Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BR1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abadi, F. M. H., Hartl, H. & Fuchs, J. (1984). *Angew. Chem.* **96**, 497.
Andersson, S. & Jagner, S. (1986). *Acta Chem. Scand. Ser. A*, **40**, 210–217.
Andersson, S. & Jagner, S. (1988). *J. Crystallogr. Spectrosc. Res.* **18**, 591–600.
Andersson, S. & Jagner, S. (1989). *Acta Chem. Scand. Ser. A*, **43**, 39–43.
Asplund, M. & Jagner, S. (1984). *Acta Chem. Scand. Ser. A*, **38**, 725–730.
Bowmaker, G. A., Clark, G. R. & Yuen, D. K. P. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2329–2334.
Gaines, J. M. & Geller, S. (1986). *J. Electrochem. Soc.* **133**, 1501–1507.
Hartl, H. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 927–928.
Hartl, H. & Abadi, F. M. H. (1984). *Angew. Chem.* **96**, 359–360.
Hartl, H. & Brudgam, I. (1989). *Z. Naturforsch. Teil B*, **44**, 936–941.
Hartl, H., Brudgam, I. & Mahdjour, F. (1990). *28th Int. Conf. Coord. Chem.* pp. 5–34.
Hartl, H. & Fuchs, J. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 569–570.
Herrschaft, G. (1990). PhD thesis, Freie Universitat, Berlin, Germany.
Hu, G. & Holt, E. M. (1994). *Acta Cryst.* C**50**. In the press.
Jagner, S. & Helgesson, G. (1991). *Adv. Inorg. Chem.* **37**, 1–41.
Murray-Rust, P., Day, P. & Prout, C. K. (1966). *J. Chem. Soc. Chem. Commun.* pp. 277–278.
Rath, N. P. & Holt, E. M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 665–667.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Acta Cryst. (1994). C**50**, 1578–1580

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

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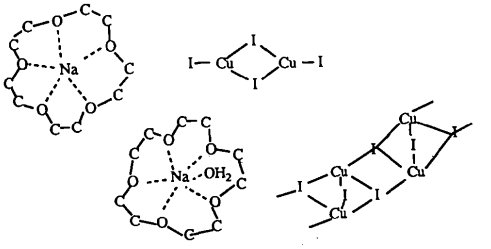
(*Received* 13 *December* 1993; *accepted* 18 *May* 1994)

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 $Cu^I_yX_z^{-(z-y)}$, 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-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,

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1985*a*), (tetraethylammonium)Cu_2I_3 and [dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium]Cu_2I_3 (Hartl & Mahdjour-Hassan-Abadi, 1981). The title structure is of this type (Fig. 2). However, (2,4,6-triphenylthiopyrylium)Cu_2I_3 (Batsanov, Struchkov, Ukhin & Dolgopolova, 1982) and K(15-crown-5)Cu_2I_3 (Rath & Holt, 1985) both display an 'up, up, down, down' bridging pattern. Each of these structures displays a weak ionic interaction with the bridging I atom (in the former, S···I, and K···I in the latter) which undoubtedly influences the conformation of the polymer.

Both conformations display Cu···Cu separations across rhombs which are shorter when the pair of Cu atoms is bridged by three I atoms and longer when the rhomb lacks the third bridging I atom.

Cu_2X_4 has been observed in the solid state for Cl, Br and I, while the Cu_2X_3 motif is known only with X = I.

