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Strontium hexabromodicadmate(II) octahydrate

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The ternary system $SrBr_2$–$CdBr_2$–H_2O was investigated at room temperature. The title phase, $SrCd_2Br_6{\cdot}8H_2O$, has been isolated from this system and its structure determined by single-crystal X-ray diffraction. The structure consists of infinite double chains of $CdBr_6$ octahedra and chains of $Sr(H_2O)_9$ polyhedra packed along the *b* axis. The interaction between these two isolated chains occurs through O—H···O and O—H···Br hydrogen bonds. The structure is compared with that of $SrCd_2Cl_6{\cdot}8H_2O$.

Comment

MCl_2–$CdCl_2$–H_2O systems (where *M* is Mg, Ca and Ba) have been intensively investigated by several authors (Bassett & Strain, 1952; Bernath & Lechner, 1940; Moshinskii & Tikhomirova, 1975). Structural studies of the phases obtained from these systems were undertaken to compare the coordination of the cations by the water molecules, and to study the arrangement of the polyhedra and particular properties (pseudosymmetry and twinning) (Ledésert & Monier, 1981; Leligny & Monier, 1978, 1982, 1983, 1989*a*,*b*; Ledésert, 1985; Ledésert & Raveau, 1987). In our previous work (Yahyaoui *et al.*, 2002) investigating the $SrCl_2$–$CdCl_2$–H_2O ternary system, we isolated the hydrated phase $SrCd_2Cl_6{\cdot}8H_2O$ and determined its structure. The room-temperature phase of this compound has a triclinic structure, space group $P\overline{1}$, and is characterized by a very persistent occurrence of twinning by pseudo-monoclinic symmetry; the twin element was found to be a twofold axis, [001]. At high temperature, $SrCd_2Cl_6{\cdot}8H_2O$ exhibits a structural phase transition at 323 K related to a higher symmetry, accompanied by a disappearance of the twin. In the present study, our interest in the $SrBr_2$–$CdBr_2$–H_2O system, which has not been reported previously in the literature, is mainly based on the structure determination of the new double-salt hydrate $SrCd_2Br_6{\cdot}8H_2O$, in order to understand the influence of the substitution of the Cl^- anion by the Br^- anion on the structural properties. We report here the synthesis of $SrCd_2Br_6{\cdot}8H_2O$ and X-ray diffraction measurements, accompanied by thermogravimetric and differential thermal analyses.

The structural arrangement in $SrCd_2Br_6{\cdot}8H_2O$ at room temperature (Fig. 1) seems to be the same as that of $SrCd_2Cl_6{\cdot}8H_2O$, with an increase in the unit-cell volume due to the large size of the Br^- ions. In the structure of $SrCd_2Br_6{\cdot}8H_2O$, there are two types of polyhedra around the Cd^{2+} and Sr^{2+} cations. The Cd^{2+} atoms are each bonded to six Br neighbours to form irregular $CdBr_6$ octahedra (Table 1), and these $CdBr_6$ octahedra are held together to generate endless double chains running along the [010] direction (Fig. 2), with four edges (Br3–Br3 × 2 and Br2–Br3 × 2) shared by four adjacent octahedra and an average Cd—Br distance of 2.7865 Å. Comparing the $CdBr_6$ octahedra in $SrCd_2Br_6{\cdot}8H_2O$ with those in $SrCd_2Cl_6{\cdot}8H_2O$, we note that the Cd—Br distances are longer than the Cd—Cl distances, leading to an elongated octahedron in $SrCd_2Br_6{\cdot}8H_2O$, as opposed to the compressed octahedron in $SrCd_2Cl_6{\cdot}8H_2O$ (mean Cd—Cl distance = 2.6339 Å).

The Sr coordination sphere consists only of O atoms, namely two O1, one O2, four O3 and two O4 atoms belonging to nine water molecules. Thus the coordination number is nine. The average Sr—O distance is 2.6665 Å. However, we noted seven O and two Cl atoms surrounding the Sr^{2+} cations in $SrCd_2Cl_6{\cdot}8H_2O$, with the mean Sr—O distance being

