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Syntheses, properties, crystal and molecular structure of a novel neutral pentanuclear copper(I) iodide species. Copper(I) complexes with tetraethylthiuram monosulfide ‡

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The reaction of copper(I) iodide with tetraethylthiuram monosulfide L^{Et} afforded the novel copper(I) pentanuclear neutral complex $[Cu_5L^{Et}{}_2I_5]\cdot EtOH\cdot MeCN$ **1**. Its crystal structure may be described as a very distorted octahedral central Cu_3I_3 cage having two additional $CuL^{Et}(I)$ units fused to the central cage by means of two iodine and one sulfur bridging atom. All copper(I) atoms in **1** are tetrahedral and both sulfur ligands are bidentate. The solvent molecules occupy intermolecular vacancies generated by the manner in which **1** is packed in space. In contrast, other copper(I) halides CuX (X = Cl or Br) with tetraethylthiuram monosulfide afforded the copper(I) complexes $[CuL^{Et}(X)]$ (X = Cl **2** or Br **3**) which exist in the solid state as monomeric units featuring three-co-ordinate copper(I). The ligands are bidentate and co-ordination is completed by the halogen atoms. The complexes were additionally characterized by IR and ^1H NMR spectra as well as magnetic susceptibility measurements. Complexes **2** and **3** can be alternatively prepared by sulfur abstraction from the disulfides, using triphenylphosphine. Copper(I) iodide and tetraethylthiuram monosulfide failed to yield a mononuclear compound under a variety of experimental conditions.

Polynuclear copper(I) complexes are scarce, and the abundance of reports stands in inverse proportion to the nuclearity of the species concerned. In particular, studies involving pentanuclear copper(I) complexes have been restricted to four reports. All these involve anionic complexes. Thus Baumgartner[1] described the structure of the tetraphenylphosphonium salt of $[Cu_5(SMe)_7]^{2-}$, a species isostructural to $[Cu_5(SPh)_7]^{2-}$ reported by Dance.[2] More related to the present work are the structures of the dianions $[Cu_5I_7]^{2-}$ [3] and $[Cu_5Br_7]^{2-}$.[4]

Relevant aspects of the ligating properties of thiuram disulfides $R_2NC(S)S{-}SC(S)NR_2$ (R = alkyl) have been reviewed in a previous paper,[5] where the significance of these compounds in the field of agriculture and medicine has been remarked upon. Particularly striking has been the application of these materials as inhibitors of human immunodeficiency viral infections such as AIDS.[6] Explanations have recently been offered as to the reasons for this wide range of biological activity.[7]

Complexes of metals with thiuram monosulfides $R_2NC(S)SC(S)NR_2$ have not been studied as extensively, and the reader is referred to previous work for a more general review of this particular topic.[5] Only the most important details will be outlined here. Straightforward 1 : 1 adducts have resulted from the interaction of tetraalkylthiuram monosulfides (L^R) and some metal halides. Some, but not all, of the examples reported are $[ML^RX_2]$ (M = Zn[8] or Hg[9]) and $[M'L^R(X)]$ (M′ = Ag[10] or Cu[11]). Carbon–sulfur bond scission of monosulfides in many cases leads to dithiocarbamate–metal–thiocarboxamide[12] or metal–dithiocarbamate[13] complexes. The ligand may also undergo a two-electron oxidation to the cyclic organic dication of 1,2,4-trithiolane-3,5-diimine, which has been isolated as a metal–halogen anionic complex.[5,14]

In a recent publication[5] we reported the crystal and molecular structures of [bis(dimethylthiocarbamoyl) sulfide]halogenocopper(I) complexes $[CuL^{Me}(X)]$ [X = Cl, Br or I; L^{Me} = $Me_2NC(S)SC(S)NMe_2$]. In all three structural studies it was found that the basic $XCuS_2$ units undergo more extensive association to afford dimers (X = Cl or I) or a polymer (X = Br). The nature and extent of the association seemed to be determined by the packing in the solid as much as by steric and electronic effects inherent to the halogen involved in each case.

