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Hydrazinium(1+) Tetrafluoroaquoindate(III)

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(*Received* 10 *October* 1975; *accepted* 27 *October* 1975)

Abstract. $N_2H_5[InF_4H_2O]$, orthorhombic, $P2_12_12_1$, $a=$ 6·768 (2), $b=$ 8·632 (2), $c=$ 9·249 (2) Å, $Z=4$, $D_m=$ 2·99, $D_c=$ 2·97 g cm^{-3}, $V=$ 540·339 Å^3, Mo $K\alpha$ ($\mu=$ 43·98 cm^{-1}). Indium atoms are in pentagonal bipyramidal coordination with six fluorine atoms and one oxygen atom. The bipyramids share their edges to form chains which are linked by hydrogen bonds.

Introduction. There are a number of fluorometallate(III) hydrates known in the literature, with the stoichiometries $M^I_2M^{III}F_5.H_2O$ and $M^IM^{III}F_4.2H_2O$. However, the only crystallographic studies reported are for $K_2AlF_5.H_2O$ (Brosset, 1942), $K_2MnF_5.H_2O$ (Edwards, 1971) and $K_2FeF_5.H_2O$ (Edwards, 1972). In the first two compounds there are octahedrally coordinated anions linked through *trans*-bridging fluorine atoms and separate water molecules. In the last case the structure consists of isolated $[FeF_5.H_2O]^{2-}$ anions.

In our first report dealing with fluorometallates(III) (Šiftar & Bukovec, 1970) we described the compound $N_2H_5[InF_4.H_2O]$. As there are no complete crystal structures known for fluoroindates and because of the unusual stoichiometry of our compound, we decided to investigate it by means of single-crystal X-ray diffraction.

Crystals of hydrazinium(1+) tetrafluoroaquoindate(III) were obtained in the form of colourless needles by isothermal evaporation of an aqueous solution containing equivalent quantities of indium trifluoride and hydrazinium(1+) fluoride.

Unit-cell dimensions were determined from $h0l$ and $hk0$ Weissenberg photographs calibrated with superimposed Al ($a_0=$ 4·04907 Å) powder lines, using Cu $K\alpha_1$ radiation. Systematic absences, $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd indicated the orthorhombic space group $P2_12_12_1$. The crystal density was measured by the flotation method in a mixture of methylene iodide and bromoform.

The intensities were collected on an Enraf–Nonius CAD-4 single-crystal automatic diffractometer, equipped with a graphite monochromator and Mo $K\alpha$ radiation. ω–2θ scan was used in the sphere with $\theta\leq$ 45°. A spherical crystal with a diameter of 0·2 mm was used for intensity measurements. A total of 5061 reflexions were collected from the hkl and $\bar{h}\bar{k}\bar{l}$ octants and were merged into a unique set of 2525 reflexions. Of these 2315 were observed and 210 were unobserved (less than $3\sigma(I_o)$ above background). Structure amplitudes were derived by application of Lorentz, polarization and absorption ($\mu=$ 0·88) corrections.

The position of the indium atom was obtained from a three-dimensional Patterson function. The positions of all non-hydrogen atoms were located by Fourier synthesis. All atomic positions, together with individual isotropic temperature factors were refined by a number of least-squares cycles with all the collected data included to $R=$ 0·071. The structure was then refined with anisotropic temperature factors to $R=$ 0·019. Hy-

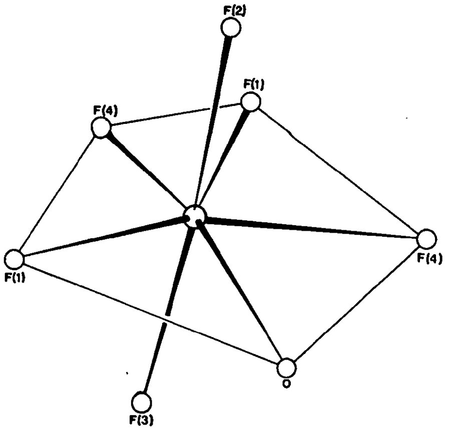

Fig. 1. Coordination polyhedron of indium.

