Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diethylammonium heptabromidedicadmium(II)

Roger D. Willett[a]* and Brendan Twamley[b]

[a]Department of Chemistry, Washington State University, Pullman, WA 99164, USA, and [b]University Research Office, University of Idaho, Moscow, ID 83844, USA

Correspondence e-mail: willett@mail.wsu.edu

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.018 Å
R factor = 0.039
wR factor = 0.082
Data-to-parameter ratio = 22.3

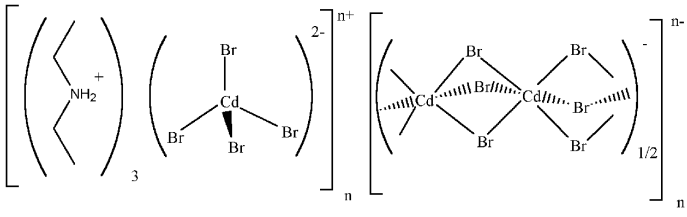
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 25 October 2001
Accepted 6 November 2001
Online 10 November 2001

The trigonal compound, $(Et_2NH_2)_3[Cd_2Br_7]$, contains Cd^{II} species with both tetrahedral and octahedral coordination. The $[CdBr_4]^{2-}$ species exist as isolated anions, stabilized by hydrogen bonding from the diethylammonium cations. The octahedral species share faces, forming $[CdBr_3]_n^{n-}$ chains parallel to the trigonal axis.

Comment

The structure of the title compound (I), as illustrated in Fig. 1, consists of a trigonal arrangement of columns of $[CdBr_3]_n^{n-}$ chains of face-shared cadmium bromide octahedra and hydrogen-bonded stacks of stoichiometry $[(DEA)_3CdBr_4]_n^{n+}$ (DEA is diethylammonium). The Cd^{II} ions in the octahedra chains (Fig. 2) have $\overline{3}$ symmetry with Cd—Br distances of 2.7848 (8) Å for Cd2 and 2.7837 (8) Å for Cd3. The octahedra are slightly elongated along the trigonal axis with interior Br—Cd—Br angles of 86.79 (2)°. This leads to Cd—Cd distances of 3.3888 (8) Å. Fig. 3 illustrates the stacks of $[CdBr_4]^{2-}$ tetrahedra hydrogen bonded by the DEA^+ cations. Each cation bridges adjacent pairs of tetrahedra, forming two N3—H···Br2 hydrogen bonds, with distances and angles given in Table 1. This forces short intra-tetrahedra Cd···Br distances of 4.1498 (19) Å and contracts the Br1···Cd1···Br2 angle to 104.04 (3)°. A packing diagram is shown in Fig. 4.



(I)

The crystal structure was determined as part of our long-standing interest in the the structure of diethylammonium halometallate(II) salts. $(Et_2NH_2)_2[CuCl_4]$ exhibits thermochromism, changing from the green room-temperature form to a yellow high-temperature form at 330 K (Bloomquist *et al.*, 1988; Simonsen & Harlow, 1977). $(Et_2NH_2)_2Cu_3Br_8(CuBr_2)$ contains planar $[Cu_3Br_8]^{2-}$ anions and neutral chains of edge-shared $CuBr_4$ tetrahedra (Fletcher *et al.*, 1983). $(Et_2NH_2)_2ZnCl_4(H_2O)_x$ exhibits a phase transition at 320 K (Bloomquist & Willett, 1981). A mixed-metal $(Et_2NH_2)_4CuCl_4AlCl_4$ species has also been reported (Martin & Leafblad, 1998). $(Et_2NH_2)_2[CeCl_6]$ contains isolated octahedrally coordinated Ce^{IV} ions (Kiselev *et al.*, 1979), while $(Et_2NH_2)_3[Ru_2Cl_9]$

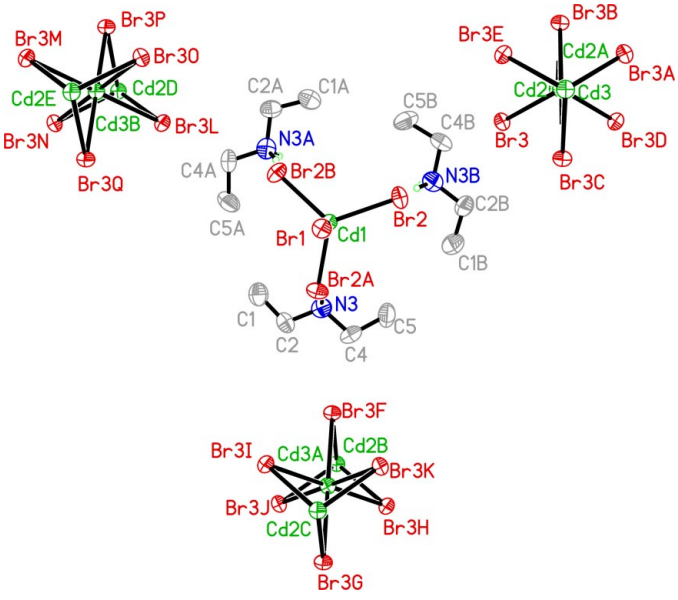


Figure 1
A section of the extended structure of (I) with atom labels and 30% probability ellipsoids.

contains tribridged dimers formed by two face-shared octahedra (Efimenko *et al.*, 1992).

The compound is isostructural with $[(CH_3)_3N]_3[Mn_2Cl_7]$ (Caputo *et al.*, 1976).

Experimental

An excess amount of diethylammonium chloride and $CdCl_2(H_2O)_4$ in a 2:1 molar ratio in water were allowed to come to equilibrium. The crystalline needles formed were separated and one selected for structural investigation.