The diversity of structures found in the solid state, which apparently show a strong dependence on the steric properties of the ligand, prompted an extension of these studies to include bulkier monosulfide ligands. Also, the unexpected sulfur abstraction from the disulfides led to an alternative method for the preparation of the materials involved.

Results and Discussion

The reaction of acetonitrile solutions of copper(I) iodide and $Et_2NC(S)SC(S)NEt_2$ (L^{Et}) which contains trace amounts of ethanol leads to a crystalline phase of composition $[(CuI)_5L^{Et}{}_2]\cdot EtOH\cdot MeCN$ **1**.§ The solid-state structure of this aggregate (Fig. 1, Table 1) may be described as formed by a central $(CuI)_3$ distorted octahedral element, plus two additional CuL(I) units fused to the central $(CuI)_3$ cage by means of sulfur and iodine bridges. The molecule displays a two-fold crystallographic axis through Cu(1) and I(1), coincident with the long axial position of the 'octahedron'. The severely bent equatorial plane of the octahedron is defined by I(2) Cu(3A), I(2A) and Cu(3). Each $CuL^{Et}(I)$ unit contains one tetrahedral copper [Cu(2)], a bidentate sulfur ligand [S(1) and S(3)] and one iodine atom [I(3)]. These units are fused to two faces of the octahedron by means of two iodine bridges [I(3) to Cu(1) and I(2) to Cu(2)] and by one sulfur bridge [S(3) to Cu(3)]. The solvent molecules are

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‡ *Non-SI units employed*: eV ≈ 1.60×10^{-19} J, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

§ Earlier experiments afforded an unsolvated solid phase $[(CuI)_5L_2]$ the crystal structure of which was solved at room temperature. The molecular geometry and structural parameters observed were comparable to those reported here. Thermal motion and an insufficient number of data led to an unsatisfactory structure solution.[15] Repeated attempts to reproduce this synthetic result were unsuccessful.

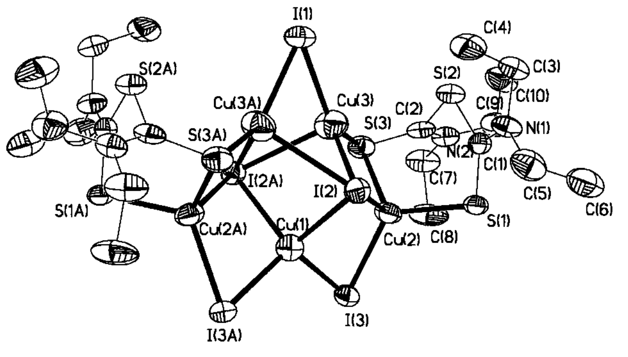


Fig. 1 Structure of $[Cu_5L^{Et}{}_2I_5]\cdot EtOH\cdot MeCN$ **1** and numbering scheme with 50% displacement ellipsoids for non-hydrogen atoms

