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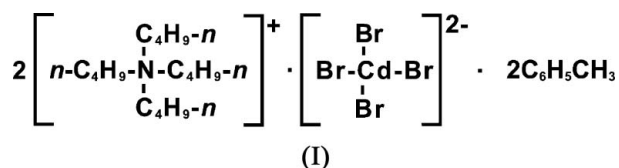
Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
Disorder in solvent or counterion
 R factor = 0.041
 wR factor = 0.095
Data-to-parameter ratio = 29.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(tetra-*n*-butylammonium) tetrabromo-
cadmate(II) toluene disolvateThe title compound, $(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{CdBr}_4] \cdot 2\text{C}_7\text{H}_8$, consists of a $[\text{CdBr}_4]^{2-}$ anion possessing 4 crystallographic symmetry and two tetra-*n*-butylammonium cations of twofold symmetry accompanied by two toluene molecules disordered around a twofold axis. The anion is enclosed within a cage formed of four cations and four solvent molecules.

Received 24 January 2006

Accepted 1 February 2006

Comment

Several compounds are known where the $[\text{CdBr}_4]^{2-}$ complex anion is accompanied by such different cations as $[\text{Ni}(\text{en})_3]^{2+}$ (Chesnut *et al.*, 1999), $(\text{PPh}_4)^+$ (Hasselgren *et al.*, 1997), diamminium derivatives such as $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)^{2+}$ (Krishnan *et al.* 1991) or pyridinium $(\text{C}_5\text{H}_5\text{NH})^+$ (Zhang & Fang, 2005), to mention just a few examples. Surprisingly, only one tetraalkylammonium tetrabromocadmate salt $(\text{Et}_4\text{N})_2[\text{CdBr}_4]$ (Geselle & Fuess, 1994) has been characterized by X-ray structural analysis and for $(\text{Me}_4\text{N})_2[\text{CdBr}_4]$ (Sato *et al.*, 1986) unit-cell data have been determined from the X-ray powder pattern.Here we report the synthesis, isolation of single crystals and structure determination of bis(tetra-*n*-butylammonium) tetrabromocadmate(II) obtained as the ditoluene solvate, (I).The compound was formed during the reaction of dimeric cadmium bis(tri-*tert*-butoxysilanethiolate) (Wojnowski *et al.*, 1992) with ammonium pyrrolidinedithiocarbamate in the presence of tetra-*n*-butylammonium bromide in a toluene/2-propanol mixture. The diffraction experiment was performed at 100 K because the characteristic octahedral crystals were not stable at room temperature and quickly became opaque. The asymmetric unit of (I) contains one fourth of a formula unit of (I). Fig. 1 gives the atom-numbering scheme and Fig. 2 presents the packing viewed along the *a* axis. The arrangement of ions and solvent molecules is shown in Fig. 3.The nearly tetrahedral $[\text{CdBr}_4]^{2-}$ anion (site symmetry: $\bar{4}$, Wyckoff letter: *a*) is enclosed within the positively charged cage formed by four tetra-*n*-butylammonium cations (site symmetry: 2, Wyckoff letter: *d*) and four toluene molecules. The toluene molecule lies on a twofold rotation axis (passing through C9 and C13, Wyckoff letter: *d*), so the methyl group is equally disordered over two symmetry-related positions.

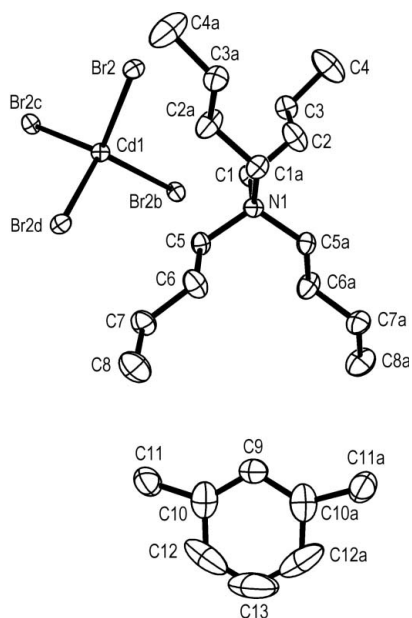


Figure 1
Ellipsoid plot of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (a) $x, -y + \frac{1}{2}, -z + \frac{1}{4}$; (b) $-x, -y, z$; (c) $-y, x, -z$; (d) $y, -x, -z$.] Both disorder components are shown

