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Structural Instability of the Water Molecule in $Sr(IO_3)_2.H_2O$, a Neutron Diffraction Study

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Abstract. Strontium diiodate(V) monohydrate, $Sr(IO_3)_2.H_2O$, $M_r = 455·44$, monoclinic, $I2/c$, $a = 8·9003\,(6)$, $b = 7·748\,(1)$, $c = 9·6496\,(8)$ Å, $\beta = 90·230\,(8)°$, $V = 665·47\,(9)$ Å^3, $Z = 4$, $D_x = 4·546\,(1)$ Mg m^{-3}, neutron radiation, $\lambda = 0·8494$ Å, μ(calc.) $= 0·0124$ mm^{-1}, $F(000) = 202·93$ fm, $T = 295$ K, $R = 0·042$ for 977 observed unique reflections. The water molecules exhibit strong librational motion perpendicular to the H_2O plane, shown by a large anisotropy of the O(4) thermal ellipsoid. The O—H bond length is 0·942 (2) Å, the H—O—H angle 114·4 (3)° and the hydrogen-bond length (H···O) is 1·864 (2) Å.

Introduction. As part of spectroscopic and structural studies on alkaline earth halate hydrates (Lutz & Klüppel, 1975; Lutz, Klüppel & Kesterke, 1976; Eckers & Lutz, 1985; Lutz, Alici & Buchmeier, 1985) with special respect to the water of crystallization in these compounds, we performed a neutron diffraction study on $Sr(IO_3)_2.H_2O$. The crystal structure of $Sr(IO_3)_2.H_2O$, which is isostructural to the $Ba(ClO_3)_2.H_2O$ (Kartha, 1952*a*,*b*) type halates $M(XO_3)_2.H_2O$ (M = Sr, Ba, Pb; X = Cl, Br, I), was determined by Manotti Lanfredi, Pellinghelli, Tiripicchio & Tiripicchio Camellini (1972) (hereafter MPTT) by X-ray single-crystal methods.

Experimental. Single cyrstals of $Sr(IO_3)_2.H_2O$ were grown by interdiffusion of $SrCl_2$ and HIO_3 solutions in an H-shaped tube with an intermediate layer of pure water at room temperature. The cell parameters were refined from Guinier powder data (Huber FR601 camera, Cu $K\alpha_1$ radiation, 52 reflections, α-quartz as internal standard, $a = 4·9136$, $c = 5·4054$ Å) by least-squares methods.

A suitable crystal (elongated monoclinic prism, $3·90 \times 0·65 \times 0·55$ mm) was mounted in a sealed quartz capillary on an Enraf–Nonius CAD-4 diffractometer in order to obtain the orientation matrix. It was then mounted on the D9 four-circle diffractometer now equipped with a two-dimensional detector system (Lehmann, Kuhs, McIntyre, Wilkinson & Allibon, 1989) at the Institut Laue-Langevin, Grenoble. A beryllium (110) monochromatized neutron beam was used. The intensities of 1263 reflections, of which 1112 were unique, were collected in the range $2 \leq 2\theta \leq 80°$; range of hkl: $-13 \leq h \leq 13$, $0 \leq k \leq 11$, $0 \leq l \leq 14$. Data reduction was performed according to Wilkinson, Khamis, Stansfield & McIntyre (1988). A numerical absorption correction did not improve the results, an intensity decrease of the standard reflection ($\bar{4}00$) was not observed during data collection.

The Sr, I and O positions obtained from X-ray data (MPTT) were used as starting values for the refinement. Scattering lengths for all atoms were taken from Sears (1986). The iodine position reported by MPTT turned out to be incorrect, possibly due to a misprint; it was therefore determined from a difference Fourier synthesis, as were the hydrogen positions. Full-matrix least-squares refinement (modified *SHELX*; Sheldrick, 1976) of positional and anisotropic thermal parameters, extinction coefficient, and scale factor based on F magnitudes of 977 reflections with $F \geq 2\sigma_F$ gave a final $R = 0·042$ [$wR = 0·035$, $w = 2·07/\sigma^2(F)$] and an extinction coefficient of $4·9\,(2) \times 10^{-7}$. The ratio of

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Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

	Site	*x*	*y*	*z*
Sr	4(*e*)	0·0	0·4083 (1)	0·25
I	8(*f*)	0·2644 (1)	0·2809 (1)	0·5598 (1)
O(1)	8(*f*)	0·0676 (1)	0·3363 (1)	0·5644 (1)
O(2)	8(*f*)	0·2620 (1)	0·0874 (1)	0·6667 (1)
O(3)	8(*f*)	0·2715 (1)	0·1840 (1)	0·3918 (1)
O(4)	4(*e*)	0·0	0·0832 (2)	0·25
H	8(*f*)	0·0846 (2)	0·0173 (3)	0·2250 (3)