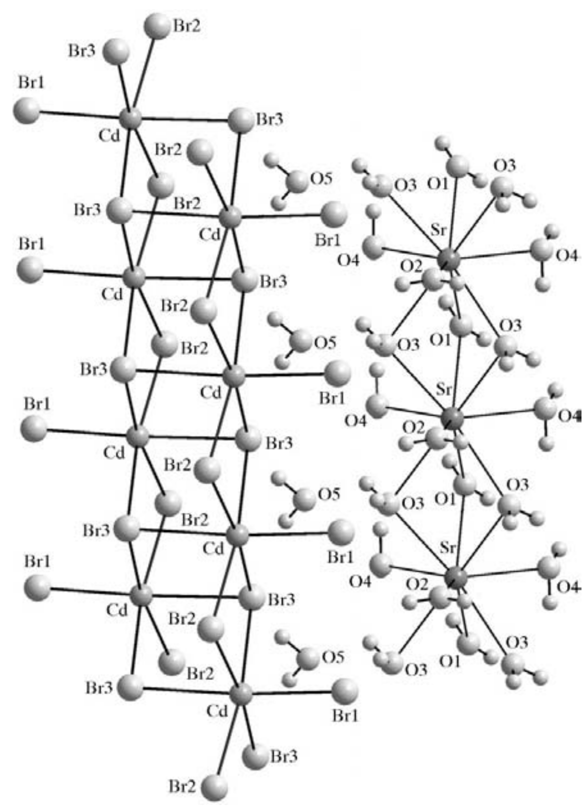

Figure 1
A view of the structure of $SrCd_2Br_6{\cdot}8H_2O$, showing the labelling of the atoms.

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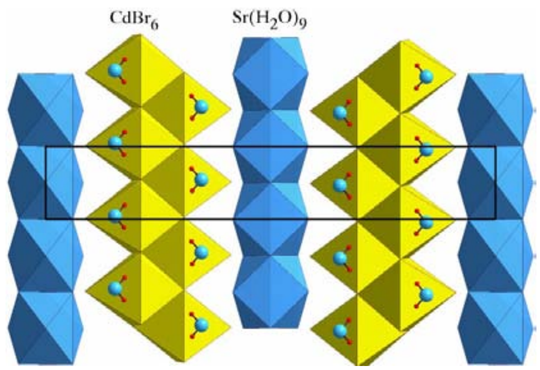

Figure 2
A polyhedral representation of $SrCd_2Br_6{\cdot}8H_2O$, viewed down the *c* axis.

2.6234 Å. The Sr polyhedron can be described as a nearly regular triangular prism, with three faces capped by three O atoms, one O2 and two O4 [Sr—O2 = 2.571 (7) Å and Sr—O4 = 2.597 (5) Å (×2); Table 1 and Fig. 3]. The two triangular bases of this polyhedron are each formed by one O1 and two O3 atoms [O1—O3 = 3.074 (6) Å (×2) and O3—O3 = 3.079 (9) Å]. The $Sr(H_2O)_9$ polyhedra are connected together to form simple chains with two shared triangular bases, with two other polyhedra in the [010] direction (Fig. 2). This chain arrangement of Sr polyhedra is found for the first time in $SrCd_2Br_6{\cdot}8H_2O$. Thus, it is the first double salt, belonging to the family of double-salt hydrates of Cd obtained from MX_2–CdX_2–H_2O systems (where *M* is Mg, Ca, Sr and Ba, and *X* is Cl or Br), containing these chains of alkaline-earth polyhedra.

We now make a comparison between the structures of $SrCd_2Br_6{\cdot}8H_2O$ and $SrCd_2Cl_6{\cdot}8H_2O$. The latter compound was found to be twinned, and exhibits a pseudo-monoclinic symmetry involving triclinic crystals defined by a twofold [001] axis and a twinned monoclinic face-centred Bravais cell described by the parameters $a1$, $b1$, $c1$, $\alpha1$, $\beta1$ and $\gamma1$, which are deduced from the triclinic parameters by the transformations $a1 = a$, $b1 = c$ and $c1 = a - 4b - c$. An examination of the orthorhombic structure of $SrCd_2Br_6{\cdot}8H_2O$ by *LEPAGE* using *PLATON* (Spek, 1990) showed the absence of any twin phenomena. We can clearly observe inside the double chains that the Cd, *X* and O atoms show two-by-two correspondence, *via* a *c*/2 pseudo-translation in the case of the Cl^- compound and a *b*/2 translation in the Br^- compound. The twin element, which was a helicoidal binary [001] axis, becomes a real helicoidal binary axis [010] in $SrCd_2Br_6{\cdot}8H_2O$.

