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Tris-(1-methylimidazoline-2(3H)-thione)copper(I) Nitrate: Preparation, Thermal Analysis and Crystal Structure

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Abstract

The preparation of a complex of 1-methylimidazoline-2(3H)-thione (*mimtH*) with copper(II) nitrate is described. A combination of elemental and thermal analysis has shown the formula to be, Cu(*mimtH*)$_3$(NO$_3$).

Magnetic measurements, infrared spectroscopy and a single crystal X-ray study have established the presence of copper(I) in distorted trigonal planar, Cu(*mimtH*)$_3^+$, cations. Averaged dimensions within the coordination sphere are: 2.249(Å) (Cu–S), 119.6° (S–Cu–S) and 107.3° (Cu–S–C).

The nitrate ions form hydrogen bonds (NH····O) with the imido groups of the ligands.

Introduction

Reactions between copper(II) salts and heterocyclic thione molecules frequently produce complexes which have unpredictable stoichiometry and stereochemistry; the metal oxidation state may also be variable.

With copper(II) nitrate, imidazolidine-2-thione, LH, produces, Cu(LH)$_4$(NO$_3$), which contains tetrahedrally coordinated copper(I) and sulphur donating ligands [1], as well as, Cu$_4$(LH)$_9$(NO$_3$)$_4$ which contains a combination of terminal and bridging sulphur donating ligands [2]. The complex, Cu(LH)$_3$(NO$_3$) (LH = pyridine-2-thione, contains a trigonal, CuS$_3$, donor set [3].

Imidazole-thione molecules react with +I and +II copper but the resultant complexes invariably contain the +I metal. A notable exception occurs in, [Cu$_{12}$L$_{12}$(MeCN)$_4$]$^{2+}$ (L$^-$ = 1-methylimidazoline-2-thiolate anion, *mimt*$^-$), which contains both Cu(I) and Cu(II) [4]. Crystallographic studies have also shown that the neutral molecule, *mimtH*, behaves as both a terminal and sulphur bridging ligand towards copper(I) in Cu$_2$(*mimtH*)$_4$Cl$_2$ [5] and Cu$_2$(*mimtH*)$_5$SO$_4$·3H$_2$O [6]. In view of this interesting donor behaviour the complex, Cu(*mimtH*)$_3$(NO$_3$), has been prepared. The diamagnetic character of this complex and the absence of any recognisable *d–d* spectra strongly suggest the +I state for the metal; we now report the further characterisation of Cu(*mimtH*)$_3$(NO$_3$).

Experimental

Starting Materials

The ligand (*mimtH*) was used as received from the Aldrich Chemical Co. Ltd; the remaining reagent chemicals were obtained from B.D.H. Ltd. and Alpha Chemicals.

Preparation and Analysis of Cu(mimtH)$_3$(NO$_3$)

A solution of the metal Cu(NO$_3$)$_2$·3H$_2$O, 0.3035 g, 1 mmol in 10 cm^3 of acetonitrile was added dropwise to a refluxing solution of the ligand (*mimtH*, 0.5700 g, 5 mmol in 10 cm^3 of acetone). After one hour of refluxing the initially light green reaction mixture became yellow, this was then cooled to room temperature. Slow evaporation of the solvent at room temperature produced large colourless crystals. These were removed by filtration and vacuum dried over silica gel. Chemical analysis for Cu(C$_4$H$_6$N$_2$S)$_3$(NO$_3$) gave: Calcd. (%): C, 30.8; H, 3.9; N, 21.0. Found (%): C, 31.3; H, 4.0; N, 20.9. The analysis was performed by Elemental Microanalysis Ltd., Beaworthy, Devon.

Physical Methods

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

Thermal analysis measurements (TG and DTG) were obtained from a Stanton-Redcroft TG750 instrument using column dried flowing air or argon and platinum crucibles. Differential thermal analysis measurements were obtained from a Stanton-Redcroft DTA673/4 instrument in flowing nitrogen

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with quartz crucibles. Sample masses were in the region of 5 mg and heating rates were either 10 or 20 °C min^{-1}. Details of the quantitative DTA method for the determination of reaction enthalpies have been published previously [7].

