Structure of Samarium(III) Iodate Monohydrate

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Abstract. $Sm(IO_3)_3.H_2O$, $M_r = 675 \cdot 11$, monoclinic, $P2_1$, $a = 10 \cdot 133$ (1), $b = 6 \cdot 6571$ (6), $c = 7 \cdot 3110$ (7) Å, $\beta = 113 \cdot 109$ (8)°, $V = 453 \cdot 6$ (2) Å^3, $Z = 2$, $D_x = 4 \cdot 94$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0 \cdot 71069$ Å, $\mu = 169 \cdot 31$ cm^{-1}, $F(000) = 586$, $T = 296$ K, final $R(F) = 0 \cdot 030$, $wR(F) = 0 \cdot 045$ for 2945 $F_m^2 > 3\sigma(F_m^2)$. The crystal is essentially isomorphous with $Nd(IO_3)_3.H_2O$, although normal probability analysis shows that the rare earth atoms depart significantly from exact isomorphism. The iodate ions form trigonal pyramids, with average I—O = $1 \cdot 812$ (14) Å and O—I—O = $98 \cdot 5$ ($2 \cdot 2$)°. Each I atom also forms longer bonds to O, resulting in two independent monocapped octahedrally coordinated and a distorted uncapped octahedrally coordinated I atom. The Sm atom is in a distorted bicapped trigonal prismatic coordination. The water molecule links all three symmetry-independent iodate ions in a three-dimensional network, with shortest distance from the water O atom to a neighboring I atom of $2 \cdot 681$ (8) Å.

Introduction. An extensive survey of the transition-metal iodates, undertaken in a search for new materials with an enhanced likelihood of possessing coupled magnetic, optic, elastic and polar properties (Abrahams, 1971), led to the synthesis and crystal growth of numerous $3d$ metal iodates (Nassau, Shiever & Prescott, 1973) and $4f$ metal iodates (Nassau, Shiever, Prescott & Cooper, 1974). The crystallographic, magnetic and nonlinear optical properties of many $3d$ iodates and their hydrates were determined by Abrahams, Sherwood, Bernstein & Nassau (1973*a,b*), Elemans & Verschoor (1973), Abrahams, Bernstein, Elemans & Verschoor (1973), Liminga, Booles, Ghose & Wan (1978), Ghose & Wan (1978), and Liminga, Abrahams & Bernstein (1975).

Abrahams, Bernstein & Nassau (1976, 1977) [hereafter ABN] investigated 13 crystallographically distinct families of $4f$ iodates, including their hydrates, with formulas $Ln(IO_3)_3.xH_2O$ for Ln from Eu to Lu including Y, and with $0 \le x \le 4$. They reported the formation of a family of isostructural monohydrates with Ln = Ce, Pr, Nd, Pm and Sm in space group $P2_1$; ABN determined the lattice constants for $Sm(IO_3)_3.H_2O$ at room temperature to be $a = 10 \cdot 080$ (7), $b = 6 \cdot 642$ (6), $c = 7 \cdot 250$ (8) Å and $\beta = 112 \cdot 9$ (1)° and noted that the family is polar, generating second harmonics with an efficiency about an order of magnitude greater than quartz. The absolute sign and magnitude of the pyroelectric and piezoelectric coefficients in $Nd(IO_3)_3.H_2O$ have been reported (Liminga & Abrahams, 1976).

In an effort to identify possibly unreported polar phases of the $4f$ iodates, crystals of $Sm(IO_3)_3.H_2O$ were found to have the same space group $P2_1$ as $Nd(IO_3)_3.H_2O$ but apparently different lattice constants. It was noted later that the cell could be transformed to that reported by ABN but, in the meantime, the crystal structure had been solved and refined independently of the previous work. The results of this study are reported below for comparison with $Nd(IO_3)_3.H_2O$ and with respect to the configuration of the three crystallographically independent IO_3^- ions, the environment about Sm^{3+} and the pyroelectric and piezoelectric properties of $Sm(IO_3)_3.H_2O$.

