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Polymeric Cyano(1-methylimidazoline-2-thione)copper(I), [Cu(mimtH)CN]$_n$: Preparation, Spectroscopy, Thermal Analysis and Crystal Structure

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Abstract

The addition of 1-methylimidazoline-2-thione (mimtH) to a solution of CuCN in aqueous (0.1 M) KCN produced a colourless crystalline solid of empirical composition Cu(mimtH)CN. The compound crystallises in a monoclinic unit cell, $a = 7.6042(4)$, $b = 7.2155(4)$, $c = 13.6004(4)$ Å, $\beta = 98.233(6)°$, space group *Pc* and $Z = 2$. The cyano groups bridge pairs of copper(I) atoms in a virtually linear manner, (Cu–C–N(mean), 175.0°; Cu–N–C(mean), 175.3°; Cu...Cu, 5.027 Å). Pairs of mimtH ligands asymmetrically bridge pairs of copper(I) atoms with the production of essentially planar Cu_2S_2 cores, (Cu–S(mean), 2.355 and 2.561 Å; Cu–S–Cu(mean), 79.4°; Cu...Cu, 3.145 Å; S...S, 3.729 Å). Each copper atom is tetrahedrally coordinated by a S_2CN donor set with angles at the metal ranging from 98.4(1) to 120.2(1)°. The effective structural unit consists of six copper(I) atoms, four cyano and four mimtH ligands, extended into a two-dimensional polymeric array. The copper atoms and the cyano groups form the essentially planar component of the polymer, which extends along the *b* and *c* axes of the unit cell, with the *a* axis representing the separation distance between adjacent planar layers. The μ_2-S bridging ligands occupy space on both sides of the planar section of the polymer. Final conventional $R = 0.0275$ for 2493 observed data ($F > 4\ \sigma(F)$). The compound is diamagnetic and appears to be indefinitely stable to aerial oxidation at room temperature. An absorption band at 190 cm^{-1} in the Raman spectrum is tentatively assigned to a bridging stretching frequency, ν(Cu–S–Cu). The compound thermally decomposes to Cu(II)O, in air, in the temperature range 145 to 800 °C and involves desulphurisation of mimtH ligands, cyanogen evolution, production of Cu(II)S and conversion of the latter to Cu(II)O.

Introduction

Stoichiometric–structural relationships among copper(I) complexes, particularly with S-donor ligands, continue to create interest. Trigonal and tetrahedral environments, with monodentate S-donor ligands, have been established for some mononuclear complexes [1–3]. Such environments form the basis of the structural chemistry of copper(I) complexes with heterocyclic thione donors [4]. Complicating features, such as the involvement of halide ions in terminal [5] or a combination of terminal and bridging environments [6], together with doubly-bridging, μ_2-S, ligands [3] and increasing nuclearity [7, 8], all tend to obscure the relationship between the stoichiometry and the structural disposition of the metal atoms and ligands in the complex. In particular, increasing nuclearity lowers the ligand-to-metal ratio, so that with dinuclear and polynuclear complexes such empirical ratios become impossible to correlate with specific structural forms. Our studies of copper(I) complexes with mimtH have produced a dinuclear complex with trigonal coordination of the metal and a symmetric μ_2-S bridging ligand $[Cu_2(mimtH)_5]^{2+}$ [9], as well as dinuclear complexes with tetrahedral coordination of the metal, together with terminal and asymmetric μ_2-S bridging ligands, $Cu_2(mimtH)_4Cl_2$ [5], $[Cu_2(mimtH)_6]^{2+}$ [10]. A tetranuclear complex of benzimidazoline-2-thione ($bzimtH_2$), $[Cu_4(bzimtH_2)_{10}]^{4+}$, with four terminal and six asymmetric μ_2-S bridging ligands together with a centrosymmetric tetranuclear rhombus of four copper atoms, each of which has an S_4 donor set, has also been reported [11].

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We have extended this range of copper(I) complexes by reacting mimtH with Cu(I)CN in KCN solution. The resulting colourless, diamagnetic complex, of empirical composition [Cu(mimtH)CN], appears to be indefinitely stable against aerial oxidation and is insoluble in all common organic solvents.

