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Sodium iodine(V) oxyfluoride, $NaIO_2F_2$

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As an extension of a general structural study concerning fluorides and oxyfluorides of cations presenting a stereochemically active electronic lone pair, until now limited to tellurium(IV) phases, the previously unknown structure of $NaIO_2F_2$ corresponds to a new structure type based on isolated $IO_2F_2^-$ polyhedra forming sheets separated by Na^+ layers. The sodium ion is octahedrally coordinated with $2/m$ site symmetry, while the I^V atom has $m2m$ symmetry with a stereochemically active lone electron pair. The O and F atoms (both with m symmetry) are bonded to the I^V atoms in a fully ordered manner. A comparison with the structure of ferroelastic KIO_2F_2 and with structures based on hexagonal close packing of anions, mainly rutile-type and $FeTeO_3F$-type, reveals differences that are attributed to the smaller ionic radius of Na^+ and the ordering of the Na and I cations.

Comment

The existence of sodium iodine(V) oxyfluoride, $NaIO_2F_2$, has been reported without structural characterization (Nikolaeva *et al.*, 1988). As an extension of a general structural study concerning fluorides and oxyfluorides of cations presenting a stereochemically active electronic lone pair, until now limited to tellurium(IV) phases, we report here the structure of $NaIO_2F_2$. Iodine(V) phases are expected to present some similarities with their tellurium(IV) homologues because of their almost identical ionic radius, in spite of their lower thermal stability.

In $NaIO_2F_2$, the Na^+ atom is in a sixfold coordination at the centre of a nearly regular NaO_2F_4 octahedron (Fig. 1 and Table 1). Each Na^+ atom is surrounded by four F atoms forming a square base and two apical O atoms.

The I^V cation is surrounded by four anions, namely two equatorial O atoms and two axial F atoms at a longer distance (Table 1). Full O/F anionic order on the O1 and F1 sites is evidenced by bond-valence calculations (Brown, 1981) (Table 2). The corresponding polyhedron (Fig. 2) can be described as a trigonal bipyramid, IO_2F_2E, the fifth corner of which is occupied by the lone pair, E. The introduction of two weaker I1—O1 bonds turns the $IO_2F_2E^-$ trigonal bipyramid into a pentagonal bipyramid, IO_4F_2E, but if the lone pair E is not included, the I^{5+} environment can also be considered as an $IO_4F_2^-$ octahedron distorted by the repulsion of this lone pair on $O1^i$ and $O1^{iv}$ [symmetry codes: (i) $x, -y, -z$; (iv) $-x + 1, -y, z + \frac{1}{2}$] (Fig. 2). This $IO_2F_2^-$ polyhedron is essentially the same as those in KIO_2F_2 (Abrahams & Bernstein, 1976) and $[N(CH_3)_4][IO_2F_2][HF_2]$ (Gerken *et al.*, 2004). Weak I1—O1 bonds are also systematically present in these structures.

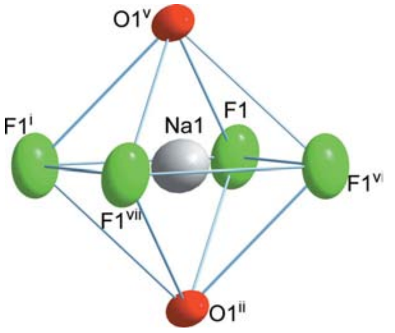

Figure 1
The coordination polyhedron of the $Na1^+$ cation in $NaIO_2F_2$. [Symmetry codes: (i) $x, -y, -z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (vi) $-x, y, -z + \frac{1}{2}$; (vii) $-x, -y, z - \frac{1}{2}$.]

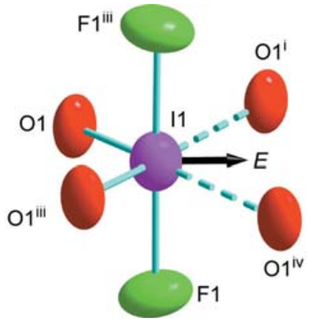

Figure 2
The anionic polyhedron around the $I1^{5+}$ cation in the structure of $NaIO_2F_2$. The arrow indicates the direction to which the lone pair E points. Dotted lines represent weak I1—O1 bonds. [Symmetry codes: (i) $x, -y, -z$; (iii) $-x + 1, y, -z + \frac{1}{2}$; (iv) $-x + 1, -y, z + \frac{1}{2}$.]