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

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

Crystal Structure Analysis

Relevant crystallographic data are listed in Table I. Unit cell dimensions, obtained initially from Weissenberg and precession photographs, were refined from the centred settings of 25 reflections. Three reflections were used as internal standards for monitoring electronic and crystal stability. The intensity data were corrected for Lorentz, polarisation and absorption effects.

TABLE I. Crystallographic Data.

Compound	$CuC_{12}H_{18}N_7O_3S_3$
Mr	468.10
a, Å	7.5684(6)
b, Å	26.9432(32)
c, Å	10.1795(9)
β, deg.	108.730(7)
U, Å^3	1965.65
Z	4
space group	$P2_1/n$
Dc, g cm^{-3}	1.58
F(000)	952.9
μ, cm^{-1}	13.81
diffractometer	Enraf-Nonius CAD-4
radiation, Å	Mo(Kα) graphite monochromated, 0.71069
2θ, deg.	3.0–54.0
total data	4284
$Fo^2 > 2\sigma(Fo^2)$	2441
R	0.0495
Rw	0.0535
w	$2.7548/[(\sigma^2)Fo + 0.000503Fo^2]$

The coordinates of the non-hydrogen atoms were obtained by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares methods with anisotropic temperature factors. Positional parameters for the imido (NH) and olefinic hydrogen atoms were also obtained from difference Fourier syntheses whereas the methylhydrogen atom positions were fixed by the program (C–H = 1.08 Å). Common isotropic temperature factors were applied to the imido, olefinic and methyl hydrogen atoms and refined to final values (U, Å^2) of 0.098(24), 0.188(30) and 0.203(27) respectively. Scattering factors for all atoms were calculated from an analytical approximation [8]. Final atomic coordinates and B_{eq} values [9] are in Table II.

TABLE II. Final Fractional Atomic Coordinates (× 10^4) with e.s.d's. in Parentheses for Non-Hydrogen Atoms and B_{eq} [9].

	x	y	z	B_{eq}(Å^2)
(a) Non-Hydrogen Atoms				
Cu	10201(1)	3866(0)	3833(1)	3.86(2)
S(21)	8658(2)	3154(1)	3867(1)	4.17(2)
C(21)	8941(7)	2778(2)	2628(5)	3.6(2)
N(11)	7866(6)	2386(2)	2065(4)	3.8(2)
C(11)	6295(8)	2215(2)	2460(5)	4.8(2)
N(31)	10266(7)	2793(2)	2008(5)	4.4(2)
C(41)	10020(9)	2409(2)	1059(6)	4.9(2)
C(51)	8529(9)	2162(2)	1093(6)	4.7(2)
S(22)	11815(2)	4170(1)	5945(1)	4.42(2)
C(22)	13954(8)	4334(2)	5914(5)	3.6(2)
N(12)	15149(6)	4636(2)	6836(5)	4.3(2)
C(12)	14781(11)	4860(3)	8036(6)	6.4(2)
N(32)	14805(6)	4194(2)	5004(4)	4.2(2)
C(42)	16535(9)	4411(3)	5348(7)	5.6(2)
C(52)	16762(8)	4677(2)	6443(7)	5.6(2)
S(23)	9796(2)	4349(1)	1975(1)	4.77(2)
C(23)	8636(7)	3995(2)	569(5)	3.7(2)
N(13)	9099(6)	3929(2)	–571(4)	3.03(2)
C(13)	10692(9)	4143(3)	–828(7)	8.6(2)
N(33)	7091(6)	3735(2)	409(4)	4.4(2)
C(43)	6565(9)	3499(2)	–863(6)	5.6(2)
C(53)	7829(10)	3623(2)	–1459(6)	5.7(2)
N(10)	13935(6)	3513(2)	2067(5)	4.1(2)
O(10)	14865(5)	3899(1)	2144(4)	5.0(2)
O(20)	13385(5)	3406(1)	3080(4)	4.8(2)
O(30)	13576(6)	3244(2)	1084(4)	5.6(2)
(b) Hydrogen Atoms				
H(31)	11302	2954	2409	
H(32)	14313	3967	4003	
H(33)	6616	3774	1155	

All calculations were performed on the NUMAC, IBM370/168 computer at the University of Newcastle upon Tyne. SHELX [10] and related programs were used in the solution. Structurally insignificant H-atom coordinates, anisotropic temperature factors, observed and calculated structure factors and selected torsion angles have been deposited with the Editor.