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**–**3**

$[Cu_5L^{Et}{}_2I_5]\cdot MeCN\cdot EtOH$ **1**			
Cu(1)–I(3)	2.625(2)	Cu(2)–S(1)	2.295(3)
Cu(1)–I(2)	2.730(2)	Cu(2)–S(3)	2.404(3)
Cu(2)–I(2)	2.840(2)	Cu(3)–S(3)	2.247(3)
Cu(2)–I(3)	2.549(2)	S(1)–C(1)	1.678(9)
Cu(3)–I(1)	2.576(2)	S(2)–C(1)	1.784(9)
Cu(3)–I(2)	2.782(2)	S(2)–C(2)	1.791(9)
Cu(3)–I(2A)	2.943(2)	S(3)–C(2)	1.702(10)
I(3)–Cu(I)–I(3A)	113.09(8)	S(3)–Cu(3)–I(2A)	91.40(10)
I(3)–Cu(1)–I(2A)	113.07(3)	I(1)–Cu(3)–I(2A)	100.61(6)
I(3)–Cu(1)–I(2)	107.37(3)	I(2)–Cu(3)–I(2A)	96.04(6)
I(2A)–Cu(1)–I(2)	102.46(7)	Cu(3)–I(1)–Cu(3A)	58.84(8)
S(1)–Cu(2)–S(3)	106.00(10)	Cu(1)–I(2)–Cu(3)	75.96(6)
S(1)–Cu(2)–I(3)	121.63(8)	Cu(1)–I(2)–Cu(2)	62.91(4)
S(3)–Cu(2)–I(3)	111.96(8)	Cu(3)–I(2)–Cu(2)	59.53(5)
S(1)–Cu(2)–I(2)	100.32(9)	Cu(1)–I(2)–Cu(3A)	73.35(5)
S(3)–Cu(2)–I(2)	109.73(8)	Cu(3)–I(2)–Cu(3A)	52.38(6)
I(3)–Cu(2)–I(2)	106.28(5)	Cu(2)–I(2)–Cu(3A)	104.94(6)
S(3)–Cu(3)–I(1)	134.80(9)	Cu(2)–I(3)–Cu(1)	68.38(6)
S(3)–Cu(3)–I(2)	116.93(9)	C(1)–S(2)–C(2)	100.8(4)
I(1)–Cu(3)–I(2)	105.00(6)		
A $-x, y, -z + \frac{1}{2}$			
$[CuL^{Et}(Cl)]$ **2**			
Cu–Cl	2.176(4)	S(2)–C(1)	1.780(8)
Cu–S(1)	2.221(5)	S(2)–C(2)	1.807(8)
Cu–S(3)	2.265(4)	S(3)–C(2)	1.687(7)
S(1)–C(1)	1.703(7)		
Cl–Cu–S(1)	124.71(14)	S(1)–C(1)–S(2)	123.1(4)
Cl–Cu–S(3)	118.9(2)	S(3)–C(2)–S(2)	117.3(4)
S(1)–Cu–S(3)	116.37(10)	C(1)–S(2)–C(2)	103.0(3)
$[CuL^{Et}(Br)]$ **3**			
Cu–Br	2.316(2)	S(2)–C(1)	1.759(12)
Cu–S(1)	2.221(3)	S(2)–C(2)	1.808(10)
Cu–S(3)	2.272(4)	S(3)–C(2)	1.695(11)
S(1)–C(1)	1.691(11)		
Br–Cu–S(1)	123.44(12)	S(1)–C(1)–S(2)	123.7(6)
Br–Cu–S(3)	120.52(10)	S(3)–C(2)–S(2)	117.0(6)
S(1)–Cu–S(3)	116.02(14)	C(1)–S(2)–C(2)	103.1(5)

found in intermolecular vacancies originated by the manner in which the units of aggregate **1** are packed in the solid. Interconnection of such vacancies generates channels along the *b* axis. These channels are shown in Fig. 2. Two different sites in the asymmetric unit are occupied by EtOH and acetonitrile respectively. Enforcement of the crystal symmetry causes the solvent positions created by the *C*2 axis to superimpose with those of the asymmetric unit. The occupancy factor for each solvent molecule is thus 0.5.

Discrete pentanuclear copper(I) complexes have been so far reported for $[Cu_5(SR)_7]^{2-}$ (R = Me or Ph) and $[Cu_5X_7]^{2-}$ (X = Br or I). The anion $[Cu_5(SPh)_7]^{2-}$ displays a molecular structure where four copper(I) atoms are found in a pseudo-cubane arrangement, with the supernumerary metal atom sitting on one of the diagonals of the face from the reference cube. A similar situation obtains in the isostructural methyl derivative. Copper in these cases shows two types of co-ordination, namely trigonal planar and linear, a situation which deviates considerably from the case reported here.[1,2]

