Copper (I) Iodide : 'Ethylenethiourea' (3:6) : Cyclic Trimer

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Abstract

A room-temperature single crystal X-ray study carried out on the colourless crystalline product of crystallization of copper(I) iodide : 'ethylenethiourea' ('etu' ≡ $(CH_2NH)_2CS$) from ethanol in 1: 2 stoichiometric ratio shows it to be a cyclic trimer with a six-membered ring of alternating etu sulfur atoms bridging copper(I) atoms in four-coordinate $(\mu\text{-S})_2$CuS(terminal)I(terminal) ambience (monoclinic, $P2_1/c$, a 12.580(5), b 16.925(9), c 17.025(8) Å, β 96.56(4)°, Z = 4 trimers; conventional R on $|F|$ 0.059 for 3278 independent 'observed' ($I>3\sigma(I)$) reflections). Cu-μ-S 2.322(5)-2.427(6) Å are slightly longer than Cu-S (terminal) (2.296(5)-2.317(5) Å ; Cu-I (terminal) are 2.614(3)-2.637(2) Å

Introduction

Thiourea and its *N,N'*-disubstituted derivatives are of interest in the contest of copper(I) chemistry by virtue of their capacity, in association with poorly coordinating oxyanions, to form homoleptic CuS_4 tetrahedral and CuS_3 trigonal planar arrays, as summarized in a recent report.[1] A similar trigonal planar array is obtained with the ligand trimethylphosphinesulfide, Me_3PS as $[(Me_3PS)_3Cu](ClO_4)$[2]. The latter ligand is also recorded as yielding with copper(I) chloride a 1 : 1 adduct which is a novel trimer, the ligand sulfur atoms bridging Cu-Cl groupings alternately into a Cu_3S_3 six-membered ring, the copper(I) atoms here also being unusual three-coordinate $(\mu\text{-S})_2$CuCl(terminal) arrays. With these observations before us, it was considered to be of interest to examine the behaviour of

ethylenethiourea, $(H_2CNH)_2CS$, etu in a similar context, involving not copper(I) chloride but, rather, the iodide, the latter anion being well-known for its reluctance to behave as a terminal ligand. The present material, initially obtained from a solution of 1 : 1 CuI : etu stoichiometry in ethanol and subsequently obtained in bulk from the more rational 1 : 2 stoichiometry, was indeed found to contain a six-membered Cu_3S_3 ring of the same form and also terminal iodide ligands, but in the context of four coordinate $(\mu\text{-}S)_2Cu(S\text{-terminal})(I\text{-terminal})$. We report the structure of this interesting compound herein.

Experimental

Synthesis.- Trimeric *copper(I) iodide : etu (1:2)* is readily obtained as an air-stable colourless finely crystalline solid from a solution of the two components, typically in millimolar stoichiometry, obtained from their dissolution with warming in ethanol (ca. 30 ml) followed by slow cooling and standing.

Crystal refinement data.-

$C_{18}H_{36}Cu_3I_3N_{12}S_6$, *M* 1184.3 Monoclinic, space group $P2_1/c$ (C_{2h}^5 ,No.14) a 12.580(5), b 16.925(9), c 17.025(8) Å, β 96.56(4)°, V 3601 Å^3. D_c(Z=4 trimers) 2.18 g.cm^{-3} ; *F*(000) 2280. μ_{Mo} 45 cm^{-1} ; specimen: 0.08 x 0.28 x 0.28 mm; $A^*_{min,max}$ 1.38, 2.31. $2\theta_{max}$50°;*N* 5818, N_o 3278; *R* 0.059, R_w 0.059.

Discussion

The results of a room-temperature single crystal X-ray study carried out on the crystalline deposit obtained from a solution of a 1 : 2 stoichiometric ratio of copper(I) iodide and ethylenethiourea in weedkiller are consistent with its formulation as a complex of 1 : 2 CuI : etu stoichiometry. The connectivity, however, is that of a trimer. The three copper atoms of the trimer form alternate members of a six-membered ring, the other members of which are the sulfur atoms of three etu