Results and Discussion

Thermal analysis, in flowing air, (Fig. 1(a)), with identification of the end products by X-ray powder diffraction, shows the complex is anhydrous and decomposes over the temperature range 140–750 °C, to copper(II) oxide. The agreement between experimental (84.2%) and theoretical mass loss (83.0%) for

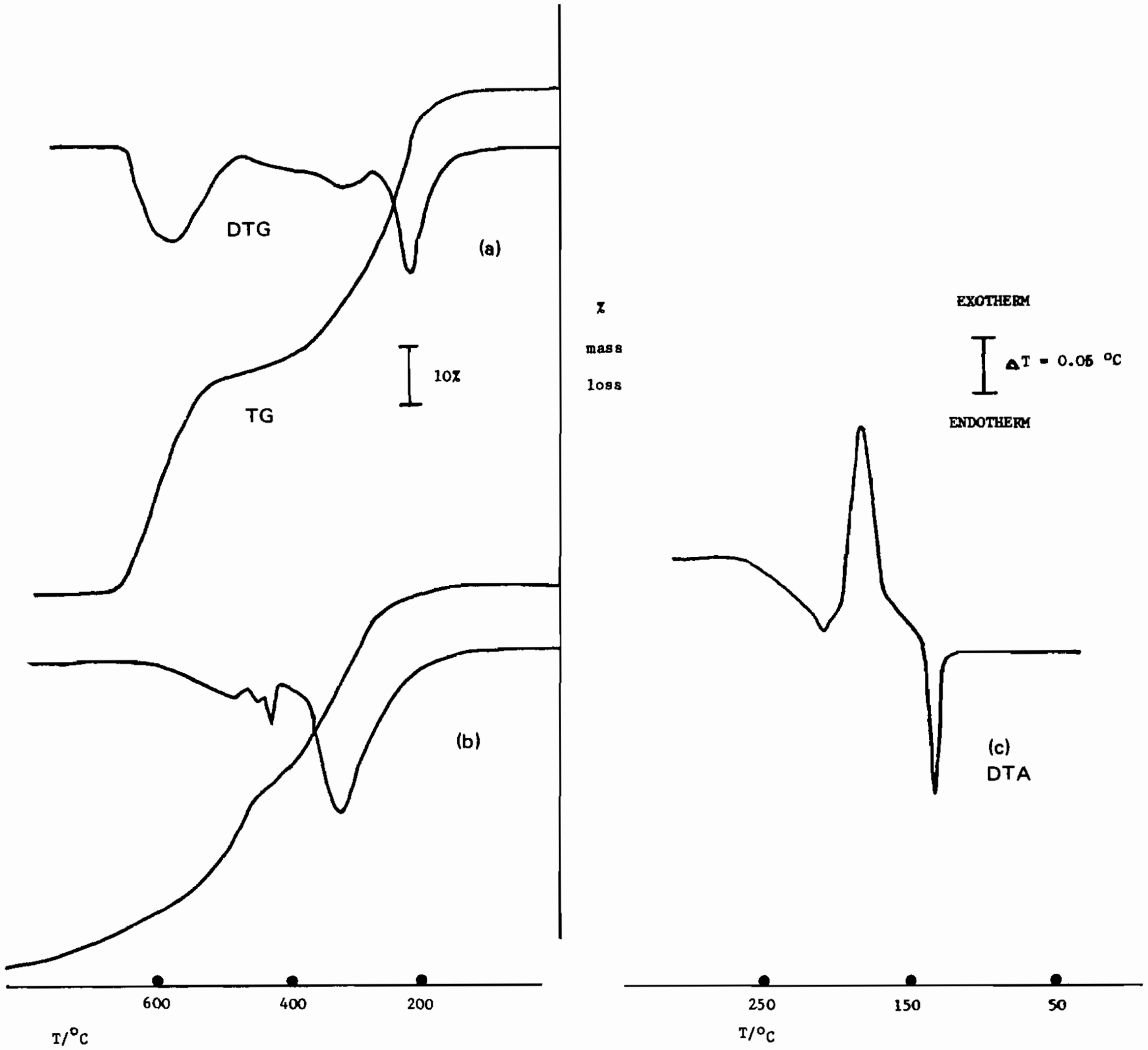

Fig. 1. Thermal analysis curves of Cu(*mimtH*)$_3$NO$_3$: (a) TG and DTG in air; (b) TG and DTG in argon; (c) DTA in nitrogen.

the above process is within experimental error (±2.0%) and confirms the formula of the complex. The TG and DTG curves show the thermal decomposition, in air, to be a two-stage process, (Fig. 1(a)). The first stage (140–465 °C) involves a 48.0% mass loss which is consistent with the evolution of two *mimtH* molecules (theor. mass loss 48.3%) and the final stage (465–600 °C) involves loss of the remaining *mimtH* molecule together with degradation of the nitrate ion. In argon, the TG and DTG curves, (Fig. 1(b)), are essentially featureless, with the exception of a slight discontinuity at 450 °C. The amorphous nature of the end products obtained from thermal decompositions in argon renders the interpretation of overall mass losses in terms of specific decomposition schemes somewhat uncertain. Although the overall mass loss in this instance, (73.0%, 200–700 °C), appears to coincide with ligand removal, (theor. mass loss 72.5%), there is evidence, from the DTA curve, that nitrate decomposition also occurs within this temperature range.

