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Structure of the Thallium-Rich Complex $[(Tl18\text{-crown-}6)_4CuBr_4][TlBr_4]_2$

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Abstract. Tetrakis[1,4,7,10,13,16-hexaoxacyclooctadecanethallium(I)] tetrabromocuprate(II) bis[tetrabromothallate(III)], $[TlC_{12}H_{24}O_6]_4[CuBr_4][TlBr_4]_2$, $M_r = 3306.0$, cubic, $F23$, $a = 20.897\,(2)$ Å, $V = 9125.6\,(9)$ Å^3, $Z = 4$, $D_m = 2.38$, $D_x = 2.406$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 161.6$ cm^{-1}, $F(000) = 6044$, $T = 295$ K, $R = 0.047$ for 604 unique observed $[I > \sigma(I)]$ reflections and 71 parameters. The two $TlBr_4^-$ [Tl—Br = 2.536 (2) and 2.553 (2) Å] and one $CuBr_4^{2-}$ [Cu—Br = 2.311 (2) Å] anions occupy sites of 23 symmetry, $CuBr_4^{2-}$ being tetrahedrally surrounded by Tl(18-crown-6)$^+$ cations on threefold axes. Thallium(I) in Tl(18-crown-6)$^+$ lies 0.9823 (7) Å out of the best plane of the six O atoms, towards $CuBr_4^{2-}$, forming contacts Tl···Br = 3.5629 (9) and Tl···Cu = 3.5893 (8) Å.

Experimental. The complex $[(Tl18c6)_4CuBr_4][TlBr_4]_2$ was prepared from 18-crown-6 (18c6), thallium(I) bromide and copper bromide in methanol using a method described previously for the chloro isomorphs (Kahwa, Miller, Mitchel, Fronczek, Goodrich, Williams, O'Mahoney, Slawin, Ley & Groombridge, 1992). The density was measured by the flotation technique using a mixture of diiodomethane ($D = 3.325$ g cm^{-3}) and bromochloromethane ($D = 1.991$ g cm^{-3}). A black square-prism crystal, 0.18 × 0.30 × 0.30 mm, was mounted on a CAD-4 diffractometer equipped with a graphite monochromator and Mo $K\alpha$ source. Cell dimensions were determined from the setting angles of 25 reflections having $10 < \theta < 12°$. Data were collected by ω–2θ scans of variable rate (0.63–4.0° min^{-1}) over an octant defined by $1 < \theta < 32°$, $0 \le h \le 31$, $0 \le k \le 31$, $0 \le l \le 31$, h, k and l all odd or all even. A total of 4358 reflections were measured, yielding 1419 unique data ($R_{\text{int}} = 0.034$), and 604 reflections having $I > 1\sigma(I)$ were considered observed and used in the refinement. Three standard reflections (600, 060,006) were monitored periodically and exhibited a 4.0% decrease in intensity, for which a linear correction was applied. Data reduction included corrections for background, Lorentz and polarization effects. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 78.1% and maximum 99.1%. The title compound was found to be isostructural with the complex $[(Tl18c6)_4CuCl_4][TlCl_4]_2$ (Kahwa *et al.*, 1992), and coordinates from that structure were used as an initial refinement model. The H atoms were idealized, assigned isotropic parameters ($B = 1.3\,B_{\text{eq}}$ of attached C atom) with C—H constrained to 0.95 Å, and allowed to ride on their parent C atoms. Non-H atoms were refined by full-matrix least squares, minimizing

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

$$B_{\text{eq}} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Tl1	0.65083 (6)	$1-x$	x	5.19 (1)
Tl2	1	1	1	3.65 (7)
Tl3	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	3.54 (7)
Cu	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	8.0 (4)
Br1	0.1861 (2)	$1-x$	$1-x$	12.92 (7)
Br2	0.9299 (1)	x	x	5.43 (3)
Br3	0.8205 (1)	x	x	5.18 (3)
O1	0.5260 (7)	0.2877 (7)	0.6530 (9)	5.4 (4)
O4	0.5917 (8)	0.2763 (8)	0.5355 (8)	5.6 (5)
C2	0.499 (1)	0.260 (1)	0.598 (1)	6.0 (6)
C3	0.552 (2)	0.228 (1)	0.561 (1)	12 (1)
C5	0.647 (1)	0.256 (2)	0.502 (1)	6.2 (7)
C6	0.679 (1)	0.313 (1)	0.474 (1)	4.5 (6)