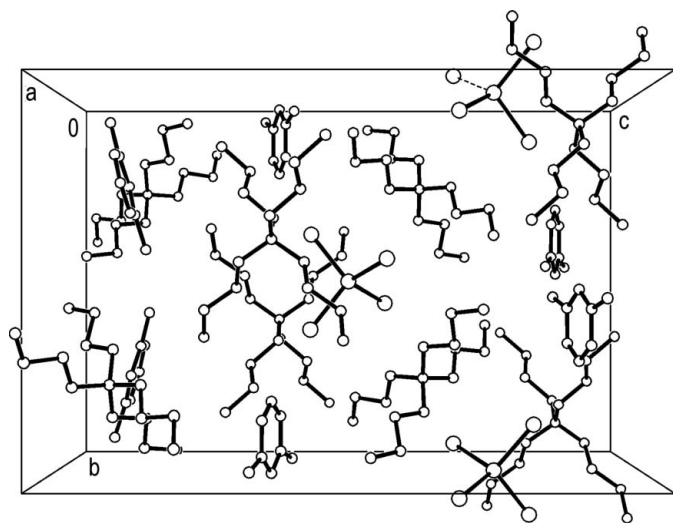


Figure 2
A packing diagram of compound (I), viewed along the a axis. H atoms have been omitted. Both disorder components are shown

The geometry of the $(n\text{-Bu}_4\text{N})^+$ ion is typical and does not deserve any elaborate discussion. The same holds for the $[\text{CdBr}_4]^{2-}$ anion; the Cd—Br bond length is within the limits reported for other complexes, *e.g.* those mentioned above.

Experimental

All commercially available reagents were of analytical or reagent grade purity and were used as received. A toluene/2-propanol mixture (5:1 v/v) was used as solvent. Cadmium bis(tri-*tert*-butoxy-silanethiolate) (0.11 g, 0.09 mmol), prepared according to a known

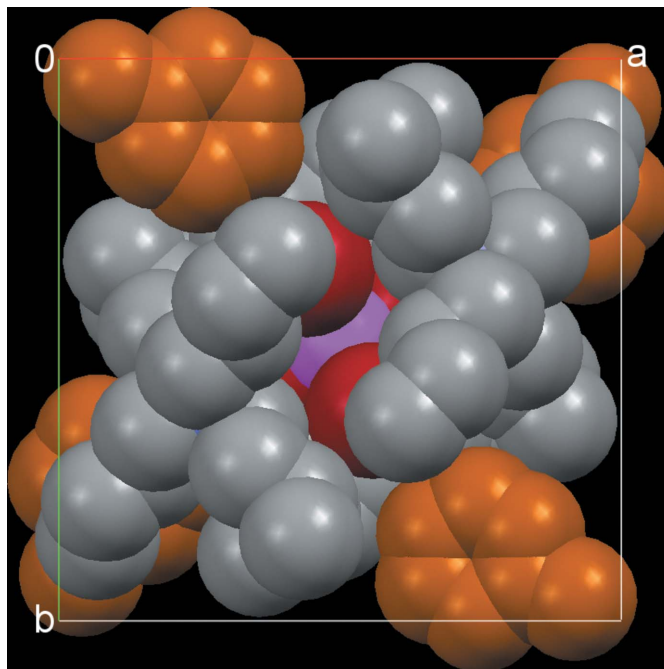


Figure 3
The tetrabromocadmiate anion within the cage formed by the cations and solvating toluene, projected along the c axis. H atoms have been omitted and the toluene methyl group is shown in only one of the two symmetry-related positions. Colour code: C(aryl) orange, C(alkyl) gray, Cd pink, Br red and N violet (hidden).