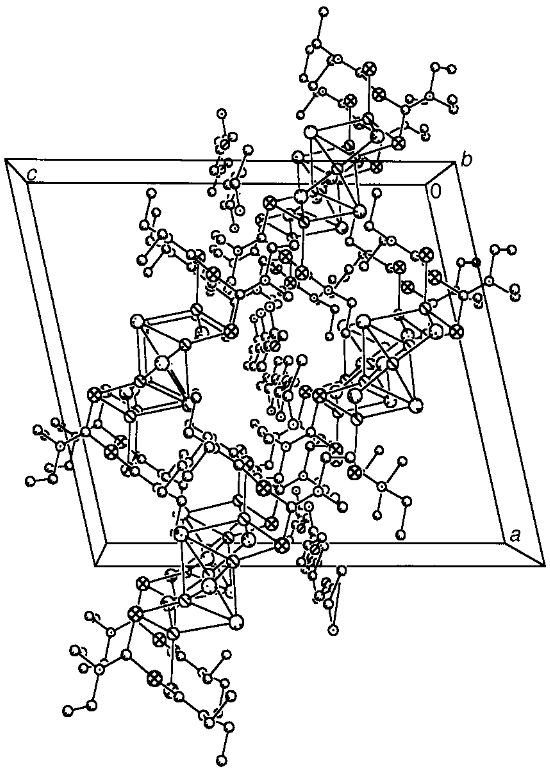


Fig. 2 Packing diagram for compound **1** showing the channels occupied by solvent molecules along the *b* axis

The anion $[Cu_5I_7]^{2-}$ has been described as a pentagonal bipyramid of seven iodine atoms, where only slight deviations from C_{5h} symmetry occur. It may be viewed as five face-sharing copper(I) iodide tetrahedra.[3] In the bromo derivative the pentagonal bipyramid of ligand atoms is more severely distorted.[4] With the hindsight afforded by the previous models we may now view the structure of **1** as consisting of the same basic structural unit, *viz.* a pentagonal bipyramid formed by the apical I(2) and I(2A) and by a distorted basal pentagonal plane I(1)–S(3)–I(3)–I(3A)–S(1A). All copper atoms display tetrahedral co-ordination and appear as three distinct sets: Cu(3) and Cu(3A) are co-ordinated to three iodines and to one sulfur atom, while the ligand entourage for Cu(2) and Cu(2A) consists of two sulfurs and two iodines; the unique Cu(1) is co-ordinated to four iodines. The shortest metal–metal distance found is 2.533(8) Å for Cu(3) · · · Cu(3A). The iodine atoms are either μ- or μ_4-bridging and the shortest I · · · I contact [4.261 Å for I(1) · · · I(2)] compares well with the one found in $[Cu_2I_4]^{2-}$ [16] and other related systems.[17]

It is clear that the pentanuclear derivative **1** is not structurally related to other copper(I) complexes of thiuram monosulfides (see below). A variety of experimental conditions have failed to yield a mononuclear copper complex in combinations of copper(I) iodide and tetraethylthiuram monosulfide. If the kinetics of complexation were slow, the available free CuI might compete with the monomeric $CuL^{Et}(I)$ for extension of the association and polynuclear complexes would result. However, all efforts to isolate a species of higher nuclearity using combinations of different copper(I) halides and methyl, Pr^n or Pr^i substituents on the ligand have not met with any success.