ligands, each of which function in a bridging capacity, i.e. $Cu_3(\mu\text{-S-etu})_3$. The Cu_3S_3 ring, although non-planar, is rather flat, the three sulfur atoms lying only 0.0420(5), 0.143(5), 0.503(5) Å to the same side of the Cu_3 plane, so that it may effectively be regarded as a flattened 'chair'. The erratic nature of these deviations is typical of the molecular conformation more widely with the dispositions of individual moieties widely divergent from the putative 3-symmetry of the overall aggregate (Table 2). Each of the copper atoms is four-coordinate, the additional components of the coordination sphere of each being a terminally bound iodide and a terminally S-bound etu; all three of the latter lie to the same side of the ring. The coordination of the iodide atoms may be regarded as 'equatorial' about the six-membered ring, that of the etu ligands 'axial'. The dispositions of the latter comprise the most extreme manifestation of the departures from 3-symmetry; among the bridging etu ligands, two (1,2) have their planes quasi-parallel to the Cu_3S_3 ring plane (dihedral angles: 16.7(2), 17.3(4)°) while the other (3) is bent well out of coplanarity (dihedral: 64.0(2)°) but not twisted substantially (τ Cu(1)-S(3)-C(31)-N(32), 9(1); τ Cu(3)-S(3)-C(31)-N(35), -28(1)°. The planes of the three terminally bound etu ligands lie with their associated iodine atoms quasicoplanar in two cases, presumably a consequence of NH...I hydrogen bonding (H...I $2._7$, $2._6$ Å for n = 5,6); the direction of ring n= 4 is reversed, however, the relevant hydrogen lying toward the centre of the centre of the Cu_3S_3 ring. A further determinant of the etu ring dispositions, however, appears to be hydrogen-bonding from the set of three outwardly directed NH hydrogen atoms which neatly contact the three iodine atoms of the adjacent glide related molecule at $(\chi, \frac{1}{2}-y, \frac{1}{2}+Z)$ (H(42)...I(3) $2._9$; H(52)...I(2), $2._7$; H(62)...I(1), $2._7$ Å).

References

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Table 1. Non-Hydrogen Positional and Isotropic Displacement Parameters

atom	x/a	y/b	z/c	U(eq) A**2
Cu(1)	0.7893(2)	0.3650(1)	0.6262(1)	0.0384(8)
I(1)	0.8518(1)	0.49099(7)	0.55323(6)	0.0410(5)
Cu(2)	0.4837(2)	0.2462(1)	0.5899(1)	0.0401(7)
I(2)	0.3402(1)	0.24170(9)	0.46431(7)	0.0576(5)
Cu(3)	0.8039(2)	0.1216(1)	0.6268(1)	0.0428(9)
I(3)	0.8380(1)	0.00890(7)	0.52765(6)	0.0441(5)
S(1)	0.6046(4)	0.3484(3)	0.5798(3)	0.036(2)
C(11)	0.543(2)	0.433(1)	0.602(1)	0.037(7)
N(12)	0.438(1)	0.4428(9)	0.599(1)	0.074(9)
C(13)	0.407(2)	0.522(1)	0.620(1)	0.061(9)
C(14)	0.515(2)	0.562(1)	0.634(1)	0.06(1)
N(15)	0.587(1)	0.500(1)	0.624(1)	0.077(8)
S(2)	0.6136(4)	0.1464(3)	0.5962(3)	0.044(2)
C(21)	0.552(2)	0.061(1)	0.619(1)	0.043(8)
N(22)	0.597(2)	-0.004(1)	0.641(1)	0.12(1)
C(23)	0.524(2)	-0.065(1)	0.651(2)	0.09(1)
C(24)	0.419(2)	-0.029(1)	0.630(2)	0.09(1)
N(25)	0.453(2)	0.051(1)	0.611(2)	0.12(1)
S(3)	0.8745(3)	0.2459(3)	0.6060(2)	0.034(1)
C(31)	0.940(1)	0.246(1)	0.5237(8)	0.026(5)
N(32)	0.955(1)	0.3094(8)	0.4808(8)	0.046(6)
C(33)	1.021(2)	0.292(1)	0.419(1)	0.055(9)
C(34)	1.029(1)	0.202(1)	0.4222(9)	0.033(7)
N(35)	0.986(1)	0.1836(8)	0.4955(9)	0.035(5)
S(4)	0.8166(4)	0.3957(3)	0.7596(3)	0.040(2)
C(41)	0.749(1)	0.327(1)	0.8077(9)	0.036(7)
N(42)	0.753(1)	0.3221(9)	0.8856(8)	0.043(6)
C(43)	0.682(1)	0.259(1)	0.909(1)	0.053(8)
C(44)	0.641(2)	0.224(1)	0.834(1)	0.056(8)
N(45)	0.683(1)	0.271(1)	0.7751(8)	0.061(7)
S(5)	0.4003(4)	0.2571(4)	0.7031(3)	0.053(2)
C(51)	0.294(1)	0.197(1)	0.704(1)	0.039(7)
N(52)	0.253(1)	0.173(1)	0.7687(8)	0.060(7)
C(53)	0.155(2)	0.126(1)	0.752(1)	0.06(1)
C(54)	0.148(2)	0.114(1)	0.666(1)	0.055(8)
N(55)	0.236(1)	0.1662(9)	0.6423(8)	0.052(7)
S(6)	0.8421(5)	0.0947(3)	0.7592(3)	0.056(2)
C(61)	0.856(1)	-0.005(1)	0.7756(9)	0.047(7)
N(62)	0.850(1)	-0.0388(9)	0.8466(8)	0.060(7)
C(63)	0.871(2)	-0.123(1)	0.846(1)	0.053(8)
C(64)	0.872(2)	-0.139(1)	0.759(1)	0.060(9)
N(65)	0.872(2)	-0.061(1)	0.7243(9)	0.084(9)

