

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)
LÄÜGT, M. & DURIF, A. (1974). *Acta Cryst.* B30, 2118–2121.

MARTIN, C., TORDJMAN, I. & DURIF, A. (1975). *Z. Kristallogr.* 141, 403–411.
PRISSET, J. L., AVERBUCH-POUCHOT, M. T. & DURIF, A. (1986). *Z. Kristallogr. A* paraître.

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Structure of Strontium Iodide Dihydrate

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Abstract. $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$, $M_r = 377.5$, orthorhombic, *Pcmm*, $a = 15.5805$ (8), $b = 4.3403$ (3), $c = 9.8814$ (7) Å, $V = 668.22$ (5) Å³, $Z = 4$, $D_x = 3.75$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 16.87$ mm⁻¹, $F(000) = 656$, $T = 293$ K, $R = 0.024$ for 1121 reflections. $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ crystallizes in a hitherto unknown structure type. The structure consists of distorted face-shared $\text{SrI}_5(\text{H}_2\text{O})_4$ tricapped trigonal prisms forming columns and channels along [010]. The Sr–I distances range from 3.372 (1) to 3.842 (1) Å; the Sr–O distances are 2.682 (2) and 2.731 (2) Å. From the infrared spectra of isotopically dilute samples it is shown that the H_2O molecules, which form weak hydrogen bonds to I^- ions, are distorted, *i.e.* there are two different H positions for each H_2O molecule.

Introduction. As part of spectroscopic and structural studies on alkaline-earth halide hydrates (Lutz & Christian, 1982, and references therein; Buchmeier, 1984; Engelen, Freiburg & Lutz, 1983), the crystal structure of $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ was determined by single-crystal X-ray methods. Strontium iodide dihydrate first described by Hüttig & Slonim (1929) was recently confirmed by thermoanalytical studies (Buzágh-Gere, Sztatisz & Gál, 1979). $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ is very sensitive to light and moisture.

Experimental. Single crystals of $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ were prepared by heating an aqueous suspension of $\text{SrI}_2 \cdot 6\text{H}_2\text{O}$ in a glass tube at 383 K (oil bath) under a nitrogen stream for removing water vapour. The dry residue was placed in an argon glove box and mixed with paraffin oil to separate the crystals from powdery material. Polycrystalline samples were obtained by rehydration of anhydrous SrI_2 with stoichiometric amounts of H_2O (Lutz, Becker, Mertins & Engelen, 1979). A needle-like crystal (0.1 × 0.1 × 0.6 mm) was mounted in a sealed glass capillary on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromatized Mo $K\alpha$ radiation was used. The intensities of 1891 unique reflections

Table 1. Fractional coordinates and equivalent isotropic temperature factors with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (Å ² × 8π ²)
Sr	0.38154 (5)	0.75	0.16797 (7)	2.30 (1)
I(1)	0.59933 (3)	0.75	0.09152 (4)	1.828 (6)
I(2)	0.34260 (3)	0.75	0.50591 (5)	2.596 (8)
O(1)	0.4599 (3)	0.25	0.2813 (5)	2.6 (1)
O(2)	0.2842 (3)	0.25	0.2114 (5)	2.6 (1)

[$2\theta \leq 80^\circ$, ω – 2θ scan, $(\sin\theta)/\lambda < 0.905$ Å⁻¹, range of hkl $0 \leq h \leq 28$, $0 \leq k \leq 7$, $0 \leq l \leq 17$] were corrected for Lorentz and polarization effects (Enraf–Nonius, 1982). 770 reflections with $I \leq 2\sigma_I$ (σ_I from counting statistics) were considered unobserved. An empirical correction for absorption (North, Phillips & Mathews, 1968) was made by ψ scans (range of transmission from 1.0 to 0.75) and for intensity decrease by measuring three standard reflections ($7\bar{2}4$, 206, $\bar{1}1\bar{6}$; 100% $\geq I \geq 88.5\%$). The Sr and I positions were determined from a Patterson synthesis, the O positions from a subsequent electron density summation using scattering factors for Sr^0 , I^0 , and O^0 (*International Tables for X-ray Crystallography*, 1974). Full-matrix least-squares refinement of positional and anisotropic thermal parameters, extinction coefficient, and scale factor ($N_p = 32$) based on the F magnitudes of 1121 reflections with $I \geq 2\sigma_I$ gave a final $R = 0.024$, $wR = 0.026$ ($w = 1/\sigma_I$), $S = 1.563$, and an extinction coefficient of $6.33(4) \times 10^{-7}$. The ratio of maximum least-squares shift to *e.s.d.* in the final cycle was 0.002 and the maximum height in the final difference Fourier synthesis 2.5 e \AA^{-3} . The final atomic coordinates and thermal parameters are given in Table 1.* Cell