Table 2. *Anisotropic thermal parameters* U_{ij} (Å^2 × 10^2) *with e.s.d.'s in parentheses*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	1·77 (4)	1·72 (4)	2·57 (5)	0	0·95 (4)	0
I	1·12 (3)	1·31 (3)	1·25 (3)	0·04 (3)	0·24 (3)	0·08 (3)
O(1)	1·42 (4)	2·29 (4)	3·02 (4)	0·30 (3)	0·34 (3)	−0·22 (3)
O(2)	2·03 (4)	1·98 (4)	2·41 (4)	0·26 (3)	0·76 (3)	0·72 (3)
O(3)	2·17 (4)	3·06 (4)	1·60 (4)	0·11 (3)	0·19 (3)	−0·55 (3)
O(4)	1·59 (7)	2·18 (7)	9·97 (17)	0	0·30 (8)	0
H	3·19 (9)	4·37 (10)	5·74 (14)	0·95 (9)	0·37 (9)	0·89 (9)

Table 3. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses, data from* MPTT *in square brackets*

Hydrogen bonding							
O(4)^{0}—H^{0,iii}	2×	0·942 (2)		H^{0,iii}···O(2)^{viii,ix}	2×	1·864 (2)	
H^{0}—O(4)^{0}—H^{iii}		114·4 (3)		O(4)^{0}···H^{0,iii}···O(2)^{viii,ix}	2×	172·8 (2)	
H^{0}···H^{iii}		1·583 (4)		H^{0,iii}···O(4)^{0}···Sr^{0}	2×	122·8 (2)	
Iodate ion							
I^{0}—O(1)^{0}		1·804 (1)	[1·806 (9)]	O(1)^{0}···I^{0}···O(2)^{0}		99·70 (6)	[99·9 (2)]
I^{0}—O(2)^{0}		1·820 (1)	[1·825 (9)]	O(1)^{0}···I^{0}···O(3)^{0}		99·21 (6)	[98·6 (3)]
I^{0}—O(3)^{0}		1·788 (1)	[1·786 (8)]	O(1)^{0}···I^{0}···O(3)^{0}		99·70 (5)	[99·2 (2)]
				I^{0}···I^{x}		3·712 (2)	
Sr coordination							
Sr^{0}—O(1)^{0,iii}	2×	3·141 (1)	[3·136 (15)]	Sr^{0}—O(3)^{0,iii}	2×	3·272 (1)	—
Sr^{0}—O(1)^{i,ii}	2×	2·738 (1)	[2·731 (8)]	Sr^{0}—O(3)^{vi,vii}	2×	2·558 (1)	[2·553 (13)]
Sr^{0}—O(2)^{iv,v}	2×	2·654 (1)	[2·664 (11)]	Sr^{0}—O(4)^{0}		2·519 (2)	[2·531 (8)]

Symmetry operations (0) x,y,z; (i) $-x,1-y,1-z$; (ii) $x,1-y,-1/2+z$; (iii) $-x,y,1/2-z$; (iv) $-1/2+x,1/2+y,-1/2+z$; (v) $1/2-x,1/2+y,1-z$; (vi) $1/2-x,1/2-y,1/2-z$; (vii) $-1/2+x,1/2-y,z$; (viii) $x,-y,-1/2+z$; (ix) $-x,-y,1-z$; (x) $1/2-x$, $1/2-y,1{\cdot}5-z$.

maximum least-squares shift/e.s.d. in the final cycle was less than 0·001. The final atomic coordinates are given in Table 1, anisotropic thermal parameters in Table 2.*

Discussion. Hitherto, the crystal structures of the Ba(ClO$_3$)$_2$.H$_2$O type halates have been described in the unconventional setting *I*2/*c* (Kartha, 1952*a*,*b*; Sikka, Momin, Rajagopal & Chidambaram, 1968; Lutz, Alici & Buchmeier, 1985) with the exception of Sr(IO$_3$)$_2$.H$_2$O (*C*2/*c*). We decided to maintain the unconventional *I*2/*c* cell and the respective numbering of atoms for this and further publications in order to allow proper comparison of the structure data.

Strontium and the water oxygen, O(4), occupy the special position 4(*e*) (site symmetry 2), the iodate ions and the H atoms are in the general position 8(*f*). Selected bond lengths and angles are given in Table 3, the coordination polyhedron of strontium is shown in Fig. 1. For a detailed description of the structure, see Lutz, Alici & Buchmeier (1985).