Analysis of the crystallographic and structural data obtained indicates that complexes $[CuL^{Et}(X)]$ (X = Cl **2** or

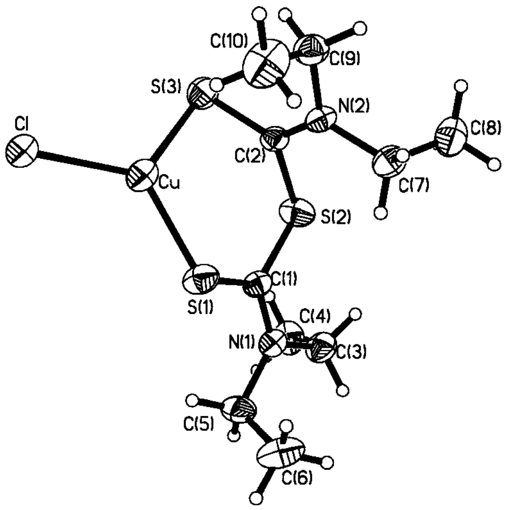


Fig. 3 Structure of $[\mathrm{CuL^{Et}(Cl)}]$ **2** and numbering scheme with 50% displacement ellipsoids for non-hydrogen atoms

Table 2 Infrared spectral data (cm^{-1}) for complexes **1**–**3**

	L^{Et}	**1**	**2**	**3**
ν(O–H)		3335		
		2940		
		2857		
ν(C≡N)		2230		
ν(C–N)	1492	1519	1500	1504
ν(C=S)	1000, 970	999	987, 960	984, 960
ν(C–S)	819	834	831	829
ν(Cu–S)			364, 329	349, 326
ν(Cu–X)			307	250

See Experimental section for band intensities.

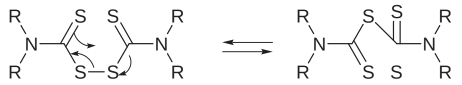
Br **3**) are isostructural (Fig. 3). Both are constituted by a bidentate ligand–copper six-membered chelate ring defined by Cu–S(1)–C(1)–S(2)–C(2)–S(3). The copper co-ordination number is three, comprising two terminal sulfur atoms from the thiuram unit and a halogen atom. The copper atom is projected out of the least-squares plane passing through Cu, S(1), S(3) and X by 0.009 Å in **2** and by 0.013 Å in **3**. The S–Cu–X angles are close to 120°. The Cu–S distances are about 2.24 Å in both compounds, values which are noticeably shorter than those found in the methyl derivatives.[5] This is to be expected on account of the non-bridging nature of the sulfur atoms in the present complexes. The effect is reflected in the values found for the Cu–S stretching frequencies in the IR spectra (Table 2), which are higher for the ethyl series. The Cu–Cl distance is also shorter by about 0.1 Å with respect to the value found in the methyl compound, a trend also reflected in the corresponding IR stretching frequencies, while the Cu–Br distance is similar to the value found in $[\mathrm{CuL^{Me}(Br)}]$. The bidentate ligand and the copper atom form a non-planar six-membered ring. The deviation from planarity is reflected in the values for the dihedral angles defined by the planes passing through X, Cu, S(1), S(3) and S(1), C(1), C(2), S(3), which are 10.1 and 10.9° for the chloro and bromo complexes respectively. Precedents for these structures are the S_2CuCl chromophore found in chlorobis(2-thiouracil)copper(I)[18] and $[\mathrm{CuCl\{Ph_2P(S)CH_2(S)PPh_2\}}]$.[19] However, striking differences are noted when comparing the results of the present work with the crystal structures of complexes $[\mathrm{CuL^{Me}(X)}]$ (X = Cl, Br or I). These features may be summarized as follows.[5] All three compounds in the methyl series consist of a basic metal–bidentate ligand six-membered chelate ring, with the halogen atom occupying a third co-ordination position on copper. Four-co-ordination about the metal is achieved by bridging. The chloro and iodo derivatives are dimers and bridging is effected by sulfur from the thiuram unit and by iodide respectively. The bromo derivative is similar to the chloro compound in that sulfur atoms from the thiuram ligand serve as bridges between copper units, but in this case a polymer is formed.

