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The Crystal Structure of Strontium Tetraiododiargentate Octahydrate, $SrAg_2I_4 \cdot 8H_2O$*

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Crystals of strontium tetraiododiargentate octahydrate, $SrAg_2I_4 \cdot 8H_2O$ belong to the tetragonal space group I422(D_4^9), with $a = 12.86 \pm 0.03$, $c = 5.56 \pm 0.02$ Å, and $Z = 2$. The structure may be described as having, in one-to-one ratio, columns formed by $[Sr(H_2O)_8]^{2+}$ entities centered at (0,0) and ($\frac{1}{2}$,$\frac{1}{2}$) and chains of edge-sharing AgI_4 tetrahedra centered at ($\frac{1}{2}$,0) and (0,$\frac{1}{2}$), the chains being linked to each other through water molecules by hydrogen bonding and through van der Waals forces between iodide ions. The crystals are obtained from a saturated aqueous solution of SrI_2 which is then saturated with AgI; dilution of this solution or addition of water to the crystals precipitates β-AgI. This demonstrates the ease with which the three-dimensional corner-sharing tetrahedra of the β-AgI transform to the edge-sharing chain arrangement of tetrahedra and vice versa. It is probable that the saturated solution itself contains $[Sr(H_2O)_8]^{2+}$ and AgI_4-chain entities.

Anhydrous compounds of strontium and barium halides with silver and copper halides appear to be unattainable at atmospheric pressure. It is speculated that this is associated with the particular coordination requirements of the alkaline earth ions.

Introduction

In continuing studies of the crystal structures and conductivities of solid electrolytes, attempts have been made to prepare compounds of alkaline earth halides with silver halides in the hope of obtaining one or more that would have substantial electrolytic conductivity. At atmospheric pressure, anhydrous compounds did not seem to form, but a hydrate of a double salt of SrI_2 and AgI, which is not a solid electrolyte, does form quite readily. The structure analysis was carried out because of the interesting properties of the crystal, because hydrates of double salts with the silver halides are uncommon (even though other "molecules of crystallization" have occurred in double salts of AgI), and to gain some understanding of the nonoccurrence of anhydrous compounds.

Experimental

In attempting to prepare compounds of SrI_2 with AgI, a new phase appeared. It occurred with all ratios of SrI_2 to AgI from 1 to 6. With ratios smaller than 1:2, excess AgI appeared; with ratios larger than 1:2, both excess $SrI_2 \cdot 6H_2O$ and AgI occurred. Subsequently, it was surmised that the formation of this new phase involved the absorption of moisture from the atmosphere. In fact, it was found that just grinding SrI_2 with AgI in a mortar in the atmosphere resulted in the formation of the new phase. It was not clear, however, what the composition of this phase was, but there was no doubt that it contained water of crystallization.

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We therefore made a few cubic centimeters of a saturated solution of SrI_2 and found that it dissolved a substantial amount of AgI. On standing, crystals formed. An X-ray powder photograph showed that this phase was identical to the one found in the aforementioned experiments.

If water was added to the concentrated solution of SrI_2 and AgI in water, AgI was precipitated. Also if water was added to the crystals, they decomposed with the precipitation of AgI. The crystals grew with either square or rectangular cross section and it seemed that those of rectangular cross section were twinned.

Buerger precession camera photographs taken with Mo$K\alpha$ radiation and Weissenberg photographs taken with Cu$K\alpha$ radiation indicated that the crystals were body-centered tetragonal with diffraction symmetry $4/mmm$. (The crystals grew with the face-centered orientation.) Other than the absent reflections indicating the body-centering, there were no systematic absences. Thus the probable space groups were $I4/mmm$ (D^{17}_{4h}), $I4mm$ (C^{9}_{4v}), $I\bar{4}m2$ (D^{9}_{2d}), $I\bar{4}2m$ (D^{11}_{2d}) and $I422$ (D^{9}_{4}) (*1*). It will be shown subsequently that the most probable space group to which the structure belongs is the last, $I422$, and that this and the trial structure itself were determined before quantitative intensity data were collected.

The composition of the phase was tentatively determined by adding water to 0.4480 g of the crystals and collecting and washing the precipitated AgI on a glass fritted disk crucible and drying and weighing the precipitate. The filtrate was also collected and the water evaporated from it. The residue was $SrI_2 \cdot 6H_2O$. The results implied that the composition was $SrAg_2I_4 \cdot 8H_2O$.

