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Tris(trimethylphenylammonium) Hexaiodotricuprate(I)

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Abstract

An anionic cuprous iodide complex of a previously unreported type, $[C_9H_{14}N]_3[Cu_3I_6]$, exists as an isosceles triangle of three Cu atoms [one unique edge 2.551 (3) Å and two longer edges averaging 2.707 (2) Å] each bound to a terminal I atom [Cu—$I_{terminal}$ 2.506 (3) Å average]. Cu atoms at the unique edge are bridged by an I atom [Cu—$I_{bridging}$ 2.646 (2) Å average] and the triangle is capped on both faces by two additional I atoms [Cu—$I_{face\ capping}$ 2.750 (3) Å average]. Thus two Cu atoms have fourfold coordination to I atoms and the other is three-coordinate. The cuprous iodide complex and one trimethylphenylammonium group are found about mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. Additional trimethylphenylammonium groups are packed between these layers.

Comment

Copper and halide combine in a variety of stoichiometries to form anionic complexes Cu_yX_z, $z > y$ (Jagner & Helgesson, 1991). The number of larger discrete (nonpolymeric) complexes with $3 < y < 56$ that have been identified by single-crystal X-ray diffraction are more notable for their differences than for their similarities. I atoms are seen in terminal, μ, μ_3 and μ_4 positions with the larger coordination numbers associated with longer Cu—I bonds. Cu atoms may be two-, three- or four-coordinate. Cu$\cdots$Cu non-bonded distances vary from

2.5 to >3.0 Å. Rhombohedra with Cu and halide atoms at alternate corners are common building blocks, and are found sharing corners or edges to form the motifs of higher nuclearity.

$[Co(C_5H_5)_2]_3Cu_3I_6$, the structure of greatest resemblance to the title compound (I), is similar as it contains an isosceles triangle of Cu atoms, but with two short Cu$\cdots$Cu distances [average 2.518 (6) Å] and one long distance [3.178 (6) Å], doubly face-capped by I atoms. The two short edges are bridged by I atoms and only the two Cu atoms of the long side have terminal I atoms. Thus transformation to the allotropic motif of the title structure requires the rupture of one bridging iodide bond with the lengthening of that side of the triangle (Hartl, 1987).