Experimental

Starting Materials

Copper(I) cyanide and the ligand, mimtH, as 2-mercapto-1-methylimidazole, were supplied by the Aldrich Chemical Company and used as supplied.

Preparation and Analysis of [Cu(mimtH)(CN]$_n$, (I)

Copper(I) cyanide (0.8950 g, 10 mmol) was dissolved in 250 ml of 0.1 M KCN. The ligand, mimtH (0.9100 g, 8 mmol) was added to 50 ml of the CuCN/KCN solution and gently refluxed for several hours. After reducing the volume of the reaction mixture to about 20 ml the reaction solution was set aside. A colourless crystalline product, including diffraction quality crystals, was obtained from the colourless residual solution after several weeks. The product was recovered by filtration and dried under vacuum. Yield, 40%.

Anal. Calc. for $CuC_5H_6N_3S$: C, 29.41; H, 2.94; N, 20.58; Cu, 31.22. Found: C, 29.73; H, 2.99; N, 21.08; Cu, 31.20%.

Physical Methods

Perkin-Elmer infrared grating spectrophotometer, 4000–200 cm^{-1}, CsI discs. Stanton-Redcroft TG750 thermal analyser, (TG, DTG), with ceramic furnace, column-dried flowing air, Pt crucibles. Stanton-Redcroft DTA 673/4, flowing N_2, quartz crucibles. Sample masses 5–8 mg, heating rates 10 to 50 °C min^{-1} (TG, DTG); 20 °C min^{-1} (DTA). Quantitative DTA method in ref. 12. Stanton Redcroft hot stage microscope, HSM-5, Hitachi DK81 video camera, JVC TM/90 PSN colour monitor. Room temperature, Newport Instruments, Gouy Balance. Guinier-Hagg parafocussing X-ray powder camera, Cu Kα_1 monochromatised radiation (λ = 1.5405 Å), Kodirex single-coated film, Siemens microdensitometer. Spex 1403, 0.85 m, double monochromator Raman spectrometer with a multi alkali Hamamatsu R928 photomultiplier tube. Spec datamate control and data acquisition system and a Spectra Physics 164-07 argon laser operating at 514.5 mm.

Crystal Structure Determination

TABLE 1. Crystallographic Data

Formula	$CuC_5H_6N_3S$
M_r	203.67
a (Å)	7.6042(4)
b (Å)	7.2155(4)
c (Å)	13.6004(7)
β (°)	98.233(6)
V (Å^3)	738.54
Reflection conditions	hkl: none $h0l$: $l = 2n$
Space group	Pc
Crystal size (mm)	0.23 × 0.27 × 0.38
Radiation, λ (Å)	Mo Kα; 0.71073
No. reflections for cell parameters	32 (20–25° 2θ)
D_x (g cm^{-3})	1.832
Z	4
F(000)	408
μ (mm^{-1})	3.16
2θ_{max} (°)	50
h ranges	−9 to 9
k ranges	0 to 8
l ranges	−16 to 16
Scan width	1.19° + α-doublet separation
Scan time (s)	14–56
T (K)	298
Standard reflections	3, no variation
Absorption correction	semi empirical
Transmission factors	0.200–0.303
Total data, all unique	2599
Observed data ($F > 4\sigma(F)$)	2493

Crystal data together with data collection and data processing details are summarised in Table 1. A Siemens AED2 diffractometer was used for the unit cell data and also for the data collection. The coordinates of the non-H atoms were obtained by a combination of Patterson and difference Fourier methods and refined by blocked-cascade least-squares methods with anisotropic thermal parameters. Positional parameters for the imido(NH) H atoms were also obtained from difference Fourier methods and refined freely, but the olefinic and methyl H atom coordinates were constrained by the program with the latter treated as a rigid group (C–H = 0.96 Å; H–C–H = 109.5°; U(H) = 1.2 U_{eq}(C)).

Final conventional $R = 0.0275$, $R_w[=(\Sigma w^{1/2}|\Delta|)/(\Sigma w^{1/2}|F_o|)] = 0.0301$ with $w = [\sigma^2(F) + 0.00049F^2]^{-1}$. Neutral atom scattering factors were taken from ref. 13, including corrections for anomalous dispersion, from which the correct polar axis direction was assigned.

Final refined coordinates are given in Table 2, bond lengths and angles in Table 3. See also 'Supplementary Material'.