Experimental. A yellow crystal, grown from the gel, with dimensions $0 \cdot 25 \times 0 \cdot 33 \times 0 \cdot 38$ mm was mounted in an Enraf–Nonius CAD-4 diffractometer. The lattice constants at 296 K were measured with Mo $K\alpha_{1,2}$ ($\lambda = 0 \cdot 70930$, $0 \cdot 71359$ Å, graphite monochromator) on the basis of 25 automatically centered reflections in the range $18 \cdot 6 \le \theta \le 25 \cdot 3°$: initial values were $a = 7 \cdot 3110$ (7), $b = 6 \cdot 6571$ (7), $c = 9 \cdot 898$ (1) Å, $\beta = 109 \cdot 684$ (8)°. The density of isostructural $Nd(IO_3)_3.H_2O$ was measured pycnometrically by ABN as

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $Sm(IO_3)_3.H_2O$ *at* 296 K

$$B_{eq} = (\tfrac{8}{3})\pi^2\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sm	0·19108 (3)	0·5000	−0·06387 (4)	0·320 (7)
I(1)	0·22518 (4)	0·02457 (7)	0·20321 (5)	0·353 (8)
I(2)	0·03487 (4)	0·48189 (8)	0·37272 (5)	0·372 (8)
I(3)	0·59203 (4)	0·35137 (8)	0·22282 (5)	0·475 (9)
O(1)	0·1507 (6)	0·1414 (9)	−0·0413 (6)	0·8 (1)
O(2)	0·2794 (6)	−0·2073 (9)	0·1208 (7)	0·9 (1)
O(3)	0·0622 (5)	−0·0501 (11)	0·2261 (9)	1·1 (2)
O(4)	0·1496 (5)	0·3666 (10)	0·6054 (6)	0·8 (1)
O(5)	0·1380 (5)	0·4143 (11)	0·2285 (7)	0·9 (1)
O(6)	−0·1016 (5)	0·2867 (10)	0·2976 (7)	0·8 (1)
O(7)	0·6057 (6)	0·0996 (10)	0·1329 (9)	1·0 (1)
O(8)	0·6632 (7)	0·2961 (12)	0·4830 (8)	1·4 (2)
O(9)	0·4002 (5)	0·3396 (10)	0·1685 (8)	1·0 (1)
O(W)	0·5810 (7)	0·7145 (12)	0·3748 (11)	1·7 (2)

4.80 (10) g cm^{-3}. Intensities were measured by means of θ–2θ scans, with a variable rate of 1·18 to 16·48° θ min^{-1} and scan range of $(1.65 + 0.53\tan\theta)°$ in 96 step intervals for subsequent profile analysis. The index range was $-13 \le h \le 13$, $-12 \le k \le 0$, $0 \le l \le 17$ for $(\sin\theta)/\lambda \le 0.90$ Å^{-1}. Five standard reflections measured at exposure intervals of 2 h exhibited an average change of $\simeq 1.3\%$, without apparent systematic trend, hence an exposure-dependent correction was not applied. A total of 3149 reflections were measured (including 25 standards), resulting in 2986 unique values of which 2945 $F_{obs}^2 > 3\sigma(F_{obs}^2)$. The integrated intensities were derived by use of a modified Lehmann & Larsen (1974) procedure (Ammon, 1986), taking 12 steps on either side of the central peak as background and with the central peak-width varied, starting at 40 steps; the average peak-width was 50 steps. Empirical absorption corrections were applied, based on systematic differences between F_{obs} and F_{calc} (Walker & Stuart, 1983); minimum and maximum absorption corrections of 0·865 and 1·335 were obtained following refinement with isotropic temperature factors. The value of $R(F^2)_{int} = 0.10$ on the basis of 118 symmetry equivalent reflections: the averaged values were included in the final 2945 F_{obs}.

