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Hydrazinium(2+) Bis[trifluorostannate(II)]*

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Abstract. $[N_2H_6][SnF_3]_2$, $M_r = 385{\cdot}44$, monoclinic, $C2/c$, $a = 10{\cdot}581\,(1)$, $b = 12{\cdot}797\,(2)$, $c = 5{\cdot}771\,(1)$ Å, $\beta = 108{\cdot}55\,(1)°$, $V = 740{\cdot}83$ Å^3, $Z = 4$, $D_x = 3{\cdot}456$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 68{\cdot}20$ cm^{-1}, $F(000) = 696$, $T = 293$ K, final $R = 0{\cdot}020$ for 979 observed reflections. The structure contains monomeric $[SnF_3]^-$ units, in the form of a trigonal pyramid. The Sn—F bond distances are 2·053 (3), 2·081 (3) and 2·096 (2) Å. The N—N bond distance in the $[N_2H_6]^{2+}$ cation is 1·428 (4) Å, with tetrahedral H—N—H and H—N—N angles in the range from 106 (3) to 114 (7)°. N—H···F hydrogen bonds are from 2·620 (4) to 2·707 (5) Å.

Introduction. Hydrazinium(2+) difluoride reacts with Lewis acids as a strong donor of fluoride ions giving ionic hydrazinium(2+) fluorometallates. $[N_2H_6]^{2+}$ is one of the very few inorganic cations that are able to form hydrogen bonds and it is the only such cation having a double charge.

In recent years a great number of hydrazinium(2+) fluorometallates have been isolated and characterized (Slivnik, Maček, Rahten & Sedej, 1980; Frlec, Gantar & Holloway, 1981; Gantar & Rahten, 1984). Crystallographic data were reported for $[N_2H_6][TiF_6]$ (Kojić-Prodić, Matković & Šćavničar, 1971), $[N_2H_6][ZrF_6]$ (Kojić-Prodić, Šćavničar & Matković, 1971), $[N_2H_6][BeF_4]$ (Anderson, Vilminot & Brown, 1973), $[N_2H_6][NbOF_5].H_2O$ (Sarin, Dudarev, Fykin, Gorbunova, Il'in & Buslaev, 1977), $[N_2H_6]_2F_2[TiF_6]$ (Golič, Kaučič & Kojić-Prodić, 1980), $[N_2H_6][SiF_6]$ (Frlec, Gantar, Golič & Leban, 1980; Cameron, Knop & Macdonald, 1983), $[N_2H_6][GeF_6].H_2O$ (Frlec, Gantar, Golič & Leban, 1981) and $[N_2H_6][BF_4]_2$ (Frlec, Gantar, Golič & Leban, 1984), revealing a variety of hydrazinium symmetries in these compounds. The present study of $[N_2H_6][SnF_3]_2$ was carried out to investigate further the structural behaviour of the $[N_2H_6]^{2+}$ group.

Recently Granier, Vilminot & Wahbi (1985) reported the results of studies of hydrazinium(1+) and hydrazinium(2+) fluorostannates(II). In their second system, $[N_2H_6]F_2$–SnF_2–H_2O, they obtained $[N_2H_6][SnF_4]$ and $[N_2H_6][SnF_3]_2$ and they determined their cell parameters and possible space groups. The cell constants obtained for $[N_2H_6][SnF_3]_2$ are very similar to ours, with the possible space groups Cc or $C2/c$. Our complete structural determination confirms the centrosymmetric alternative, $C2/c$.

Experimental. In the reaction of the aqueous solutions of hydrazinium(2+) difluoride and tin(II) hydroxide in 1:1 molar ratio and excess of 38% hydrofluoric acid the crystals of $[N_2H_6][SnF_4]$ were isolated. Among these, a few crystals of $[N_2H_6][SnF_3]_2$ appeared.

D_m not determined. Single crystal *ca* 0·15 × 0·15 × 0·36 mm. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters by least-squares refinement of setting angles of 60 centred reflections ($10 \leq \theta \leq 15°$). Intensities of reflections with $0{\cdot}03 < (\sin\theta)/\lambda < 0{\cdot}70$ Å^{-1} measured at room temperature, h $-14\rightarrow0$, k $-18\rightarrow18$, l $-8\rightarrow8$. ω–2θ scan mode, scan angle $\Delta\omega = (0{\cdot}80 + 0{\cdot}30\tan\theta)°$. Three reflections ($\bar{3}\bar{5}2$, $\bar{4}21$, $\bar{2}\bar{4}2$) monitored after every 240 intensities measured; no significant variation in intensity. Of 1083 independent reflections measured, 979 with $I_o > 3\sigma(I_o)$ considered as observed, 104 unobserved. Empirical absorption corrections applied. Structure solved with Patterson method to locate Sn atoms. Subsequent Fourier map revealed positions of the other non-H atoms. Refinement by full-matrix least squares on F of positional and anisotropic thermal parameters of all non-H atoms and an isotropic extinction parameter (final value $9{\cdot}6 \times 10^{-3}$) converged to an R value of 0·024. A difference Fourier map revealed the positions of the H atoms, which were included in the refinement with isotropic temperature factors. Refinement converged to final $R = 0{\cdot}020$ and $wR = 0{\cdot}020$. $(\Delta/\sigma)_{\max} = 0{\cdot}11$. 58 parameters. Weighting function $w = W_F.W_S$ determined empirically from $W_F(|F_o| < 40) = (|F_o|/40)^2$, $W_F(|F_o| > 100) = (100/|F_o|)$, and $W_F(40 <$

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* This work is part of a diploma thesis by Gašperšič-Škander (1984).