procedure (Wojnowski *et al.*, 1992), was dissolved in 7 ml of warm solvent. The ammonium salt of pyrrolidinecarbodithioic acid (0.029 g, 0.18 mmol) and tetra-*n*-butylammonium bromide (0.058 g, 0.18 mmol) were each dissolved in 7 ml of hot solvent. The dithiocarbamate and bromide solutions were mixed together, filtered and to the filtrate the solution of the cadmium complex was added dropwise. The mixture was stirred under reflux for *ca.* 1.5 h, then cooled and the small amount of precipitate removed by decantation. The clear solution was left to stand at *ca.* 278 K. After one month, octahedral crystals suitable for X-ray analysis were collected [m.p. 565 K (decomposition)]. The yield was *ca.* 35% and was not optimized.

Crystal data

$(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{CdBr}_4] \cdot 2\text{C}_7\text{H}_8$
 $M_r = 1101.22$
 Tetragonal, $I\bar{4}2d$
 $a = 15.1535$ (9) Å
 $c = 23.3816$ (18) Å
 $V = 5369.1$ (6) Å³
 $Z = 4$
 $D_x = 1.362$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 13314 reflections
 $\theta = 2.8\text{--}32.6^\circ$
 $\mu = 3.41$ mm⁻¹
 $T = 100$ (2) K
 Octahedron, colourless
 $0.20 \times 0.16 \times 0.11$ mm

Data collection

Kuma KM-4 diffractometer with Oxford Diffraction Sapphire-2 CCD detector
 ω scans
 Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2005), based on Clark & Reid (1998)]
 $T_{\min} = 0.403$, $T_{\max} = 0.476$

18127 measured reflections
 3926 independent reflections
 3769 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\max} = 30^\circ$
 $h = -21 \rightarrow 20$
 $k = -21 \rightarrow 15$
 $l = -32 \rightarrow 32$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.095$
 $S = 1.09$
 3926 reflections
 132 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 17.459P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 1.19 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.72 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 1779 Friedel pairs
 Flack parameter: $-0.021 (10)$

Table 1

Selected geometric parameters (Å, °).

Br2—Cd1	2.5901 (4)	C6—C7	1.514 (6)
C1—C2	1.491 (5)	C7—C8	1.516 (6)
C1—N1	1.515 (4)	C9—C10	1.405 (7)
C2—C3	1.512 (5)	C10—C12	1.364 (10)
C3—C4	1.511 (6)	C10—C11	1.471 (12)
C5—N1	1.515 (4)	C12—C13	1.326 (11)
C5—C6	1.518 (5)		
Br2 ⁱ —Cd1—Br2	108.833 (16)	C5 ⁱⁱⁱ —N1—C5	111.3 (4)
Br2 ⁱⁱ —Cd1—Br2	109.791 (8)	C12—C10—C9	119.0 (6)
C1—N1—C1 ⁱⁱⁱ	110.8 (4)	C12—C10—C11	108.0 (8)
C1—N1—C5 ⁱⁱⁱ	110.6 (2)	C9—C10—C11	133.1 (8)
C1—N1—C5	106.76 (19)		

Symmetry codes: (i) $-x, -y, z$; (ii) $-y, x, -z$; (iii) $x, -y + \frac{1}{2}, -z + \frac{1}{4}$.

All H atoms ($-\text{CH}_3$, $-\text{CH}_2$ and $\text{C}_{\text{ar}}\text{H}$, except H10) were positioned geometrically ($\text{C}-\text{H} = 0.95\text{--}0.99 \text{ Å}$) and refined as riding with their U_{iso} values constrained to be 1.2 times U_{eq} of the parent atoms. The

C10—H10 bond was restrained to $0.95 (1) \text{ Å}$. The highest peak is located 1.36 Å from atom Br2.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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