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42753 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters were determined by precession photographs (Enraf-Nonius precession camera) and refined by least-squares methods from Guinier powder data (Huber FR 601 camera, Cr $K\alpha_1$ radiation, 46 reflections, α -quartz as internal standard, $a = 4.9136$, $c = 5.4054$ Å). The systematic absences $h + k = 2n + 1$ for $hk0$ and $l = 2n + 1$ for $0kl$ indicate space group $Pmna$ (D_{2h}^{16}) (No. 62) (*International Tables for X-ray Crystallography*, 1952). Because of the structural relationship to the monohydrate (Engelen, Freiburg & Lutz, 1983; Buchmeier, 1984) the non-standard setting $Pcmm$ was used in this work. Infrared spectra of isotopically dilute samples, *i.e.* deuterated about 5% (Nujol mulls), were recorded at liquid-nitrogen temperature on a Perkin-Elmer Model 580 spectrophotometer (resolution $< 1 \text{ cm}^{-1}$).

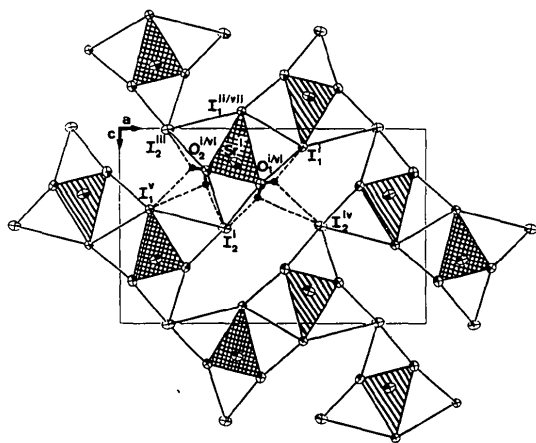


Fig. 1. Structure of $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ [projection along [010]; line-shaded areas, mirror planes at $y = -0.25$ and 0.75 ; cross-hatched areas, mirror planes at $y = 0.25$ and 1.25 ; distorted tricapped trigonal $\text{SrI}_5(\text{H}_2\text{O})_4$ prisms, full lines; possible hydrogen bonds, dashed lines].

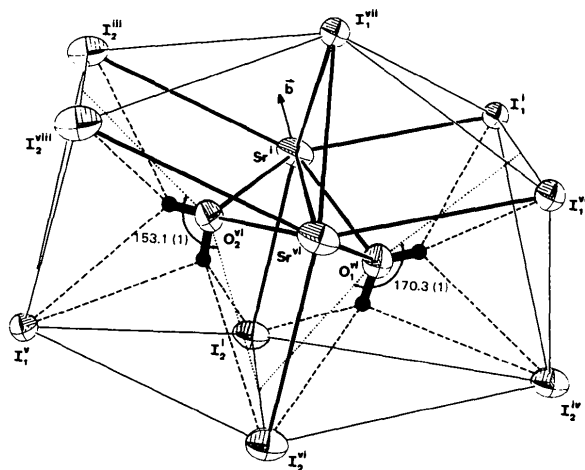


Fig. 2. Environment of the water molecules in $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ [possible hydrogen bonds, dashed lines; angles ($^\circ$), dotted lines].

Table 2. *Interatomic distances* (Å) in $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ (for angles see Fig. 2)

