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Bis[bis(12-crown-4)potassium] hexaiodotetracuprate(I)

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Key indicators

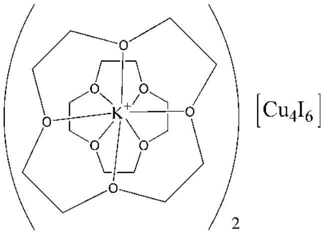
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.006 Å
R factor = 0.027
wR factor = 0.061
Data-to-parameter ratio = 22.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

From 12-crown-4, KI, and CuI in an acetone solution, the title compound, $[K(C_{16}H_{32}O_8)_2]_2[Cu_4I_6]$, was obtained. It consists of sandwich-type $[(12\text{-crown-}4)_2K]^+$ complex cations and polymeric $[Cu_4I_6]^{2-}$ anions. The latter consist of CuI_4 tetrahedra, which share edges and faces to form infinite chains.

Comment

Iodocuprates exhibit a wealth of structures with quite a number of different structural motifs. Depending on the nature of the counter-ion, different coordination numbers are realized: coordination number 2 in compounds such as (18-crown-6)$KCuI_2$ (Rath & Holt, 1986), which contains infinite zigzag $KCuI_2$ chains, and coordination number 3 in trigonal-planar CuI_3 groups. The latter are present in compounds such as methyltriphenylphosphonium diiodocuprate (Bowmaker *et al.*, 1984) and cobaltocenium triiodocuprate (Hartl & Bruedgam, 1989). The most common structural motif is, however, the more or less distorted tetrahedral environment. These CuI_4 tetrahedra can be linked in many different ways; numerous different structures can be obtained, from small iodocuprate clusters such as $(Cu_3I_6)^{3-}$ in tris(trimethylphenylammonium) hexaiododicuprate(I) (Hu & Holt, 1994*a*) to chain structures. In the latter, different geometries of chains of the basic composition $[Cu_2I_3]^-$ or $[Cu_4I_6]^{2-}$ are most common and can be found in structures such as bis[aqua(15-crown-5)sodium] bis[(15-crown-5)sodium] hexaiodotetracuprate(I) tetraiododicuprate(I) (Hu & Holt, 1994*b*) and tetramethylammonium triiododicuprate(I) (Andersson & Jagner, 1985).



(I)

In our investigation of possible electrolytes for use in photoelectrochemical solar cells, we obtained crystals of the title compound, $[(12\text{-crown-}4)_2K]_2[Cu_4I_6]$, (I), from a solution of potassium iodide, copper iodide and 12-crown-4 in acetone. It is interesting to note that a completely different compound had been obtained previously from essentially the same reaction medium (Rath & Holt, 1986). The title compound contains two crystallographically independent $[(12\text{-crown-}4)_2K]^+$ complex cations, whose geometry is unexceptional. The

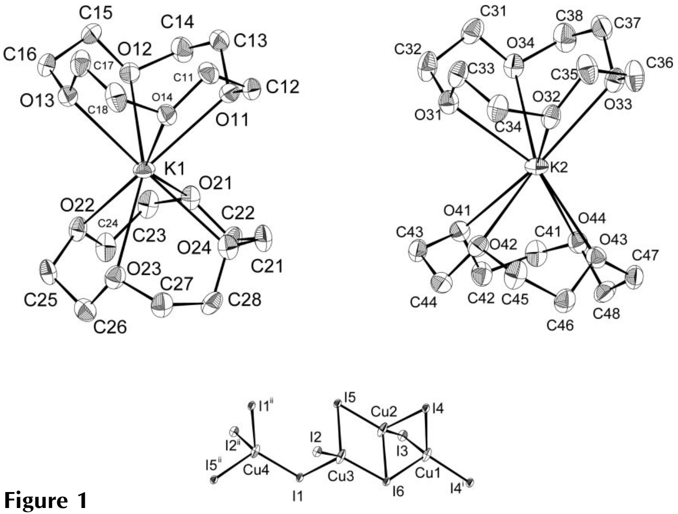


Figure 1

The $[(12\text{-crown-}4)_2K]^+$ cations and the ${}^1_\infty[Cu_4I_6]^{2-}$ anions in the structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atom have been omitted.

