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Structure of Dicalcium Cadmium Hexabromide Dodecahydrate

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Abstract. $Ca_2CdBr_6.12H_2O$, $M_r = 888{\cdot}20$, monoclinic, $C2/c$ {Hall symbol $-C2_c^y$ [Hall (1981). *Acta Cryst.* A**37**, 517–525]}, $a = 18{\cdot}288\,(4)$, $b = 10{\cdot}341\,(2)$, $c = 13{\cdot}527\,(2)$ Å, $\beta = 117{\cdot}16\,(1)°$, $V = 2276{\cdot}1\,(7)$ Å^3, $Z = 4$, $D_x = 2{\cdot}59$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 11{\cdot}68$ mm^{-1}, $F(000) = 1672$, room temperature, $R = 0{\cdot}045$ ($wR = 0{\cdot}046$) for 1333 unique observed [$I > 3\sigma(I)$] reflections. Cd is octahedrally coordinated by six Br atoms (ave. Cd—Br = 2·78 Å). The environment of Ca consists of six H_2O molecules (ave. Ca—O = 2·38 Å) and one Br atom (Ca—Br$_1$ = 3·22 Å) shared with Cd. The centrosymmetric $[Ca(H_2O)_6][CdBr_6][Ca(H_2O)_6]$ molecules are extended along the [310] direction and are linked together by O—H···Br and O—H···O hydrogen bonds. Comparison is made between this structure and related structures of compounds of the same formula type.

Introduction. $Ca_2CdBr_6.12H_2O$ was first reported as one of the three double salts found in the equilibrium $CaBr_2$—$CdBr_2$—H_2O system at 297 K (Balarew, Duhlev & Panaiotov, 1982). In their crystallochemical classification Duhlev & Balarew (1987) pointed out that the $2MX_2.M'X_2.12H_2O$ double salts belong to four different structural types depending on the ratios of softness and size of M^{2+} and M'^{2+} and they predicted that $Ca_2CdBr_6.12H_2O$ would be of the same structural type as $Ca_2CdCl_6.12H_2O$ (Leligny & Monier, 1978), built from two $Ca(H_2O)_6^{2+}$ and one $CdBr_6^{4-}$ ions sharing ligands.

Experimental. An aqueous solution of $CaBr_2$ and $CdBr_2$ in a molar ratio 2·5:1 was left in a desiccator under vacuum until the colourless extremely hygroscopic crystals of $Ca_2CdBr_6.12H_2O$ started to form. A crystal with dimensions 0·47 × 0·40 × 0·25 mm was coated with liquid paraffin, sealed in a thin-walled capillary under dry nitrogen and mounted on a Syntex $P2_1$ diffractometer. Unit-cell parameters were determined from 15 well centred strong reflections in the range $19 < 2\theta < 29°$. Intensities were measured for 2316 reflections with $0 \le h \le 21$, $0 \le k \le 12$, $-16 \le l \le 14$ and $2\theta < 50°$ and were corrected for Lorentz and polarization effects. The intensities of the $\bar{3}17$ and $93\bar{3}$ reflections were monitored after every 48 measurements and showed variations less than 1·8%. Empirical absorption corrections were derived from ψ scans of 24 reflections (maximum correction factor of 3·02 for the intensity of reflection 711). Equivalent reflections were then averaged ($R_{\rm int} = 0{\cdot}009$) to give 2028 unique reflections. Since one third of these were weak, only the 1333 unique reflections with $I > 3\sigma(I)$ were used for the refinement. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). The positions of the H atoms were determined from the difference map and from chemical considerations and were held fixed. We used a weighting function $w = [\sigma^2(F_o) + \kappa F_o^2]^{-1}$, where $\sigma(F_o)$ is the uncertainty derived from counting statistics and κ was refined to 0·00108. The scale factor, weighting factor (κ), secondary-extinction coefficient and all variable (non-hydrogen) positional and atomic displacement factors were refined by least squares [function minimized = $\sum w(|F_o| - |F_c|)^2$] with *SHELX*76 (Sheldrick, 1976). The final cycle of the refinement gave $R = 0{\cdot}045$ ($wR = 0{\cdot}046$) and a goodness of fit $S = 1{\cdot}17$. The average shift/e.s.d. = 0·001 (max. = 0·002). The final difference electron density has maximum and minimum values of +0·77 and −1·62 e Å^{-3} respectively. The secondary-extinction coefficient (Larson, 1967) $g = 0{\cdot}00048\,(4)$. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates and temperature factors are given in Table 1.†