The DTA curve in nitrogen, (Fig. 1(c)), consists of a sharp melting endotherm (Tp 135 °C; ΔH_m 65.5 ± 3.0 kJ mol^{-1}) followed by a substantial exotherm (Tp 260 °C; ΔH_D 290 ± 20 kJ mol^{-1}). The presence of a decomposition exotherm in the DTA trace of the complex is in marked contrast to the behaviour of *mimtH* and Cu(NO$_3$)$_2$·3H$_2$O, both of which show endothermic decomposition, together with melting and in the case of the metal salt, dehydration endotherms. We propose that the exothermic degradation of Cu(*mimtH*)$_3$(NO$_3$) in nitrogen arises from the oxidative degradation of the ligands by the nitrate ion.

Ionic nitrate is indicated by the presence of an intense band at 1355 cm^{-1} (ν_1) as well as a band of medium intensity at 830 cm^{-1} (ν_2) in the solid state infrared spectrum of the complex [11, 12].

Changes to the ligand spectrum upon coordination are slight and are limited to the thioamide IV band which is converted from its clearly resolved components (770, 740 cm^{-1}) in the uncoordinated molecule [13] to a peak (740 cm^{-1}) and shoulder (765 cm^{-1}) in the complex. Slight changes (±10 cm^{-1}) also occur in the δ(C–S) (670 cm^{-1}) and π(C–S) (530 cm^{-1}) bands. The general indication is one of perturbation in the thione region (800–500 cm^{-1}) of the spectrum which usually signifies sulphur donation by the ligand [14]. No associated ν(M–S) activity was observed in this complex however.

The nitrate oxygen atoms and the ligand imido (NH) groups form an extensive network of NH····O hydrogen bonds [Table III(d)]. Each imido hydrogen atom is asymmetrically bifurcated to a pair of oxygen atoms either from the same nitrate group [H(32) and O(10), O(20)] or a pair of symmetry-related nitrate groups. Consequently, chains of hydrogen bonds are generated along *a*. The O····H distances involving the O(10) and O(20) atoms are relatively short and strong whereas those involving O(30) are longer and weaker (Fig. 2).