Table 2 reports characteristic IR frequencies for the complexes prepared. While the data do not add to the features found by the crystal structure determination, the co-ordination is confirmed. Particularly noteworthy are the shifts of the $C–NR_2$ frequencies in the spectra of the complexes, compared to those of the free tetraalkylthiuram monosulfide[20] and the appearance of the Cu–S and Cu–X stretchings[21] referred to above. For **1**, absorptions at 3335 and 2940 cm^{-1} confirm the presence of ethanol in the solid. Similarly, the presence of acetonitrile is evident from the band at 2230 cm^{-1}.

Solution characterization of the complexes included conductivity measurements in acetonitrile. In all three cases the values obtained were consistent with a non-electrolyte behavior. Low solubility (for **1**) or lack of solution stability (for **2** and **3**) frustrated attempts at molecular weight determinations by osmometry.

The ^1H NMR data for the complexes are reported in the Experimental section. The temperature dependence of the ^1H NMR spectra of thiuram sulfides has been interpreted in terms of restricted rotation about the C–N bond which causes inequivalence of the alkyl groups and broadening of the signals at temperatures close to ambient.[22] This is apparent in the spectra of the complexed $[\mathrm{CuL^R(X)}]$ and free L^R. Two sets of alkyl resonances are present in all the cases studied. Absorptions for acetonitrile and ethanol are also observed in the spectra of the pentanuclear complex.

The mononuclear complexes **2** and **3** can alternatively be isolated from the reaction of tetraethylthiuram *disulfides* and copper(I) halides in the presence of triphenylphosphine (halide = Cl or Br, not I). A possible explanation for these observations involves the onset of equilibrium (1). The position



(1)

of this equilibrium must lie well to the left in solutions of the disulfide which contain triphenylphosphine only, since the monosulfide is not isolated in the absence of a metal halide.[23] Addition of copper(I) halides to these solutions causes a shift in the equilibrium position and appearance of deep red colors. Thus complexes **2** and **3** may be isolated in good yield.

Experimental

Reagents, spectroscopy and analyses

Handling of reagents, instrumentation, methods of analyses and preparation of the copper(I) halides have been described previously.[5] Magnetic measurements at ambient temperature were performed on the solid samples; the results were corrected for diamagnetism of the ligands. Electron spectroscopy for chemical analysis (ESCA) was performed on a Fissons Instruments Escalab 220 iXL spectrometer with a monochromatic X-ray source. Charge compensation was achieved using a coaxial electron source. Spectra were calibrated using the carbon 1s line at binding energy 284.8 eV. Samples were mounted on double-sided adhesive tape. Tetraethylthiuram disulfide (Aldrich) and triphenylphosphine (Merck) were used as supplied. Tetraethylthiuram monosulfide was prepared by desulfurization of the disulfide with alcoholic KCN. **CAUTION**: acid hydrolysis of potassium cyanide generates HCN, an exceedingly poisonous gas. The ethanol solution was concentrated by evaporation and diluted with water. The orange-brown solution was extracted

