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The Structures of Potassium Lead Triiodide Dihydrate and Ammonium Lead Triiodide Dihydrate

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Abstract

$KPbI_3.2H_2O$, $NH_4PbI_3.2H_2O$ and $RbPbI_3.2H_2O$ are isostructural and crystallize in space group *Pnma* with $Z = 4$. $KPbI_3.2H_2O$: $a = 10.168$ (2), $b = 4.577$ (1), $c = 22.484$ (5) Å. $NH_4PbI_3.2H_2O$: $a = 10.262$ (2), $b = 4.611$ (1), $c = 22.613$ (5) Å. $RbPbI_3.2H_2O$: $a = 10.276$ (5), $b = 4.715$ (3), $c = 22.623$ (9) Å. The structures of the first two compounds have been determined and refined to $R = 0.030$ and $R = 0.039$, respectively. The structures contain $[PbI_3]^-$ double chains of edge-sharing PbI_6 octahedra. The chains extend along **b** and are connected by alkali ions and water molecules. Pb–I bonds average 3.241 Å. The structures can be regarded as hydrated variants of the NH_4CdCl_3 structure type, in which anhydrous $RbPbI_3$ and $CsPbI_3$ are known to crystallize. Close relationships to the structures of $NH_4HgCl_3.H_2O$ and $NaHgCl_3.2H_2O$ are noted.

Introduction

PbI_2 is only slightly soluble in water but dissolves readily in hot concentrated aqueous solutions of alkali iodides. On evaporation or cooling of the solutions, $APbI_3.nH_2O$ double salts are obtained, where $A =$ Li, Na, K, NH_4, Rb or Cs and $n = 0$, 2 or 4, depending on the alkali ion and, in part, on the conditions of formation (*Gmelins Handbuch der Anorganischen Chemie*, 1970). Of this family, only the structures of the two isotypic anhydrous salts $RbPbI_3$ (Haupt, Huber & Preut, 1974) and $CsPbI_3$ (low-temperature form; Møller, 1959) are known. In this work we present the crystal structures of $KPbI_3.2H_2O$ and $NH_4PbI_3.2H_2O$, together with crystal data for $RbPbI_3.2H_2O$.

Experimental

Crystals of the NH_4 and K salts were obtained by saturating solutions of alkali iodide (50 wt% in water) with PbI_2 at 353 K and cooling them slowly to 313 K. When we applied this method for the Rb salt we obtained only anhydrous $RbPbI_3$, a simple preparation method not, however, known in the literature. We finally obtained the desired dihydrate by crystallization at room temperature.

$KPbI_3.2H_2O$, $NH_4PbI_3.2H_2O$ and $RbPbI_3.2H_2O$ are isomorphous; they form thin flexible pale-yellow needles. The crystals are very similar in habit to anhydrous $RbPbI_3$ and $CsPbI_3$, the only obvious

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difference being the pronounced brighter yellow of the latter. $RbPbI_3.2H_2O$ is unstable in air at room temperature and dehydrates readily. The K and NH_4 salts are stable, but dehydrate gradually above 303 K.

Structure determination

Weissenberg photographs of the three hydrated salts showed them to be orthorhombic and isotypic. Systematic extinctions were consistent with the space groups *Pnma* or *Pn2₁a*. Statistical tests on the normalized structure factors indicated centro-symmetry and hence *Pnma*, which was confirmed by the structure determination. Crystals ~ 0.02 mm in diameter and $0.3-0.5$ mm long (parallel to **b**) were mounted on a Philips PW 1100 four-circle diffractometer for determining accurate lattice constants (Table 1). The values for the K salt agree well with those given by Nardelli, Cavalca & Braibanti (1956). Graphite-monochromatized Mo $K\alpha$ radiation was used to collect data in the range $\theta = 3 - 30°$ with the ω-scan technique and a scan width of $1.5°$. 1707 and 1748 symmetry-independent reflections were measured for $KPbI_3.2H_2O$ and $NH_4PbI_3.2H_2O$, respectively. The

data were processed to obtain F_o's without corrections for absorption.

