The Structure of SrPb₂I₆.7H₂O

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The structure of the salt $SrPb_2I_6.7H_2O$ has been investigated. The compound crystallizes in the tetragonal system, with cell constants

$$a = 11{\cdot}77 \pm 0{\cdot}02, \quad c = 17{\cdot}32 \pm 0{\cdot}02 \text{ Å}.$$

The space group is $D_{4h}^{19}-I4_1/amd$.

The structure is characterized by a three-dimensional framework of octahedra $[PbI_{6/2}]$ joined to one another through all the corners. The empty spaces of this framework are occupied by the strontium ions and by the water molecules. Six water molecules octahedrally surround each strontium ion.

The errors in the intensities due to the particularly high absorbing power of the substance ($\mu = 962$ cm.⁻¹) do not affect the coordinates of the heavy atoms but do not allow an exact determination of the coordinates of the water molecules.

Introduction

Strontium and lead(II) salts are often isotypic and form solid solutions. But in some compounds, such as $SrPb_2I_6.7H_2O$ the two ions are combined in a definite ratio. The study of the salt $SrPb_2I_6.7H_2O$ has been undertaken in order to detect any specific characteristics of the two elements. The research has shown that lead(II) forms partially covalent bonds with iodine and that strontium is surrounded by six water molecules, forming an octahedron of the type observed in simple hexahydrated salts.

Experimental

Crystals were prepared by evaporating an aqueous solution of strontium iodide in the presence of undissolved lead iodide. Their habit is pseudooctahedral and their color ranges from orange to brown. The chemical analysis was in good agreement with those of Mosnier (1897) and consistent with the formula $SrPb_2I_6.7H_2O$.

All the crystals used were small bipyramids. Photographs were taken with Cu $K\alpha$ radiation ($\bar{\lambda} = 1{\cdot}5418$ Å). Cell dimensions were determined from oscillation- and Weissenberg photographs (rotation axis [001]). The unit cell is tetragonal:

$$a = 11{\cdot}77 \pm 0{\cdot}02, \quad c = 17{\cdot}32 \pm 0{\cdot}02 \text{ Å}$$

and contains four stoichiometric units $SrPb_2I_6.7H_2O$. The observed density $d_4^{26} = 4{\cdot}32$ g.cm.⁻³ is somewhat lower than the calculated one $d_c = 4{\cdot}56$ g.cm.⁻³.

Observed reflections were hkl for $h+k+l=2n$; $hk0$ for $h=2n$ and $k=2n$; hhl for $l=2n$, which indicated the space group $D_{4h}^{19}-I4_1/amd$.

Intensity data for the $hk0$ and $0kl$ zones were evaluated photometrically from the Weissenberg photographs using the multiple-film technique.

The absorption corrections ($\mu = 962$ cm.⁻¹) using the Henshaw method (1958) were limited to an average section for the $hk0$ zone and to two sections for the $0kl$ zone. The Lorentz and polarization factors were obtained graphically. The atomic scattering factors used were taken from Sagel (1958).

Determination of the structure

Atomic coordinates were found by trial and error, most of the atoms being in special positions. Good agreement between calculated and observed intensities was found assuming six iodine atoms to be disposed octahedrally around each lead atom. Hypotheses based
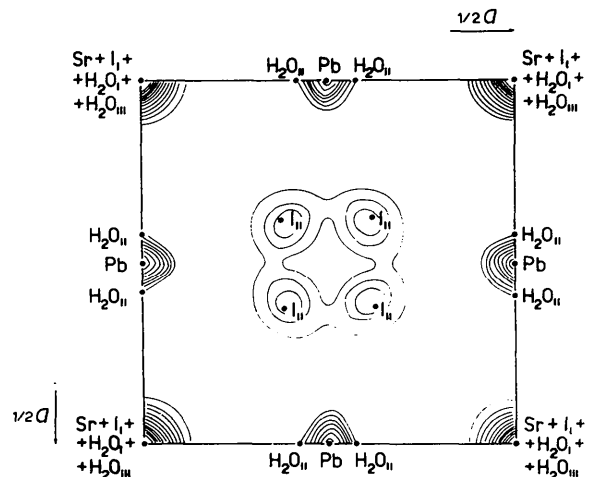