A comparison between I^V and Te^{IV} is very meaningful because their lone pairs have the same stereochemical activity (Glay *et al.*, 1975). Some isolated polyhedra displaying such activity that can be compared with $IO_2F_2^-$ include $TeOF_4^{2-}$ in Cs_2TeOF_4 (Jansen & Kessler, 2001), and IOF_3 (Edwards & Taylor, 1974), TeF_4 (Kniep *et al.*, 1984) and IF_5 (Burbank & Jones, 1974) in the corresponding phases.

Depending on the respective distribution of O and F anions in these structures, the classical umbrella effect resulting from the stereochemical activity of the lone pair E is more or less marked. In TeF_4, the axial angle F2—Te1—F4 is 161.31 (19)° and the equatorial angle F1—Te1—F3 is 87.59 (21)°. In IF_5, the average of the axial F—I1—F angles is 163.0 (6)°. In oxyfluorides, these angles increase, *e.g.* in IOF_3 the axial F1—I1—F2 angle is 165.92 (11)° and the equatorial O1—I1—F3 angle is 102.02 (13)°; the average value of the axial F—Te1—F angles in $TeOF_4^{2-}$ is 177.55°. These last two polyhedra are the

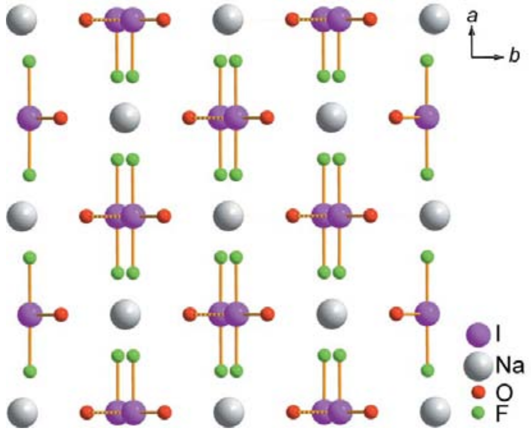

Figure 3
A projection of the structure of $NaIO_2F_2$ along [001], showing the pseudo-cubic subcell.

most similar to the $IO_2F_2^-$ configuration, in which the axial angle F1—I1—F1^{iii} is 179.55 (10)° and the equatorial angle O1—I1—O1^{iii} is 103.72 (12)° [symmetry code: (iii) $-x + 1, y, -z + \frac{1}{2}$]. Therefore, in these oxyfluorides the umbrella effect, characterized in a first approximation by axial angles lower than 180°, is partly or almost completely counterbalanced by the repulsion between the equatorial O anions and the axial F anions.

A projection along the [001] direction (Fig. 3) shows that the Na^+ cations and $IO_2F_2^-$ complex anions form a CsCl-like lattice (Hyde & Andersson, 1989). The pseudo-cubic Na1 subcell is in fact tetragonal, with $a = 5.02$ Å and $c = 3.68$ Å, and its centre is occupied by an $IO_2F_2^-$ complex anion which is responsible for the distortion.

The IO_4F_2E pentagonal bipyramids (or IO_4F_2 distorted octahedra), incorporating two weak I1—O1 bonds, form linear $[IO_2F_2^-]_n$ chains extending along the c axis through O–O edge sharing. Along this same axis, NaO_2F_4 octahedra share F–F edges, also forming parallel linear chains alternating with $[IO_2F_2^-]_n$ chains and shifted by $c/4$ (Fig. 4). Successive I1 and Na1 chains are connected along the [100] direction through F1 corners forming sheets. Along [010], these sheets are interconnected only *via* O1 corners of NaO_2F_4 octahedra (Fig. 3). In this way, the structure can be described as a smooth three-dimensional array of nearly perfect edge-sharing NaO_2F_4 octahedra and distorted IO_4F_2 octahedra. From this point of view, the structure of $NaIO_2F_2$ is derived from a rutile superstructure (Fig. 5) by a cationic I1/Na1 ordering in such a way that $a = (a_{\rm rutile})^{1/2}$, $b = (a_{\rm rutile})^{1/2}$ and $c = (c_{\rm rutile})^{1/2}$. This kind of structure is well adapted to cations presenting a stereochemically active electronic lone pair. For example, the structure of BiOF and PbFCl is described by Hyde & Andersson (1989) as being derived from the rutile type. The puckering of the anionic hexagonal close-packed planes, common in rutile phases and in TiO_2 itself, accommodates in $NaIO_2F_2$ the distortion resulting from the lone-pair activity of I^{5+}.

