Structure of the Heptaaquacalcium Salt of the Polymeric Hexabromodicadmate(II) Anion

BY R. FAGGIANI, M. VILLELLA AND I. D. BROWN

Institute of Materials Research, McMaster University, Hamilton, Ontario, Canada L9H 3B7

Abstract. $[Ca(H_2O)_7][Cd_2Br_6]$, $M_r = 870.44$, monoclinic, $P2_1/c$ {Hall symbol $\bar{P}2^y_{bc}$ [*Acta Cryst.* (1981), A37, 517–525]}, $a = 8.079$ (2), $b = 18.677$ (6), $c = 12.176$ (5) Å, $\beta = 96.60$ (3)°, $V = 1825.08$ Å^3, $Z = 4$, $D_x = 3.17$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 9.95$ mm^{-1}, $F(000) = 1584$, $T = 198$ K, $R = 0.065$ for 2259 reflections. The sample was prepared from a saturated solution containing a 1:1.5 molar mixture of $CaBr_2$ and $CdBr_2$. When the sealed container was opened to the air the crystals which had originally formed dissolved and colourless crystals of the title compound appeared. The structure consists of discrete $Ca(H_2O)_7^{2+}$ ions (Ca—O = 2.36–2.47 Å) hydrogen bonded to an infinite $Cd_2Br_6^{2-}$ anion extended along the *a* axis. One Cd is octahedrally coordinated (Cd—Br = 2.75–2.81 Å). It shares edges with two crystallographically equivalent CdBr$_6$ octahedra and shares corners with two CdBr$_4$ tetrahedra (Cd—Br = 2.53–2.61 Å).

Experimental. A crystal 0.5 × 0.3 × 0.3 mm sealed in a thin-walled quartz capillary, Nicolet *P*2$_1$ diffractometer equipped with a Nicolet LT1 cooling device. Unit cell from 15 strong reflections in the range $20 \le \theta \le 30°$. No absorption correction was used. Intensities for 2665 reflections in the range $-8 \le h \le 8$, $0 \le k \le 20$, $0 \le l \le 13$ ($2\theta \le 45°$). The standard reflections ($\bar{4}15$ and 272) showed non-systematic variations of about 1%. Equivalent reflections were averaged ($R = 0.021$) to give 2259 unique reflections. Structure by direct methods (*MULTAN*80, Main *et al.*, 1980), scale factor, weighting factor (k) and all variable (non-hydrogen) positional and anisotropic displacement parameters refined with *SHELX*76 (Sheldrick, 1976), $w = [\sigma^2(F) + kF_o^2]^{-1/2}$ [where $k = 0.0035$ and $\sigma(F)$ is the error derived from counting statistics] to give $R = 0.065$, $wR = 0.076$ and a goodness of fit of $S = 1.02$. The average shift/e.s.d. $= 0.01$ (max. $= 0.03$). Hydrogen atoms could not be located on the final difference map where the largest feature was 2.13 and the smallest -1.67 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1.* The

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42812 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

principal interatomic distances are listed in Table 2 and the structure is illustrated in Fig. 1.

Table 1. *Atomic positions* (×10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^4)

$$U_{eq} = \tfrac{1}{3}\mathrm{Tr}\mathbf{U}.$$

	x	y	z	U_{eq}
Ca	2083 (5)	8081 (2)	4434 (3)	234
Cd(1)	6910 (2)	5937 (1)	2106 (1)	197
Cd(2)	5000	5000	5000	164
Cd(3)	0	5000	5000	152
Br(1)	−225 (2)	5339 (1)	2742 (1)	177
Br(2)	4369 (2)	5327 (1)	2771 (1)	225
Br(3)	2562 (2)	5967 (1)	5436 (1)	169
Br(4)	6841 (3)	5866 (1)	−23 (2)	323
Br(5)	7082 (2)	7311 (1)	2445 (2)	244
Br(6)	2429 (2)	4002 (1)	4718 (1)	195
O(1)	4665 (16)	7413 (7)	4454 (12)	361
O(2)	31 (16)	8555 (7)	3051 (10)	263
O(3)	−422 (19)	7755 (9)	5203 (11)	447
O(4)	3007 (17)	7825 (7)	6320 (11)	362
O(5)	1241 (18)	7061 (7)	3204 (11)	319
O(6)	1761 (22)	9203 (8)	5275 (13)	489
O(7)	3621 (17)	8696 (8)	3182 (11)	373

Table 2. *Interatomic distances* (Å) *and angles* (°)

Environment of Ca

Ca—O(6)	2.36 (2)	Ca—O(3)	2.40 (2)
Ca—O(7)	2.37 (2)	Ca—O(1)	2.43 (1)
Ca—O(4)	2.38 (1)	Ca—O(5)	2.47 (1)
Ca—O(2)	2.39 (1)		

Tetrahedral environment of Cd(1)

Cd(1)—Br(2)	2.559 (2)	Cd(1)—Br(5)	2.600 (2)
Cd(1)—Br(4)	2.590 (3)	Cd(1)—Br(1)	2.606 (2)

Br(4)—Cd(1)—Br(2)	111.6 (1)	Br(2)—Cd(1)—Br(5)	114.8 (1)
Br(4)—Cd(1)—Br(5)	101.8 (1)	Br(2)—Cd(1)—Br(1)	115.6 (1)
Br(4)—Cd(1)—Br(1)	101.0 (1)	Br(5)—Cd(1)—Br(1)	110.3 (1)

Octahedral environment of Cd(2) (site symmetry C_i)

Cd(2)—Br(3)	2.768 (2)	Br(3)—Cd(2)—Br(2)	90.6 (1)
Cd(2)—Br(2)	2.771 (2)	Br(3)—Cd(2)—Br(6)	94.4 (1)
Cd(2)—Br(6)	2.783 (2)	Br(2)—Cd(2)—Br(6)	91.4 (1)