drogen atoms were found in a difference electron-density synthesis. These atoms were included with fixed, positional and isotropic thermal parameters ($B_H = 4{\cdot}0$ Å^2), but the R value did not change. Atomic scattering factors for neutral In, F, O, N (Cromer & Mann, 1968) and for neutral H (Stewart, Davidson & Simpson, 1965) together with anomalous scattering coefficients $\Delta f'$ and $\Delta f''$ for In (Cromer, 1965) were used in F_{calc}. An extinction parameter (Larson, 1967) was included in the refinement, and its final value was $2{\cdot}229 \times 10^{-3}$. Unobserved reflexions were not considered in the refinement. The following weighting scheme was used:

$F_{\text{obs}} < 10$: $WF = (F_{\text{obs}}/10)^{2{\cdot}0}$
$F_{\text{obs}} > 75$: $WF = (75/F_{\text{obs}})^{2{\cdot}0}$
$10 < F_{\text{obs}} < 75$: $WF = 1{\cdot}0$
$\sin\theta < 0{\cdot}7$: $WS = (\sin\theta/0{\cdot}7)^{1{\cdot}5}$
$\sin\theta > 0{\cdot}9$: $WS = (0{\cdot}9/\sin\theta)^{1{\cdot}0}$
$0{\cdot}7 < \sin\theta < 0{\cdot}9$: $WS = 1{\cdot}0$
Weight $(F_{\text{obs}}) = WF \times WS$.

The final agreement indices are

$$R_1 = \sum \big||F_{\text{obs}}| - |F_{\text{calc}}|\big| / \sum |F_{\text{obs}}| = 0{\cdot}019$$
$$R_2 = \{ \sum w(F_{\text{obs}} - F_{\text{calc}})^2 / \sum wF^2_{\text{obs}} \}^{1/2} = 0{\cdot}021 \,.$$

All calculations were carried out on the CDC CYBER 70 computer of RRC Ljubljana using the X-RAY 72 system of crystallographic programs (Stewart, Kundell & Baldwin, 1972).*

Table 1. *Final atomic coordinates* ($\times 10^5$)

	x	y	z
In	13477 (2)	21557 (1)	5099 (1)
F(1)	44318 (21)	16571 (22)	10167 (20)
F(2)	17445 (30)	40996 (27)	17120 (28)
F(3)	11444 (32)	2169 (25)	−7547 (31)
F(4)	32792 (21)	30352 (26)	−11599 (18)
O	12542 (40)	6171 (59)	23815 (46)
N(1)	−501 (45)	17860 (30)	59866 (30)
N(2)	15162 (34)	29247 (32)	61267 (23)
H(1)	766	−601	25433
H(2)	22500	−375	28954
H(3)	7037	7117	59253
H(4)	−4614	15575	70715
H(5)	19737	26860	72004
H(6)	24798	30164	52286
H(7)	7086	39762	60761