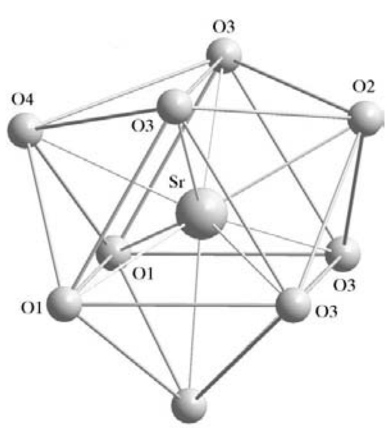

Figure 3
The Sr polyhedron in $SrCd_2Br_6{\cdot}8H_2O$, *viz*. the tricapped triangular prism.

The structure of $SrCd_2Br_6{\cdot}8H_2O$ contains four water molecules (H_2O1, H_2O2, H_2O3 and H_2O4), surrounding Sr atoms, and one water molecule (H_2O5), which is not coordinated to any cations. Thus, there are two categories of water molecules, which are differently coordinated to Sr, Br and O atoms.

The cohesion of the structure of $SrCd_2Br_6{\cdot}8H_2O$ is ensured by the presence of two kinds of hydrogen bonds, O—H···Br and O—H···O. The first type connects different polyhedra through all the Br atoms, and the distances range from 3.444 (5) to 3.536 (6) Å. As seen in Table 2, the three Br atoms link differently to the O atoms. Atom Br1 establishes the most hydrogen bonds, with nearly all O atoms coordinated to Sr^{2+} cations (O1, O2, O3 and O4). Atom Br2 has two hydrogen bonds to atom O5 of the free water molecule H_2O5, while atom Br3 establishes only one hydrogen bond to atom O5. There are O—H···O hydrogen bonds between nearly all the water molecules present in the structure. The shortest links atom O5 to atoms O3 and O4, at distances of 2.712 (7) and 2.747 (9) Å, respectively. It is also noted that a comparison of the hydrogen bonds in $SrCd_2Br_6{\cdot}8H_2O$ and $SrCd_2Cl_6{\cdot}8H_2O$ shows an increase in the O—H···*X* bond lengths and a decrease in the O—H···O bond lengths, which may be explained by the decrease in electronegativity on going from Cl to Br.

From these comparisons, it follows that the substitution of Cl^- by Br^- in $SrCd_2Cl_6{\cdot}8H_2O$ has led to an extension of the unit cell due to the large size of the Br^- ions. An important point in the present structure is the disappearance of the twin phenomenon already observed in crystals of $SrCd_2Cl_6{\cdot}8H_2O$. One can conclude that the substitution of one atom by another, less electronegative, atom acts as a chemical pressure leading to an increase of symmetry. The same effect was observed when heating $SrCd_2Cl_6{\cdot}8H_2O$ to 323 K. On the other hand, this substitution has conserved the environment of the different cations. However, it has induced a new arrangement of $Sr(H_2O)_9$ polyhedra in isolated chains with a reduction in the distortion of the polyhedra. A lengthening of the Cd—Br and Sr—O bonds has also been observed.

Experimental

Single crystals of $SrCd_2Br_6{\cdot}8H_2O$ were prepared from a heated mixture of strontium carbonate and cadmium bromide in HBr in a molar ratio of 1:1 at 363 K. This solution was cooled to room temperature and allowed to evaporate. A few days later, colourless hygroscopic needle-shaped crystals were obtained. Characterizations of the compound were performed by X-ray powder patterns and elemental chemical analysis. The water content was determined by thermogravimetric analysis and the formula was confirmed by density measurements and refinement of the crystal structure. Differential thermal and thermogravimetric analyses were performed on polycrystalline samples using a SETARAM TGDTA92 instrument between 303 and 573 K. Seven sharp weight losses were detected between 333 and 498 K, of 7.49, 5.77 and 1.92% of the original weight, and these were assigned to the loss of two water molecules and six water molecules of crystallization per unit formula.

Crystal data

$SrCd_2Br_6{\cdot}8H_2O$
$M_r = 936.01$
Orthorhombic, $P2_12_12$
$a = 25.247$ (2) Å
$b = 4.0827$ (10) Å
$c = 8.764$ (2) Å
$V = 903.4$ (3) $Å^3$
$Z = 2$
$D_x = 3.441$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 2$–11°
$\mu = 18.56$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.20 × 0.06 × 0.04 mm

Data collection

Oxford Instruments Xcalibur point-detector diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*JANA*2000; Petříček & Dušek, 2000)
$T_{min} = 0.135$, $T_{max} = 0.408$
3930 measured reflections
1982 independent reflections
1494 reflections with $I > 2\sigma(I)$
$R_{int} = 0.063$
$\theta_{max} = 27°$
$h = 0 \rightarrow 32$
$k = -5 \rightarrow 5$
$l = -11 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.070$
$S = 1.07$
1982 reflections
81 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.43$ e $Å^{-3}$
$\Delta\rho_{min} = -1.53$ e $Å^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0018 (2)
Flack parameter = 0.336 (17)