The structure of $NH_4PbI_3.2H_2O$ was solved by direct methods with *MULTAN* and, subsequently, difference maps. The parameters of the K and NH_4 salts were then refined by least-squares methods minimizing $\sum w(F_o - F_c)^2$ with $w = [\sigma(F_o) + 0.01F_o]^2$. Anisotropic temperature factors were used for Pb and I. For $KPbI_3.2H_2O$ the final agreement factors were $R = 0.030$ and $R_w = 0.025$ for only the 1050 reflections with $F_o > 6\sigma(F_o)$. The corresponding values for the NH_4 salt are $R = 0.039$ and $R_w = 0.031$ for 1070 reflections. Difference syntheses showed no unusual features. Scattering functions and anomalous-dispersion corrections for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are given in Table 2.*

Discussion

$KPbI_3.2H_2O$ and $NH_4PbI_3.2H_2O$ are isostructural and show only minor differences in bond lengths and

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35026 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data*

Space group	$KPbI_3.2H_2O$	$NH_4PbI_3.2H_2O$	$RbPbI_3.2H_2O$
	Pnma	*Pnma*	*Pnma*
a (Å)	10.168 (2)	10.262 (2)	10.276 (5)
b (Å)	4.577 (1)	4.611 (1)	4.715 (3)
c (Å)	22.484 (5)	22.613 (5)	22.623 (9)
V (Å³)	1046.4	1070.0	1096.1
Z	4	4	4
M_r	663.03	641.97	709.40
D_c (Mg m⁻³)	4.21	3.98	4.30
μ(Mo $K\alpha$) (mm⁻¹)	24.4	25.3	28.1

Table 2. *Positional parameters (x and $z \times 10^5$) and isotropic temperature factors (Å²)*

The *B*'s for Pb and I were calculated from the anisotropic temperature factors.

	x	y	z	B
(a) $KPbI_3.2H_2O$				
Pb	54326 (4)	¼	40497 (2)	2.74 (2)
I(1)	41562 (8)	¼	28312 (3)	3.36 (4)
I(2)	74850 (7)	¾	36729 (4)	3.46 (4)
I(3)	66135 (7)	¼	54934 (3)	2.95 (4)
K	14112 (28)	¾	29991 (14)	4.92 (6)
O(1)	5936 (81)	¼	36294 (39)	5.19 (20)
O(2)	6274 (79)	¼	48710 (37)	5.00 (20)
(b) $NH_4PbI_3.2H_2O$				
Pb	54173 (5)	¼	40578 (2)	2.94 (2)
I(1)	41652 (9)	¼	28466 (4)	3.47 (4)
I(2)	74554 (9)	¾	36938 (4)	3.61 (4)
I(3)	66064 (8)	¼	54903 (4)	3.18 (4)
NH_4	13868 (91)	¾	30053 (43)	2.98 (20)
O(1)	4960 (90)	¼	36485 (44)	4.97 (24)
O(2)	6109 (90)	¼	48526 (43)	5.38 (24)

Table 3. *Interatomic distances (Å) and angles (°)*

		$KPbI_3.2H_2O$	$NH_4PbI_3.2H_2O$
Pb–I(1)		3.032 (1)	3.025 (1)
–I(2)	2×	3.211	3.220
–I(3)	2×	3.259	3.267
–I(3)'		3.461	3.462
Mean		3.239	3.243
K,NH_4–I(1)	2×	3.629 (3)	3.684 (9)
–I(1)'	2×	3.739	3.772
–I(2)		3.915	3.996
–I(2)'		4.270	4.324
–I(3)		3.940	3.977
–O(1)	2×	2.817	2.875
O(1)–I(1)		3.595 (9)	3.646 (8)
–I(2)	2×	3.904 (7)	3.881 (8)
–K,NH_4	2×	2.817 (5)	2.875 (8)
–O(2)		2.792 (12)	2.725 (14)
O(2)–I(2)		3.795 (8)	3.840 (9)
–I(3)	2×	3.712 (6)	3.751 (7)
–O(1)		2.792 (12)	2.725 (14)
–O(2)'	2×	2.684 (9)	2.708 (10)
I(1)–Pb–I(2)	2×	92.28 (2)	92.55 (3)
–I(3)	2×	90.66	90.76
–I(3)'		174.96	175.50
I(2)–Pb–I(2)		90.91	91.46
–I(3)	2×	89.86	89.29
–I(3)	2×	176.93	176.57
–I(3)'	2×	91.26	90.59
I(3)–Pb–I(3)		89.21	89.78
–I(3)'	2×	85.75	86.06

KPbI₃·2H₂O
S.G. Pnma
a = 10.168 Å
b = 4.577
c = 22.484

(a)