Discussion. The bond distances and angles are shown in Table 2. Six Br atoms lie in an octahedron around Cd. Ca is coordinated by six water molecules and one bromine from the $CdBr_6$ complex. The molecular complexes $[Ca(H_2O)_6][CdBr_6][Ca(H_2O)_6]$ with Cd at a centre of symmetry (Fig. 1) are extended in the [310] direction and are linked by an extensive network of O—H···Br and O—H···O bonds as shown in Fig. 2.

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† Lists of structure factors, anisotropic atomic displacement factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51031 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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In a recent crystallochemical classification of compounds with the formula $2MX_2.M'X_2.12H_2O$, Duhlev & Balarew (1987) explained the variety of structures which these salts show in terms of the softness and size of the ions. If M^{2+} is the harder and M'^{2+} the softer (Balarew & Duhlev, 1984) ion, the stoichiometrically identical compounds fall into two distinct structural classes: $2MX_2.M'X_2.12H_2O$ and $MX_2.2M'X_2.12H_2O$. $Ca_2CdBr_6.12H_2O$ belongs to the former class which, when M^{2+} is small, is composed of independent $M(H_2O)_6^{2+}$ and $M'X_6^{4-}$ octahedra; when M^{2+} exceeds a certain critical size (as is the case with Ca^{2+}), sharing of some of the ligands occurs to increase the coordination number of M^{2+}. As was pointed out by Duhlev & Balarew (1987), the polymerized structures with $M = Ca$ can be regarded as derived from the structures with independent octahedra by bringing the octahedra closer together until they penetrate each other and share one or more ligands.

Crystallographic parameters for the seven reported structures of $[M(H_2O)_6]_2[M'X_6]$ compounds are compared in Table 3 and the motifs in their structures are compared in Fig. 3. Despite belonging to five different space groups, the structures have many similar lattice spacings. All the structures are based on hexagonal-closed-packed layers composed of two $M(H_2O)_6^{2+}$ cations and one $M'X_6^{4-}$ anion. In the structures with small M^{2+} ions (Mg^{2+}, Ni^{2+}) (Fig. 3*a*) the layers display strict trigonal symmetry and are stacked in cubic ($R\bar{3}$) or hexagonal ($P3$, $P31c$) close-packed arrays. As the ratio $r_{M^{2+}}/r_{X^-}$ increases, the coordination number around M^{2+} increases from 6 to 7 by the introduction of a halogen from an adjacent $M'X_6^{4-}$ ion into the coordination sphere (Fig. 3*b*). The result is a centrosymmetric triplet molecule composed of two complex

Table 1. *Atomic positions and equivalent isotropic atomic displacement factors* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\rm eq}$
Cd	$\frac{1}{4}$	$\frac{3}{4}$	0	0·0306
Br(1)	0·36059 (8)	0·55076 (12)	0·10787 (9)	0·0434
Br(2)	0·32745 (7)	0·80482 (14)	−0·12611 (10)	0·0486
Br(3)	0·35969 (8)	0·91540 (11)	0·16903 (10)	0·0426
Ca	0·40719 (14)	0·2966 (2)	0·01084 (17)	0·0364
O(1)	0·3094 (5)	0·1428 (9)	−0·1157 (7)	0·056
O(2)	0·3225 (5)	0·4323 (9)	−0·1382 (6)	0·051
O(3)	0·5307 (5)	0·3992 (10)	0·1297 (8)	0·071
O(4)	0·3424 (6)	0·2309 (9)	0·1180 (8)	0·073
O(5)	0·4739 (5)	0·2748 (10)	−0·1062 (7)	0·061
O(6)	0·4804 (5)	0·1020 (10)	0·0888 (9)	0·074