As the terminal Cu—X distance is always shorter than the bridging Cu—X distance, the Cu—X—Cu bridge sometimes displays unequal bond distances. Flexibility of the rhomb is indicated by the range of Cu···Cu separations observed: 2.660 (3)–2.937 (3) Å. The rhomb may be planar or folded about the bridging halide atoms. Planar rhombs are observed in [VO(SALen)H_2O]$_2Cu_2Cl_4$ (Banci, Bencini, Dei & Gatteschi, 1984), bis(phenyltrimethylammonium)Cu_2Br_4 (Andersson & Jagner, 1985*b*), bis(methyltriphenylphosphonium)Cu_2Br_4 (Andersson & Jagner, 1987*b*), bis(tetraethylammonium)Cu_2Br_4 (Asplund & Jagner, 1984*a*), bis(tetraethylphosphonium)Cu_2Br_4 (Andersson & Jagner, 1987*a*), TTTCu_2Br_4 (Shibaeva & Kaminskii, 1981), bis(tetrabutylammonium)Cu_2I_4 (Asplund, Jagner & Nilsson, 1982) and bis(tetrapropylammonium)Cu_2I_4 (Asplund & Jagner, 1984*b*), whereas bis(tetraphenylarsoniumonium)Cu_2I_4 (Asplund & Jagner, 1984*b*) displays a fold angle of 146.61 (4)° and both planar and nonplanar (fold angle 146.34°) bis(tetraphenylphosphonium)-Cu_2I_4 (Hartl, Brudgam & Mahjour-Hassan-Abadi, 1985) have been reported.

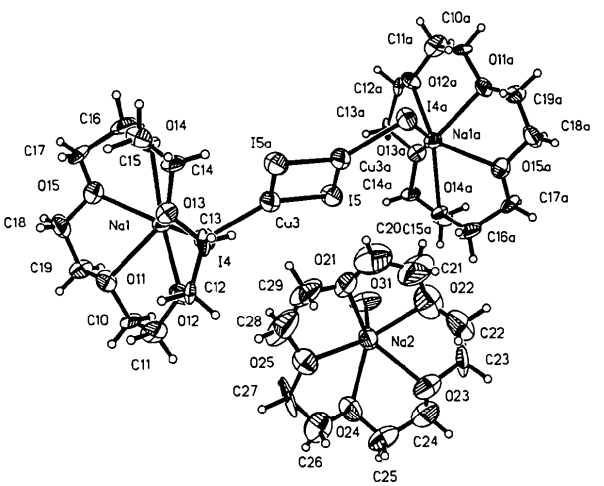

Fig. 1. Projection view of [Na(15-crown-5)]$_2$[Na(15-crown-5)(H_2O)]$_2$-[Cu_2I_4][Cu_4I_6]$_x$. Displacement ellipsoids are plotted at the 50% probability level.

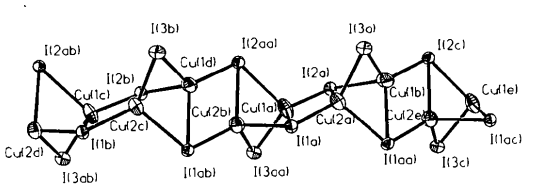

Fig. 2. View of the [Cu_4I_6]$_x$ polymer. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

CuI (0.38 g, 2 mmol) was dissolved in 20 ml of saturated NaI solution with ascorbic acid added to retard copper oxidation. Acetone (20 ml) and 15-crown-5 (1 ml, 5 mm) were added resulting in a yellow solution which was heated to reflux under nitrogen for 5 h, cooled to ambient temperature and filtered. Colorless needles formed on cooling the filtrate to 278 K for 48 h.

Crystal data

[$Na(C_{10}H_{20}O_5)$]$_2$[$Na(C_{10}H_{20}O_5)(H_2O)$]$_2$[$Cu_2I_4$][$Cu_4I_6$]
M_r = 2659.36
Monoclinic
$P2_1/c$
a = 14.046 (3) Å
b = 33.013 (7) Å
c = 8.425 (2) Å
β = 96.11 (3)°
V = 3884.5 (15) Å^3
Z = 2
D_x = 2.273 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 21 reflections
θ = 6.79–10.634°
μ = 5.631 mm^{-1}
T = 295 (2) K
Needle
0.4 × 0.3 × 0.2 mm
Colorless