SHELXTL [14] and related programs were used in the analysis.

Results and Discussion

The presence of the cyano group ν(CN) in the vibrational spectrum of the complex is indicated by a strong, sharp and resonably narrow ($\Delta\nu_{1/2}$ *ca.*

TABLE 2. Final Fractional Atomic Coordinates ($\times 10^4$) for Refined Atoms[a]

Atom	x	y	z
Cu(1)	5000	3613.8(6)	5000
Cu(2)	5465.9(9)	7147.8(7)	3708.3(4)
C(1)	5205(6)	1262(5)	4398(3)
N(1)	5342(5)	9748(5)	4146(3)
C(2)	5283(5)	6687(5)	2312(3)
N(2)	5188(5)	3540(5)	6488(2)
S(21)	7724(1)	5574(1)	4765(1)
C(21)	7944(5)	6632(6)	5901(3)
N(11)	8807(4)	5931(5)	6765(3)
C(11)	9674(8)	4155(7)	6843(5)
N(31)	7260(4)	8264(5)	6130(2)
H(31)	6843(54)	8976(58)	5718(34)
C(41)	7624(6)	8570(7)	7150(3)
C(51)	8579(6)	7116(7)	7534(3)
S(22)	2771(1)	5688(1)	4334(1)
C(22)	2514(4)	7223(6)	5259(3)
N(12)	1650(5)	8844(5)	5179(3)
C(12)	703(7)	9591(8)	4255(5)
N(32)	3203(5)	7087(5)	6226(3)
H(32)	3706(57)	6375(68)	6404(37)
C(42)	2786(7)	8612(8)	6734(4)
C(52)	1829(7)	9697(7)	6090(5)

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

10 cm^{-1}) band at 2100 cm^{-1} (IR) and also at 2100 cm^{-1} (R). These values represent a downward shift in ν(CN) relative to solid CuCN (2172 cm^{-1}, IR) [15] and a slight upward shift, relative to free cyanide ion (2080 cm, IR) in aqueous solution [16]. In aqueous solution linear [Cu(CN)$_2$]$^-$ has a ν(CN) band at 2125 cm^{-1} which is significantly greater than the values reported for [Cu(CN)$_3$]$^{2-}$ (2094 cm^{-1}) and [Cu(CN)$_4$]$^{3-}$ (2076 cm^{-1}), also in aqueous solution [16]. In view of the essentially linear character of the Cu–CN–Cu bond in I, the position of ν(CN) seems to be in reasonable agreement with that of the linear [Cu(CN)$_2$]$^-$ ion and would seem to indicate greater σ (donor) than π (acceptor) behaviour for the cyano group in such linear environments. The IR spectrum of solid mimtH consists of a strong, broad peak at 3120 cm^{-1} with superimposed bands at 3020 and 2900 cm^{-1} which are caused by ν(NH) and ν(CH). The character of this activity is due to extensive H-bonding in solid mimtH [17]. In I the IR spectrum consists of sharp, strong, reasonably well separated peaks at 3300 cm^{-1} ν(NH), as well as 3240 and 3115 cm^{-1} ν(CH). Similarly, the Raman spectrum is converted from a broad region (3000–3400 cm^{-1}) of ill-defined activity in solid mimtH to reasonably well resolved peaks (3160, 3120 and 2930 cm^{-1}) in I. These observations suggest the

TABLE 3. Bond Lengths (Å) and Angles (°)[a]