(I)
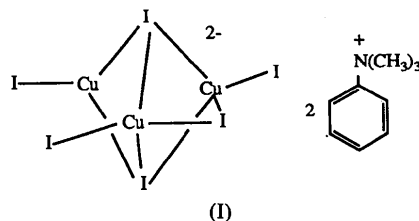
There is no obvious relationship to any of the motifs of higher copper content. The bridged tetrahedron of Cu atoms seen in $Cu_4X_6^{2-}$, isolated with $X = I$ and triphenylmethylphosphonium (Bowmaker, Clark & Yuen, 1976) and K[12-crown-4] (Rath & Holt 1985) cations, and with $X = Br$ and butyltriphenylphosphonium (Andersson & Jagner, 1986) and tetrapropylammonium (Asplund & Jagner, 1984) cations, is unrelated, as are the corner-sharing rhombohedra of tris(tetrapropylammonium)Cu_4I_7 (Hartl, Brudgam & Mahdjour, 1990) and $[Co(C_5H_5)_2]_4[Cu_4I_8]$ (Hartl, 1987), and the pentagons of Cu atoms, edge bridged and doubly face capped by halide atoms, as seen in bis(tetrapropylammonium)Cu_5I_7 (Hartl & Abadi, 1984) and bis(methyltributylammonium)Cu_5Br_7 (Andersson & Jagner, 1988). Cu_6X_{11}, a trigonal prism with five face-capping I atoms and a terminal I atom bound to each Cu atom, has been observed only with $X = I$ {hexakis(tetraethylammonium)$(Cu_6I_{11})I$ (Abadi, Hartl & Fuchs, 1984) and $[Co(C_5H_5)_2]_9(Cu_6I_{11})(Cu_6I_8)_2$ (Hartl & Brudgam, 1989)}. Similarly, the known motifs with greater copper content, $[K_7(12$-crown-$4)]_6(Cu_8I_{13})(Cu_4I_6)$ (Rath & Holt, 1985), $[N,N$-(dimethyl)isopropylideneammonium]$_5Cu_8I_{13}$ (Herrschaft, 1990) and (pyridinium)$_{24}(Cu_{36}I_{56})I_4$ (Hartl & Fuchs, 1986), are known only with $X = I$. However, there are known $X = Br$ and $X = Cl$ varieties of higher copper stoichiometry, such as $[Co(NH_3)_6]_4(Cu_5Cl_{16})Cl$ (Murray-Rust, Day & Prout, 1966), tris(methyltriethylammonium)Cu_6Br_9 (Andersson & Jagner, 1989), tetrakis(phenyltrimethylammonium)Cu_6Br_{10} (Hu & Holt, 1994) and $Rb_4Cu_9Cl_{13}$ (Gaines & Geller, 1986).
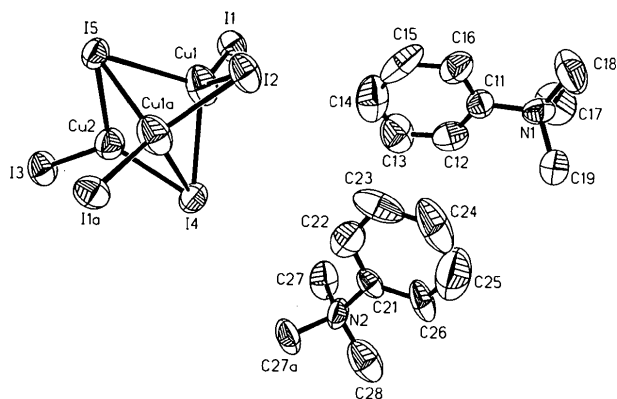
Fig. 1. Projection of the structure of tris(trimethylphenylammonium) hexaiodotricuprate(I).

Experimental

Trimethylphenylammonium iodide (0.26 g, 1 mmol) and CuI (0.19 g, 1 mmol) were added to 10 ml of diethylglycol. The resulting mixture was heated until the solid material dissolved and was then cooled to room temperature. Acetone (30 ml) was added and the resulting solution heated under reflux for 4 h. After cooling to room temperature, filtering and cooling to 278 K for 48 h, light yellow rhombic crystals were seen to form.

Crystal data

$(C_9H_{14}N)_3[Cu_3I_6]$
$M_r = 1360.7$
Orthorhombic
$Pnma$
$a = 26.364$ (2) Å
$b = 15.055$ (2) Å
$c = 10.027$ (1) Å
$V = 3979.7$ (6) Å^3
$Z = 4$
$D_x = 2.271$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 56 reflections
$\theta = 3.5-25.0°$
$\mu = 6.263$ mm^{-1}
$T = 298$ (2) K
Rhombohedron
$0.6 \times 0.5 \times 0.4$ mm
Light yellow

Data collection

Siemens $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: semi-empirical
$T_{min} = 0.025$, $T_{max} = 0.055$
4605 measured reflections
3439 independent reflections
1759 observed reflections
$[F > 4\sigma(F)]$