Octahedral environment of Cd(3) (site symmetry C_i)

Cd(3)—Br(3)	2.752 (2)	Br(3)—Cd(3)—Br(6)	93.6 (1)
Cd(3)—Br(6)	2.756 (2)	Br(3)—Cd(3)—Br(1)	90.2 (1)
Cd(3)—Br(1)	2.807 (2)	Br(6)—Cd(3)—Br(1)	90.1 (1)

Possible H bonds

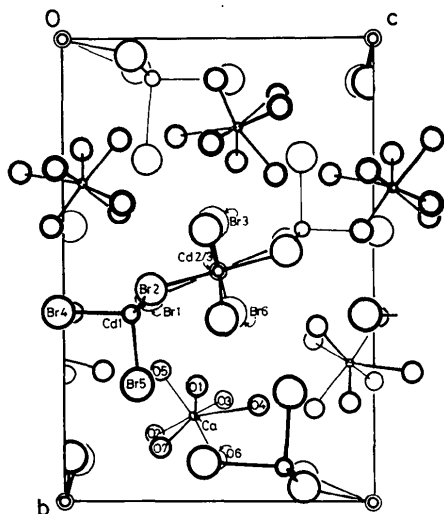| X	O···X	Ca—O···X		X	O···X	Ca—O···X
O(1)···Br(5)	3.31 (1)	127 (1)		O(5)···Br(5)	3.41 (1)	105 (1)
Br(3)	3.47 (1)	87 (1)		Br(1)	3.45 (1)	152 (1)
Br(6)	3.60 (1)	156 (1)		Br(3)	3.47 (1)	87 (1)
Br(4)	3.68 (1)	87 (1)		O(6)···Br(4)	3.33 (2)	137 (1)
O(2)···Br(2)	3.35 (1)	108 (1)		Br(2)	3.60 (2)	120 (1)
Br(1)	3.48 (1)	120 (1)		Br(1)	3.67 (2)	130 (1)
O(3)···Br(4)	3.39 (2)	110 (1)		O(7)···Br(4)	3.30 (1)	97 (1)
Br(5)	3.58 (2)	152 (1)		Br(3)	3.41 (1)	129 (1)
Br(6)	3.67 (2)	129 (1)		Br(2)	3.70 (1)	152 (1)
O(4)···O(5)	2.85 (2)	129 (1)				
Br(5)	3.43 (1)	126 (1)				
Br(3)	3.64 (1)	84 (1)				

Fig. 1. $[Ca(H_2O)_7][Cd_2Br_6]$ viewed down the a axis.

Discussion. Crystals of the title compound were formed when a flask containing a saturated solution of $CaBr_2$:$CdBr_2$ in equilibrium with the solid was opened to the air. The original crystals which dissolved at the same time have the composition $CaCd_2Br_6.6H_2O$ (Balarew, Duhlev & Panaiotov, 1982). The bonding of

Ca to water and Cd to Br in $[Ca(H_2O)_7][Cd_2Br_6]$ confirms the predictions of Balarew & Duhlev (1984) whose work prompted the present study. The interatomic distances are close to those expected. The $Ca(H_2O)_7^{2+}$ and infinite chain $Cd_2Br_6^{2-}$ ions are linked by hydrogen bonds with $O\cdots Br$ distances ranging from 3.30 to over 3.60 Å.

References

BALAREW, C. & DUHLEV, R. (1984). *J. Solid State Chem.* **55**, 1–6.
BALAREW, C., DUHLEV, R. & PANAIOTOV, V. (1982). *Bulg. Acad. Sci. Commun. Dep. Chem.* **15**, 187–195.
HALL, S. R. (1981). *Acta Cryst.* A**37**, 517–525.
International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Structure of Lead(II) Copper(I) Arsenate(V)

BY F. PERTLIK

Institut für Mineralogie und Kristallographie der Universität Wien, Dr Karl-Lueger-Ring 1, A-1010 Vienna, Austria

Abstract. $PbCuAsO_4$, $M_r = 409.65$, triclinic, $P\bar{1}$, $a = 4.832$ (1), $b = 5.837$ (1), $c = 7.995$ (2) Å, $\alpha = 78.68$ (2), $\beta = 74.95$ (1), $\gamma = 84.04$ (1)°, $V = 213.2$ Å^3, $Z = 2$, $D_x = 6.382$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.710688$ Å, $\mu = 50.3$ mm^{-1}, $F(000) = 352$, room temperature, $R = 0.030$ for 1039 observed reflections up to $\sin\theta/\lambda = 0.70$ Å^{-1}. $PbCuAsO_4$ crystallizes in a network structure built up by three characteristic cation coordination polyhedra. The Pb atom is irregularly [4 + 2] coordinated by six O atoms. The monovalent Cu atom has a linear [2] coordination, and the pentavalent As atom has the usual tetrahedral [4] coordination by O atoms. $PbCuAsO_4$ was synthesized under hydrothermal conditions [490 (5) K, saturation vapour pressure].

Introduction. The oxidation state of arsenic in oxygen compounds indicates in mineralogy the conditions of formation of various ore deposits and their weathering during geologic periods. Therefore investigations within the system PbO, CuO, As_2O_3 and H_2O under hydrothermal conditions were performed to learn the different conditions for the formation of arsenite and arsenate minerals (Pertlik, 1977).

Experimental. $PbCuAsO_4$ is a product of the following chemical reaction: 2 g of an equimolar mixture of PbO, CuO, and As_2O_3 were placed in a 'Teflon'-coated vessel ($V \simeq 6000$ mm^3) and the vessel was filled to ~80% of its volume with 1 M acetic acid. After heating for 4 d,