated ligands.

TABLE IX. Cu$_2$S$_2$ Core Dimensions.

Compound	Reference	Cu–S (Å)	Cu–S–Cu (°)	S····S (Å)	Cu····Cu (Å)
[Cu$_2$(thiourea)$_6$]$^{2+}$	[36]	2.367(3); 2.429(3)	72.6(1)	3.865(1)	2.840(3)
[Cu$_2$(S-dimethylthiourea)$_6$]$^{2+}$	[36]	2.325(3); 2.461(3)	72.3(1)	3.868(5)	2.828(3)
[Cu(purinium-6-thione)Cl$_2$]$_2$	[32]	2.244(5); 2.741(6)	87.5(2)	3.629(9)	3.456(3)
	[33]	2.253; 2.734	–	–	–
Cu$_2$(mimtH)$_4$Cl$_2$	[this work]	2.301(1); 2.572(1)	73.2(1)	3.916(1)	2.914(1)

The terminal chlorine atoms and imido (NH) groups of the ligands form intra-molecular N–H····Cl hydrogen bonds. There are no other significantly short contacts between the dimers.

Stoichiometric-Structural Relationships among the Complexes

Crystallographic studies on complexes involving copper(I) chloride and heterocyclic thiones have established the presence of trigonal and tetrahedral environments for the metal as well as terminal and bridging sulphur donation for the ligands (Table VIII). Sufficient structural information now exists to permit exploration of the stoichiometric-structural relationships among the complexes contained in this report.

Formulation of the imtH$_2$ complexes, Cu(imtH$_2$)X (X = Cl, Br, I), may be rationalised on the basis of a trigonal environment for the metal, terminal chlorine and bridging (μ_2) thione sulphur.

A structure which supports the above arrangement is that of [Cu(I)(purinium-8-thione)Cl$_2$]$_n$. The ligand is protonated in this complex, hence the extra chloride; consequently the metal has a tetrahedral, rather than a trigonal, environment. However, the bridging (μ_2) thione sulphur links the metal centres into an infinite polymeric chain.

In contrast to this, the previously reported complexes, Cu(imtH$_2$)$_2$X (X = Cl, Br, I) [14], which were described as dimeric, could be reasonably expected to have structures similar to [Cu(mimtH)$_2$Cl]$_2$.

The combination of similar X-ray powder diffraction patterns and the crystal structure of the chloro complex suggests dimeric formulae, [Cu(mimtH)$_2$X]$_2$, for the mimtH complexes and tetrahedral geometry for the metal.

Two of the Cu–S distances (2.271(1) and 2.301(1) Å) are 'normal' in the sense that they are less than the sum of their respective tetrahedral covalent radii (2.36 Å) [25] and are within the range of Cu–S distances reported for polynuclear copper complexes (2.241–2.356 Å) [26]. Conventional coordination is proposed for these two bonds involving electron donation from sp^2 hybrid orbitals (sulphur) to sp^3 hybrid orbitals (metal). The remaining Cu(1′)–S(21) distance (2.572(1) Å) is much longer; furthermore, both the bridging Cu(1)–S(21)–Cu(1′) angle (73.2(1)°) and the Cu(1′)–S(21)–C(21) angle (96.3(1)°) indicate that the S(21) atom does not use its remaining non-bonded (sp^2) electron-pair in order to complete the Cu(1)–S(21)–Cu(1′) bridge. In view of the fact that the bridging ligand (plane 1, Table VII) is virtually normal (93.3°, Table VII) to the Cu$_2$S$_2$ core (plane 5, Table VII) the most likely bonding mode involves electron donation from the thioamide π-MO of the heterocycle to a vacant sp^3 orbital on the metal. This bonding scheme also provides an explanation for the fact that the C(21)–S(21) bond is significantly lengthened upon coordination while that of the terminal mimtH molecule is essentially the same as that of the uncoordinated ligand. Negative chemical shifts to the N(1s) binding energies of the coordinated mimtH molecules (Table V) suggest that back-donation of electron density to the heterocycle complements the bonding process.

The Cu$_2$S$_2$ core dimensions for Cu$_2$(mimtH)$_4$Cl$_2$ and other centro-symmetric dimers with related ligands are listed in Table IX.

The factors which govern Cu$_2$S$_2$ core formation are a combination of the bonding and steric requirements of the bridging ligand and soft attractive Cu(I)····Cu(I) coupling [27, 28]. Thiourea molecules, not surprisingly, generate Cu$_2$S$_2$ cores which are similar to that of Cu$_2$(mimtH)$_4$Cl$_2$. The bridging angle in three cases is similar to that calculated for an idealised tetrahedral dimer (70.5°) [27]. Among the complexes listed it can be seen that opening up of the bridging (Cu–S–Cu) angle is accompanied by a shortening of the S····S separation distance together with increases in metal–metal separation and in the longer of the two Cu–S distances. It is probable that the latter contact is the crucial component in the dimerisation process and its inherent flexibility is evident from the distances involved, (2.429(3) to 2.741(6) Å Table IX).

Formulation of the dmimt complexes, Cu(dmimt)$_2$X (X = Cl, Br, I) may be equated with monomeric formulae and trigonal metal environments. The presence of methyl groups on both of the imidazole nitrogen atoms precludes intramolecular hydrogen bond formation, similar to that which is present in [Cu(mimtH)$_2$Cl]$_2$, and which is one of the factors helping to stabilise the dimeric form of the complex and the tetrahedral geometry of the metal. A trigonal monomeric arrangement has been reported for Cu(1,3-dimethylimidazolidine-2-thione)$_2$Cl (Table VIII) [8]; which serves as an excellent model for the above dmimt complexes.