$R_{int} = 0.0350$
$\theta_{max} = 22.5°$
$h = -1 \rightarrow 31$
$k = -17 \rightarrow 1$
$l = -1 \rightarrow 11$
3 standard reflections monitored every 97 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.0426$
$wR = 0.0446$
$S = 0.91$
1759 reflections
197 parameters
H atoms refined using a riding model
$w = 1/[\sigma^2(F) + 0.0006F^2]$
$(\Delta/\sigma)_{max} = 0.070$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Extinction correction: SHELXS86 (Sheldrick, 1990)
Extinction coefficient: 0.00010 (1)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu1	0.1233 (1)	0.1642 (1)	0.2266 (2)	0.081 (1)
Cu2	0.0463 (1)	1/4	0.3808 (3)	0.066 (1)
I1	0.1114 (1)	−0.0003 (1)	0.2458 (1)	0.063 (1)
I2	0.1909 (1)	1/4	0.0802 (2)	0.070 (1)
I3	−0.0338 (1)	1/4	0.5160 (2)	0.077 (1)
I4	0.1363 (1)	1/4	0.4801 (1)	0.065 (1)
I5	0.0369 (1)	1/4	0.1255 (1)	0.056 (1)
N1	0.4287 (4)	−0.0257 (8)	0.2531 (12)	0.062 (4)
N2	0.2910 (5)	1/4	0.7217 (16)	0.053 (6)
C11	0.3740 (4)	0.0013 (9)	0.2471 (17)	0.055 (5)
C12	0.3476 (6)	−0.0040 (9)	0.3658 (17)	0.068 (6)
C13	0.2975 (7)	0.0211 (12)	0.3703 (22)	0.092 (9)
C14	0.2753 (7)	0.0509 (12)	0.2578 (28)	0.101 (9)
C15	0.3021 (7)	0.0542 (11)	0.1363 (21)	0.094 (8)
C16	0.3512 (6)	0.0290 (10)	0.1354 (17)	0.071 (6)
C17	0.4348 (6)	−0.1180 (11)	0.3043 (17)	0.106 (9)
C18	0.4538 (6)	−0.0205 (12)	0.1187 (16)	0.103 (9)
C19	0.4575 (5)	0.0351 (13)	0.3465 (18)	0.121 (10)
C21	0.3218 (7)	1/4	0.5963 (20)	0.045 (7)
C22	0.2970 (9)	1/4	0.4801 (28)	0.081 (10)
C23	0.3243 (12)	1/4	0.3594 (23)	0.092 (12)
C24	0.3774 (12)	1/4	0.3725 (38)	0.117 (16)
C25	0.4003 (11)	1/4	0.4962 (44)	0.132 (18)
C26	0.3735 (7)	1/4	0.6042 (28)	0.072 (10)
C27	0.2581 (4)	0.1681 (9)	0.7304 (14)	0.072 (6)
C28	0.3247 (7)	1/4	0.8482 (21)	0.083 (10)

Table 2. *Selected geometric parameters* (Å, °)

Cu1···Cu2	2.861 (3)	Cu1···Cu1^i	2.584 (4)
Cu1—I1	2.504 (2)	Cu2—I3	2.507 (3)
Cu1—I2	2.646 (2)	Cu2—I4	2.573 (3)
Cu1—I4	2.871 (2)	Cu2—I5	2.572 (3)
Cu1—I5	2.808 (2)	Cu2···Cu1^i	2.861 (3)
Cu2···Cu1—I1	108.4 (1)	Cu1···Cu2—I4	63.5 (1)
Cu2···Cu1—I2	123.9 (1)	I3—Cu2—I4	124.5 (1)
I1—Cu1—I2	127.6 (1)	Cu1···Cu2—I5	62.0 (1)
Cu2···Cu1—I4	53.3 (1)	I3—Cu2—I5	117.2 (1)
I1—Cu1—I4	113.1 (1)	I4—Cu2—I5	118.2 (1)
I2—Cu1—I4	101.0 (1)	Cu1···Cu2···Cu1^i	53.7 (1)
Cu2···Cu1—I5	54.0 (1)	Cu1—I4—Cu2	63.1 (1)
I1—Cu1—I5	112.4 (1)	Cu1—I4—Cu1^i	53.5 (1)
I2—Cu1—I5	97.0 (1)	Cu1—I5—Cu2	64.1 (1)
I4—Cu1—I5	102.1 (1)	Cu1—I5—Cu1^i	54.8 (1)
Cu1···Cu2—I3	152.8 (1)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

Data collection, cell refinement and data reduction: Siemens *XSCANS*. Structure solution and refinement: *SHELXS86* (Sheldrick, 1990). Molecular graphics: *SHELXS86*. Software used to prepare material for publication: *SHELXS86*. Dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 4.2.4.2, respectively).