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

Polyhedron $Ca(H_2O)_6Br$

Ca	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	Br(1)
O(1)	2·422 (8)	3·030 (13)		3·074 (14)	3·253 (14)	3·117 (11)	
O(2)	78·5 (3)	2·363 (8)	3·178 (15)	3·916 (14)	3·069 (14)		3·309 (9)
O(3)	162·0 (4)	111·5 (3)	2·344 (9)	3·793 (16)	3·146 (14)	3·182 (14)	3·373 (11)
O(4)	80·1 (3)	112·2 (4)	107·8 (4)	2·352 (13)		3·035 (17)	3·333 (10)
O(5)	84·6 (3)	79·9 (3)	82·8 (4)	157·7 (4)	2·411 (12)	3·142 (15)	
O(6)	80·9 (3)	153·7 (4)	84·6 (3)	79·7 (4)	81·9 (4)	2·380 (10)	
Br(1)	125·1 (3)	70·7 (2)	72·6 (3)	71·5 (3)	130·6 (3)	135·1 (3)	3·222 (3)

Octahedron $CdBr_6$

Cd	Br(1)	Br(1$^{\rm i}$)	Br(2)	Br(2$^{\rm i}$)	Br(3)	Br(3$^{\rm i}$)
Br(1)	2·7875 (13)		3·9416 (20)	3·859 (2)	3·8621 (18)	4·0749 (17)
Br(1$^{\rm i}$)	179·85 (4)	2·7875 (13)	3·859 (2)	3·9416 (19)	4·0749 (17)	3·8621 (18)
Br(2)	91·15 (4)	88·73 (4)	2·7283 (16)		3·930 (2)	3·927 (2)
Br(2$^{\rm i}$)	88·73 (4)	91·15 (4)	179·86 (4)	2·7283 (16)	3·927 (2)	3·930 (2)
Br(3)	86·87 (4)	93·01 (4)	89·98 (4)	89·90 (4)	2·8267 (11)	
Br(3$^{\rm i}$)	93·01 (4)	86·87 (4)	89·90 (4)	89·98 (4)	179·86 (4)	2·8267 (11)

Hydrogen bonds and angles

O—H···X	O—H	H···X	O···X	O—H···X	H—O—H
O(1)—H(11)···Br(3$^{\rm ii}$)	1·06	2·46	3·483 (11)	163	101
O(1)—H(12)···Br(2$^{\rm iii}$)	0·98	2·60	3·519 (9)	156	
O(2)—H(21)···Br(2$^{\rm iv}$)	0·79	2·80	3·382 (7)	133	111
*O(2)—H(22)···Br(3$^{\rm i}$)	1·03	2·56	3·533 (10)	159	
O(3)—H(31)···Br(2$^{\rm v}$)	1·01	2·55	3·362 (11)	137	111
O(3)—H(31)···O(2$^{\rm v}$)	1·01	2·52	3·159 (15)	120	
O(3)—H(32)···Br(1$^{\rm vi}$)	0·99	2·62	3·545 (10)	156	
O(4)—H(41)···Br(3$^{\rm iii}$)	1·08	2·32	3·320 (10)	152	122
O(4)—H(42)···O(1$^{\rm i}$)	0·94	2·17	3·055 (16)	155	
O(5)—H(51)···Br(1$^{\rm v}$)	0·99	2·66	3·532 (10)	147	119
O(5)—H(52)···Br(3$^{\rm vii}$)	1·00	2·63	3·417 (8)	136	
O(6)—H(61)···Br(3$^{\rm iii}$)	1·01	2·51	3·460 (12)	156	102
O(6)—H(62)···Br(2$^{\rm v}$)	0·97	2·71	3·451 (11)	133	

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii) $x, -y, -\frac{1}{2}+z$; (iii) $x, -1+y, z$; (iv) $\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (v) $1-x, 1-y, -z$; (vi) $1-x, y, \frac{1}{2}-z$; (vii) $x, 1-y, -\frac{1}{2}+z$.