Bond lengths (Å)			
Cu(1)–C(1)	1.900(4)	Cu(1)–N(2)	2.010(3)
Cu(1)–S(21)	2.565(1)	Cu(1)–S(22)	2.344(1)
Cu(2)–N(1)	1.975(4)	Cu(2)–C(2)	1.914(4)
Cu(2)–S(21)	2.366(1)	Cu(2)–S(22)	2.556(1)
C(1)–N(1b)	1.155(5)	N(1)–C(1a)	1.155(5)
C(2)–N(2d)	1.125(5)	N(2)–C(2c)	1.124(5)
S(21)–C(21)	1.710(4)	C(21)–N(11)	1.359(5)
C(21)–N(31)	1.342(5)	N(11)–C(11)	1.438(6)
N(11)–C(51)	1.381(6)	N(31)–H(31)	0.793(43)
N(31)–C(41)	1.394(5)	C(41)–C(51)	1.339(7)
S(22)–C(22)	1.708(4)	C(22)–N(12)	1.338(5)
C(22)–N(32)	1.348(5)	N(12)–C(12)	1.460(7)
N(12)–C(52)	1.372(7)	N(32)–H(32)	0.665(46)
N(32)–C(42)	1.361(7)	C(42)–C(52)	1.315(8)
Bond angles (°)			
C(1)–Cu(1)–N(2)	114.3(2)	C(1)–Cu(1)–S(21)	108.7(1)
N(2)–Cu(1)–S(21)	101.4(1)	C(1)–Cu(1)–S(22)	120.2(1)
N(2)–Cu(1)–S(22)	110.5(1)	S(21)–Cu(1)–S(22)	98.7(1)
N(1)–Cu(2)–C(2)	117.7(2)	N(1)–Cu(2)–S(21)	109.5(1)
C(2)–Cu(2)–S(21)	117.6(1)	N(1)–Cu(2)–S(22)	102.5(1)
C(2)–Cu(2)–S(22)	108.1(1)	S(21)–Cu(2)–S(22)	98.4(1)
Cu(1)–C(1)–N(1b)	171.8(3)	Cu(2)–N(1)–C(1a)	177.5(4)
Cu(2)–C(2)–N(2d)	178.3(4)	Cu(1)–N(2)–C(2c)	173.1(3)
Cu(1)–S(21)–Cu(2)	79.1(1)	Cu(1)–S(21)–C(21)	96.3(1)
Cu(2)–S(21)–C(21)	107.7(1)	S(21)–C(21)–N(11)	126.0(3)
S(21)–C(21)–N(31)	127.6(3)	N(11)–C(21)–N(31)	106.3(3)
C(21)–N(11)–C(11)	123.7(4)	C(21)–N(11)–C(51)	109.1(3)

(continued)

TABLE 3. *(continued)*

C(11)–N(11)–C(51)	126.9(4)	C(21)–N(31)–H(31)	122.3(33)
C(21)–N(31)–C(41)	110.0(3)	H(31)–N(31)–C(41)	127.1(33)
N(31)–C(41)–C(51)	106.5(4)	N(11)–C(51)–C(41)	108.0(4)
Cu(1)–S(22)–Cu(2)	79.7(1)	Cu(1)–S(22)–C(22)	106.4(1)
Cu(2)–S(22)–C(22)	99.2(1)	S(22)–C(22)–N(12)	127.8(3)
S(22)–C(22)–N(32)	127.0(3)	N(12)–C(22)–N(32)	105.1(4)
C(22)–N(12)–C(12)	124.7(4)	C(22)–N(12)–C(52)	109.5(4)
C(12)–N(12)–C(52)	125.8(4)	C(22)–N(32)–H(32)	122.3(44)
C(22)–N(32)–C(42)	110.5(4)	H(32)–N(32)–C(42)	127.1(43)
N(32)–C(42)–C(52)	106.8(5)	N(12)–C(52)–C(42)	108.0(5)

Symmetry operators: (a) $x, 1+y, z$; (b) $x, -1+y, z$; (c) $x, 1-y, z$; (d) $x, -1-y, z$. [a]e.s.d.s given in parentheses.

absence of H-bonding in I. Thioamide band activity is more evident in the IR than in the Raman spectrum of I. The most significant evidence for coordinated mimtH occurs in the 800 to 500 cm^{-1} region of the spectrum. Thioamide IV is clearly resolved from its original components in mimtH (770, 740 cm^{-1}) into a sharp band (745 cm^{-1}) with associated and weaker shoulder (720 cm^{-1}). Modest shifts (10 cm^{-1}) and band-splitting also occur with δ(CS) (670 cm^{-1}) and π(CS) (530 cm^{-1}) in I. The general indication is one of significant perturbation in the thione region, which usually signifies sulphur donation by the ligand [4]. A weak band at 190 cm^{-1} (R) is tentatively assigned to bridging stretching activity originating within the Cu_2S_2 core.