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Bis[aqua(15-crown-5)sodium] Bis[(15-crown-5)sodium] Hexaiodotetracopper(I) Tetraiododicopper(I)

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Abstract

$[Na(C_{10}H_{20}O_5)]_2[Na(C_{10}H_{20}O_5)(H_2O)]_2[Cu_2I_4][Cu_4I_6]$ crystallizes with two different copper(I) halide motifs in the unit cell: a polymer of edge-sharing Cu_2I_2 rhombs in which the tetrahedral Cu atoms of every second rhomb are bridged by an additional I atom (which projects alternately up and down) [Cu—I 2.706 (3) Å average] and a discrete planar rhomb in which two trigonal planar Cu

atoms, each of which is bonded to a terminal I atom [Cu—I$_{terminal}$ 2.484 (3) Å], are bridged by another two I atoms [Cu—I$_{bridging}$ 2.572 (4) Å average]. While both motifs have been seen independently in other crystalline materials, the observation of the two in one material is highly unusual. Four 15-crown-5 rings, each coordinated to an Na atom [Na—O 2.42 (2) Å average], balance the charge within the asymmetric unit. Two of the Na(15-crown-5) groups have a water molecule coordinated to the metal atom [Na—O 2.29 (2) Å]. The remaining two Na(15-crown-5) groups display Na···I$_{terminal}$ distances of 3.220 (8) Å. In the crown ether the average C—O distance is 1.392 (3) Å and the average C—C distance is 1.48 (5) Å. Cu···Cu separations are 2.472 Å when the two Cu atoms have three bridging I atoms (within the polymeric unit) and average 2.660 (5) Å when the pair of Cu atoms are bridged only by two I atoms (as seen in the polymeric unit and the discrete dimer).

Comment

Many copper halide complexes of the formula $Cu_y^I X_z^{-(z-y)}$, where X = Cl, Br, I, have been identified. They may be discrete, for example, tetrahedral $Cu_4X_6^{2-}$ or rhombohedral $Cu_2I_4^{2-}$, or polymeric $(Cu_2I_3)_x$ (Jagner & Helgesson, 1991). While the incidence of the copper halide motif is apparently influenced by the size and shape of the cation, there are many cases where the same cation is observed with different copper halide motifs in different crystals and, indeed, a synthetic product often contains several of these. However, it is very unusual to observe more than one copper halide motif within the same unit cell, as in the title compound (I) (Fig. 1). $K_7(12\text{-crown-4})_6Cu_4I_6^{2-}(Cu_8I_{13})^{5-}$ (Rath & Holt, 1985), in which two discrete copper(I) halide clusters exist in the asymmetric unit with a tetrahedron of Cu atoms with edge-bridging I atoms and a cubic arrangement of eight Cu atoms centered about an I atom with all cube edges bridged by an I atom, is the only other known example.
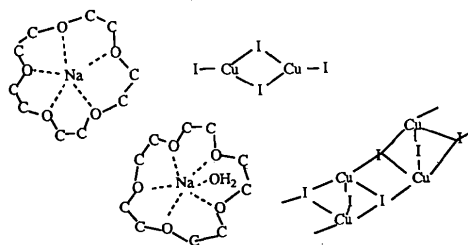
The $Cu_2I_3^-$ motif, a polymeric series of edge-sharing Cu_2I_2 rhombs with alternate rhombs bridged by an additional I atom, exists as two versions in the literature differing in the pattern of direction of projection of the bridging I atom. An alternating 'up, down, up, down' pattern of projection has been observed for (tetramethylammonium)Cu_2I_3 (Andersson & Jagner,