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Table 1. *Final atomic coordinates* ($\times 10^5$ *for* Sn, $\times 10^4$ *for* F *and* N, $\times 10^3$ *for* H) *and* U_{eq} *values (for non-*H *atoms,* $U_{\rm iso}$ *for* H *atoms), with e.s.d.'s in parentheses*

$$U_{\rm eq} = (U_{11}.U_{22}.U_{33})^{1/3}.$$

	x	y	z	$U_{\rm eq}$ or $U_{\rm iso}$(Å^2)
Sn(1)	19267 (2)	10163 (2)	2288 (4)	1·96 (1)
F(1)	3244 (2)	−3 (2)	2681 (4)	2·76 (10)
F(2)	3618 (2)	1905 (2)	856 (4)	3·01 (10)
F(3)	1752 (2)	1631 (2)	3450 (4)	3·12 (11)
N(1)	4495 (3)	1620 (2)	6335 (5)	2·15 (13)
H(1)	403 (5)	218 (4)	628 (9)	1·82 (102)
H(2)	402 (6)	108 (5)	629 (11)	3·36 (133)
H(3)	476 (6)	165 (5)	533 (12)	2·88 (131)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

(*a*) [SnF$_3$]$^-$ group			
Sn(1)—F(1)	2·096 (2)	Sn(1)···F(1$^{\rm i}$)	2·663 (3)
Sn(1)—F(2)	2·053 (3)	Sn(1)···F(2$^{\rm ii}$)	2·752 (3)
Sn(1)—F(3)	2·081 (3)		
		F(1)—Sn···F(1$^{\rm i}$)	73·6 (1)
F(1)—Sn(1)—F(2)	82·6 (1)	F(1)—Sn···F(2$^{\rm ii}$)	143·3 (1)
F(1)—Sn(1)—F(3)	82·0 (1)	F(2)—Sn···F(1$^{\rm i}$)	77·7 (1)
F(2)—Sn(1)—F(3)	87·3 (1)	F(2)—Sn···F(2$^{\rm ii}$)	67·2 (1)
		F(3)—Sn···F(1$^{\rm i}$)	152·7 (1)
		F(3)—Sn···F(2$^{\rm ii}$)	76·5 (1)
		F(1$^{\rm i}$)···Sn···F(2$^{\rm ii}$)	117·0 (1)
(*b*) [N$_2$H$_6$]$^{2+}$ group			
N(1)—N(1$^{\rm iii}$)	1·428 (4)	H(1)—N(1)—H(2)	110 (6)
N(1)—H(1)	0·86 (5)	H(1)—N(1)—H(3)	107 (6)
N(1)—H(2)	0·85 (7)	H(2)—N(1)—H(3)	114 (7)
N(1)—H(3)	0·73 (8)	H(1)—N(1)—N(1$^{\rm iii}$)	106 (3)
		H(2)—N(1)—N(1$^{\rm iii}$)	107 (4)
		H(3)—N(1)—N(1$^{\rm iii}$)	113 (4)
(*c*) Hydrogen-bond contacts			
N(1)—H(1)···F(3$^{\rm iv}$)	2·620 (4)		
N(1)—H(2)···F(1$^{\rm v}$)	2·700 (4)		
N(1)—H(3)···F(2$^{\rm vi}$)	2·707 (5)		

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

$|F_o| < 100) = 1{\cdot}0$, and $W_S(\sin\theta < 0{\cdot}35) = (\sin\theta/0{\cdot}35)^2$, $W_S(\sin\theta > 0{\cdot}45) = (0{\cdot}45/\sin\theta)$, and $W_S(0{\cdot}35 < \sin\theta < 0{\cdot}45) = 1{\cdot}0$. Final difference Fourier map shows max. height of 2·27 e Å^{-3} close to the Sn atom.

All calculations were carried out using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors for non-H atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion correction for non-H atoms from Cromer & Liberman (1970).

Discussion. The final atomic coordinates, bond lengths and bond angles are given in Tables 1 and 2.* The atom-numbering scheme is shown in Fig. 1.