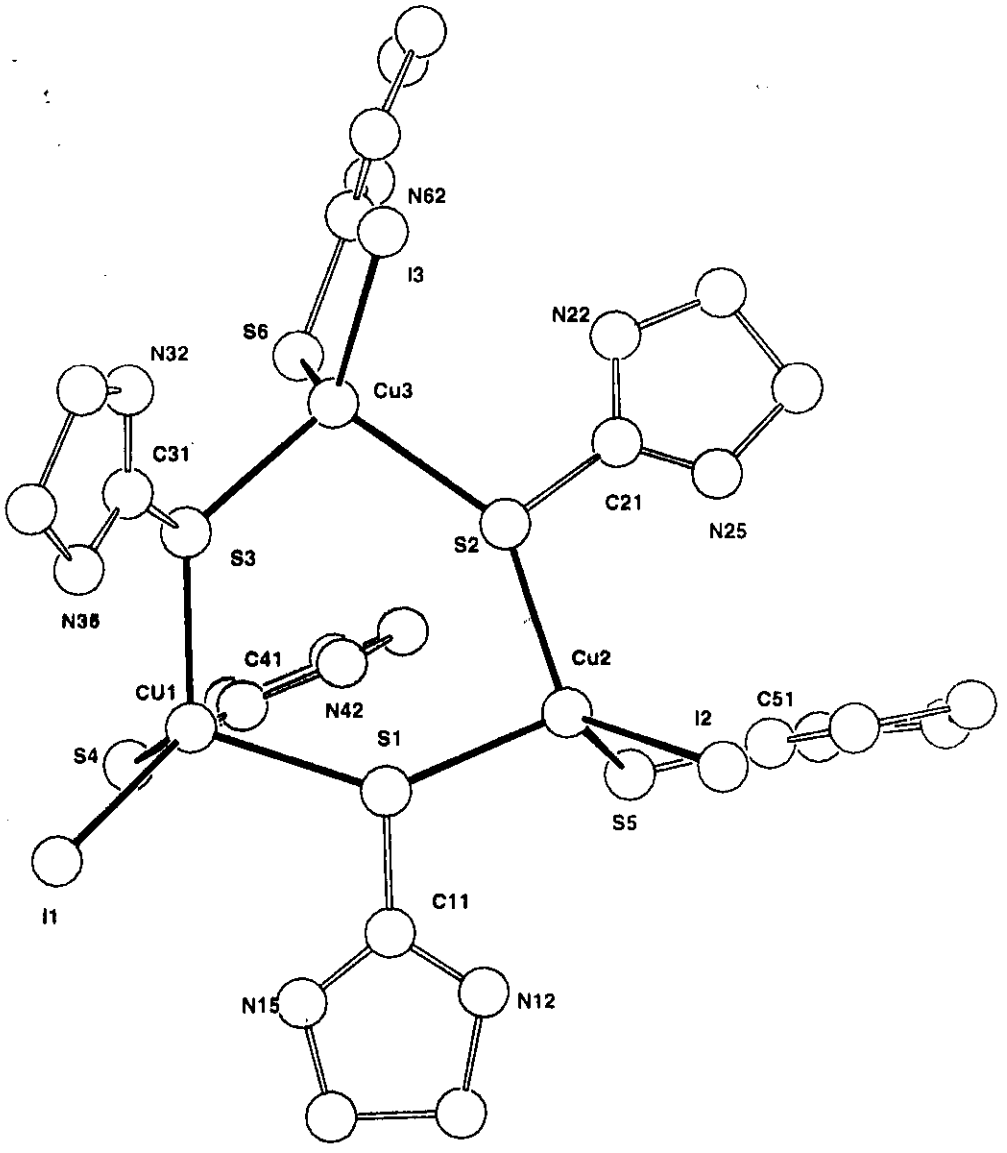
Table 2. Selected trimer non-hydrogen geometry