The density of the crystals was measured by the flotation technique. This required a rather dense liquid; it was found that iodoform dissolved in diiodomethane gave a suitable density range. The density found for the crystals is 3.41 gcm^{-3}, with possible error of 1–2%.

The lattice constants determined from the Buerger precession camera photographs are $a = 12.86 \pm 0.03$, $c = 5.56 \pm 0.02$ Å. With a cell content of 2 $SrAg_2I_4 \cdot 8H_2O$, the X-ray density is 3.45 gcm^{-3}, in good agreement with the measured density.

An attempt was made to grind spherically shaped crystals with a sphere grinder designed (*2*) to handle fragile crystals. However, although spheres were obtained, they were severely damaged to the extent that they gave essentially powder photographs. In one case, it seemed that a good sphere had been obtained because it gave a very good precession camera photograph. However, again although the sphere remained intact, the damage eventually destroyed the crystal coherence. This was not caused by the X rays because a sphere ground at the same time as the one mentioned above and photographed later, showed essentially powder lines. Consequently, a crystal of 0.2 × 0.2 mm cross section and 4.2 mm long was mounted on a glass fiber with *c*-axis as rotation axis and data collected on it.

The absorption of Mo$K\alpha$ radiation by the crystal was too high and would very likely have required absorption corrections to obtain reasonable values for the parameters of the water molecules. It was therefore decided to use Ag$K\alpha$ radiation. For absorption correction, the crystal was assumed to be cylindrical with an average diameter of 0.24 mm, that is, the average between the edge and diagonal of the square. This introduced a maximum error of about 10% in the measured *F*-values. Because of the simplicity of the structure and the expense of calculating individual absorption corrections, this was considered adequate. The final results appear to justify this conclusion, although the thermal parameters may be less reliable than indicated by the calculated standard errors.

Intensities of independent reflections in the range $10° \leq 2\theta \leq 50°$ (Ag$K\alpha$ radiation, $\lambda = 0.5608$ Å, Pd and Mo balanced filters), were collected with a Buerger–Supper diffractometer automated by a Nova 1200 computer.

Each reciprocal lattice point was scanned at the rate of 1.5°/min over the range (1.5 + 0.5 Lp) where Lp is the Lorentz-polarization-Tunnel factor. The maximum scan range for any peak was limited to 5°. Background counts were taken at the beginning and at the end of the scan interval at $\frac{1}{4}$ the scan time of each scan.

Intensity decrease was rather rapid with increasing θ, and in fact, it appeared that all reflections with $l = 7$ and 8 had intensities below their threshold values. Therefore, subsequent refinement of the structure included only data with $l = 0$ to 6. The total number of independent reflections measured, in the range $10° \leq 2\theta \leq 50°$, $0 \leq l \leq 6$, was 468 of which 158 were below the 150 count threshold. Total background counts were rather high, probably partially because of the quality of the crystal and partially because of the quality of the radiation.

The linear absorption coefficient, μ, of $SrAg_2I_4 \cdot 8H_2O$ for Ag*Kα* radiation is 5.78 mm^{-1}, while for Mo*Kα* radiation, it is 11.11 mm^{-1} (see above). (Values of μ/ρ for this calculation were obtained from Ref. *3*.)

It should be mentioned that the crystal turned black on continued irradiation; however, this did not appear to have a significant effect on the intensities of several reflections which were checked.

The Trial Structure

One could expect that the Ag^+ ions would be tetrahedrally coordinated to the iodide ions. It was unlikely that the iodide tetrahedra would predominantly share faces in this structure, both because the crystals appeared to be electrically highly resistive (see for example, Ref. *4*) and because of spatial considerations. It also seemed very unlikely that the iodide tetrahedra would share corners as in the β- and γ-AgI. This leaves edge-sharing as most likely and only one of the probable space groups could accommodate it readily: $I422$[1] has 4_2 screw axes at $(0,\frac{1}{2})$ and at $(\frac{1}{2},0)$ (1). Thus the iodide ions were very likely in the 8j positions $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) + x, \frac{1}{2} + x, \frac{1}{4}; \bar{x}, \frac{1}{2} - x, \frac{1}{4}; \bar{x}, \frac{1}{2} + x, \frac{3}{4}; x, \frac{1}{2} - x, \frac{3}{4}$. It was expected that the Ag^+—I^- distance would be somewhat larger than the 2.80 Å in γ-AgI; the value 2.86 Å was assumed, leading to $x = 0.1375$.