Fig. 1. $\varrho_0(x, y)$. Contours are drawn at approximately 20 e.Å⁻², starting with 20 e.Å⁻².
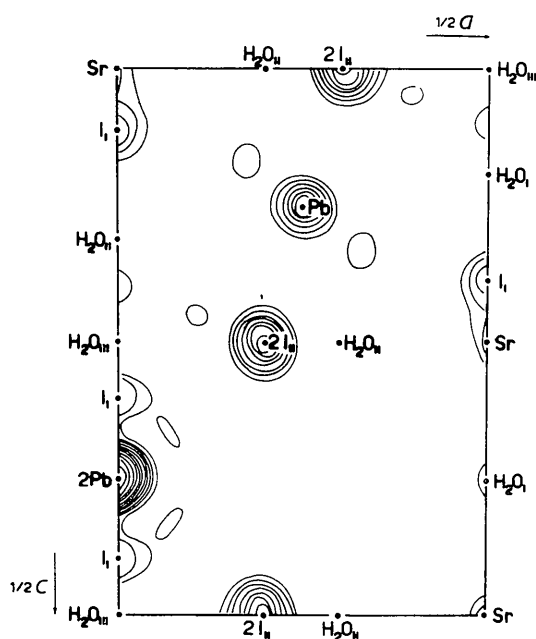
Fig. 2. $\varrho_0(y, z)$. Contours are drawn at approximately 20 e.Å^{-2}, starting with 20 e.Å^{-2}.

Table 1. *Observed and calculated structure factors for the hk0 reflections*

$hk0$	F_o	F_c	$hk0$	F_o	F_c
020	—	−55	440	908	890
040	1240	1189	460	372	−382
060	766	−759	480	554	532
080	354	241	4,10,0	172	−233
0,10,0	461	−513	4,12,0	254	305
0,12,0	284	283	4,14,0	—	−102
0,14,0	—	−50	660	—	−117
220	271	−294	680	—	35
240	334	432	6,10,0	—	−108
260	286	276	6,12,0	84	91
280	533	563	6,14,0	—	44
2,10,0	224	212	880	601	619
2,12,0	227	182	8,10,0	—	18
2,14,0	—	−35	8,12,0	228	253
			10,10,0	—	−101

The structure factors are calculated with the axis origin at $2/m$.

on a linear arrangement I–Pb–I were excluded. Six water molecules were assumed to surround octahedrally each strontium ion; the seventh water molecule can occupy the (b) position only, which is at the centre of an empty space between the octahedra formed by iodine and lead.

