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Cadmium Rubidium Iodide Monohydrate

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Abstract. $RbCdI_3.H_2O$ crystallizes at room temperature from aqueous solution in the monoclinic system, space group *Cc* (C_s^4), $a = 10{\cdot}911\,(2)$, $b = 10{\cdot}030\,(2)$, $c = 8{\cdot}778\,(2)$ Å, $\beta = 90{\cdot}6\,(2)°$; $D_m = 3{\cdot}90\,(5)$, $D_x = 4{\cdot}12$ g cm^{-3}, $Z = 4$. The structure, determined by X-ray diffraction ($R_2 = 0{\cdot}072$), is similar to $KHgI_3.H_2O$, consisting of CdI_4 tetrahedra linked through I atoms into chains running along **c** [Cd–I(terminal) = 2·728; Cd–I(bridging) = 2·820 Å]. Each Rb is surrounded by seven I atoms at distances ranging from 3·753 to 4·141 Å and two water molecules (Rb–O = 2·92 Å), each of which hydrogen-bonds to five I atoms.

Introduction. Crystals of $RbCdI_3.H_2O$ were originally prepared by Natarajan & Secco (1976) who, however, reported them as $RbCdI_3$. A colourless needle-shaped crystal from the same source was employed for the X-ray structure determination. Precession photographs showed the following condition for reflexion: *hkl*, $h + k = 2n$ and *h*0*l*, $l = 2n$, consistent with the space groups *Cc* and *C*2/*c*. Statistical tests on the normalized structure factors (program *NORM SF*) indicated that the noncentrosymmetric space group *Cc* was correct and this was confirmed by the final structure. Accurate lattice parameters were obtained by a least-squares fit to the angular settings of 15 reflexions ($20° < 2\theta < 25°$) measured with a Syntex $P\bar{1}$ automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). A single crystal of $RbCdI_3.H_2O$ ground to a cylinder of radius 0·075 mm and length 0·3 mm (along **c**) was used for measuring intensities on the same diffractometer. With a $\theta/2\theta$ scan a total of 1059 symmetry-independent reflexions were measured out to $2\theta = 55°$ in the quadrant with $h \geq 0$, $k \leq 0$. They were corrected for Lorentz, polarization and absorption effects ($\mu = 17{\cdot}5$ mm^{-1}). The structure was solved from the Patterson function and difference electron density maps. Atomic positions were refined by minimizing $\Sigma\omega(|F_o| - |F_c|)^2$ with the locally written full-matrix least-squares program *CUDLS* (CDC 6400). The weighting function, $\omega = [\sigma + (0{\cdot}025F)^2]^{-1}$, where σ is the standard error attributable to counting statistics, was chosen so that $\langle\omega(|F_o| - |F_c|)^2\rangle$ was relatively independent of $|F_o|$.[†] The 39 reflexions for which $I < 3\sigma(I)$ and $|F_c| < |F_o|$ were given zero weight. In the final refinements an extinction correction given by $F^* = F[1 + 0{\cdot}18 \times 10^{-6}\beta(2\theta)F^2]^{-1/2}$ (Larson, 1967) was applied. The atomic scattering factors corrected for anomalous dispersion for Rb, Cd, I and O^- were taken from *International Tables for X-ray Crystallography* (1962) and the origin was defined by the *x* and *z* coordinates of Cd. The final agreement indices were $R_1 (= \Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0{\cdot}061$ and $R_2\{= [\Sigma\,\omega(|F_o| - |F_c|)^2/\Sigma\,\omega F_o^2]^{1/2}\} = 0{\cdot}072$. A difference synthesis showed no significant features. The final positional and temperature coordinates are given in Table 1, the interatomic distances and angles in Table 2.[‡]

Table 1. *Atomic positional* (×10^4) *and thermal* (×10^3) *coordinates*

The temperature factor is given by: $\exp(-2\pi^2\Sigma U_{ij}H_iH_ja_i^*a_j^*)$. The coordinates of the hydrogen atoms have been assigned on chemical grounds.

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	3980 (5)	8891 (4)	3267 (5)	112 (3)	60 (2)	49 (2)	13 (2)	−2 (2)	−2 (2)
Cd	0	337 (2)	0	49 (1)	43 (1)	39 (1)	−0 (1)	1 (1)	−0 (1)
I(1)	901 (3)	2868 (2)	−54 (3)	57 (1)	47 (1)	55 (1)	−13 (1)	−0 (1)	−0 (1)
I(2)	3407 (2)	4930 (2)	7488 (3)	45 (1)	48 (1)	32 (1)	0 (1)	−0 (1)	−0 (1)
I(3)	6733 (3)	3371 (2)	−60 (3)	54 (1)	56 (1)	60 (1)	12 (1)	−0 (1)	−0 (1)
O	3910 (24)	1400 (23)	1544 (28)	99 (17)	48 (12)	50 (12)	6 (12)	11 (12)	−10 (10)
H(1)	3200	1900	1770						
H(2)	4620	1900	1770						

[†] For the largest and smallest reflexions $\langle\omega(|F_o| - |F_c|)^2\rangle$ was ~5 but in the intermediate range it was ~2.