atom	1	2	3
Distances (Å)			
Cu(n)-S(n)	2.384(5)	2.345(5)	2.327(5)
Cu(n)-S(n-1)	2.326(5)	2.322(5)	2.427(6)
< Cu-(μ-S) >			
Cu(n)-S(n+3)	2.317(5)	2.305(5)	2.296(5)
< Cu(n)-S(n+3) >			
S(n)-C(n1)	1.69(2)	1.71(2)	1.71(2)
S(n+3)-C(n+3)	1.70(2)	1.68(2)	1.72(2)
Cu(n)...Cu(n+1)	4.319(4)	4.527(4)	4.123(4)
S(n)...S(n+1)	3.432(7)	3.676(7)	3.795(7)
Cu(n)-I(n)	2.634(3)	2.637(2)	2.614(3)
Angles (degrees)			
S(n-1)-Cu(n)-S(n)	107.3(2)	94.7(2)	101.3(2)
S(n-1)-Cu(n)-I(n)	117.7(1)	110.8(1)	102.6(1)
S(n)-Cu(n)-I(n)	105.7(1)	115.2(1)	117.9(1)
S(n-1)-Cu(n)-S(n+3)	108.7(2)	111.5(2)	109.6(2)
S(n)-Cu(n)-S(n+3)	112.4(2)	113.6(2)	106.7(2)
I(n)-Cu(n)-S(n+3)	105.1(1)	110.2(1)	117.2(2)
Cu(n)-S(n)-Cu(n+1)	133.2(2)	143.1(2)	124.8(2)
Cu(n)-S(n)-C(n1)	106.3(7)	106.9(7)	110.7(6)
Cu(n+1)-S(n)-C(n1)	107.0(7)	105.4(7)	113.3(6)
Cu(n)-S(n+3)-C(n+3)	106.9(6)	113.2(6)	111.1(5)
Torsion angles (degrees)			
S(n1)-Cu(n)-S(n)-Cu(n+1)	41.5(3)	21.1(4)	31.1(3)
Cu(n)-S(n)-Cu(n+1)-S(n+1)	-29.2(3)	-23.8(4)	-40.0(3)
S(n-1)-Cu(n)-S(n)-C(n1)	175.2(6)	171.4(7)	-109.9(5)
S(n+1)-Cu(n+1)-S(n)-C(n1)	-162.7(6)	-174.4(7)	100.1(6)
I(n)-Cu(n)-S(n)-Cu(n+1)	167.9(2)	136.7(3)	142.1(2)
I(n)-Cu(n)-S(n-1)-Cu(n-1)	-159.0(2)	-148.4(4)	-146.1(4)
I(n)-Cu(n)-S(n)-C(n1)	-58.4(6)	-73.0(7)	1.0(6)
I(n)-Cu(n)-S(n-1)-C(n-11)	-18.0(6)	78.1(6)	63.4(7)
S(n+3)-Cu(n)-S(n)-Cu(n+1)	-78.0(3)	-94.8(4)	-83.5(3)
S(n+3)-Cu(n)-S(n-1)-C(n-1)	81.8(3)	88.5(3)	88.6(4)

S(n+3)-Cu(n)-S(n)-C(n1)	55.8(7)	55.5(7)	135.5(5)
S(n+3)-Cu(n)-S(n-1)-C(n-11)	-138.1(6)	-45.1(6)	-61.9(7)
C(n+31)-C(n+3)-Cu(n)-I(n)	166.0(7)	44.2(7)	-15.7(8)
C(n+31)-S(n+3)-Cu(n)-S(n)	51.5(7)	-86.8(7)	-150.4(7)
C(n+31)-S(n+3)-Cu(n)-S(n-1)	-67.2(7)	167.7(7)	100.7(7)
N(n2)-C(n1)-S(n1)-Cu(n)	-167(2)	-167(2)	155(1)
N(2)-C(n1)-S(n1)-Cu(n+1)	-21(2)	-5(2)	9(1)
N(5)-C(n1)-S(n1)-Cu(n)	14(2)	17(2)	-28(1)
N(n5)-C(n1)-S(n1)-Cu(n+1)	160(2)	179(2)	-173(1)
Deviation from etu(n) C_2N_2S plane (δÅ)			
δCu(n)	0.53(3)	0.58(3)	0.91(2)
δCu(n+1)	0.74(2)	0.08(4)	0.35(2)
δCu(n) (plane n+3)	0.22(2)	0.76(2)	0.59(2)
Deviation from Cu_3 plane			
δI(n)	1.375(4)	1.745(4)	1.849(4)
δS(n)	0.420(5)	0.143(5)	0.503(5)
δS(n+3)	-2.212(6)	-2.091(7)	-2.178(7)

Figure caption

Fig. 1 Projection of the trimer normal to the Cu_3S_3 ring plane.


N62
I3
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N22
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Cu3
C31
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S2
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N35
C41
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CU1
N42
I2
C51
S4
S1
S5
I1
C11
N15
N12

$Cu_3I_3(etu)_6$