Rb Pb I₃
S.G. Pnma
a = 10.274 Å
b = 4.773
c = 17.381

(b)
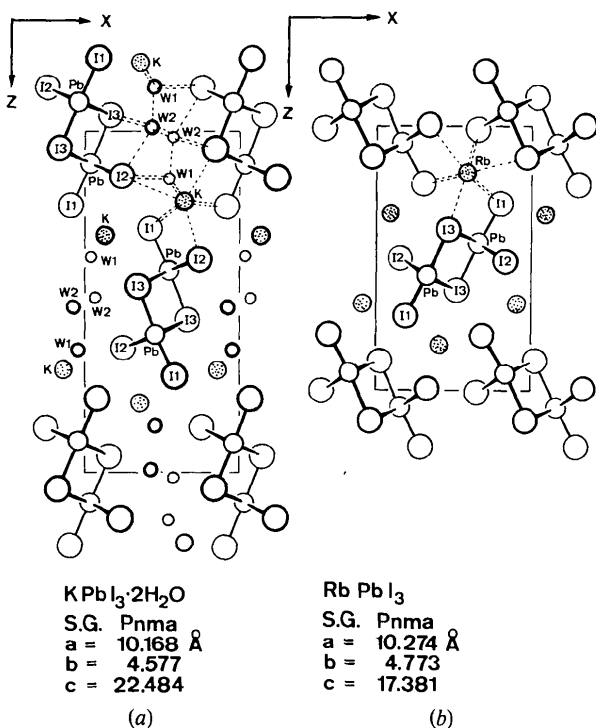
Fig. 1. The crystal structures of (a) KPbI₃.2H₂O compared to (b) RbPbI₃ (Haupt, Huber & Preut, 1974; transformed from space group *Pnam* to *Pnma*). All atoms lie on mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$.

angles (Table 3). The structures contain [PbI₃]⁻ double chains of edge-sharing PbI₆ octahedra. These chains extend along **b** and are bonded together by alkali ions and water molecules which occupy channels between them (Fig. 1a). The structures can be regarded as hydrated variants of the anhydrous salts RbPbI₃ (Fig. 1b; Haupt, Huber & Preut, 1974) and CsPbI₃ (Møller, 1959), which crystallize with the NH₄CdCl₃ structure type (Brasseur & Pauling, 1938; Rolies & De Ranter, 1978) and also contain the [PbI₃]⁻ double chains.

Although the PbI₆ octahedra are distorted, a stereochemical effect of the Pb electron lone pair is unlikely (Haupt, Huber & Preut, 1974). Pb—I lengths increase with the number of Pb atoms to which the three different kinds of I atoms are bonded. Thus the terminal Pb—I(1) (3·03 Å) is shorter than the two bridging Pb—I(2) (2 × ~3·22 Å) and these again are shorter than the three bridging Pb—I(3) (2 × ~3·26 and 1 × 3·46 Å). Individual Pb—I lengths and their average values differ by <0·02 Å from the values found for RbPbI₃, except the Pb—I(3)′ which are ~0·08 Å longer in the hydrates than in the anhydrous salt.

The repeat periods of the [PbI₃]⁻ chains and, consequently, certain I—Pb—I angles, vary considerably with the alkali ion. Repeat periods range from b = 4·577 Å for KPbI₃.2H₂O to 4·773 Å for RbPbI₃ and 4·797 Å for CsPbI₃. Since the alkali ions have their

shortest distances parallel to the chain directions, a repulsion between them, increasing with the size of the ions, is most likely responsible for this effect. As a consequence the I—Pb—I angles subtended by I(2) and I(3) differ by about 5° between KPbI₃.2H₂O and RbPbI₃.

The coordination figure of the alkali ions is a tricapped trigonal prism (Fig. 1a) similar to that found in RbPbI₃ (Fig. 1b), except that two I atoms are replaced by H₂O molecules in the hydrated salts. As expected, the NH₄—I,O distances are about 0·05 Å longer than the corresponding distances for the K salt.