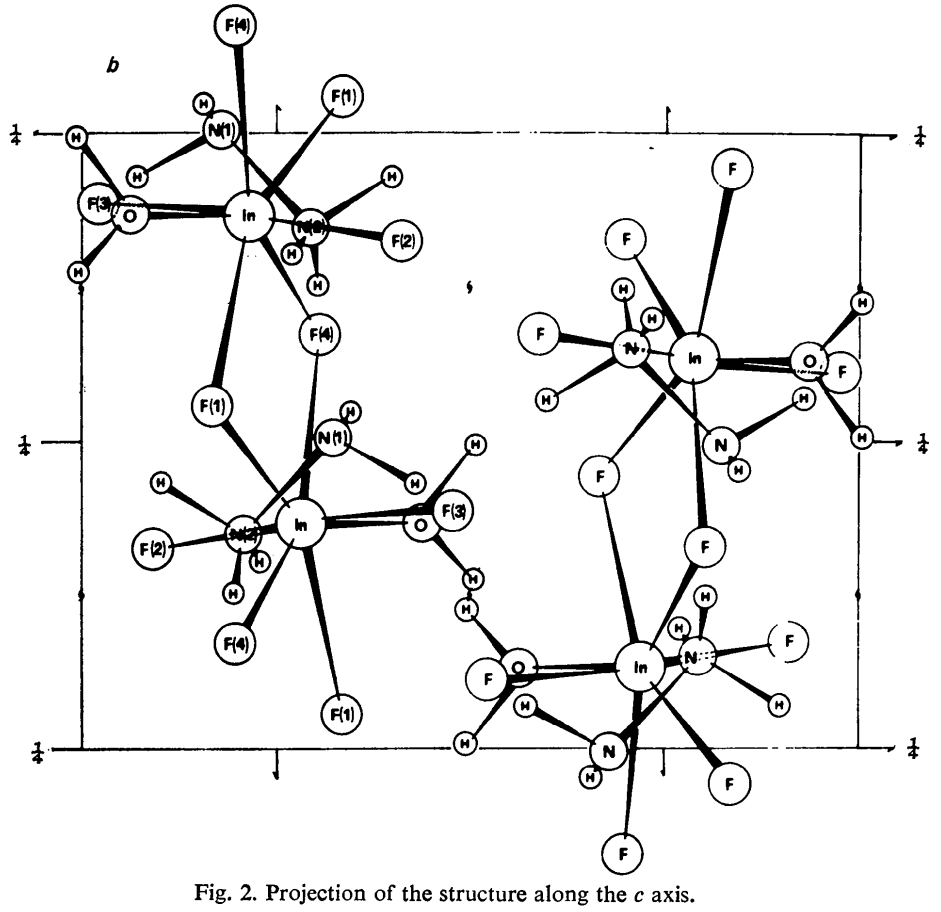

Fig. 2. Projection of the structure along the c axis.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31489 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Anisotropic thermal parameters* ($\times 10^2$)

The temperature factors are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2klb^*c^*U_{23})]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In	73 (0)	122 (0)	122 (0)	3 (0)	3 (0)	1 (0)
F(1)	99 (4)	250 (6)	223 (6)	7 (1)	1 (4)	−101 (5)
F(2)	202 (6)	311 (8)	400 (10)	8 (6)	−4 (7)	−204 (8)
F(3)	255 (8)	269 (7)	556 (14)	−93 (6)	154 (9)	−248 (9)
F(4)	93 (4)	387 (10)	187 (5)	−25 (5)	10 (3)	−115 (6)
O	140 (7)	1025 (30)	690 (21)	−125 (13)	−97 (11)	710 (24)
N(1)	308 (10)	205 (7)	238 (8)	126 (7)	−37 (8)	−12 (7)
N(2)	213 (7)	264 (8)	199 (6)	33 (8)	−19 (6)	3 (7)

Discussion. The structural arrangement is illustrated in Figs. 1 and 2. Each indium atom has a pentagonal bipyramidal coordination with two terminal and four bridging fluorine atoms and a water molecule, forming endless chains parallel to the *a* axis. The oxygen and the bridging fluorine atoms have nearly the same bond distances to the central atom, thus giving an almost regular pentagon (the sum of the in-plane angles equals 360·42°). As there are no structures of fluoroindates known, In–F and In–O bond distances may be compared with those of $InF_3.3H_2O$ containing octahedrally coordinated indium (In–F, 2·07; In–O, 2·13 Å) (Bokij & Hodašova, 1956). The two terminal *trans*-fluorine atoms in $N_2H_5[InF_4.H_2O]$ are therefore somewhat closer to the central atom, the four bridging fluorines however are at distances longer than expected for an octahedral coordination. The hydrogen atoms of the water are at the same distances from the oxygen and form strong hydrogen bonds to the adjacent chain with O···F(2), 2·557 and O···F(3), 2·567 Å.

The N(1)–N(2) bond distance of 1·451 Å is similar to reported values, *e.g.* 1·390–1·466 Å in $(N_2H_5)_3CrF_6$ (Kojić-Prodić, Šćavničar, Liminga & Šljukič, 1972) or 1·432 Å in $N_2H_5BF_4$ (Conant & Roof, 1970). The hydrazinium(1+) cation thus links together three anionic chains.

As shown by contact distances in Table 3, each part of hydrazinium(1+), NH_2 and NH_3^+ respectively forms three hydrogen bonds.