The 16 water molecules must form an 8-coordination polyhedron about the Sr^{2+} ions and must be in the general positions of the space group. If there were 9 H_2O per $SrAg_2I_4$, two oxygens must be in positions $2b$: $(00\frac{1}{2})$, $(\frac{1}{2}\frac{1}{2}0)$, thus giving a coordination polyhedron of 10 vertices. This seemed unlikely because it would put some water molecules too close to each other (but see next section).

The Sr^{2+} ions were assumed to be in positions 2a: (000), $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, the centers of the H_2O polyhedra. The Ag^+ ions were assumed to be in $4c$: $(000; \frac{1}{2}\frac{1}{2}\frac{1}{2}) + 0\frac{1}{2}0; \frac{1}{2}00$, the centers of the iodide tetrahedra.

Refinement of the Structure

Initially, the parameters taken for the oxygens were $x = y = 0.11$, $z = 0.23$.[2] In the early least-squares cycles, water molecules at $(00\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$ were included; these were rejected by the calculation as indicated by the increase of the B value to greater than 20. Initially the data used had $0 \leq l \leq 3$. The Ag^+ ions do not contribute to reflections with l odd; therefore, the remainder of the data to $l = 6$ were soon used in the calculations.

Because of the layering at multiples of $c/4$, it was not possible to vary the scale factors of layers with l even but greater than 0 and thermal parameters involving l even (>0) (especially, β_{33} of the Ag^+ ion) simultaneously. However, it was possible to vary the scale factors for $l = 0, 1, 3, 5$ and all other

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[1] As of 1967, the Systematic Tables of Crystal Data (*5*) show that no structures were then known to belong to this space group.

[2] This is equivalent to Sr^{2+}–H_2O distances of 2.37 Å, actually much too short.

parameters simultaneously. In the final two cycles, all the scale factors, having converged, were held constant. The final discrepancy factor, $R = \sum ||F_0| - |F_c||/\sum |F_0|$ is 0.088; the standard error of an observation of unit weight is 1.00. The observed data were weighted according to

$$\begin{aligned} \sigma &= 0.07\,(40.0 - F) + 4.0, && F < 40.0, \\ \sigma &= 0.08\,F, && 40.0 \le F < 200.0, \\ \sigma &= \exp(F/72.14), && F \ge 200.0, \end{aligned}$$

and $w = 1/\sigma^2$.

In the final least-squares cycle, no parameter changed by more than 0.01 of its estimated standard error. More than half the parameters changed by <0.005 of their estimated standard errors.

In the calculations (which were done with the NUCLS5 (*6*) program), the atomic scattering factors used were all taken from the paper by Cromer and Mann (*7*). Corrections for the real parts of anomalous dispersion were taken from Ref. *3*.

A table of $|F|_{\text{calc}}$ vs $|F|_{\text{obs}}$ is available from the senior author if specifically requested. Eleven F values from reflections with large intensities were omitted from the final calculations. These suffered mainly from "streaking" contributions. No attempt was made to correct for extinction because about as many of the high F_{obs}'s were larger than their F_{calc}'s as were lower. Again the effect of "impure" radiation could be seen in the data and particularly noticeable for the *h*0*l* and *hhl* data.

A table of $|F_{\text{threshold}}|$ vs $|F_{\text{calc}}|$ for the unobserved reflections is also available upon specific request. There are no really large discrepancies, although these calculations indicate that perhaps the threshold count should have been set higher. The maximum $|F_{\text{threshold}}|$ is 13; F_{000} for this structure is 848.

The final parameter values and their estimated standard errors are listed in Table I. It is probable that some of the error in the data caused by the approximate absorption corrections has been compensated by error in the thermal parameters. However, it is unlikely that the error in the data affects significantly the overall correctness of the structure. The large standard errors of the positional parameters of the oxygen, relative to that of the positional parameter of the iodide ion is to be expected, even if the data were considerably better. It should be noted that the standard error in the iodide x-parameter is equivalent to only 0.0017 Å; for the x-parameter of oxygen, it is 0.026 Å.