[‡] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31971 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. $RbCdI_3.H_2O$ contains chains of corner-sharing CdI_4 tetrahedra extending along **c**. Between the chains lie the Rb ions and H_2O molecules, each O bonding to two Rb ions and hydrogen-bonding to five I atoms. $KHgI_3.H_2O$ crystallizes with an almost identical structure (Nyqvist & Johansson, 1971) in the space group $P2_1cn$ (converted from $Pna2_1$ for comparison), the only difference between the two structures being the arrangements of adjacent chains. In $RbCdI_3.H_2O$ the chains are related by translational symmetry but in $KHgI_3.H_2O$ they are related by the 2_1 and *n*-glide symmetry elements.

The CdI_4 tetrahedron is slightly distorted with the bridging Cd—I bonds being longer than the terminal bonds. The observed angles are very close to those predicted from the equation (Brown, 1976) $\theta = 109{\cdot}5 + 45\Delta S - 40{\cdot}5\Delta S^2$ where ΔS is the sum of the differences between the valences of the defining bonds and 0·5, their average value (Table 3).

Although the H atoms were not included in the refinement, their positions (Table 2) can be assigned by completing the tetrahedral coordination around O and setting O—H = 0·95 Å. The final difference electron density map shows positive density at the expected H positions but the peaks are not significantly above the background. Both H atoms make contacts with three I atoms leading to weak trifurcated hydrogen bonds. I(2) is linked to O by two hydrogen bonds. As a check on the final structure, bond valences (Brown & Shannon, 1973) were calculated[*] (Table 3) and were found to give sums with a standard deviation of 0·01 valence units from the atomic valences.

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

Predicted I—Cd—I angles are given in brackets (see text).

Cd—I(1)	2·723 (3)	Rb—I(3)	3·830 (9)	
Cd—I(2)	2·818 (5)	Rb—I(3)′	3·973 (6)	
Cd—I(2)′	2·823 (5)	Rb—I(3)″	4·029 (7)	
Cd—I(3)	2·733 (3)			
Rb—O	2·893 (25)	I(1)—Cd—I(2)	109·2 (1)	[110·4]
Rb—O′	2·937 (24)	I(1)—Cd—I(2)′	109·9 (1)	[110·4]
Rb—I(1)	3·752 (8)	I(1)—Cd—I(3)	115·0 (1)	[115·0]
Rb—I(1)′	4·083 (7)	I(2)—Cd—I(2)′	102·2 (1)	[103·5]
Rb—I(1)″	4·131 (6)	I(2)—Cd—I(3)	112·3 (3)	[109·5]
Rb—I(2)	3·942 (5)	I(2)—Cd—I(3)	107·5 (1)	[109·5]

Hydrogen bonds	O···I	H···I	O—H···I
O—H(1)···I(1)	3·75 (3)	3·12	136
O—H(1)···I(3)	3·93 (3)	3·24	123
O—H(1)···I(2)	3·81 (2)	3·25	120
O—H(2)···I(2)		3·50	102
O—H(2)···I(1)	3·85 (3)	3·11	126
O—H(2)···I(3)	3·84 (3)	3·18	138

Table 3. *Bond valences in valence units*

See footnote on this page for method of calculation.

	Rb	Cd	H(1)	H(2)	Sum
I(1)	0·14 0·08 0·07	0·58	0·06	0·06	0·99
I(2)	0·10	0·44 0·44	0·03	0·01	1·02
I(3)	0·12 0·10 0·09	0·56	0·06	0·06	0·99
O	0·16 0·14		0·85	0·87	2·02
Sum	1·00	2·02	1·00	1·00	

The temperature factors indicate that the CdI_3 chains are librating about their axes. The Rb and O atoms both undergo large thermal vibrations (r.m.s. displacement = 0·33 Å) in the plane perpendicular to the Rb—O bonds.

One of the more remarkable features of $RbCdI_3.H_2O$ is its low density (4·12) compared to $RbCdBr_3$ (4·69 g cm^{-3}). The latter structure is very compact (Iyer, Faggiani & Brown, 1977) with the Cd atoms octahedrally coordinated. The larger size of I forces the Cd atoms into tetrahedral coordination in the present compound and results in a much more open structure which is responsible for the much higher ionic conductivity in the iodide compared with the bromide (Natarajan & Secco, 1976).

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[*] Bond valences (S) were calculated from the bond lengths (R) by the expression $S = (R/R_0)^{-N}$ where the values of R_0 and N were taken from Brown & Wu (1976) for Rb—O, and for the other bonds were the values given below obtained by fitting to the structures listed. Rb—I: $R_0 = 843$, $N = 7$ [RbI (2 phases), Rb_2SnI_6 (Werker, 1939), $RbPbI_3$ (Haupt, Huber & Preut, 1974)]. Cd—I: $R_0 = 2{\cdot}535$, $N = 7{\cdot}6$ {$RbCdI_3.H_2O$, $Cd[N(C_2H_4NCH_3)_2]I.Cd_2I_6$ (Orioli & Ciampolini, 1972)}. Valences of bonds to H atoms were assigned in accordance with the expected H—I distances to give the best fit for the sums. It was the failure of the valence sum around Rb to equal 1·0 during the refinement that first drew our attention to the presence of water in these crystals.