The structure of [N$_2$H$_6$][SnF$_3$]$_2$ consists of monomeric [SnF$_3$]$^-$ units and [N$_2$H$_6$]$^{2+}$ ions, held together by hydrogen bonds. In the [SnF$_3$]$^-$ ion the atoms form a trigonal pyramid, with the Sn—F bond distances from 2·053 (3) to 2·096 (2) Å and with the F—Sn—F angles from 82·0 (1) to 87·3 (1)° (Table 2). The observed dimensions of the [SnF$_3$]$^-$ ion are in agreement with the Sn—F bond distances and F—Sn—F bond angles found in the literature. The reported values for Sn—F bond distances are from 2·07 in Na[Sn$_2$F$_5$] (McDonald, Larson & Cromer, 1964) to 2·26 Å in Sn$_3$F$_5$Br (Donaldson, Laughlin & Puxley, 1977), and for the F—Sn—F angles from 69·2 to 89·3° (Bergerhoff & Goost, 1974; Bergerhoff & Namgung, 1978). In the structure there are also two close Sn···F contact distances of 2·663 (3) and 2·752 (3) Å. Calculated F—Sn···F angles, listed in Table 2, show a one-sided coordination of the Sn atom by all five F atoms. Although the two Sn···F contact distances are shorter than the expected intermolecular (van der Waals) distance, it is not possible in this structure to recognize

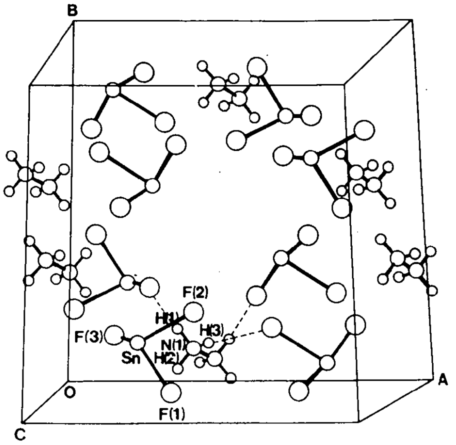

Fig. 1. A view of the unit cell with the atom-numbering scheme.

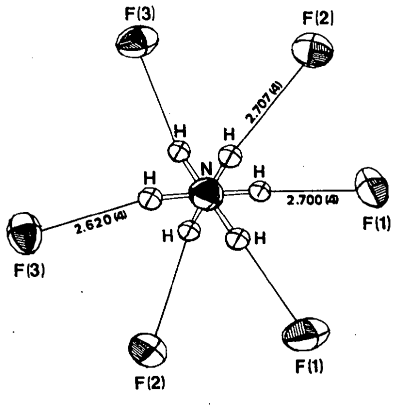

Fig. 2. Projection of the [N$_2$H$_6$]$^{2+}$ ion down the N—N bond and the hydrogen bonds (distances in Å).

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* Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44935 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the Sn···F interactions as being secondary bonds (Alcock, 1972).

The observed N—N distance in the $[N_2H_6]^{2+}$ ion of 1·428 (4) Å is as expected for the hydrazinium(2+) ion (*International Tables for X-ray Crystallography*, 1962). The $[N_2H_6]^{2+}$ cation forms six N—H···F hydrogen bonds. A projection of the $[N_2H_6]^{2+}$ ion down the N—N bond is shown in Fig. 2. The hydrogen-bond distances are in the usual range of 2·620 (4) to 2·707 (5) Å (Table 2) (Anderson *et al.*, 1973; Kojić-Prodić, Šćavničar & Matković, 1971; Golič & Lazarini, 1974; Golič *et al.*, 1980). There are some additional N···F contact distances [2·850 (4), 2·956 (4) Å], which suggest bifurcated hydrogen bonds. The tetrahedral H—N—H and H—N—N angles range from 106 (3) to 114 (7)° (Table 2).

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The Synthesis and Structure of Heptacobalt Tetrakis(hydrogenphosphate) Bis(phosphate)

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Abstract. $Co_7(PO_4)_2(HPO_4)_4$, $M_r = 986{\cdot}4$, triclinic, $P\bar{1}$, $a = 6{\cdot}466$ (4), $b = 9{\cdot}480$ (2), $c = 7{\cdot}871$ (2) Å, $\alpha = 104{\cdot}29$ (2), $\beta = 101{\cdot}35$ (3), $\gamma = 109{\cdot}10$ (3)°, $V = 421{\cdot}0$ Å^3, $D_x = 3{\cdot}884$ g cm^{-3}, $Z = 1$, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 74{\cdot}1$ cm^{-1}, $F(000) = 475$, room temperature, $R = 0{\cdot}017$, $wR = 0{\cdot}021$ for 2122 unique reflections, $I > 3\sigma(I)$. The new phase was synthesized hydrothermally, and is isostructural with $Mn_7(PO_4)_2(HPO_4)_4$. The structure is based on a framework of edge- and corner-sharing CoO_6, CoO_5 and PO_4 polyhedra, isotypic with that found in the mixed-valence iron phosphate $Fe_7(PO_4)_6$. In the present case, the cobalt is found purely in the divalent state, the

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