* Hydrogen bond formed within the triplet.

Table 3. *Crystal data for related* $[M(H_2O)_6]_2[M'X_6]$ *compounds*

Compound	Reference	Space group	*a*	*b*	*c*	β	γ	*Z*	$c_{\text{hexag.}} = c\cos\beta$	$a_{\text{monocl.}} = a\cos(\gamma - 90)$	$a_{\text{hexag.}} = a/\cos(120-\gamma)$	$r_{M^{2+}}/r_{X^-}$	Figure
$[Mg(H_2O)_6]_2[CdBr_6]$	(*a*)	$R\bar{3}$	10·4	10·4	17·8	90	120	3	3 × 5·9	9·0	10·4	0·33	3(*a*)
$[Mg(H_2O)_6]_2[CaCl_6]$	(*b*),(*c*)	$R\bar{3}$	10·1	10·1	17·3	90	120	3	3 × 5·8	8·7	10·1	0·36	3(*a*)
$[Ni(H_2O)_6]_2[CdCl_6]$	(*d*)	*P*3	10·0	10·0	11·2	90	120	2	2 × 5·6	8·7	10·0	0·38	3(*a*)
$[Mg(H_2O)_6]_2[CdCl_6]$	(*e*)	*P*31*c*	10·0	10·0	11·6	90	120	2	2 × 5·8	8·7	10·0	0·36	3(*a*)
$[Ca(H_2O)_6]_2[CdBr_6]$	(*f*)	*C*2/*c*	18·3	10·3	13·5	117	90	4	2 × 6·0	2 × 9·1	2 × 10·6	0·51	3(*b*)
$[Ca(H_2O)_6]_2[CdCl_6]$	(*g*)	$P2_1/c$	8·8	10·1	12·7	114	90	2	2 × 5·8	8·8		0·55	3(*c*)
$[Ca(H_2O)_6]_2[CaCl_6]$ $= \beta\text{-}CaCl_2.4H_2O$	(*h*)	$P2_1/c$	8·9	10·2	12·8	115	90	2	2·58	8·9		0·55	3(*c*)

(*a*) Duhlev, Faggiani & Brown (1987); (*b*) Leclaire, Borel & Monier (1980); (*c*) Clark, Evans & Erd (1980); (*d*) Leclaire & Borel (1982); (*e*) Ledésert & Monier (1981); (*f*) this paper; (*g*) Leligny & Monier (1978); (*h*) Leclaire & Borel (1978).