Table 3 Crystallographic data and refinement details for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{24}H_{49}Cu_5I_5N_5OS_6$	$C_{10}H_{20}ClCuN_2S_3$	$C_{10}H_{20}BrCuN_2S_3$
M	1568.24	363.45	407.91
Space group	$C2/c$ (no. 15)	$P2_1$ (no. 4)	$P2_1$ (no. 4)
Crystal size/mm	0.32 × 0.24 × 0.18	0.78 × 0.40 × 0.15	0.50 × 0.34 × 0.30
a/Å	17.795(4)	7.376(16)	7.371(2)
b/Å	13.831(6)	12.686(23)	12.846(4)
c/Å	20.034(4)	9.121(18)	9.185(3)
β/°	103.12(5)	107.92(16)	107.31(2)
U/Å^3	4802(3)	812.1(3)	830.3(4)
Z	4	2	2
D_c/g cm^{-3}	2.169	1.49	1.63
F(000)	2968	376	412
μ/mm^{-1}	5.679	1.88	4.08
θ Range/°	1.88 to 25.00	2.35 to 22.54	2.32 to 22.55
Index ranges	$0 \leqslant h \leqslant 21, 0 \leqslant k \leqslant 16, -23 \leqslant l \leqslant 23$	$-2 \leqslant h \leqslant 7, -2 \leqslant k \leqslant 13, -9 \leqslant l \leqslant 9$	$0 \leqslant h \leqslant 7, -2 \leqslant k \leqslant 13, -9 \leqslant l \leqslant 9$
Collected reflections	4378	1942	1520
Independent reflections (R_{int})	4234 (0.0724)	1335 (0.035)	1367 (0.016)
Observed reflections [$F^2>2\sigma(F^2)$]	2771	1297	1293
Absorption correction	Semiempirical (ψ scans)	None	None
Maximum, minimum transmission	0.084 and 0.042	—	—
Data, restraints, parameters	4175, 4, 236	1335, 1, 155	1367, 1, 155
Goodness of fit S on F^2	0.934	1.027	1.091
$R1$, $wR2$ [$F^2>2\sigma(F^2)$]	0.0490, 0.1147	0.038, 0.107	0.041, 0.127
(all data)	0.0820, 0.1435	0.039, 0.109	0.043, 0.128
Maximum difference peak, hole/e Å^{-3}	1.023, −1.007	1.01, −0.65	0.39, −0.36

Details in common: λ(Mo-Kα) = 0.710 73 Å; monoclinic; red prisms; $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$; $R1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

with diethyl ether and the extract was left in a freezer. Failure to crystallize prompted the evaporation of the solution to dryness and use of the resulting syrup with no further attempts to isolate the compound.[24]

Crystallography

Diffraction intensities were collected on a Siemens P3 diffractometer, which included a beam monochromator. The data were collected at room temperature (293 K) for complexes **2** and **3**, and 183 K for **1**, in order to diminish thermal motion. Two standard reflections checked every 98 showed no significant crystal decay. Intensities were corrected for Lorentz-polarization effects. The structures were solved by direct methods using the program package SHELXTL PLUS[25] (personal computer version), and refined by full-matrix least squares on F^2 using the program SHELXL 93.[26] All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were included in their idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Full details are given in Table 3.

CCDC reference number 186/864.

Preparation of the complexes

(a) From tetraethylthiuram monosulfide. The monosulfide (0.79 g, 3.0 mmol) was dissolved in acetonitrile (15 cm^3) and the solution added dropwise to a stirred, cooled (ice–salt bath) solution of copper(I) halide (3.0 mmol) in the same solvent (25 cm^3). The resulting red solutions were treated with diethyl ether (15 cm^3), layered on top of the acetonitrile solution. Standing in a freezer for 3 h produced a crop of black needles of the known bis(diethyldithiocarbamato)copper(II) $Cu(Et_2NCS_2)_2$, m.p. 198 °C. This undesired product was filtered off, the solution was treated with additional ether (5 cm^3) and returned to the freezer overnight, when large orange-red prismatic crystals separated. These were isolated by decanting the solvent, washing with fresh ether and drying in air. The procedure was successful for all three halides. A change in the experimental stoichiometry for the iodide derivative did not alter the nature of the product obtained.

(b) From tetraethylthiuram disulfide and triphenylphosphine. Triphenylphosphine (0.79 g, 3.0 mmol) in MeCN (40 cm^3) was added to a solution of the disulfide (0.89 g, 3.0 mmol) in the same solvent (20 cm^3). The solution was cooled in ice and a solution of copper(I) halide (3.0 mmol, halide = Cl or Br but not I) in MeCN (25 cm^3) was added dropwise with stirring. Approximately half of the solvent was stripped off in a rotary evaporator and the solution allowed to stand in ice for 1 h. The dark amorphous powder produced was filtered off, washed with ether and dried. Yield: 0.08 to 0.10 g. IR: 1546s, 1518s, 1501s, 395s and 360s (chloro derivative): 1537s, 1516s, 1501s, 390s and 355s cm^{-1} (bromo derivative). Spectral (IR and ESCA) and magnetic properties of these samples matched those found for authentic samples of $[Cu_2(Et_2NCS_2)_3X_2]$ (X = Cl or Br), reported previously.[27] The red mother-solution mixed with the wash ether was left in a freezer overnight and produced yellow needles which were separated by decanting the solvent. Yield: 0.60 to 0.70 g triphenylphosphine sulfide. m.p. 162–165 °C. IR: 3059vw, 1477m, 1433s, 1388w, 1309w, 1102s, 991w and 710vs cm^{-1}. The mother-solution was treated with an additional portion of Et_2O (20 cm^3) and returned to the freezer. After 12 h the orange-red prismatic crystals were isolated as described under (a).