Description of the Structure

The interatomic distances, calculated with use of the computer program ORFFEC (*8*),

TABLE I

FINAL PARAMETER VALUES AND ESTIMATED STANDARD ERRORS

Atom		Sr^{2+}	Ag^{+}	I^{-}	O_{H_2O}
Position		2*a*	4*c*	8*j*	16*k*
Site symmetry		$422(D_4)$	$222(D_2)$	$2(C_2)$	$1(C_1)$
x		0	$\frac{1}{2}$	0.13866(13)	0.0667(20)
y		0	0	$=\frac{1}{2}+x$	0.1600(13)
z		0	0	$\frac{1}{4}$	0.2471(40)
10^5	β_{11}	403(19)	1245(65)	491(7)	1197(200)
	β_{22}	$=\beta_{11}$	983(56)	$=\beta_{11}$	493(112)
	β_{33}	1979(142)	12409(509)	6320(117)	4211(777)
	β_{12}	0	0	46(13)	124(106)
	β_{13}	0	0	40(37)	−594(422)
	β_{23}	0	0	$=-\beta_{13}$	−515(341)

TABLE II

INTERATOMIC DISTANCES (AND STANDARD ERRORS), Å, IN $SrAg_2I_4 \cdot 8H_2O$

Sr^{2+}–H_2O	(8)2.62(2)
Ag^+–I^-	(4)2.879(2)
–Ag^+	(2)2.78(1)
I^-–Ag^+	2.879(2)
–I^-	(4)4.522(4), (2)4.912(3), 5.044(4)
–H_2O	(2)3.70(2), (2)3.80(3), (2)3.90(2), (2)3.92(2)
H_2O–Sr^{2+}	2.62(2)
–H_2O	(2)3.15(3), 3.23(4), 3.24(4), 3.28(4), 3.29(5)
–I^-	3.70(2), 3.80(3), 3.90(2), 3.92(2)

Note: The number in parentheses in front of the distance, is equal to the number of neighbors at exactly the same distance.

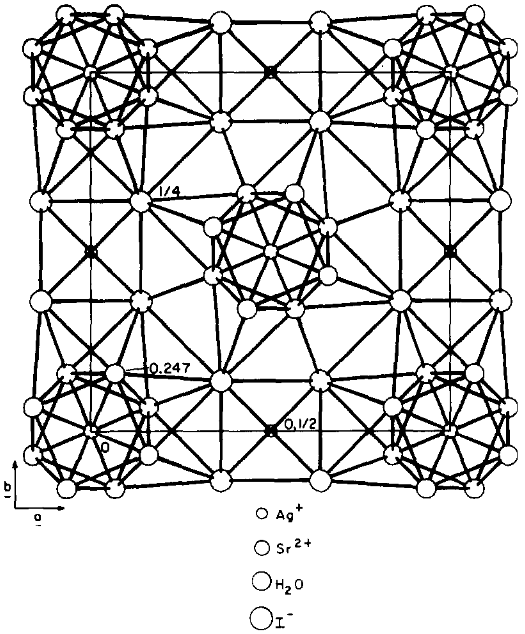

FIG. 1. Top view of the structure of $SrAg_2I_4 \cdot 8H_2O$.

are listed in Table II. A projection of the structure down the *c*-axis is shown in Fig. 1 and a stereoscopic view (almost) down the *c*-axis (out of the paper) is shown in Fig. 2. These figures were drawn with the use of the computer program ORTEP (*9*).

Table II and Figs. 1 and 2 show that each Sr^{2+} ion is coordinated to eight water molecules at a distance of 2.62 ± 0.06 Å.[3] The polyhedron of water molecules is an antiprism with square bases parallel to (001). Each water molecule is coordinated to six others at distances ranging from 3.15 ± 0.09 Å to 3.29 ± 0.15 Å. The first four distances listed in Table II are to other water molecules in the same polyhedron; the last two are to the