The positions of the Sm and I atoms were determined from a sharpened Patterson function, and subsequent difference Fourier synthesis yielded the location of all remaining atoms except for the H atoms. Full-matrix least-squares refinement of all position coordinates and anisotropic thermal parameters (a total of 127 parameters varied), minimizing $\Sigma[1/\sigma^2(F_{obs})] \times (F_{obs} - F_{calc})^2$ with $\sigma^2(F_{obs}) = (2LpI_{obs})^{-2}[P + t^2(B_1 + B_2) + (0.03P)^2]$ for P = peak scan intensity, B_1 and B_2 the two background intensities and t = (peak scan time)/(total background time), gave the results in Table 1 with $R(F) = 0.030$, $wR(F) = 0.045$ and $S = 2.01$. Atomic and anomalous scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974), and a secondary-extinc-

tion parameter was varied (Zachariasen, 1968) in the final refinement cycles giving $g = 16.8 \times 10^{-6}$; the maximum extinction correction was 17·8%, for $F(2\bar{1}1)$. The maximum ratio of parameter shift/e.s.d. in the final refinement cycle was 0·06 and the minimum, maximum in the final difference Fourier synthesis was −3·3, +4·3 e Å^{-3}. Transformation to the cell isomorphous with Nd(IO$_3$)$_3$.H$_2$O (Liminga *et al.*, 1975) by the matrix 101/0$\bar{1}$0/$\bar{1}$00 gives $a = 10.133$ (1), $b = 6.6571$ (1), $c = 7.3110$ (7) Å, $\beta = 113.109$ (8)°. The origin was taken at $y(\text{Sm}) = \tfrac{1}{2}$, for direct comparison with the previous results on Nd(IO$_3$)$_3$.H$_2$O, and all atoms are numbered as in the earlier study. The absolute sense of the polar axis could not be determined in the present analysis since only a quadrant of reciprocal space was measured. All calculations were made with the *TEXSAN* (1987) system and a DEC MicroVAX II computer.*

Discussion. A stereoview of the Sm(IO$_3$)$_3$.H$_2$O structure, based upon the atomic coordinates in Table 1, is given in Fig. 1 as viewed along the b axis. The atomic coordinates in Table 1 may conveniently be compared with those of isostructural Nd(IO$_3$)$_3$.H$_2$O, as determined by Liminga *et al.* (1975), in a half-normal probability plot (Abrahams & Keve, 1971). The two largest normal deviates are those for $x(\text{Sm})$ and $z(\text{Sm})$ at 7·9 and 11·6 joint e.s.d.'s respectively, indicating that the $4f$ atom in the two structures does not occupy identical positions (but is nevertheless very close). The remaining normal deviates $\delta m = |m_1 - m_2|/(\sigma^2 m_1 +$
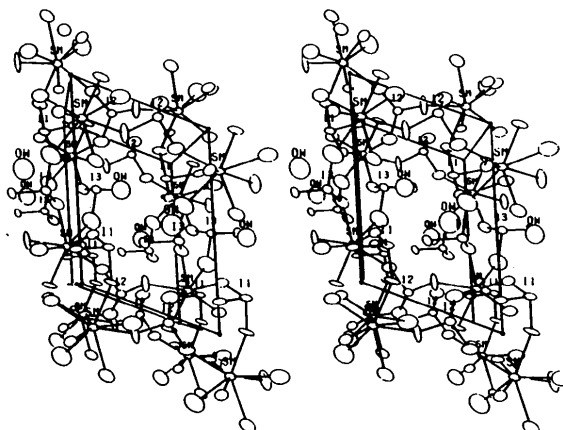
Fig. 1. Stereoview of content of Sm(IO$_3$)$_3$.H$_2$O unit cell at 296 K as viewed along the b axis with the a axis vertical. The thermal ellipsoids represent probability densities greater than 98%.

$\sigma^2 m_2)^{1/2}$ exhibit two distinct distributions, with 26 of the remaining 39 δm close to normal and having a slope of 1·4. The outlying 13 δm are also linearly distributed, but have a slope of about 3·4. It may be noted that the only atom, apart from Sm, with δm for all x, y and z coordinates occupying the higher slope distribution is I(1). The inference may thus be drawn that either the two iodate monohydrates are not exactly isomorphous or the joint estimated standard deviation of the difference between corresponding atomic coordinates has been underestimated by a factor between 1·4 and 3·4.