$[(CuI)_5L^{Et}{}_2]_2\cdot EtOH\cdot MeCN$[15] **1**: dark red prisms, m.p. 122–145 °C (decomp.) (Found: C, 18.6; H, 3.14; Cu, 20.5; I, 40.8. $C_{24}H_{49}Cu_5I_5N_5OS_6$ requires C, 18.4; H, 3.2; Cu, 20.3; I, 40.5%). IR: 3335m, 2973m, 2940m, 2927w, 2857w, 2230w, 1519s, 1440s, 1361m, 1275s, 1203m, 1157m, 1071w, 999w, 907w, 834w and 755w cm^{-1}. δ_H(CDCl$_3$) 4.03 (q, J 7, 8), 3.90 (s, 1), 3.63 (q, J 7, 8), 3.60 (q, J 7, 2), 1.94 (s, 3), 1.46 (t, J 7, 12), 1.35 (t, J 7, 12) and 1.17 (t, J 7 Hz, 3). μ_{eff}(solid samples): 0.00 μ_B. Λ_M(MeCN): 17–22 Ω^{-1} cm^2 mol^{-1} (10^{-3}–10^{-4} M).

$[CuL^{Et}(Cl)]$ **2**: orange-red prisms, m.p. 118–120 °C (decomp.) (Found: C, 33.2; H, 5.4; Cl, 9.7; Cu, 17.4. $C_{10}H_{20}ClCuN_2S_3$ requires C, 33.0; H, 5.6; Cl, 9.8; Cu, 17.5%). IR: 2980m, 2936m, 2861w, 1500s, 1428s, 1376w, 1349m, 1267s, 1193s, 1145m, 1069m, 987w, 960w, 904m, 831m, 775w, 364w, 329 (sh) and 307s cm^{-1}. δ_H(CDCl$_3$) 4.02 (q, J 7, 4), 3.73 (q, J 7, 4), 1.39 (t, J 7, 6) and 1.32 (t, J 7 Hz, 6). μ_{eff}(solid samples): 0.00 μ_B. Λ_M(MeCN): 25–30 Ω^{-1} cm^2 mol^{-1} (10^{-3}–10^{-4} M).

[CuL^{Et}(Br)] **3**: orange-red prisms, m.p. 115–117 °C (decomp.) (Found: C, 29.4; H, 4.9; Br, 19.2; Cu, 15.7. $C_{10}H_{20}BrCuN_2S_3$ requires C, 29.4; H, 5.0; Br, 19.6; Cu, 15.6%). IR: 2980s, 2962s, 2927m, 2868w, 1504s, 1495s, 1430s, 1373w, 1347m, 1295w, 1269s, 1197s, 1143m, 1088w, 1069m, 984w, 960w, 905m, 829m, 777w, 349w, 326m and 250s cm^{-1}. δ_H($CDCl_3$) 4.02 (q, *J* 7, 4), 3.66 (q, *J* 7, 4), 1.44 (t, *J* 7, 6) and 1.34 (t, *J* 7 Hz, 6). μ_{eff}(solid samples): 0.00 μ_B. Λ_M(MeCN): 28–38 Ω^{-1} cm^2 mol^{-1} (10^{-3}–10^{-4} M).

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