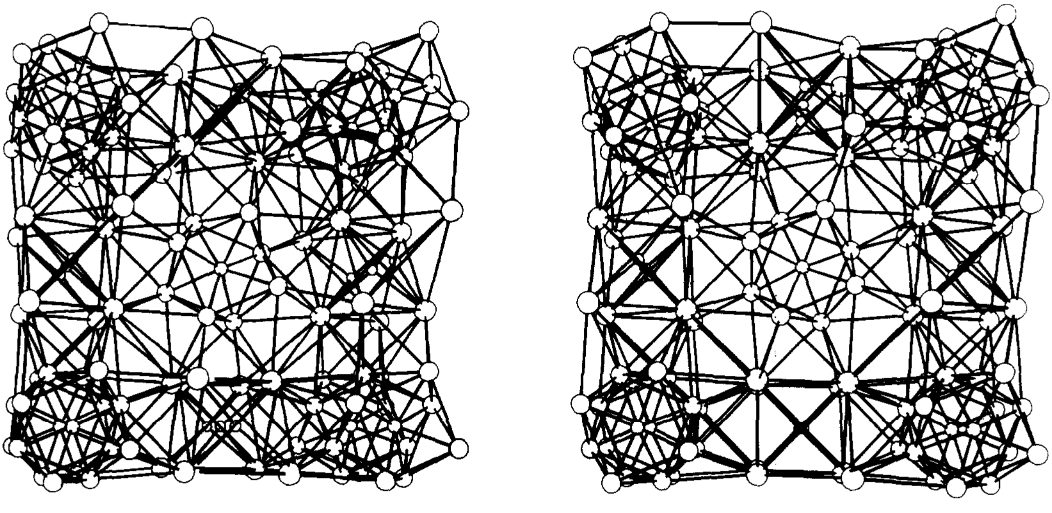

FIG. 2. Stereoscopic drawing of the structure of $SrAg_2I_4 \cdot 8H_2O$, looking nearly along *c*. (There is a 5° rotation about the *b*-axis.)

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[3] *Limits* of error rather than the estimated standard error are used throughout this section.

nearest neighbor water molecules in the next polyhedron along the *c*-axis. These are not significantly longer than the distances within the polyhedron. Thus (see Figs. 1 and 2), there are columns of the water polyhedra enclosing Sr^{2+} ions parallel to the *c*-axis, the water molecules isolating the Sr^{2+} ions from the I^- ions as in the hexahydrates of the strontium halides (*10*). Each water molecule is also coordinated to four iodide ions at distances from 3.70 ± 0.06 Å to 3.92 ± 0.04 Å.

Each iodide ion has seven iodide neighbors (see Table II and Figs. 1 and 2) at distances ranging from 4.522 ± 0.012 Å to 5.044 ± 0.012 Å. Within a given tetrahedron, there are four equal I^-–I^- distances of 4.522 Å involving atoms in the layers at $\pm c/4$. Within each of the layers, the I^-–I^- distance is 5.044 Å giving an average I^-–I^- distance in the tetrahedron of 4.696 ± 0.012 Å. Each iodide also makes contact with two other iodides at 4.912 ± 0.009 Å in a neighboring chain.

The Ag^+ ions are coordinated to four I^- ions at the corners of a tetrahedron, all at 2.879 ± 0.005 Å from the Ag^+ ion. It is rather remarkable to find that the Ag^+ ions are very close (2.78 ± 0.02 Å) to two others along the chain of edge-sharing iodide tetrahedra (see Fig. 2). The individual chains of iodide tetrahedra are linked by water molecules, probably through some hydrogen bonding, each iodide being coordinated to eight water molecules (see Table II and Fig. 2). One may thus describe the structure simply as having, in one-to-one ratio, along the *c*-axis, columns formed by $[Sr(H_2O)_8]^{2+}$ entities centered at (0,0) and $(\frac{1}{2},\frac{1}{2})$ and chains of edge-sharing AgI_4 tetrahedra[4] centered at $(\frac{1}{2},0)$ and at $(0,\frac{1}{2})$, the chains being linked to each other through water molecules by hydrogen bonding and through van der Waals forces between iodide ions.

As to comparison with related structures: the hexahydrates of $SrCl_2$, $SrBr_2$, and SrI_2 are isostructural but quantitative structure analysis has been done only on the first, and that, some time ago (*10*). In $SrCl_2 \cdot 6H_2O$, Sr^{2+} is coordinated to $9H_2O$ molecules, 6 at 2.80 Å, and 3 at 2.65 Å. In $SrBr_2 \cdot H_2O$ (*11*) the Sr^{2+} ion is coordinated to seven Br^- ions and two water molecules, the latter at a distance of 2.63 Å. The H_2O–H_2O distances in $SrCl_2 \cdot 6H_2O$ are as follows: each H_2O molecule in 3*e* (*1*, *10*) has two *e*-type neighbors at 4.59 Å and four *f*-type neighbors at 3.13 Å; the H_2O molecules in 3*f* have four *e*-type neighbors at 3.13 Å and two *f*-type neighbors at 3.30 Å, distances comparable with those in $SrAg_2I_4 \cdot 8H_2O$.

The Ag^+–I^- distance, 2.879 ± 0.005 Å, in $SrAg_2I_4 \cdot 8H_2O$ is close to that found in other compounds in which iodide tetrahedra share two edges. In $PyAg_5I_6$ (*12*), it is 2.861 ± 0.003; in both $Ag_6I_8C_8H_{22}N_2$ (*13*) and $Ag_4I_6C_4H_{12}N_2 \cdot 4C_2H_6SO_2$ (*14*) the reported average Ag–I distance is 2.87 Å; in $Ag_2I_4C_8H_{22}N_2$ (*15*) the reported average Ag–I distance is 2.857 ± 0.009 Å.