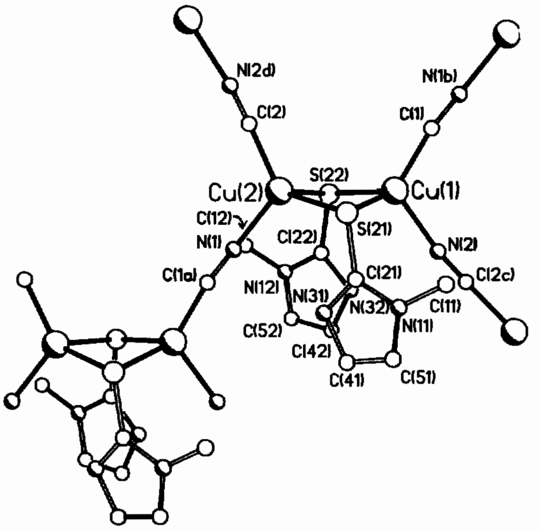

Fig. 1. Perspective view of a section of the structure showing the atom numbering for the asymmetric unit; H atoms omitted.

With four monomers of empirical composition Cu(mimtH)CN in a non-centrosymmetric monoclinic cell the asymmetric unit (Fig. 1) contain pairs of, respectively, copper atoms, mimtH ligands and cyano ligands. Each copper atom is coordinated by two μ_2-S bridging mimtH ligands together with a carbon atom and a nitrogen atom from different cyano groups. Consequently, each copper(I) atom has a S_2CN-donor set and a distorted tetrahedral environment with angles at the metal ranging from 98.4(1)° to 120.2(1)°. Pairs of mimtH ligands asymmetrically bridge pairs of copper atoms with the resultant production of a Cu_2S_2 core. Dimensions within the Cu_2S_2 core are summarised and compared with related systems in Table 4. The major characteristics of the Cu_2S_2 core in I, as well as in other structures, are an alternating sequence of short and long Cu–S distances, narrow angles at the bridging sulphur

TABLE 4. Cu_2S_2 Core Dimensions

	Reference	Cu–S (Å)	Cu–S–Cu (°)	S–Cu–S (°)	S...S (Å)	Cu...Cu (Å)
$[Cu_2(thiourea)_6]^{2+}$	18	2.367(3); 2.429(3)	72.6(1)	107.4(1)	3.865(1)	2.840(3)
$[Cu_2(S\text{-dimethylthiourea})_6]^{2+}$	18	2.325(3); 2.461(3)	72.3(1)	107.7(1)	3.868(1)	2.828(3)
$[Cu(purinium\text{-}6\text{-}thione)Cl_2]_2$	19	2.244(5); 2.741(6)	87.5(2)		3.629(9)	3.456(3)
$[Cu_2(mimtH)_4Cl_2]$	5	2.301(1); 2.572(1)	73.2(1)	105.5(1)	3.916(1)	2.914(1)
$[Cu_2(mimtH)_6]^{2+}$	10	2.358(1); 2.459(1)	77.2(1)	110.1(1)	3.766(1)	3.007(1)
$[Cu_4(benzimidazole\text{-}2\text{-}thione)_{10}]^{4+}$	11	2.355(3); 2.370(4) 2.365(3); 2.494(4)	69.1(1) 66.9(1)	109.2(1) 113.2(9)	3.817(1)	2.681(2)
$[Cu(mimtH)CN]_n$	this work	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)

atoms, somewhat larger angles at the copper atoms, together with a relatively large separation between the bridging sulphur atoms and moderate separation between the copper atoms. The four atoms of the Cu_2S_2 core deviate from coplanarity by approximately +0.16 Å (plane 1; Table 5).