The alkali ions and water molecules are connected in ribbons parallel to **b** (Fig. 2). Hydrogen bonds between H₂O molecules are indicated by O···O distances of 2·68–2·79 Å. Disorder must be assumed for the O(2)···O(2) bonds since the O atoms are related by a symmetry center, but the O—H vectors should point locally in one direction only. Apparently, the H₂O molecules are also engaged in interactions with I atoms which must be weak because all I—O distances are >3·59 Å. Although H atoms were not included in the refinement their positions can be assigned by completing the tetrahedral coordination around the O atoms and setting O—H = 0·96 Å. The predicted H positions and the geometries of the corresponding hydrogen bonds are given for KPbI₃.2H₂O in Table 4. Comparable data on O—H···I bonds are rare. Fairly linear O—H···I bonds with O···I = 3·59–3·65 Å and H···I = 2·65–2·82 Å have been deduced from X-ray and ¹H NMR data for NaI.2H₂O (Verbist, Piret & Van
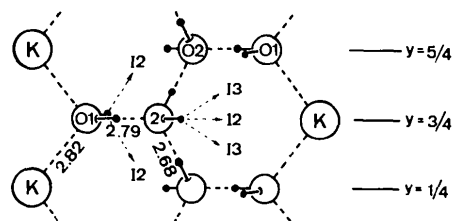
Fig. 2. Bonding scheme of K and H₂O in KPbI₃.2H₂O.

Table 4. *Hydrogen bonds in* KPbI₃.2H₂O

(a) Hydrogen-atom parameters (×10⁴), assigned on chemical grounds

	x	y	z
H(1)	0983	2500	4018
H(2)	−0347	2500	3666
H(3)	0161	4213	4998*
H(4)	1492	2500	5042

(b) Hydrogen-bond geometry (O—H = 0·96 Å, H—O—H = 109·5°)

D—H···A		D···A	H···A	∠D—H···A	
O(1)—H(1)···O(2)		2·79 Å	1·95 Å	145°	
—H(2)···I(2)	2×	3·90	3·18	134	bifurcated
O(2)—H(3)···O(2)		2·68	1·73	172	
—H(4)···I(2)		3·80	3·07	133	trifurcated
···I(3)	2×	3·71	3·22	113	

* Half occupancy due to disorder (see text).

Meerssche, 1970). Values more comparable with those of $KPbI_3.2H_2O$ have been given for $RbCdI_3.H_2O$ (structurally not related to the Pb salt; Natarajan Iyer, Faggiani & Brown, 1977): $O\cdots I$ distances of 3·75–3·93 Å have been found and $H\cdots I$ distances of 3·11–3·50 Å within two trifurcated hydrogen bonds were deduced.

Related structures

The close structural relationships between the hydrated salts K-, NH_4- and $RbPbI_3.2H_2O$ and the NH_4CdCl_3-type structures of $RbPbI_3$ and $CsPbI_3$ are evident from Fig. 1. The hydrated salts lose water very easily on heating; the K salt, for instance, dehydrates completely at ~373 K. When completely dehydrated, the $[PbI_3]^-$ chains and adjacent alkali ions need only to be rotated by ~45° about the chain axes to transform the structure into the NH_4CdCl_3 type. For rearrangement only the longest alkali–I bond (K–I = 4·27 Å) must be broken, while three new, shorter bonds are gained. We have obtained experimental evidence for this transformation in $RbPbI_3.2H_2O \rightarrow RbPbI_3$, which takes place at temperatures between 373 and 473 K. Further investigations on this subject are in progress.

An interesting connection also exists with NH_4Hg-$Cl_3.H_2O$ (Sagisawa, Kitahama, Kiriyama & Kiriyama, 1974) and $NaHgCl_3.2H_2O$ (Malčič, 1959). Both salts crystallize in space group $Pnma$, $Z = 4$, with $a = 8·727$, $b = 4·344$, $c = 17·73$ Å and $a = 9·372$, $b = 4·037$, $c = 18·71$ Å, respectively. They contain $[HgCl_3]^-$ double chains of the same type and with the same arrangement as the $[PbI_3]^-$ chains of the alkali lead iodide dihydrates. Compared to the PbI_6 octahedra, the $HgCl_6$ octahedra are smaller and strongly compressed in the direction equivalent to $I(1)–Pb–I(3)'$. In $NH_4HgCl_3.H_2O$ the $H_2O(2)$ molecules of the lead iodide hydrates are absent. Due to the smaller $[HgCl_3]^-$ chains there is room for only an $H_2O(1)$-type molecule, which lies, in terms of the Pb salts, halfway between a pair of connected $H_2O(1)$ and $H_2O(2)$ molecules. The structure of $NaHgCl_3.2H_2O$ can be derived from those of the alkali lead iodide hydrates by exchanging the positions of the alkali ions and $H_2O(1)$ molecules. Moderate shifts of the atomic sites then give the Na ions a distorted octahedral coordination with three H_2O and three Cl.

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