It may be seen from Fig. 1 that each of the three I atoms forms an independent trigonal pyramid with the three closest O atoms, and that each deviates significantly from $3m$ point symmetry. I(1) is closely bonded to O(1), O(2) and O(3) with average I—O = 1·811 (10) Å, I(2) to O(4), O(5) and O(6) with average I—O = 1·813 (6) Å and I(3) to O(7), O(8) and O(9) with average I—O = 1·813 (22) Å {the e.s.d. of the

average $\bar{x} = \frac{1}{n} \sum\limits_{i=1}^{n} x_i$ is taken here and elsewhere in this

paper as $[1/(n-1) \sum\limits_{i=1}^{n} (x_i - \bar{x})^2]^{1/2}$}. For all nine short I—O bonds the average is 1·812 (14) Å, which compares well with the value in LiIO$_3$ measured by neutron diffraction over the temperature range 20–295 K (Svensson, Albertsson, Liminga, Kvick & Abrahams, 1983) of 1·8081 (3) Å.

As found in other iodates, where between two and five additional nearest-neighbor O atoms form weak I—O bonds of length 2·5–3·2 Å with the central I atom (Ghose & Wan, 1974), each of the I atoms in Sm(IO$_3$)$_3$.H$_2$O occupies an irregular polyhedron. Thus, I(1) forms a monocapped octahedron (see Table 2) with I(1)···O(W) = 3·197 (7) Å. I(2) forms a distorted uncapped octahedron, and I(3) a second independent distorted monocapped octahedron, as in Nd(IO$_3$)$_3$.H$_2$O (Liminga et al., 1975). The coordination about Sm may be described either as distorted bicapped trigonal prismatic or as distorted bisphenoidal, with Sm—O = 2·420 (54) Å on average (see Table 3).

The water molecule links all three independent iodate groups in a three-dimensional network, with O(W)···I distances as short as 2·681 (8) Å, see Table 4. The H-atom positions were not detectable in the final difference Fourier series and have not been inferred from the structure.

The model relating the measured pyroelectric coefficient of + 22 × 10^{-6} C m^{-2} K^{-1} and the positive piezoelectric d_{22} coefficient ($0 < d_{22} < 30 \times 10^{-12}$C N^{-1}) in Nd(IO$_3$)$_3$.H$_2$O to the structure (Liminga & Abrahams, 1976) applies equally to Sm(IO$_3$)$_3$.H$_2$O.

Table 2. *Interatomic* I—O *distances* (Å) *less than* 3·30 Å *and* O—I—O *angles* (°) *within the three independent iodate ions*

I(1)—O(1)	1·820 (5)	O(1)—I(1)—O(2)	95·7 (3)
I(1)—O(2)	1·819 (6)	O(1)—I(1)—O(3)	99·7 (3)
I(1)—O(3)	1·794 (6)	O(2)—I(1)—O(3)	101·8 (3)
I(1)—O(5)	2·770 (7)		
I(1)—O(8′)	2·611 (6)		
I(1)—O(9)	2·822 (6)		
I(1)—O(W′)	3·197 (7)		
I(2)—O(4)	1·812 (5)	O(4)—I(2)—O(5)	97·9 (2)
I(2)—O(5)	1·808 (6)	O(4)—I(2)—O(6)	96·5 (3)
I(2)—O(6)	1·819 (5)	O(5)—I(2)—O(6)	101·0 (3)
I(2)—O(1′)	2·638 (4)		
I(2)—O(4′)	3·212 (6)		
I(2)—O(6′)	3·017 (6)		
I(3)—O(7)	1·825 (7)	O(7)—I(3)—O(8)	97·9 (3)
I(3)—O(8)	1·788 (6)	O(7)—I(3)—O(9)	96·2 (3)
I(3)—O(9)	1·826 (5)	O(8)—I(3)—O(9)	100·0 (3)
I(3)—O(W)	2·681 (8)		
I(3)—O(2′)	3·276 (7)		
I(3)—O(7′)	3·069 (6)		
I(3)—O(6)	2·964 (5)		

Symmetry code: (′) $\bar{x}$, $\frac{1}{2}+y$, $\bar{z}$.

Table 3. *Bicapped trigonal prismatic coordinated* Sm—O *distances* (Å)

Sm—O(1)	2·439 (6)	Sm—O(5)	2·468 (5)
Sm—O(2)	2·339 (6)	Sm—O(6′)	2·484 (6)
Sm—O(3′)	2·391 (5)	Sm—O(7′)	2·398 (7)
Sm—O(4)	2·453 (6)	Sm—O(9)	2·386 (5)

For symmetry code see Table 2.