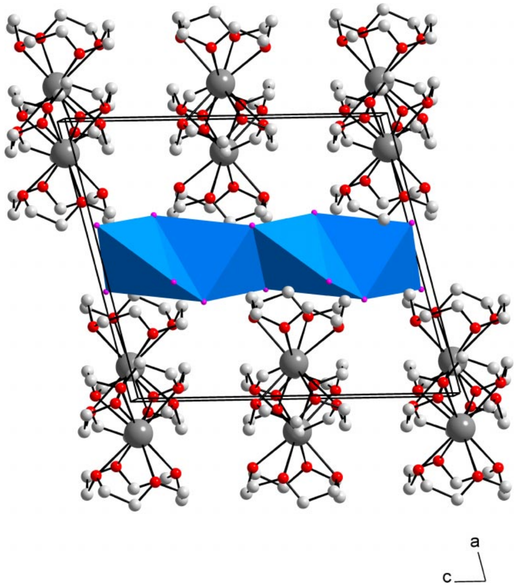


Figure 2

The contents of the unit cell of (I), viewed along *b*, with CuI_4 tetrahedra in the polyhedral representation. H atoms have been omitted.

anion, ${}^1_\infty[Cu_4I_6]^{2-}$, contains four crystallographically independent Cu^+ ions that are each coordinated by four iodide ions. I1, I3, I4, and I5 function as bridging ligands, coordinating to two Cu^+ ions each, whereas I2 is coordinated to Cu3 only and I6 coordinates to three Cu^+ ions. The Cu—I bond lengths are between 2.5449 (5) and 2.8516 (5) Å, and, thus, in the same range as in other iodocuprates. The CuI_4 tetrahedra are rather distorted and some of the I—Cu—I angles deviate by as much as 15° from the ideal value.

Experimental

Potassium iodide (2 g, 12 m*M*), 12-crown-4 (0.88 g, 5 m*M*) and copper(I) iodide (1 g, 5 m*M*) were dissolved in acetone (50 ml). The solution was stored for a week in a crystallization bowl at 252 K. After this time, potassium iodide had crystallized. From the yellow solution obtained upon filtering off the precipitate, single crystals of the title compound were obtained within one day by evaporation of the solvent at room temperature.

Crystal data

$[K(C_{16}H_{32}O_8)_2]_2[Cu_4I_6]$
$M_r = 1798.63$
Triclinic, $P\bar{1}$
$a = 14.5859\ (1)$ Å
$b = 14.6371\ (1)$ Å
$c = 15.6526\ (2)$ Å
$\alpha = 67.4428\ (5)^\circ$
$\beta = 69.0664\ (4)^\circ$
$\gamma = 64.1181\ (4)^\circ$
$V = 2703.11\ (4)$ Å^3

$Z = 2$
$D_x = 2.210$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34261 reflections
$\theta = 4.1\text{–}27.5^\circ$
$\mu = 5.19$ mm^{-1}
$T = 150$ K
Irregular, colourless
0.30 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997).
$T_{\min} = 0.463$, $T_{\max} = 0.745$
62318 measured reflections

12337 independent reflections
10176 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 27.5^\circ$
$h = -18 \rightarrow 18$
$k = -19 \rightarrow 19$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.061$
$S = 1.03$
12337 reflections
541 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 5.5412P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.88$ e Å^{-3}
$\Delta\rho_{\min} = -1.68$ e Å^{-3}

Table 1

Selected interatomic distances (Å).

Cu1—I4$^{\rm i}$	2.5449 (5)	K1—O21	2.705 (2)
Cu1—I3	2.6207 (5)	K1—O13	2.721 (2)
Cu1—I6	2.7514 (5)	K1—O23	2.754 (3)
Cu1—I4	2.8516 (5)	K1—O24	2.754 (3)
Cu2—I5	2.5451 (5)	K1—O14	2.764 (2)
Cu2—I3	2.6330 (5)	K1—O11	2.770 (2)
Cu2—I4	2.7665 (6)	K1—O12	2.776 (3)
Cu2—I6	2.7871 (5)	K1—O22	2.795 (3)
Cu3—I6	2.5431 (5)	K2—O32	2.708 (2)
Cu3—I2	2.6320 (5)	K2—O44	2.737 (2)
Cu3—I1	2.7624 (6)	K2—O41	2.752 (2)
Cu3—I5	2.8264 (6)	K2—O34	2.757 (3)
Cu4—I1	2.5511 (5)	K2—O31	2.769 (3)
Cu4—I2$^{\rm ii}$	2.6293 (5)	K2—O42	2.771 (3)
Cu4—I5$^{\rm ii}$	2.7483 (5)	K2—O33	2.775 (3)
Cu4—I1$^{\rm ii}$	2.8296 (5)	K2—O43	2.776 (3)

Symmetry codes: (i) $1-x, 2-y, -z$; (ii) $1-x, 1-y, 1-z$.

H atoms were placed in calculated positions (C—H = 0.96 Å) and were refined using a riding-model approximation, with $U_{\rm iso}$ equal to $1.2U_{\rm eq}$ of the carrier atom. The highest peak and the deepest hole in the difference map are located 0.82 and 0.73 Å, respectively, from Cu2.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: maXus (Mackay *et al.*, 1999).

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