Data collection

Siemens $P3$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.352, T_{max} = 0.794
9004 measured reflections
6829 independent reflections
1887 observed reflections [$F > 4\sigma(F)$]
R_{int} = 0.0563
θ_{max} = 25.00°
$h = -16 \rightarrow 16$
$k = -39 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections monitored every 97 reflections
intensity variation: 0.009%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0690
$wR(F^2)$ = 0.1673
S = 1.197
6778 reflections
370 parameters
H atoms refined using a riding model
$w = 1/[\sigma^2(F_o^2) + (0.0896P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.030
$\Delta\rho_{max}$ = 1.821 e Å^{-3}
$\Delta\rho_{min}$ = −1.003 e Å^{-3}
Extinction correction: negligble
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}
I1	0.3005 (1)	0.7313 (1)	0.0456 (2)	0.050 (1)
I2	0.5668 (1)	0.7759 (1)	0.3699 (2)	0.054 (1)
I3	0.4424 (1)	0.6581 (1)	0.4338 (2)	0.062 (1)
I4	0.1389 (1)	0.4202 (1)	0.2899 (2)	0.080 (1)
I5	0.0553 (1)	0.5482 (1)	0.3552 (2)	0.084 (1)
Cu1	0.4753 (2)	0.7733 (1)	0.0948 (4)	0.095 (1)
Cu2	0.3996 (2)	0.7311 (1)	0.3167 (3)	0.081 (1)
Cu3	0.0496 (2)	0.4728 (1)	0.4241 (4)	0.078 (1)
Na1	0.0670 (5)	0.3534 (2)	0.5288 (10)	0.062 (2)
O11	0.1873 (9)	0.3045 (5)	0.4837 (17)	0.068 (4)
O12	0.1988 (9)	0.3497 (4)	0.7444 (17)	0.062 (4)
O13	0.0158 (9)	0.3326 (5)	0.7858 (17)	0.066 (4)
O14	−0.1054 (8)	0.3446 (4)	0.5125 (18)	0.061 (4)
O15	0.0088 (10)	0.3080 (5)	0.3055 (17)	0.075 (4)
C10	0.2735 (13)	0.3228 (7)	0.5289 (28)	0.072 (7)
C11	0.2785 (15)	0.3286 (7)	0.6991 (24)	0.074 (7)
C12	0.1773 (15)	0.3420 (8)	0.8952 (27)	0.077 (7)
C13	0.0733 (14)	0.3553 (7)	0.9056 (25)	0.070 (7)
C14	−0.0844 (12)	0.3385 (7)	0.7877 (27)	0.069 (6)
C15	−0.1350 (14)	0.3210 (7)	0.6404 (28)	0.069 (7)
C16	−0.1411 (14)	0.3313 (8)	0.3600 (30)	0.082 (8)
C17	−0.0817 (13)	0.2947 (7)	0.3001 (26)	0.069 (7)
C18	0.0794 (14)	0.2783 (7)	0.2681 (30)	0.075 (7)
C19	0.1758 (14)	0.2942 (8)	0.3092 (25)	0.072 (7)
Na2	0.3481 (6)	0.5424 (3)	0.7462 (10)	0.072 (2)
O21	0.2072 (15)	0.5076 (7)	0.8119 (24)	0.108 (6)
O22	0.2550 (22)	0.5826 (8)	0.9020 (32)	0.155 (10)
O23	0.4495 (12)	0.5851 (7)	0.9163 (23)	0.108 (6)
O24	0.5151 (15)	0.5293 (8)	0.7248 (25)	0.121 (8)
O25	0.3762 (15)	0.4707 (6)	0.7778 (26)	0.112 (6)
O31	0.2999 (11)	0.5693 (7)	0.5004 (21)	0.115 (7)
C20	0.1500 (31)	0.5250 (18)	0.9003 (69)	0.223 (27)
C21	0.1693 (26)	0.5643 (17)	0.9442 (62)	0.222 (30)
C22	0.3013 (26)	0.6043 (12)	1.0127 (40)	0.128 (13)
C23	0.4034 (29)	0.6189 (8)	0.9566 (34)	0.135 (15)
C24	0.5337 (21)	0.5931 (11)	0.8510 (42)	0.126 (13)
C25	0.5802 (24)	0.5514 (17)	0.8106 (48)	0.190 (24)
C26	0.5373 (25)	0.4878 (11)	0.7388 (43)	0.131 (12)
C27	0.4634 (28)	0.4641 (10)	0.6853 (45)	0.140 (14)
C28	0.2962 (32)	0.4507 (12)	0.7405 (55)	0.206 (24)
C29	0.2165 (22)	0.4656 (12)	0.8151 (55)	0.165 (18)