Crystal data

$(C_4H_{11}N)_3[Cd_2Br_7]$
M_r = 1006.61
Trigonal, $P\overline{3}$
a = 15.5665 (11) Å
c = 6.7777 (6) Å
V = 1422.31 (19) Å^3
Z = 2
D_x = 2.350 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 776 reflections
θ = 2.6–18.6°
μ = 11.33 mm^{-1}
T = 297 (2) K
Hexagon, colorless
0.12 × 0.09 × 0.07 mm

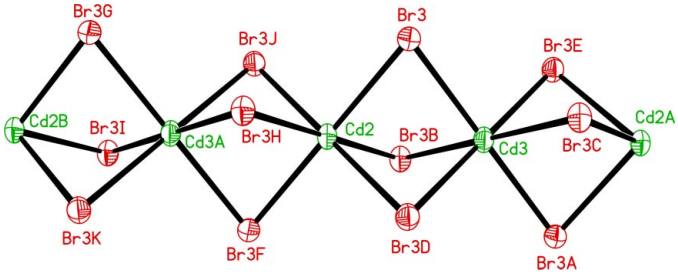


Figure 2
A view of the $[CdBr_3]_n^{n-}$ chain of face-shared cadmium bromide octahedra.

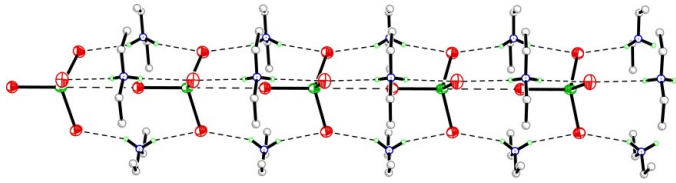


Figure 3
A view, parallel to [001], of the intermolcular hydrogen bonding, indicated by dashed lines. Only the H atoms involved in this bonding are shown. The DEA^+ cations are shown in ball-and-stick format, the $CdBr_4$ units have displacement ellipsoids at the 30% probability level.

Data collection

Siemens SMART 1K diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1999)
T_{min} = 0.343, T_{max} = 0.504
15545 measured reflections
1675 independent reflections
1137 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 25.0°
$h = -18 \rightarrow 18$
$k = -18 \rightarrow 18$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.082
S = 1.02
1675 reflections
75 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 3.3912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0027 (2)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···Br2^{i}	0.90	2.74	3.556 (8)	151
N3—H3B···Br2^{ii}	0.90	2.70	3.555 (8)	160

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

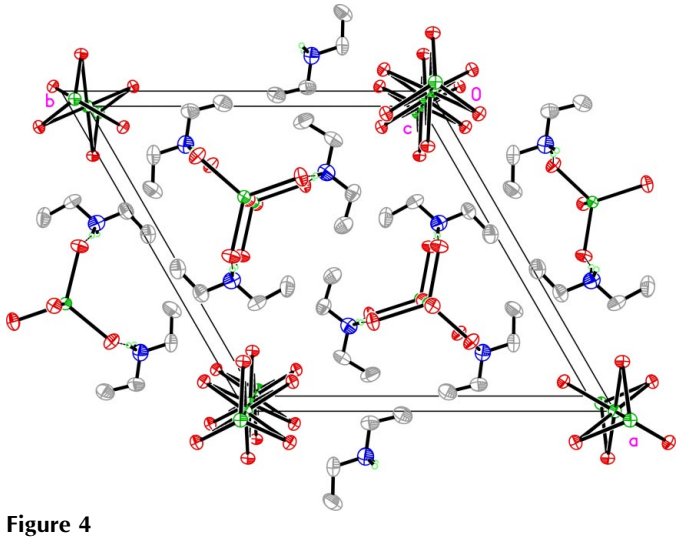


Figure 4
A packing diagram of (I) with intermolecular hydrogen bonding shown by dashed lines. For clarity, only the H atoms involved in intermolecular bonding are shown. Displacement ellipsoids are at the 30% probability level.

There is a high positive residual density of 1.61 e $Å^{-3}$ near the Cd1 center. It lies along the Cd1—Br1 vector.

Data collection: *SMART* (Bruker, 1997–1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *XS* in *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

References

Bloomquist, D. R., Pressprich, M. R. & Willett, R. D. (1988). *J. Am. Chem. Soc.* **110**, 7391–7398.

Bloomquist, D. R. & Willett, R. D. (1981). *Acta Cryst.* B**37**, 1353–1356.

Bruker (1997–1998). *SMART*. Version 5.059. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1998). *SHELXTL* (*XCIF, XL, XP, XS*). Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SADABS* (Version 2.01) and *SAINT-Plus* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Caputo, R. E., Roberts, S., Willett, R. D. & Gerstein, B. C. (1976). *Inorg. Chem.* **15**, 820–823.

Efimenko, I. A., Balakaeva, T. A., Kurbakove, A. P, Kanishcheva, A. S., Chuvaev, A. V., Stepanovich, V. M. & Mikhailov, Yu. N. (1992). *Zh. Neorg. Khim*, **37**, 1312–1319.

Fletcher, R., Hansen, J. J., Livermore, J. & Willett, R. D. (1983). *Inorg. Chem.* **22**, 330–334.

Kiselev, Yu. M., Brandt, A., Martynenko, L. I. & Spitsyn, V. I. (1979). *Dokl. Akad. Nauk. SSSR*, **246**, 879–884.

Martin, J. J. & Leafblad, B. R. (1998). *Angew. Chem. Int. Ed.* **37**, 3318–3320.

Simonsen, S. H. & Harlow, R. L. (1977). *Am. Crystallogr. Assoc. Ser.* **2**, 25.