The initial coordinates were confirmed and refined

Table 2. *Observed and calculated structure factors for the 0kl reflections*

$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c
004	295	−413	0,3,15	—	38	0,6,18	—	104	0,10,6	275	186
008	773	986	0,3,17	—	−50	0,6,20	—	96	0,10,8	85	−129
0,0,12	—	−145	0,3,19	162	−244	071	—	16	0,10,10	234	146
0,0,16	440	586	0,3,21	—	85	073	477	−486	0,10,12	140	146
0,0,20	—	−78	040	948	1140	075	308	206	0,10,14	—	99
011	537	−461	042	—	—	077	—	96	0,10,16	—	−151
013	329	437	044	260	256	079	—	−47	0,11,1	125	212
015	—	−17	046	—	—	0,7,11	148	−144	0,11,3	125	−57
017	271	164	048	424	313	0,7,13	279	259	0,11,5	—	−76
019	244	−206	0,4,10	—	—	0,7,15	—	−20	0,11,7	127	−119
0,1,11	—	−16	0,4,12	268	184	0,7,17	—	—	0,11,9	120	123
0,1,13	168	−219	0,4,14	—	—	0,7,19	—	−115	0,11,11	—	49
0,1,15	121	181	0,4,16	275	321	080	283	219	0,11,13	65	37
0,1,17	—	−116	0,4,18	—	—	082	—	—	0,11,15	—	−98
0,1,19	—	81	0,4,20	—	37	084	529	557	0,12,0	223	232
0,1,21	—	3	051	542	−568	086	—	—	0,12,2	—	—
020	—	−55	053	135	102	088	—	−133	0,12,4	208	150
022	646	584	055	310	334	0,8,10	—	—	0,12,6	—	—
024	481	−377	057	432	312	0,8,12	353	332	0,12,8	56	38
026	540	483	059	445	−319	0,8,14	—	—	0,12,10	—	—
028	621	514	0,5,11	—	−141	0,8,16	—	68	0,12,12	86	106
0,2,10	361	346	0,5,13	—	−65	0,8,18	—	—	0,12,14	—	—
0,2,12	200	−232	0,5,15	197	230	091	93	−72	0,13,1	—	44
0,2,14	280	228	0,5,17	100	−80	093	315	308	0,13,3	187	214
0,2,16	—	14	0,5,19	—	18	095	—	−101	0,13,5	127	−119
0,2,18	133	136	0,5,21	—	37	097	—	−23	0,13,7	—	−73
0,2,20	—	−46	060	604	−721	099	174	−6	0,13,9	—	54
0,2,22	—	75	062	368	391	0,9,11	114	77	0,13,11	—	85
031	—	−187	064	343	387	0,9,13	—	−167	0,14,0	53	−38
033	770	−959	066	484	340	0,9,15	—	40	0,14,2	92	95
035	645	485	068	—	−144	0,9,17	—	−19	0,14,4	—	−23
037	375	297	0,6,10	274	258	0,10,0	391	−446	0,14,6	86	84
039	—	−196	0,6,12	102	193	0,10,2	216	214	0,14,8	—	63
0,3,11	447	−308	0,6,14	214	202	0,10,4	278	258	0,15,1	—	72
0,3,13	442	463	0,6,16	142	−217				0,15,3	—	−38

Structure factors are calculated with the axis origin at $2/m$.

by electron-density projections $\varrho_0(x, y)$ and $\varrho_0(y, z)$ (Fig. 1, 2). A $\varrho_0 - \varrho_P(x, y)$ projection ($\varrho_P =$ calculated electron-density projection due to the heavy atoms) showed that water molecules were in the positions of high density. However, their localization was not possible because the density values of the corresponding peaks were similar in magnitude to those of peaks ascribable to absorption and other experimental errors. The standard deviation of $\varrho_0(x, y)$ was $\sigma(\varrho) = 3.5$ e. Å^{-2}.

In $\varrho_0(x, y)$ the electron-density projection maxima corresponding to Pb, Sr, I_I, I_{II} appear clearly; $\sigma(\varrho)$ was 6.29 e. Å^{-2}.

Observed and calculated structure factors for $hk0$ reflections are reported in Table 1. The temperature factor was found graphically to be $B = 2.7$ Å^2 and the discrepancy index was $R_{hk0} = 0.08$. (Unobserved reflections are not included.) In Table 2 are reported the observed and calculated structure factors for $0kl$ reflections. The temperature factor was $B = 3.5$ Å^2. The value of R_{0kl} 0.20, was higher than that for $hk0$ reflections. Nevertheless it did not seem worthwhile to try to reduce the value. In fact, though the range of R was greatly changed by introducing absorption corrections derived from fairly accurate graphical methods, the plot of R_{hk0} versus $x_{I_{II}}$ and of R_{0kl} versus z_{I_I} always showed a minimum at nearly the same value of $x_{I_{II}}$ and z_{I_I} respectively. Therefore these minima are independent of absorption and depend only on $x_{I_{II}}$ and z_{I_I}. Intensity data very roughly corrected never changed the $x_{I_{II}}$ coordinate by more than 0.004. Moreover $\varrho_0 - \varrho_P(x, y)$ shows that experimental errors in the F_o's are always too high for the determination of the water coordinates, even if R is low. The index R is consequently an unreliable indication of the accuracy. This implies that we cannot use any expression depending on $F_o - F_c$ to assess the standard deviation in atomic coordinates. Therefore we assumed the value ± 0.004 as standard deviation for atomic coordinates of both iodine atoms. The final coordinates are reported in Table 3.