Table 2. *Selected geometric parameters* (Å)

I1—Cu2	2.545 (3)	I4—Cu3	2.484 (3)
I1—Cu2^{i}	2.787 (3)	I4···Na1	3.220 (8)
I1—Cu1	2.811 (3)	I5—Cu3	2.557 (4)
I2—Cu1	2.530 (3)	I5—Cu3^{iii}	2.587 (3)
I2—Cu2	2.771 (3)	Cu1···Cu2^{i}	2.472 (4)
I2—Cu1^{ii}	2.897 (4)	Cu1···Cu2	2.643 (4)
I3—Cu2	2.649 (4)	Cu3···Cu3^{iii}	2.678 (6)
I3—Cu1^{ii}	2.655 (4)		

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $-x, 1-y, 1-z$.

Data collection, cell refinement and data reduction: Siemens *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXS*86. Software used to prepare material for publication: *SHELXL*93. Extinction effects were observed to be negligble. Absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Table 4.2.4.2).

The authors acknowledge NSF grant EHR-9108771.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Andersson, S. & Jagner, S. (1985*a*). *Acta Chem. Scand. Ser. A*, **39**, 181–186.
Andersson, S. & Jagner, S. (1985*b*). *Acta Chem. Scand. Ser. A*, **39**, 423–428.
Andersson, S. & Jagner, S. (1987*a*). *Acta Chem Scand. Ser. A*, **41**, 230–236.
Andersson, S. & Jagner, S. (1987*b*). *Acta Chem Scand. Ser. C*, **43**, 1089–1091.
Asplund, M. & Jagner, S. (1984*a*). *Acta Chem. Scand. Ser. A*, **38**, 135–139
Asplund, M. & Jagner, S. (1984*b*). *Acta Chem. Scand. Ser. A*, **38**, 297–301
Asplund, M., Jagner, S. & Nilsson, M. (1982). *Acta Chem. Scand.* **A36**, 751–755
Banci, L., Bencini, A., Dei, A. & Gatteschi, D. (1984). *Inorg. Chim. Acta*, L11–L12.
Batsanov, A. S., Struchkov, Yu. T., Ukhin, L. Yu. & Dolgopolova, N. A. (1982). *Inorg. Chim. Acta*, **63**, 17–22.
Hartl, H., Brudgam, I. & Mahjour-Hassan-Abadi, F. (1985). *Z. Naturforsch. Teil B*, **40**, 1032–1039.
Hartl, H. & Mahdjour-Hassan-Abadi, F. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 772–773.
Jagner, S. & Helgesson, G. (1991). *Adv. Inorg. Chem.* **37**, 1–41.
Rath, N. P. & Holt, E. M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 665–667.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
Shibaeva, R. P. & Kaminskii, V. F. (1981). *Sov. Phys. Crystallogr.* **26**, 188–190.

Acta Cryst. (1994). C**50**, 1580–1582

3,5-Diphenyl-1,2-dithiolium Diiodoauride(I)

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(*Received* 30 *July* 1993; *accepted* 18 *January* 1994)

Abstract

The title complex, $(C_{15}H_{11}S_2)[AuI_2]$, consists of a 3,5-diphenyldithiolium cation and a diiodoauride anion. The Au^I center is linearly coordinated by two I atoms.