The absolute structure parameter was calculated using *SHELXL*97 (Sheldrick, 1997). The Flack (1983) parameter x is 0.336 (17). From the full text of Flack & Bernardinelli (2000), one can understand that the standard uncertainty of 0.017 indicates that the inversion-distinguishing power is strong and the domains around x should be well defined and clearly distinguishable from one another. The value of the Flack parameter indicates that the crystal is twinned by inversion (Flack & Bernardinelli, 1999) and it is not possible to determine the absolute structure of such a crystal, which is considered to be constituted of a mixture of inverted structures. H atoms were located in geometrically idealized positions after their location, and were given riding constraints with regard to their positional and displacement parameters, with O—H distances of 0.9 Å, O—H—O angles of 106°, Sr—O—H angles of 120° and U_{iso}(H) values of $1.5U_{eq}$(O).

Data collection: *KM*4*B*8 (Galdecki *et al.*, 1996); cell refinement: *KM*4*B*8; data reduction: *JANA*2000 (Petříček & Dušek, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 1
Selected geometric parameters (Å, °).

Cd—Br1	2.6870 (9)	Sr—O4^{iv}	2.597 (5)
Cd—Br2	2.7218 (10)	Sr—O1^{iii}	2.700 (4)
Cd—Br2^{i}	2.7596 (11)	Sr—O1	2.700 (4)
Cd—Br3^{i}	2.7734 (11)	Sr—O3^{i}	2.702 (6)
Cd—Br3	2.8537 (11)	Sr—O3^{v}	2.702 (6)
Cd—Br3^{ii}	2.9240 (9)	Sr—O3^{vi}	2.715 (6)
Sr—O2	2.571 (7)	Sr—O3	2.715 (6)
Sr—O4^{iii}	2.597 (5)		
Br1—Cd—Br2	94.38 (3)	O4^{iii}—Sr—O4^{iv}	110.5 (2)
Br2—Cd—Br3^{i}	170.40 (3)	O2—Sr—O1^{iii}	130.88 (11)
Br2^{i}—Cd—Br3^{i}	85.01 (3)	O4^{iii}—Sr—O1^{iii}	67.71 (15)
Br2^{i}—Cd—Br3	170.74 (3)	O2—Sr—O3^{i}	70.68 (11)
Br1—Cd—Br3^{ii}	174.12 (3)	O4^{iii}—Sr—O3^{i}	74.14 (17)
Br3—Cd—Br3^{ii}	83.45 (3)	O1^{iii}—Sr—O3^{i}	141.75 (11)
O2—Sr—O4^{iii}	124.73 (12)	O2—Sr—O3^{v}	70.68 (11)
O2—Sr—O4^{iv}	124.73 (12)		

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, -z$; (iii) $x, 1+y, z$; (iv) $1-x, -1-y, z$; (v) $1-x, 1-y, z$; (vi) $1-x, -y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O4^{i}	0.91	2.47	2.982 (6)	116
O1—H1*A*···Br1^{ii}	0.91	2.72	3.444 (5)	138
O2—H2*A*···Br1^{iii}	0.90	2.80	3.468 (4)	132
O2—H2*A*···Br1^{iv}	0.90	2.83	3.519 (4)	134
O3—H3*A*···O2^{i}	0.91	2.57	3.052 (7)	113
O3—H3*A*···Br1^{i}	0.91	2.67	3.522 (5)	156
O3—H3*B*···O4^{v}	0.90	2.48	3.195 (8)	136
O3—H3*B*···O5^{i}	0.90	2.01	2.712 (7)	133
O4—H4*A*···O1	0.91	2.42	2.952 (6)	118
O4—H4*A*···O5	0.91	2.26	2.747 (9)	113
O4—H4*B*···Br1^{ii}	0.91	3.09	3.536 (6)	112
O5—H5*A*···Br3	0.93	2.74	3.512 (6)	140
O5—H5*A*···Br2^{vi}	0.93	2.89	3.430 (5)	118
O5—H5*B*···Br2^{vii}	0.95	2.60	3.493 (6)	157

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y, 1+z$; (iii) $1-x, -1-y, z$; (iv) $1-x, -y, z$; (v) $x, 2+y, z$; (vi) $\frac{3}{2}-x, y-\frac{1}{2}, -z$; (vii) $x, y-1, 1+z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1605). Services for accessing these data are described at the back of the journal.

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