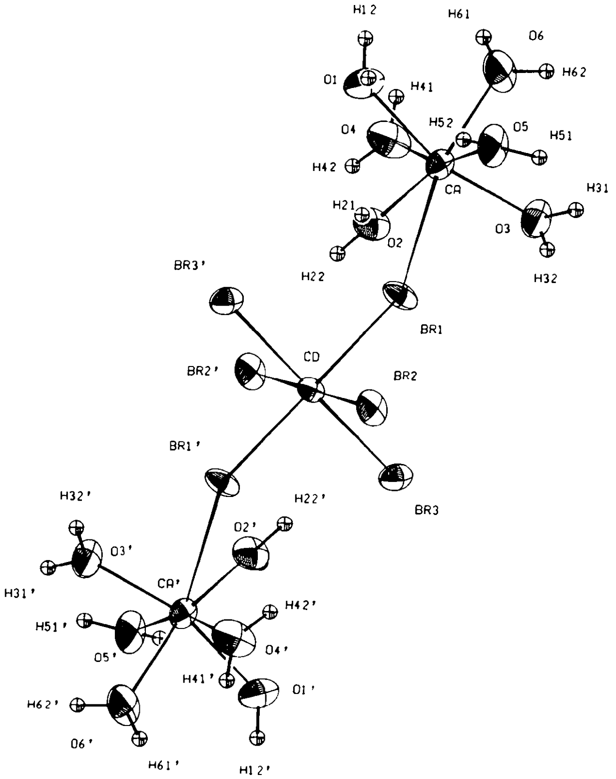

Fig. 1. Molecular structure of $Ca_2CdBr_6.12H_2O$ with thermal ellipsoids.

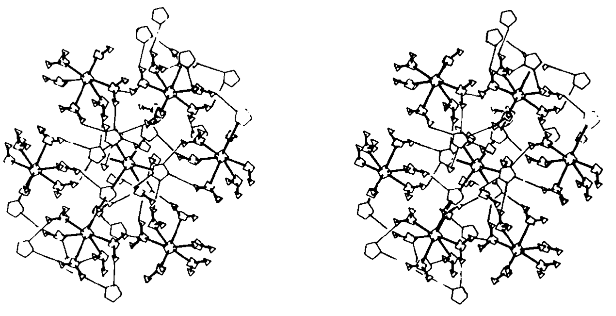

Fig. 2. Stereoscopic view of $Ca_2CdBr_6.12H_2O$. The viewing direction is approximately perpendicular to the *a* (horizontal to the right) and *b* (downwards) axes. Hydrogen bonds are indicated by thin lines.

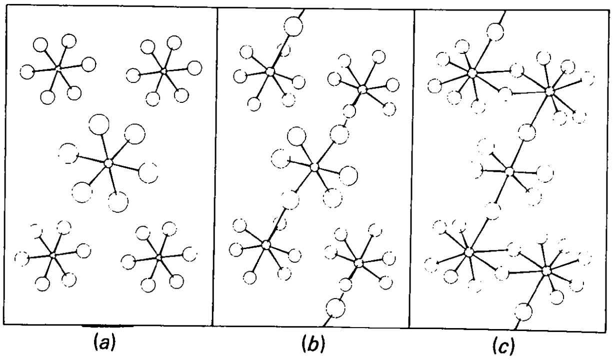

Fig. 3. Projections of the $[M(H_2O)_6]_2[M'X_6]$ structures onto (001), the plane containing the metal ions. In all cases the *b* axis is vertically downwards. Small circles are metal ions, medium circles H_2O, large circles *X*. H atoms are not shown. See Table 3 for further details.

cations and one complex anion. The formation of these triplets is achieved with only small displacements of the atoms from their ideal trigonal positions within the layers, though the stacking of the layers is somewhat different. As the radius ratio ($r_{M^{2+}}/r_{X^-}$) increases further the coordination number of M^{2+} increases from 7 to 8 by the sharing of two water molecules between adjacent $M(H_2O)_6^{2+}$ ions linking the triplets into chains along the **b** direction (Fig. 3*c*). Although the hexagonal structure is still closely preserved within the chains, adjacent chains are now shifted by half a lattice translation along **b** to change the lattice from *C*-centred to primitive. The bridging atoms (Br, Cl or O) in all these structures are bonded asymmetrically with the stronger bond being the one found in the trigonal structure. The present compound thus clearly belongs in the middle of a sequence of closely related structures formed between two hydrated cations and a single octahedral anion.