Table 4. *Interatomic distances* (Å) *between the water molecule and its nearest atoms less than* 3·3 Å *apart*

O(W)···I(1′)	3·197 (7)	O(W)···O(7)	3·179 (11)
O(W)···I(3)	2·681 (8)	O(W)···O(8)	2·926 (11)
O(W)···O(2)	2·933 (8)	O(W)···O(8′)	3·086 (11)
O(W)···O(4′)	2·861 (9)	O(W)···O(9)	3·113 (9)

For symmetry code see Table 2.

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The Structure of Aluminium Iron Molybdate

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Abstract. Synthetic $AlFe(MoO_4)_3$, $M_r = 562.64$, monoclinic, $P2_1/a$, $a = 15.509$ (1), $b = 9.1320$ (2), $c = 18.021$ (1) Å, $\beta = 125.306$ (5)°, $V = 2082.9$ (5) Å^3, $Z = 8$. The structure has been refined by Rietveld analysis of constant wavelength neutron powder diffraction data ($\lambda = 1.909$ Å) recorded at $T = 4.2$ K [$R_I = 3.40$, $R_p = 6.38$, $R_{wp} = 7.12$, $R_{exp} = 6.63\%$]. It is isomorphous with the end member molybdates, $Fe_2(MoO_4)_3$ and $Al_2(MoO_4)_3$, without any detectable cation ordering. No magnetic ordering occurs at 4.2 K.

Introduction. The title compound was studied as part of our investigations into magnetic, structural and catalytic properties of $M_2(XO_4)_3$ type systems. Previous work has included $Fe_2(SO_4)_3$ (Long, Longworth, Battle, Cheetham, Thundathil & Beveridge, 1979), $Fe_2(MoO_4)_3$ (Battle, Cheetham, Long & Longworth, 1982), $Cr_2(MoO_4)_3$ (Battle, Cheetham, Harrison, Pollard & Faber, 1985), $Fe_2(WO_4)_3$ (Harrison, Chowdhry, Machiels, Sleight & Cheetham, 1986) and $Al_2(MoO_4)_3$ (Harrison, Cheetham & Faber, 1988). Pure, well characterized $M_2(MoO_4)_3$ type mixed molybdates of Fe, Cr and Al have been reported by Harrison (1986) and the catalytic properties of the aluminium-substituted iron molybdate, $Al_xFe_{2-x}(MoO_4)_3$ (Machiels, Chowdhry, Harrison & Sleight, 1985) have been discussed. The present work investigates the crystal structure of $AlFe(MoO_4)_3$.

Experimental. $AlFe(MoO_4)_3$ was synthesized from analytical grade reagents following the method of Machiels, Chowdhry, Harrison & Sleight (1985). X-ray powder diffraction patterns and analytical electron microscopy (Cheetham & Skarnulis, 1981) indicated that the product was single phase, homogeneous and crystalline. Neutron powder diffraction data were collected on the diffractometer D1a at ILL, Grenoble (Hewat & Bailey, 1976): mean neutron wavelength $\lambda = 1.909$ Å; $6° \leq 2\theta \leq 145°$ in steps of $0.05°$; vanadium tailed liquid helium 'orange' cryostat at 4.2 K; cylindrical vanadium sample can. Absorption was negligible and no correction was made. Data from the ten ^3He detectors were collated and normalized before refinement commenced (Hewat, 1978). A model was refined using the Rietveld profile method (Rietveld, 1969; Hewat, 1978) on a VAX 11-780 computer at Oxford University Computing Centre. A preliminary background subtraction was determined by extrapolation between those parts of the pattern containing no Bragg reflections at low angle and extended linearly to high angles. The structure of centrosymmetric monoclinic $Fe_2(MoO_4)_3$ (Chen, 1979) was used as a trial model. Coherent neutron scattering lengths were taken as: $Fe/Al = 6.495$ fm, $Mo = 6.95$ fm, $O = 5.805$ fm (Bacon, 1975). A total of 115 variable parameters including scale factor, four unit-cell constants, counter zero point error, empirical low-angle 'asymmetry correction', three Gaussian peak half-width variation parameters, 102 general atomic positional parameters and three atom-type isotropic thermal factors were included in the final full-matrix cycle of least-squares refinement. Refinement was terminated