Table 3. *Atomic coordinates*

Atom	Number of atoms	Crystall. position	x/a	y/a	z/c
Sr	4	a	0	0	0
Pb	8	d	0	0.250	0.625
I	8	e	0	0	*0.310*
I	16	g	*0.309*	0.309	0
H_2O_I	8	e	0	0	*0.141*
H_2O_{II}	16	h	*0.208*	*0.000*	0
H_2O_{III}	4	b	0	0	0.500

Axis origin at $\bar{4}2m$. Add 0 to x/a; 0.250 to y/a; -0.125 to z/c for the origin at $2/m$.

The numbers in italics are the variable independent parameters.

Discussion of the structure

The structure of $SrPb_2I_6 . 7H_2O$ is shown diagrammatically in Fig. 3. Distances between Pb and I

Fig. 3. Structure of $SrPb_2I_6 . 7 H_2O$.
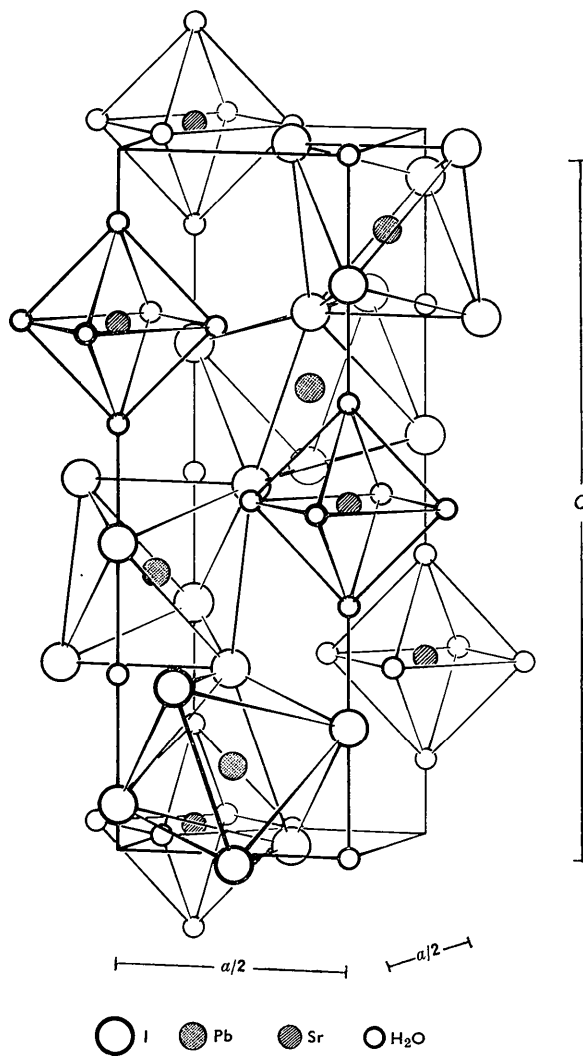A quarter of a unit cell is represented.

($Pb-I_{II} = 3.20 \pm 0.02$, $Pb-I_I = 3.14 \pm 0.04$ Å) are somewhat shorter than the sum of the ionic radii (Pauling, 1927). The covalent bond length of Pb–I was found by Lister & Sutton (1941) to be 2.79 ± 0.02 Å in gaseous PbI_2. Our value thus favours a partially covalent character of Pb–I bonds, in agreement with the considerations of Powell & Tasker (1937) concerning the Pb–Br bonds in $NH_4Pb_2Br_5$; in this compound, however, coordination around Pb is not octahedral.