Table 3. *Interatomic distances* (Å) *and angles* (°)

Distances and angles of In polyhedron

In–F(1)	2·182 (2)	In–F(4)	2·161 (2)
In–F(1$^{\mathrm{i}}$)	2·174 (2)	In–F(4$^{\mathrm{i}}$)	2·168 (2)
In–F(2)	2·031 (2)	In–O	2·183 (5)
In–F(3)	2·046 (2)		
F(1)–In–F(1$^{\mathrm{i}}$)	143·43 (6)	F(2)–In–F(3)	176·00 (9)
F(1)–In–F(2)	85·35 (8)	F(2)–In–F(4)	91·20 (9)
F(1)–In–F(3)	91·48 (8)	F(2)–In–F(4$^{\mathrm{i}}$)	92·16 (8)
F(1)–In–F(4)	69·16 (7)	F(2)–In–O	94·15 (15)
F(1)–In–F(4$^{\mathrm{i}}$)	147·31 (7)	F(3)–In–F(4)	85·38 (9)
F(1)–In–O	74·77 (9)	F(3)–In–F(4$^{\mathrm{i}}$)	91·83 (8)
F(1$^{\mathrm{i}}$)–In–F(2)	92·58 (8)	F(3)–In–O	87·35 (15)
F(1$^{\mathrm{i}}$)–In–F(3)	88·52 (9)	F(4)–In–F(4$^{\mathrm{i}}$)	143·53 (6)
F(1$^{\mathrm{i}}$)–In–F(4)	74·40 (6)	F(4)–In–O	142·94 (9)
F(1$^{\mathrm{i}}$)–In–F(4$^{\mathrm{i}}$)	69·18 (7)	F(4$^{\mathrm{i}}$)–In–O	72·91 (9)
F(1$^{\mathrm{i}}$)–In–O	141·69 (8)		

Other bond distances and angles

N(1)–N(2)	1·451 (4)	N(2)–H(6)	1·060 (2)
N(1)–H(3)	1·060 (3)	N(2)–H(7)	1·061 (3)
N(1)–H(4)	1·060 (3)	O——H(1)	1·000 (4)
N(2)–H(5)	1·060 (2)	O——H(2)	1·000 (4)
N(2)–N(1)–H(3)	104·2 (2)	N(1)–N(2)–H(7)	101·5 (2)
N(2)–N(1)–H(4)	103·5 (2)	H(5)–N(2)–H(6)	124·7 (2)
H(3)–N(1)–H(4)	90·8 (2)	H(5)–N(2)–H(7)	111·0 (2)
N(1)–N(2)–H(5)	99·5 (2)	H(6)–N(2)–H(7)	102·6 (2)
N(1)–N(2)–H(6)	115·5 (2)	H(1)–O——H(2)	97·8 (4)

Contact distances and angles involving hydrogen atoms

H(1)···F(2$^{\mathrm{ii}}$)	1·587 (2)	H(4)···F(2$^{\mathrm{iv}}$)	2·272 (2)
H(2)···F(3$^{\mathrm{iii}}$)	1·662 (3)	H(5)···F(4)	1·781 (2)
H(3)···F(1$^{\mathrm{iii}}$)	2·049 (2)	H(6)···N(1$^{\mathrm{v}}$)	2·022 (3)
H(4)···F(1$^{\mathrm{i}}$)	2·347 (2)	H(7)···F(3$^{\mathrm{vi}}$)	1·676 (2)
O——H(1)···F(2$^{\mathrm{ii}}$)	162·0 (3)	N(1)–H(4)···F(2$^{\mathrm{iv}}$)	137·2 (2)
O——H(2)···F(3$^{\mathrm{iii}}$)	148·3 (3)	N(2)–H(5)···F(4)	155·4 (2)
N(1)–H(3)···F(1$^{\mathrm{iii}}$)	148·2 (3)	N(2)–H(6)···N(1$^{\mathrm{v}}$)	162·1 (1)
N(1)–H(4)···F(1$^{\mathrm{i}}$)	126·8 (1)	N(2)–H(7)···F(3$^{\mathrm{vi}}$)	160·1 (2)

Equivalent positions

(i)	$x-\frac{1}{2}$, $\frac{1}{2}-y$, $\bar{z}$	(iv)	$x-\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$
(ii)	$\bar{x}$, $y-\frac{1}{2}$, $\frac{1}{2}-z$	(v)	$x+\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$
(iii)	$\frac{1}{2}-x$, $\bar{y}$, $\frac{1}{2}+z$	(vi)	$\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}+z$

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