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Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Tl1—Br1	3.5629 (9)	O1—Tl1—O1	113.8 (5)
Tl2—Br2	2.536 (2)	O4—Tl1—O4	105.5 (5)
Tl3—Br3	2.553 (2)	O1—Tl1—O4	55.9 (5)
Cu—Br1	2.311 (2)	O1—Tl1—O4	142.0 (5)
Cu—Tl1	3.5893 (8)	Br1—Tl1—Br1	64.0 (1)
Tl1—O1	2.91 (2)	O1—C2—C3	108 (2)
Tl1—O4	3.11 (2)	O4—C3—C2	109 (2)
O1—C2	1.40 (3)	O4—C5—C6	110 (2)
O1—C6	1.47 (3)	O1—C6—C5	109 (2)
O4—C3	1.41 (4)	C2—O1—C6	108 (2)
O4—C5	1.41 (3)	C3—O4—C5	118 (2)
C2—C3	1.49 (4)		
C5—C6	1.47 (4)		

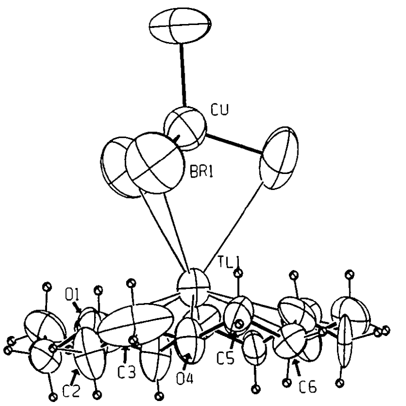

Fig. 1. *ORTEP* (Johnson, 1965) view of the Tl18c6$^+$ cations coordinated to the $CuBr_4^{2-}$ anion. Note the large thermal ellipsoids of Cu, Br1 and C3.

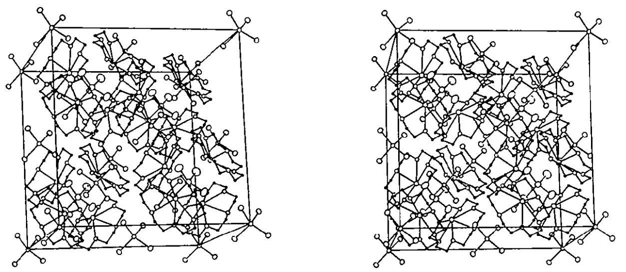

Fig. 2. Stereoview of the unit cell, illustrating the packing of ions.

$\sum w(|F_o| - |F_c|)^2$, with weights $w = 4F_o{}^2[\sigma^2(I) + (0.02F_o{}^2)^2]^{-1}$, using Enraf-Nonius programs (Frenz & Okaya, 1980). Maximum shift in final cycle was 0.06σ; maximum and minimum residual electron densities were 1.06 and -1.26 e Å^{-3}. The extinction coefficient refined to $1.9(1) \times 10^{-7}$.

Final $R = 0.047$, $wR = 0.050$ and $S = 1.796$ for 71 variables. The inversion-related structure was refined under identical circumstances, yielding $R = 0.055$. $wR = 0.057$ and $S = 2.042$; thus the absolute configuration is shown to be that given in Table 1.

The atomic coordinates* are given in Table 1 and selected interatomic distances and angles are shown in Table 2. An *ORTEP* view (Johnson, 1965) of the $CuBr_4^{2-}$ anion coordinated to the Tl18c6$^+$ cation is shown in Fig. 1, and a stereoview of the unit cell is shown in Fig. 2.

Related literature. This work is a continuation of our studies on MX_4^{2-} (X = Cl, Br) anions as concentrators of toxic thallium, which was reported in detail recently (Kahwa *et al.*, 1992). The structure of the $[(Tl18c6)_4CuBr_4][TlBr_4]_2$ complex is isomorphous with that of $[(Tl18c6)_4CuCl_4][TlCl_4]_2$ and from powder X-ray diffraction studies (Fairman, Gallimore, Spence & Kahwa, 1992), the compounds $[(Tl18c6)_4MCl_4][TlCl_4]_2$, M = Mn, Co, Cu, Zn, are isostructural. The $TlBr_4^-$ and $CuBr_4^{2-}$ anions at the 23 site have perfect tetrahedral geometry; however, the $CuBr_4^{2-}$ ion exhibits large thermal parameters for the Br atom indicating that the $CuBr_4^{2-}$ is probably of low symmetry and distorted. One of the three independent C atoms of the 18-crown-6 macrocycle of the bromo complex also exhibits large thermal parameters.

See also, Pressprich & Willet (1991), Chaudhuri, Banerjee, Roy, Bocelli & Deb Purkayastha (1990), Hasebe, Asahi & Gesi (1990), and Halvorson, Patterson & Willet (1990).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55543 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0592]

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