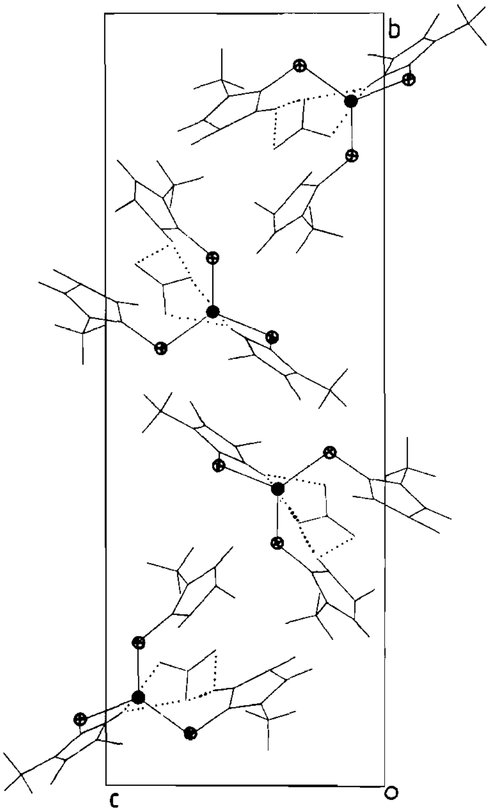

Fig. 2. Unit cell contents viewed down *a** with partial hydrogen bonding, ● = Cu, ⊕ = S.

The nitrate groups are effectively planar with normal dimensions [15, 16].

A perspective diagram of the Cu(*mimtH*)$_3^+$ cation is shown in Fig. 3, with atomic numbering.

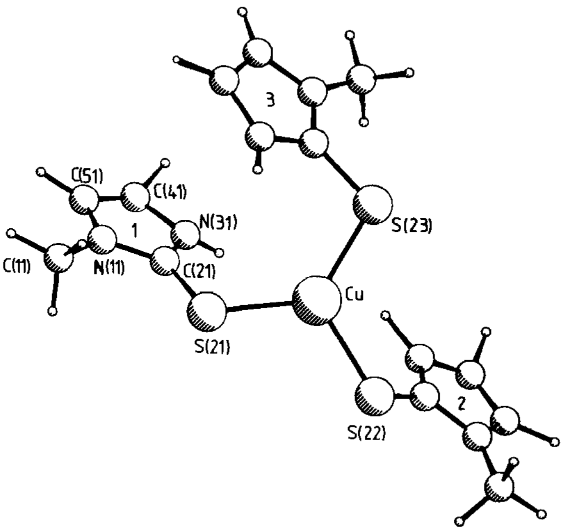

Fig. 3. Perspective diagram of the Cu(*mimtH*)$_3^+$ cation with atomic numbering.

The copper(I) atom is clearly coordinated by three thione sulphur atoms from three *mimtH* molecules in a distorted trigonal configuration. Similar structures, also with copper(I), have been reported with thiourea [17], tetramethyl thiourea [18], ethylenethiourea [18], thiophenolate [19] and pyridine-2-thione [3]. The extent of the distortion is apparent from the range of S–Cu–S angles (Table III), all of which deviate from the ideal value, as well as by the displacement of the metal from the CuS$_3$ coordination plane (Table IV). The overall distortion is the net result of the steric and bonding requirements of the *mimtH* molecules.

A further consequence of these requirements is that the ligands 'twist' about their respective Cu–S(2A)–C(2A) planes; they also 'tilt' about the Cu–S$_3$ coordination plane, as well as towards one another; the relevant dihedral angles are in Table IV.

The three Cu–S distances (Table III) are within the range of values (2.213–2.280 Å) reported for trigonally coordinated copper(I) with heterocyclic thione–sulphur donors [18, 19]. Two of the three Cu–S distances, [S(21) & S(22): 2.253 & 2.258 Å], are similar to one another and are significantly longer than the third, [2.235 Å, S(23)]; this distinction is also maintained after librational correction of the data.