$\text{Sr}^{\text{I}}-\text{O}(2)^{\text{vi/vi}}$	2.682 (2)	$\text{O}(1)^{\text{i}}-\text{I}(1)^{\text{ii}}$	3.798 (4)
$\text{Sr}^{\text{I}}-\text{O}(1)^{\text{v/vi}}$	2.731 (2)	$\text{O}(2)^{\text{vi}}-\text{I}(1)^{\text{v}}$	3.477 (4)
$\text{Sr}^{\text{I}}-\text{I}(1)^{\text{ii/vii}}$	3.372 (1)	$\text{O}(2)^{\text{j}}-\text{I}(1)^{\text{ii}}$	3.500 (4)
$\text{Sr}^{\text{I}}-\text{I}(2)^{\text{j}}$	3.394 (1)	$\text{O}(2)^{\text{vi/vi}}-\text{I}(2)^{\text{iii}}$	3.569 (3)
$\text{Sr}^{\text{I}}-\text{I}(1)^{\text{j}}$	3.476 (1)	$\text{O}(2)^{\text{vi/vi}}-\text{I}(2)^{\text{j}}$	3.742 (3)
$\text{Sr}^{\text{I}}-\text{I}(2)^{\text{iii}}$	3.842 (1)	$\text{I}(1)^{\text{i}}-\text{I}(1)^{\text{ii/vii}}$	4.191 (1)
$\text{Sr}^{\text{I}}-\text{Sr}^{\text{vi}}$	4.340 (1)	$\text{I}(1)^{\text{ii/vii}}-\text{I}(2)^{\text{iii}}$	4.472 (1)
$\text{O}(1)^{\text{j}}-\text{O}(2)^{\text{j}}$	2.824 (1)		
$\text{O}(1)^{\text{vi/vi}}-\text{I}(1)^{\text{j}}$	3.598 (3)		
$\text{O}(1)^{\text{vi/vi}}-\text{I}(2)^{\text{j}}$	3.602 (3)		
$\text{O}(1)^{\text{vi}}-\text{I}(2)^{\text{iv}}$	3.726 (4)		

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

Discussion. $\text{SrI}_2 \cdot 2\text{H}_2\text{O}$ crystallizes in a hitherto unknown structure type. Sr, I(1), I(2), O(1), and O(2) occupy the special position 4(c). Sr is coordinated by five I and four O atoms in the form of a distorted tricapped trigonal prism (see Fig. 1). The Sr–I and Sr–O distances (see Table 2) are similar to those of other iodide hydrates. One of the four different Sr–I distances is larger than the sum of the ionic radii of Sr and I, so that an 8 + 1 coordination is present. The $\text{SrI}_5(\text{H}_2\text{O})_4$ polyhedra are face-shared with common triangular basal planes in [010] forming $[\text{SrI}_4(\text{H}_2\text{O})_2]_n$ columns. These $[\text{SrI}_4(\text{H}_2\text{O})_2]_n$ columns, which are edge-connected in (010) with common I[−] ions, are arranged in such a manner that channel-like cavities along [010] are formed. Both crystallographically different water molecules (type B after Chidambaram, Sequeira & Sikka, 1964) have similar surroundings (see Fig. 2). The H atoms are obviously in the channels discussed above (see Fig. 1). As shown from the infrared spectra of isotopically dilute samples, there are four different H positions. This means that both water molecules are distorted, *i.e.* effective site symmetry lower than $mm2$. The OD stretching modes of the HDO molecules present in such samples, namely at 2560, 2513, probably $\text{H}_2\text{O}(1)$, 2548, and 2543 cm^{-1} , $\text{H}_2\text{O}(2)$, at 95 K, reveal weak hydrogen bonds to adjacent I[−] ions.

References

- BUCHMEIER, W. (1984). Dissertation, Univ. of Siegen.
 BUZÁGH-GERE, E., SZTATISZ, J. & GÁL, S. (1979). *J. Therm. Anal.* **17**, 501–505.
 CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.
 ENGELEN, B., FREIBURG, C. & LUTZ, H. D. (1983). *Z. Anorg. Allg. Chem.* **497**, 151–156.
 Enraf-Nonius (1982). *Structure Determination Package (SDP)*. Frenz & Associates, College Station, Texas (USA), and Enraf-Nonius, Netherlands.
 HÜTTIG, G. F. & SLONIM, CH. (1929). *Z. Anorg. Chem.* **181**, 65–77.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LUTZ, H. D., BECKER, W., MERTINS, C. & ENGELEN, B. (1979). *Z. Anorg. Allg. Chem.* **457**, 84–90.
 LUTZ, H. D. & CHRISTIAN, H. (1982). *J. Mol. Struct.* **96**, 61–72.
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

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Structures of 26 New Polytypes of Tin Disulfide*