Furthermore, the Cu_2S_2 core in **I** is non-centrosymmetric whereas the remaining cores listed in Table 4 are either inherently centrosymmetric or result from crystallographic centres of symmetry within the unit cell and are hence planar. Each bridging sulphur atom forms a Cu–S distance (Cu–S(mean) 2.355 Å) and Cu–S–C angle (Cu–S–C(mean) 107.0°) which are typical of copper(I) tetrahedrally coordinated by heterocyclic thione donors [10, 11]; conventional coordination is proposed for these contacts. In addition, the sulphur atoms complete their bridging function by forming a somewhat longer distance (Cu–S(mean) 2.561 Å) and smaller angle (Cu–S–C(mean) 97.8°). With the bridging ligands virtually normal to the Cu_2S_2 core, (planes 1, 4, 5; Table 5), as well as the relevant Cu–S–C planes (planes 2, 3; Table 5) and narrow angles at the bridging sulphur atoms (Cu–S–Cu(mean) 79.4°) it is proposed that completion of the bridging function by the sulphur atom involves the thioamide pπ MO of the heterocycle. Geometric considerations preclude the use of both electron pairs by the sulphur atom of mimtH in such bridging environments. Similar bonding schemes for μ_2-S bridging have been proposed for thiourea [18] and mimtH [5, 10]. As a result of coordination the C–S distance in the ligands (mean 1.709 Å) is lengthened relative to the value in the the free mimtH (mean 1.681 Å) [17]. Such a change in the C–S distance is consistent with the coordinating characteristics of the ligands. The function of the cyano groups in **I** is to bridge pairs of copper(I) atoms in a virtually linear array, (Cu–C–N(mean) 175.0°; Cu–N–C(mean) 175.3°). Mean attachments, Cu–C (1.907 Å), Cu–N (1.993 Å), as well as the triple bond in the cyano group (1.140 Å) are similar to those reported for other cyano-bridged polymeric Cu(I) structures [20–25].

The asymmetric unit (Fig. 1) is linked by cyano bridges to symmetry-equivalent units, so that the overall structural unit involves a more extensive arrangement of the components. The packing diagrams (Figs. 2 and 3) clearly show that the effective structural unit consists of six copper(I) atoms, four bridging cyano groups and four bridging mimtH molecules extended into a two dimensional infinite polymeric array by sharing their Cu atoms. The resultant hexanuclear unit is distorted because the separation distances between the cyano bridged copper atoms (5.027 Å) are longer than those (3.145 Å) which result from mimtH bridging (Fig. 2). The copper(I) atoms and the cyano groups form the

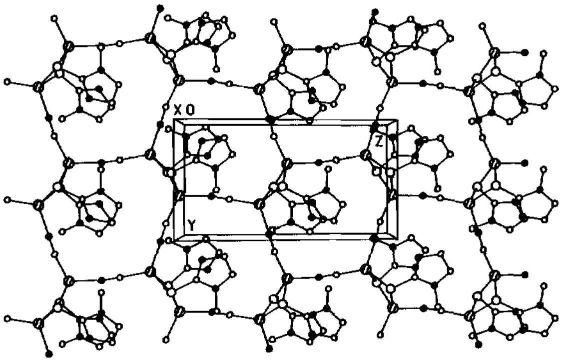

Fig. 2. Perspective view of the unit cell contents in *a* projection.

TABLE 5. Least-squares Mean Planes in the Form $ax + by + cz + d = 0$

Plane	Atoms	*a* (Å)	*b* (Å)	*c* (Å)	*d* (Å)	Largest deviations (Å)	
1	Cu(1), Cu(2), S(21), S(22)	−0.873	4.174	11.097	−6.7812	Cu(1)	−0.1607
						Cu(1)	−0.1596
						S(21)	0.1592
						S(22)	0.1611
2	Cu(1), S(21), C(21)	4.192	−5.328	4.155	−2.2476		
3	Cu(2), S(22), C(22)	3.960	−3.995	7.733	−2.1767		
4	S(21), C(21), N(31), C(41), C(51), N(11), C(11)	6.647	3.309	−3.885	−5.1740	N(11)	0.0353
5	S(22), C(22), N(32), C(42), C(52), N(12), C(12)	6.587	3.353	−4.159	−1.9099	S(22)	0.0197

Dihedral angles (°)	Planes	Angle (°)
	1/4	87.9
	1/5	88.8
	2/4	85.3
	3/5	85.7
	2/3	18.5

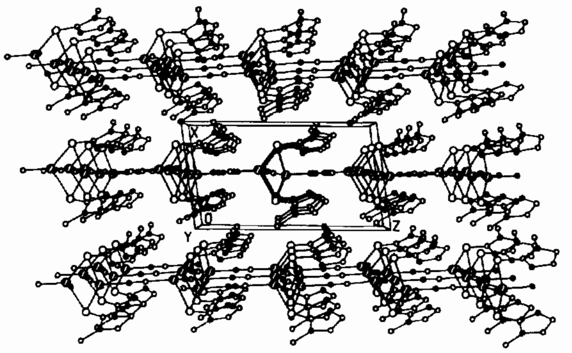

Fig. 3. Perspective view of the unit cell contents in *b* projection.

planar component of the layers with the bridging mimtH ligands occupying the space on either side (Fig. 3).