The coordination of the water molecule is trigonal, type *D* after Chidambaram, Sequeira & Sikka (1964), *i.e.* there is only one metal atom coordinated to the water oxygen O(4) (see Fig. 1). The thermal ellipsoid of O(4) exhibits large anisotropy. This behaviour of O(4), which was found by X-ray structure determination for all *M*(*X*O$_3$)$_2$.H$_2$O (Kartha, 1952*a*,*b*; MPTT, 1972; Lutz, Alici & Buchmeier, 1985) and by neutron diffraction on Ba(ClO$_3$)$_2$.H$_2$O (Sikka, Momin, Rajagopal & Chidambaram, 1968), indicates a structural instability. However, a refinement of O(4) and/or H on split positions due to a possible orientational disorder of the water molecule was not successful. Dynamic disorder of the water molecules at room temperature is indicated by IR and Raman bandwidths as well as by measurements of the dielectric constant (Lutz & Lange, undated) while a structural phase transition detectable by X-rays or DSC (differential scanning calorimetry) is not observed. Therefore, a neutron diffraction study at low temperatures is desirable in order to investigate this effect.

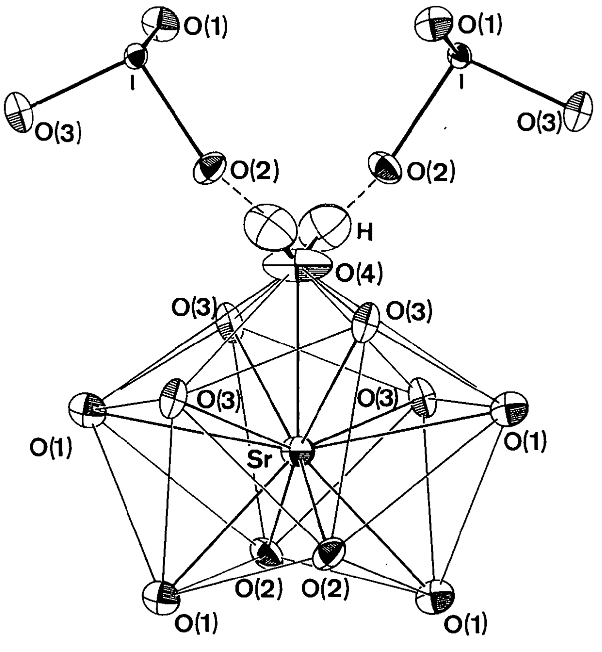

Fig. 1. Strontium–oxygen coordination polyhedron with the water molecule and the hydrogen-bond acceptor iodate ions, viewed approximately down [100]; dashed lines represent hydrogen bonds.

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* Lists of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52611 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Additionally, it must discussed whether the structural instabilities caused by a trigonal planar coordination of water molecules can be compensated by a deviation from sp^3 hydridization of the water oxygen, *i.e.* partly sp^2 hybridization. This could explain the enlarged intramolecular H—O—H angle (see Table 3), which is obviously due to metal–oxygen interaction. This interaction might also be responsible for the low frequency of the H_2O bending fundamental (1604 cm^{-1}, 95 K; Henning, 1988); see the discussion given by Falk (1984) and Lutz (1988).

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Actinide Structural Studies. 19.* Structure of *af*-Dinitrato-*bd*-dioxo-*ce*-bis(urea)uranium(VI)

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Abstract. $[U(NO_3)_2(O)_2(CH_4N_2O)_2]$, $M_r = 514{\cdot}09$, monoclinic, $P2_1/c$, $a = 14{\cdot}109\ (3)$, $b = 7{\cdot}727\ (3)$, $c = 11{\cdot}210\ (3)$ Å, $\beta = 99{\cdot}02\ (2)°$, $V = 1207{\cdot}0\ (5)$ Å^3, $Z = 4$, $D_m = 2{\cdot}81$, $D_x = 2{\cdot}83$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 128{\cdot}4$ cm^{-1}, $T = 290$ K, $R = 0{\cdot}028$ for 1799 unique observed $[I/\sigma(I) \geq 2{\cdot}0]$ reflections. The title compound contains a UO_2 group [mean U—O 1·754 (6) Å] coordinated by two *trans* urea molecules [mean U—O 2·345 (4) Å] and two *trans* bidentate nitrate groups [mean U—O 2·530 (5) Å]. Two weak intramolecular N—H···O bonds are formed between urea molecules and one of the uranyl O atoms [N···O 3·15 (1) Å].

Introduction. All uranyl complexes with urea previously studied by X-ray and neutron diffraction show pentagonal bipyramidal coordination by O atoms around the uranyl group. In the case of nitrate complexes, the coordination about the UO_2 group was reported to consist either of five oxygens contributed by the urea molecules (Zalkin, Ruben & Templeton, 1979) or of four oxygens belonging to the urea molecules and one water molecule respectively (Dalley, Mueller & Simonsen, 1972), and in each

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* Part 18: Alcock, Kemp, Leciejewicz & Pennington (1989).

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