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Abstract. Structures of 26 new polytypes of SnS_2 grown from the vapour phase are reported (t - o - f /Zhdanov notations): 12 hexagonal polytypes: $12H_3$: $tf5f1f2f1f1/21211212$; $14H_3$: $f5f1f2f1f1f2f1/1211212112$; $16H_1$: $(tf5f1f1)_2/(21212)_2$; $24H_2$: $(t)_2f5f1f1f5f1of1f5f1f1/2212121211121212$; $24H_3$: $(f5f1of1)_2f2f2f1f1/(121112)_2111212$; $38H_1$: $(f1f5f1)_6o/(2121)_611$; $44H_2$: $(f1f5f1)_4[f1f5f1(o)_2]_2/(2121)_4[2121(11)]_2$; $58H_1$: $(f1f5f1)_9(o)_2/(2121)_9(11)_2$; $76H_1$: $[f1f5f1(o)_3]_6(o)_2/[2121(11)]_3]_6(11)_2$; $78H_1$: $(t)_2(f5f1f1)_6f5f1of1(f5f1f1)_3/22(1212)_6121112(1212)_5$; $80H_1$: $[f1f5f1(o)_6]_2(o)_4f1f5f1(o)_{15}/[2121(11)]_6]_2(11)_42121(11)_{15}$; $92H_1$: $(f1f5f1)_{15}o/(2121)_{15}11$; and 14 rhombohedral polytypes: $42R_3$: $(f1f5f1)_2o/(2121)_211$; $48R_3$: $f5f1f1tf5tf1f1/1212212212$; $60R_1$: $(f1f5f1)_2(o)_4/(2121)_2(11)_4$; $78R_3$: $(f1f5f1)_4o/(2121)_411$; $90R_1$: $f5f1f1f2f2f1f1f5f1f1f2of2f1f1/121211121212121(11)_212$; $90R_2$: $(t)_2(f5f1f1)_2f5f1of1f5f1f1/22(1212)_21211121212$; $96R_3$: $(f1f5f1)_5o/(2121)_511$; $102R_2$: $[f1f5f1(o)_2]_2(o)_7/[2121(11)]_2]_2(11)_7$; $138R_2$: $[f1f5f1(o)_3f1f5f1o]_2f1f5f1/[2121(11)_3212111]_22121$; $144R_2$: $(f1f5f1)_6of1f5f1(o)_2/(2121)_6112121(11)_2$; $156R_2$: $(t)_2(f5f1f1)_8/22(1212)_8$; $192R_1$: $[f1f5f1(o)_3]_4(o)_8/[2121(11)]_3]_4(11)_8$; $246R_1$: $(f1f5f1)_{13}(o)_2/(2121)_{13}(11)_2$; $258R_1$: $(f1f5f1)_{14}o/(2121)_{14}11$.

Introduction. Although only a little is known about the origin of polytypism, in some cases it is possible to predict the structures (stacking sequences) which can form in crystals under given conditions. As discussed many times in the literature most of the large-period polytypes may be divided into structural series: groups of structures having similar construction. To explain these regularities a screw-dislocation mechanism has been suggested by numerous authors; but the geometrical rules for constructing polytypes on the basis of a growth mechanism appear to have only limited use. According to the geometrical concepts of polytypism, to create a polytype in the crystal it should be enough to have one structure grown in given conditions. In most cases, however, the structures observed in real crystals do not conform with those predicted in this way.

A much more useful and reasonable approach for understanding the rules governing polytypism of crystals is to consider polytype structures as mixed phases – the structures intermediate between simple (basic) polytypes. On developing this concept for polytype structure determination it was found that the formation of structural series of polytypes as well as the growth of polytypes in only some specific conditions may be easily explained. Using the same assumptions (rules) to predict the stacking sequences for different MX_2 compounds the structure determination of tens of CdI_2 , PbI_2 , SnSe_2 and SnS_2 polytypes has been performed.

In the present work several very-large-period polytypes of SnS_2 are given. As discussed the large number of layers in the polytypes of SnS_2 , much larger than in typical polytypes of CdI_2 or PbI_2 , is a direct consequence of the formation of mixed phases from the basic polytypes of this material: $2H$, $4H$ and $18R$. The polytypes composed only of $2H$ and $4H$ stackings were not found in SnS_2 .

* *Editorial note:* The Zhdanov notation used in this paper is a simplified version of the recommendations approved by the International Union of Crystallography *Ad-Hoc* Committee on the Nomenclature of Disordered, Modulated and Polytype Structures [Guinier, Bokij, Boll-Dornberger, Cowley, Đurović, Jagodzinski, Krishna, de Wolff, Zvyagin, Cox, Goodman, Hahn, Kuchitsu & Abrahams (1984). *Acta Cryst.* **A40**, 339–404].

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