The polymeric layers are extended along the *b* and *c* axes of the unit cell and are stacked along *a*. The axial separation distance ($a = 7.6042(4)$ Å) represents the effective separation distance between adjacent layers. Unlike many complexes of mimtH there are no H bonds initiated by the ligands' (NH) imido groups [1, 9, 10]. Thermal analysis in flowing air (Fig. 4a) shows that the polymeric complex decomposes over the temperature range 145 to 800 °C to copper(II) oxide. The agreement between experimental (60.5%) and theoretical mass losses (60.8%) for the above process is within experimental error (+2.0%).

Both the TG and the DTG curves show the thermal decomposition to be, essentially, a three-stage process. The first stage (145–503 °C) involves 40.0% mass loss and is consistent with the evolution of 1-methylimidazole (M_r 82) as a result of the desulphurisation of coordinated mimtH. This process is somewhat protracted. From the slope of the TG curve and the presence of two DTG components the decomposition process also appears to be kinetically variable and composed of slow (145–248 °C), rapid (248–341 °C) and slow (341–503 °C) stages, probably due to the polymeric nature of the complex.

The second major decomposition (503–512 °C) consists of a rapid mass loss (13%, M_r 26) due to the evolution of cyanogen from the CuS–CuCN residues. Solid CuCN is reported to decompose at 473 °C [26]. Progress of the final decomposition stage is dependent on sample mass and heating rate. With relatively large sample masses (8 mg <) and rapid heating rates (20 °C min^{-1} <) there is a pronounced increase in the mass of the residue as some of the CuS is oxidised to CuSO$_4$. This tendency is less pronounced with smaller sample masses and slower heating rates, which tends to suggest that the CuS to CuSO$_4$ oxidation is superficial rather than total, in character. The residual mixture then decomposes to Cu(II)O.

The above decomposition procedures have been verified by collection and IR examination of evolved 1-methylimidazole, by X-ray powder diffraction studies of the cooled melt initially obtained at about 500 °C and by visual observation of the decomposition by hot-stage microscopy.

The DTA curve in dinitrogen (Fig. 4b) shows two essentially contiguous endotherms in the temperature ranges 192–279 and 279–363 °C. The first, and larger, endotherm ($\Delta H_r = 62.9(\pm 4)$ kJ mol^{-1}) represents desulphurisation of coordinated mimtH with concomitant evolution of 1-methylimidazole and copper sulphide formation. The second endotherm ($\Delta H_r = 32.1(\pm 2.0)$ kJ mol^{-1}) represents the endothermic requirements of cyanogen evolution from the copper sulphide and copper cyanide residues. Visual observation of the decomposition by hot-stage microscopy indicates that the first stage occurs in the solid and the second stage is accompanied by melting. Both endotherms clearly represent the residual endothermic requirements for combinations of chemical processes.

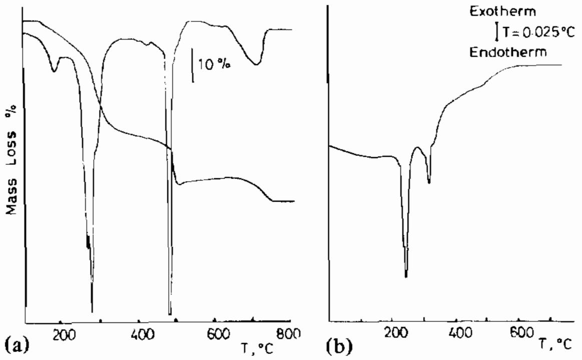

Fig. 4. Thermal analysis curves: (a) TG, DTG in flowing air, 20 °C min^{-1}; (b) DTA in flowing N$_2$, 20 °C min^{-1}.

Supplementary Material

H atom coordinates with isotropic thermal parameters, anisotropic thermal parameters and structure factor tables are available from the authors on request.

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