Discussion

The Ag^+–I^-, I^-–I^-, H_2O–Sr^{2+}, H_2O–H_2O, and H_2O–I^- distances all appear to be reasonable relative to these or related (e.g., H_2O–Br^-) interatomic distances in other structures. However, as already mentioned above, the Ag^+–Ag^+ distances are remarkably short; the iodide tetrahedra are also rather flattened in the *c*-axis direction. In $PyAg_5I_6$ (*12*) which involves a three-dimensional network of iodide ions, the separation of the pairs of iodides forming the shared edges is 3.71 Å, while in $SrAg_2I_4 \cdot 8H_2O$, this separation is again only 2.78 Å. This must be associated with the relative instability of the latter and the ease with which the AgI_4 chains transform to the β-AgI arrangement. The rather large thermal parameters of the Ag^+ ions may also be indicative of instability.

On the other hand, the β-AgI arrangement readily transforms to the chain arrangement in the presence of SrI_2 and moisture, forming readily when SrI_2 and AgI are simply ground

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[4] Formally, for charge balance, the repeating entity may be taken as $[Ag_2I_4]^{2-}$.

together even in an atmosphere of low relative humidity. The key is the amount of water present. The inference to be drawn is that in the concentrated solution of AgI in SrI_2 itself, there already exist the chains of iodide tetrahedra and the entities $[Sr(H_2O)_8]^{2+}$ and even perhaps columns of these entities. Some iodide chain increments and $[Sr(H_2O)_8]^{2+}$ column increments may even, to some extent, be associated in solution. Too much water must change this arrangement and precipitate the AgI. Hydrogen bonding must play an important role in both the solution and the crystal. Needless to say, a study of the species existing in solution might prove very elucidating if, of course, the problem is tractable.

Attempts were made to prepare, either by melting or by solid state reaction, the following: $SrI_2 \cdot nAgI$, $1 \leq n < 6$, $SrBr_2 \cdot 6CuBr$, $SrI_2 \cdot 4CuI$, $BaI_2 \cdot 3CuCl$, $BaI_2 \cdot SrI_2 \cdot 8AgI$, $SrCl_2 \cdot 4CuCl$. In all cases, the X-ray powder photographs indicated that no reaction had taken place. The clue to the failure of the formation of such anhydrous compounds has already been given in a paper by Dyke and Sass (*11*) on $SrBr_2 \cdot H_2O$, in which they have pointed out that the 9-coordination of Sr^{2+} in this compound is similar to the 9-coordination of Ba^{2+} in the anhydrous barium halides (*16*). While it is true that in anhydrous SrI_2 (*17*), Sr^{2+} has seven coordination to iodides, Sr^{2+} prefers higher coordination, besides which the 7-coordination that occurs in anhydrous SrI_2 (*17*) is very likely unachievable in a compound with AgI—at least, at atmospheric pressure.

Dyke and Sass (*11*) have pointed out that although anhydrous $SrBr_2$ has eight coordination of Sr^{2+} to Br^- ions, the greater stability of $SrBr_2 \cdot H_2O$ results primarily from its allowing Sr^{2+} to have 9-coordination, i.e., seven Br^- and two H_2O nearest neighbors; Sr^{2+} cannot have nine nearest Br^- neighbors because of its small size relative to Ba^{2+}.

It appears that an $SrI_2 \cdot H_2O$ isostructural with $SrBr_2 \cdot H_2O$ exists (*18*); we can infer from this and the structures of anhydrous SrI_2 and $SrBr_2$ that Sr^{2+} cannot have more than seven nearest neighbor iodide ions because of their large size and the small size of Sr^{2+}.[5] More important, we can conclude that the alkaline earths will not form structures similar to that of $RbAg_4I_5$ (*19*) and isomorphs, because they do not favor six-coordination with halogenide ions and it is likely that the nets formed on "condensation" of iodide polyhedra to face- or edge-sharing are not conducive to the coordinations that the alkaline earths prefer. This is seen also in the failure to form a compound between anhydrous $SrBr_2$ and CuBr or $SrCl_2$ and CuCl.

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[5] Sr^{2+} is substantially smaller than Rb^+, and comparable in size with K^+.

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