Two of the ligand, C(2A)–S(2A), distances, [S(21) & S(22): 1.683 & 1.688 Å], are essentially the same as the corresponding value (1.685 Å) in the uncoordinated molecule [20]. The C(23)–S(23)

TABLE III. Bond Distances (Å) and Angles (°) with e.s.d's. in Parentheses. Symmetry code, superscript; none, *x*, *y*, *z*; ('), −1 + *x*, *y*, *z*.

(a) The coordination sphere

Bond	(Å)	Angle	(°)
Cu–S(21)	2.253(2)	S(22)–Cu–S(21)	114.7(1)
Cu–S(22)	2.258(2)	S(23)–Cu–S(21)	125.4(1)
Cu–S(23)	2.235(2)	S(23)–Cu–S(22)	118.7(1)
S(21)····S(22)	3.799	Cu–S(21)–C(21)	108.0(2)
S(21)····S(23)	3.987	Cu–S(22)–C(22)	107.8(2)
S(22)····S(23)	3.865	Cu–S(23)–C(23)	106.1(2)

(b) The nitrate ions

Bond	(Å)	Angle	(°)
N(10)–O(10)	1.244(6)	O(20)–N(10)–O(10)	117.8(4)
N(10)–O(20)	1.263(7)	O(30)–N(10)–O(10)	121.3(5)
N(10)–O(30)	1.217(6)	O(30)–N(10)–O(20)	120.9(5)

(c) The heterocyclic molecules

(A = 1, 2 or 3)	Molecule 1	Molecule 2	Molecule 3
Bond lengths (Å)			
S2(A)–C2(A)	1.683(5)	1.688(6)	1.709(5)
C2(A)–N1(A)	1.345(6)	1.348(6)	1.328(8)
N1(A)–C1(A)	1.447(8)	1.467(9)	1.435(9)
C2(A)–N3(A)	1.346(8)	1.341(8)	1.328(7)
N3(A)–C4(A)	1.386(7)	1.372(8)	1.381(7)
C4(A)–C5(A)	1.321(10)	1.290(10)	1.331(11)
C5(A)–N1(A)	1.383(8)	1.405(9)	1.364(7)
Bond angles (°)			
S2(A)–C2(A)–N1(A)	125.9(5)	125.4(5)	126.7(4)
S2(A)–C2(A)–N3(A)	128.8(4)	128.0(4)	126.4(4)
N1(A)–C2(A)–N3(A)	105.3(4)	106.6(5)	106.9(4)
C2(A)–N1(A)–C1(A)	124.8(5)	124.3(5)	125.3(5)
C1(A)–N1(A)–C5(A)	125.4(4)	128.2(5)	125.2(5)
C2(A)–N1(A)–C5(A)	109.8(5)	107.5(5)	109.5(5)
C2(A)–N3(A)–H3(A)	119.2(5)	132.4(5)	112.9(4)
H3(A)–N3(A)–C4(A)	126.5(6)	117.8(5)	137.3(5)
C2(A)–N3(A)–C4(A)	110.6(6)	109.6(5)	109.7(5)
N3(A)–C4(A)–C5(A)	106.4(6)	108.0(7)	106.1(5)
C4(A)–C5(A)–N1(A)	107.9(5)	108.3(5)	107.9(5)

(d) Hydrogen bonding

Bond	Lengths			Angle
A····H–D	A····D	A····H	H–D	A···H–D
O(10)····H(32)–N(32)	3.032	2.072	1.144	139.2
O(10')····H(33)–N(33)	2.841	1.934	0.945	160.1
O(20)····H(31)–N(31)	2.800	1.936	0.874	169.6
O(20)····H(32)–N(32)	2.854	1.798	1.144	151.2
O(30')····H(33)–N(33)	3.222	2.682	0.945	116.9
O(30)····H(31)–N(31)	3.203	2.646	0.874	122.6

TABLE IV. Equations of Mean Planes Referred to Orthogonal Axes with Distances (Å) of Relevant Atoms from the Planes in Square Brackets.