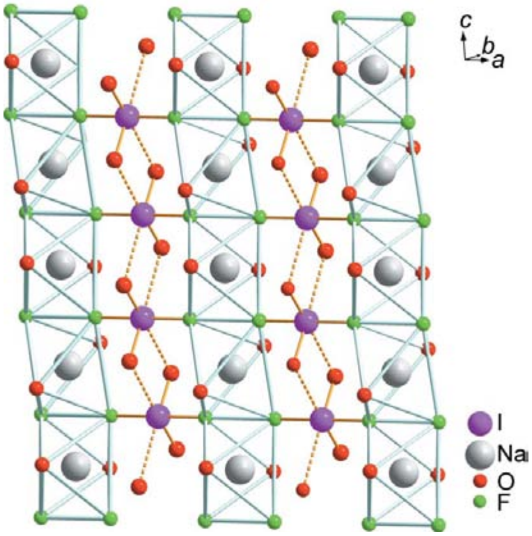

Figure 4
The parallel chains of the I1 and Na1 polyhedra of $NaIO_2F_2$.

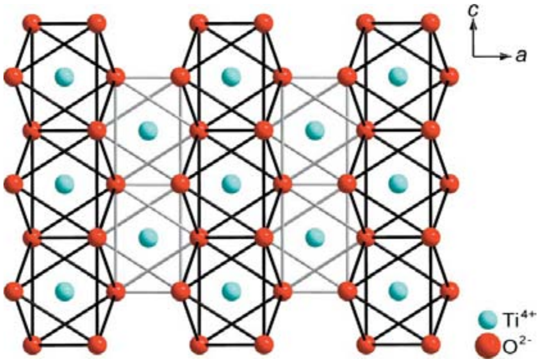

Figure 5
The rutile structure, for comparison with $NaIO_2F_2$.

In the MIO_2F_2 series, only the KIO_2F_2 structure was known before the present work. Described in the polar space group $Pca2_1$, it is also derived from CsCl, but the much greater size of K^+ compared with Na^+ leads to a complete separation of corrugated planes of $IO_2F_2^-$ polyhedra, alternating with slightly twisted K^+ square layers.

There is no evidence for noncentrosymmetry in $NaIO_2F_2$, as attempts to refine in a subgroup of *Cmcm* did not lead to a significantly better refinement. Moreover, no unusually large atomic displacement parameters for F and O are detected as in KIO_2F_2.

In conclusion, in $NaIO_2F_2$, as in KIO_2F_2, the $IO_2F_2^-$ complex ion is present and seems to be a very stable unit. The crystal structure of $NaIO_2F_2$, in spite of some analogies with KIO_2F_2, is clearly different as a consequence of the difference in size between Na^+ and K^+. If weak I1—O1 bonds are considered, the CsCl-derived stacking of isolated M^+ and $IO_2F_2^-$ ions is better described as a three-dimensional array of octahedra derived from the TiO_2 rutile type with cationic Na1/I1 long-range ordering. A parallel can also be established with the structure of $FeTeO_3F$ (Laval *et al.*, 2008), which is derived from the α-PbO_2 type (to which belongs TiO_2 under high pressure) but with Fe/Te long-range ordering. It would be interesting to see if $NaIO_2F_2$ under pressure presents the classical rutile→α-PbO_2 transition between these two main types of hexagonal close-packed anionic array (Hyde & Andersson, 1989).

Experimental

$NaIO_2F_2$ was prepared by progressive evaporation at 373 K of a 2:1 molar mixture of NaF and I_2O_5 dissolved in hydrofluoric acid (40%) in a Teflon beaker. After full evaporation, transparent air-stable single crystals suitable for X-ray studies were obtained, growing on the surface of a second pink-coloured amorphous phase.

Crystal data

$NaIO_2F_2$
$M_r = 219.89$
Orthorhombic, *Cmcm*
$a = 6.9287$ (10) Å
$b = 7.2735$ (13) Å
$c = 7.3503$ (13) Å
$V = 370.42$ (11) Å^3
$Z = 4$
Mo *Kα* radiation
$\mu = 8.65$ mm^{-1}
$T = 293$ (2) K
0.10 × 0.10 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2001)
$T_{min} = 0.478$, $T_{max} = 0.846$
3335 measured reflections
312 independent reflections
303 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.010$
$wR(F^2) = 0.023$
$S = 0.74$
312 reflections
22 parameters
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3127). Services for accessing these data are described at the back of the journal.

Table 1
Selected bond lengths (Å).

I1—O1	1.7647 (17)	Na1—O1^{ii}	2.3124 (18)
I1—F1	2.0040 (17)	Na1—F1	2.3627 (11)
I1—O1^{i}	2.8185 (19)		

Symmetry codes: (i) $x, -y, -z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Table 2
Bond valences.

Atom	Na1	I1	V_{ij}
O1	0.253	1.903 + 0.110	2.27
O1	0.253	1.903 + 0.110	2.27
F1	2 × 0.157	0.718	1.07
F1	2 × 0.157	0.718	1.07
V_{ij}	1.14	5.46	

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