Acknowledgements

We are grateful to S.E.R.C. and Dr. M. B. Hursthouse, Department of Chemistry, Queen Mary College, University of London, for the provision of X-ray intensity data.

References

1 T. Morgan and H. Burstall, *J. Chem. Soc.*, 143 (1928).
2 F. Devillanova and G. Verani, *Transition Met. Chem.*, *2*, 120 (1977).
3 F. Devillanova and G. Verani, *Transition Met. Chem.*, *3*, 42 (1978).
4 F. A. Devillanova, F. Isaia and G. Verani, *J. Inorg. Nucl. Chem.*, *43*, 2749 (1981).

5 P. Castan, *Transition Met. Chem.*, *6*, 14 (1981).

6 K. D. Karlin and J. Zubieta (eds.), 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives', Adenine, New York, 1983.

7 B. Donnelly, T. C. Downie, R. Grzeskowiak, H. R. Hamburg and D. Short, *Corros. Sci.*, *18*, 109 (1978).

8 F. A. Devillanova, G. Verani, L. P. Battaglia and A. Bonnamartini Corradi, *Transition Met. Chem.*, *5*, 362 (1980).

9 L. P. Battaglia, A. Bonnamartini Corradi, F. A. Devillanova and G. Verani, *Transition Met. Chem.*, *4*, 264 (1979).

10 L. P. Battaglia, A. Bonnamartini Corradi, M. Nardelli and M. E. Vidoni Tani, *J. Chem. Soc., Dalton Trans.*, 143 (1976).

11 M. R. Caira and L. R. Nassimbeni, *J. Chem. Soc., Dalton Trans.*, 4 (1976).

12 A. L. Crumbliss, L. J. Gestaut, R. C. Rickard and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 545 (1974).

13 Y. Agnus, R. Louis and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 946 (1980).

14 R. Shunmugam and D. N. Sathyanarayana, *J. Coord. Chem.*, *12*, 151 (1983).

15 M. E. O'Neill, E. S. Raper and J. A. Daniels, *Inorg. Chim. Acta*, *54*, L25 (1981).

16 A. R. W. Jackson, E. S. Raper and D. J. Gardiner, *Anal. Proc.*, *21*, 9 (1984).

17 'International Tables for X-ray Crystallography, Vol. IV', Birmingham, Kynoch Press, 1974.

18 B. T. M. Willis and A. W. Pryor, 'Thermal Vibrations in Crystallography', Cambridge Univ. Press, 1975.

19 G. M. Sheldrick, 'SHELX', Programs for Crystal Structure Determination, Univ. of Cambridge, 1976.

20 (a) C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, *18*, 541 (1962). (b) B. Singh and K. P. Thakur, *J. Inorg. Nucl. Chem.*, *36*, 1735 (1974).

21 (a) E. S. Raper and P. H. Crackett, *Inorg. Chim. Acta*, *50*, 159 (1981); (b) E. S. Raper and J. L. Brooks, *J. Inorg. Nucl. Chem.*, *39*, 2163 (1977); (c) E. S. Raper and I. S. Rowell, *J. Inorg. Nucl. Chem.*, *43*, 3137 (1981).

22 E. R. Atkinson, D. J. Gardiner, A. R. W. Jackson and E. S. Raper, *Inorg. Chim. Acta*, *98*, 35 (1985).

23 (a) E. S. Raper and I. W. Nowell, *Acta Crystallogr., Sect. B:*, *35*, 1600 (1979); (b) I. W. Nowell, A. G. Cox and E. S. Raper, *Acta Crystallogr., Sect. B:*, *35*, 3047 (1979).

24 E. S. Raper, J. R. Creighton, R. E. Oughtred and I. W. Nowell, *Acta Crystallogr., Sect. B: 39*, 355 (1983).

25 L. Pauling 'The Nature of the Chemical Bond, 3rd edn., Ithaca, Cornell Univ. Press, 1960.

26 D. M. L. Goodgame, G. A. Leach, A. C. Skapski and K. A. Woode, *Inorg. Chim. Acta*, *31*, L375 (1978).

27 R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, *98*, 7240 (1976).

28 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, *17*, 2187 (1978).

29 T. Yoshida, *Bull. Chem. Soc. Jpn.*, *53*, 1449 (1980).

30 T. Yoshida, K. Yamasaki and S. Sawada, *Bull. Chem. Soc. Jpn.*, *52*, 2908 (1979).

31 G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 869 (1973).

32 M. R. Caira and L. R. Nassimbeni, *Acta Crystallogr.*, *1331*, 1339 (1975).

33 A. L. Shoemaker, P. Singh and D. J. Hodgson, *Acta Crystallogr.*, *1332*, 979 (1976).

34 J. M. Bret, P. Castan, G. Jugie, A. Dubourg and R. Roques, *J. Chem. Soc., Dalton Trans.*, 301 (1983).

35 W. A. Spofford and E. L. Amma, *Acta Crystallogr., Sect. B:*, *26*, 1474 (1970).

36 L. F. Taylor, M. S. Weininger and E. L. Amma, *Inorg. Chem.*, *13*, 2835 (1974).