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Zinc Bromide Dihydrate $ZnBr_2.2H_2O$: a Double-Salt Structure

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Abstract. $[Zn(H_2O)_6][Zn_2Br_6] = (ZnBr_2.2H_2O)_3$, $M_r = 783{\cdot}66$, orthorhombic, *Immm* {Hall symbol $\bar{I}22$ [Hall (1981). *Acta Cryst.* A**37**, 517–525]}, $a = 10{\cdot}435$ (1), $b = 10{\cdot}367$ (1), $c = 7{\cdot}961$ (1) Å, $V = 861{\cdot}2$ (2) Å^3, $Z = 2$, $D_x = 3{\cdot}02$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 17{\cdot}68$ mm^{-1}, $F(000) = 720$, room temperature, $R = 0{\cdot}045$ ($wR = 0{\cdot}046$) for 327 unique observed [$I > 2\sigma(I)$] reflections. Prepared from a saturated aqueous solution of $ZnBr_2$ at 297 K. The compound is isostructural with $MgZn_2Br_6.6H_2O$ and consists of independent octahedral $Zn(H_2O)_6^{2+}$ complexes (ave. Zn—O = 2·07 Å) and dimeric tetrahedral $Zn_2Br_6^{2-}$ complexes [Zn—Br = 2·48 (bridging) and 2·36 Å (terminal)], linked together by O—H···Br hydrogen bonds.

Introduction. Although $ZnBr_2.2H_2O$ is a well known material its crystal structure has not previously been reported. Brehler (1961) reported the space group to be *I2mm*, with $a = 10{\cdot}4$, $b = 10{\cdot}4$, $c = 7{\cdot}94$ Å, $Z = 6$. In their review of the structures of $MX_2.nH_2O$ salts, Balarew, Duhlev & Spassov (1984) pointed out that $ZnBr_2.2H_2O$ has different lattice parameters and hence probably a different structure from other $MX_2.2H_2O$ (M = Ca, Mn, Fe, Co, Ni, Cu; X = F, Cl, Br) compounds which are all composed of infinite chains of $MX_4(H_2O)_2$ octahedra sharing X—X edges.

Duhlev & Balarew (1986), in a study of solubility phase diagrams and X-ray powder diffraction patterns, found a continuous series of mixed crystals between $ZnBr_2.2H_2O$ and the double salt $MgZn_2Br_6.6H_2O$, suggesting that the two end members were isostructural. Using a method (Balarew & Duhlev, 1984) based on the relative softness and size of the ions, Duhlev & Balarew (1986) predicted that the structures of $MgZn_2Br_6.6H_2O$ and $ZnBr_2.2H_2O$ are composed of independent $Mg(H_2O)_6$ [or $Zn(H_2O)_6$] octahedra and $ZnBr_4$ tetrahedra, the latter either sharing corners to link into infinite chains $(ZnBr_3)_\infty$ or sharing edges to form discrete Zn_2Br_6 dimers. Further modelling of the structures (Duhlev, Faggiani & Brown, 1987) showed that the $[Mg(H_2O)_6][Zn_2Br_6]$ (or $[Zn(H_2O)_6][Zn_2Br_6]$) motifs fit well into the cell reported by Brehler (1961). These results are confirmed by the X-ray analysis of $MgZn_2Br_6.6H_2O$ (Duhlev, Faggiani & Brown, 1987) and $ZnBr_2.2H_2O$ (present work).

The successful prediction of the $ZnBr_2.2H_2O$ structure shows how unconventional sources such as solubility studies of three-component systems can sometimes be used to predict crystal structures.

Experimental. $ZnBr_2.2H_2O$ was obtained as colourless extremely hygroscopic crystals from saturated aqueous $ZnBr_2$ solution at room temperature. A crystal with dimensions 0·47 × 0·37 × 0·27 mm was coated with liquid paraffin, sealed in a thin-walled capillary under dry nitrogen and mounted on a Syntex $P2_1$ diffractometer. Unit-cell parameters were determined from 15 well centered strong reflections in the range $25 < 2\theta < 38°$. Intensities were measured for 891 reflections with $0 \le h \le 12$, $0 \le k \le 12$, $-9 \le l \le 9$, $2\theta < 50°$ and were corrected for Lorentz and polarization effects. The intensities of the $07\bar{1}$ and $2\bar{5}\bar{1}$

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