The shortening of the Pb–I bond length as compared with the sum of the ionic radii is relatively small and is probably due to the sharing of the iodine atoms by two lead atoms. Actually it was observed in $NbCl_5$ (Zalkin & Sands, 1958) and in $Cs_3Cr_2Cl_9$ (Wessel & IJdo, 1957) that chlorine atoms shared by two octahedra are farther from the metal than the unshared ones (2.56 Å for shared Cl against 2.25–2.30 Å for unshared Cl in $NbCl_5$ or 2.52 Å for shared Cl against

2·34 Å for unshared Cl in $Cs_3Cr_2Cl_9$). The shortening of the metal–halogen bond length was observed in 1927 (Ferrari & Baroni) in compounds of divalent transition metals containing chlorine atoms forming octahedral complexes with metals. It was confirmed by later researches (Brasseur & Pauling, 1938; MacGillavry et al., 1939).

The main part of the structure are the octahedra $[PbI_{6/2}]$ joined to one another through two opposite corners (occupied by I_I) to form linear chains throughout the whole crystal. There are two sets of such chains; the set 1 (see Fig. 4) includes chains parallel to [010] and the set 2 (see Fig. 4) includes chains parallel to [100]. The axes [010] and [100] can be interchanged. Chains in the same set are shifted $\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}c$. The two sets are joined to one another through the remaining corners of the octahedra (occupied by I_{II}). It follows that it is made up of a
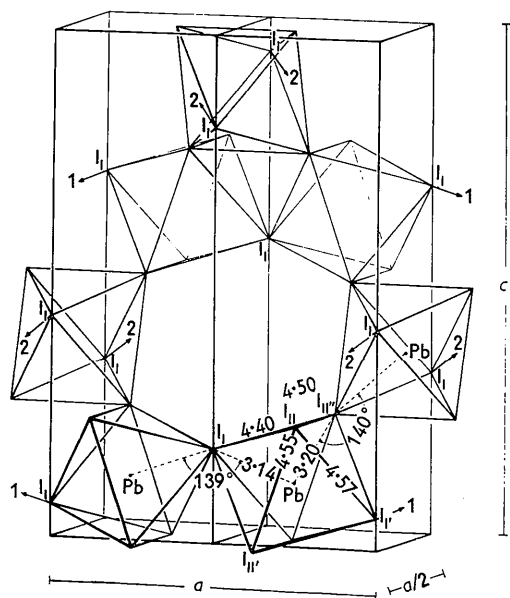

Fig. 4. Part of the three-dimensional framework formed of $[PbI_{6/2}]$ octahedra sharing all corners. Corners not labelled are occupied by I_{II}. The arrows from I_I show the next bond I_I–Pb in the chain. The numbers 1, 2 indicate the chains parallel to [010] and [100] respectively.

three-dimensional framework formed of octahedra which share all corners (Fig. 4).

Each iodine atom is bound to two lead atoms. The angles between the two bond directions are practically equal in I_I and in I_{II}: $< Pb–I_I–Pb = 139° \pm 2°$; $< Pb–I_{II}–Pb = 140° \pm 2°$. Distances I–I, which are the edges of the octahedra, are: $I_{II}–I_{II'} = 4·55 \pm 0·04$ Å; $I_I–I_{II} = 4·40 \pm 0·03$ Å; $I_{I'}–I_{II''} = 4·50 \pm 0·04$ Å; $I_I–I_{II} = 4·57 \pm 0·03$ Å.

The empty spaces of the framework formed by the octahedra $[PbI_{6/2}]$ are occupied by the strontium ions and by the water molecules. The coordinates of the water molecules could be determined only approximately, due to the presence of the heavy atoms and to absorption errors. Their octahedral arrangement around each strontium ion agrees well with the packing of atoms. The octahedron $Sr(OH_2)_6$ is of the same type as is found in $SrI_2.6H_2O$ and other related compounds (Hermann, 1931): assuming a distance $Sr–OH_2 = 2·45$ Å we find $H_2O_I–I_I = 2·93$ Å.

The distance between H_2O_{III} and its neighbouring atoms are: $H_2O_{III}–I_I = 3·38 \pm 0·02$ Å and $H_2O_{III}–Pb = 3·65 \pm 0·02$ Å. These distances exclude chemical bonds. Hence H_2O_{III} is to be considered as of zeolyte- or clathrate-type.

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