Plane A	Cu, S(21), S(22), S(23) −6.6420X + 12.5702Y + 3.9308Z + 0.3000 = 0.0 [Cu, −0.108; S21, 0.036; S22, 0.034; S23, 0.038]
Plane B	Cu, S(21), C(21) 4.8689X − 10.3577Y + 4.2795Z − 2.6018 = 0.0
Plane C	Cu, S(22), C(22) −1.9430X + 24.7301Y − 2.0786Z − 6.7835 = 0.0
Plane D	Cu, S(23), C(23) 7.1783X − 8.3502Y − 3.7379Z − 2.6609 = 0.0
Plane E	Ligand 1 2.9283X − 15.8726Y + 5.5736Z + 0.3171 = 0.0 [S21, 0.001; C21, −0.008; N11, −0.016; C11, 0.013; N31, 0.010: C41, 0.003; C51, −0.002; Cu, −0.697]
Plane F	Ligand 2 1.7324X − 21.3945 + 4.6798Z + 4.0890 = 0.0 [S22, −0.006; C22, −0.005; N12, −0.005; C12, 0.005; N32, 0.022; C42, −0.018; C52, 0.006; Cu, −0.623]
Plane G	Ligand 3 3.3716X − 21.3031Y + 2.5923Z + 5.4563 = 0.0 [S23, 0.003; C23, 0.016; N13, 0.002; C13, −0.010; N33, −0.020; C43, 0.004; C53, 0.006; Cu, 1.6521]

Dihedral Angles

Planes	Angle (°)
A/E	57.6
A/F	59.4
A/G	44.5
B/E	19.1
C/F	16.7
D/G	50.2
E/F	17.1
E/G	20.6
F/G	14.9

distance however, (1.709 Å), is significantly longer than the value reported for *mimtH* and corresponds to 43.0% π-character [21] in the C–S bond compared with 52.0% in the uncoordinated ligand [20]. No other significant changes occur to the bond lengths and angles within the *mimtH* molecules upon coordination.

The Cu–S(2A)–C(2A) angles (106.1–108.0°) are typical of coordinated *mimtH* molecules [20] in being close to the tetrahedral value.

In common with many trigonal $Cu-S_3$ systems the Cu–S distances in $Cu(mimtH)_3^+$ are all significantly less than the sum of their tetrahedral covalent radii (2.36 Å) [22]. The major bonding mode however probably involves electron donation from sp^2 hybrid orbitals on the sulphur atoms to vacant sp^2 hybrid orbitals on the metal. There is an indication from the data that one of the *mimtH* molecules (ligand 3) may be bonded somewhat differently than the other two. It is possible, that the combination of relatively short Cu–S(23) and long C(23)–S(23) distances, coupled with the greatest 'twisting' (50.2°) and smallest 'tilting' (44.5°) of the molecule about the coordination plane, are part of a process which seeks to optimise a π-interaction between the metal and the ligand.

Of the various possibilities available a metal–ligand, d_π–d_π interaction, appears to be the most likely in view of the involvement of the thione sulphur p_z orbital in the p_π–p_π component of the carbon–sulphur bond of the ligands [20]. Conventional ligand field splitting for a complex of idealised D_{3h} symmetry shows two sets of doubly degenerate orbitals: $d_{x^2-y^2}$, d_{xy} and d_{xz}, d_{yz} [23]. Suitable overlap may occur between either of the latter pair of orbitals and a corresponding *d*-orbital on the sulphur.

A likely consequence of metal–sulphur d_π–d_π bonding is a lengthening of the exocyclic carbon–sulphur bond and a redistribution of π-electron density from the carbon–sulphur bond to the carbon–nitrogen bonds of the ligand. Support for such a redistribution comes from an X-ray p.e.s. study of *mimtH* and the complex, $Cu_2(mimtH)_4Br_2$, which reveals a negative shift in the N(1s) electron core binding energies from 404.5 eV (*mimtH*) to 400.5 eV; the $S(2p_{3/2})$ values show a corresponding positive shift from 162.9 eV (*mimtH*) to 164.9 eV [5].

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