

stuffed derivatives of the *H*-cristobalite structure. Almost all of the stuffed derivatives of silica-structure-type compounds are reported to be of the tridymite type and cristobalite-type compounds are rather uncommon.

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Hydrazinium(2+) Difluoride Hexafluorotitanate(IV)

BY LJUBO GOLIČ AND VENČESLAV KAUČIČ*

Department of Chemistry, University 'Edvard Kardelj', 61000 Ljubljana, Yugoslavia

AND BISERKA KOJIĆ-PRODIĆ

Institute 'Rudjer Bošković', 41000 Zagreb, Yugoslavia

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Abstract. $(\text{N}_2\text{H}_6)_2\text{F}_2[\text{TiF}_6]$, orthorhombic, *Pccn*, $a = 5.481$ (1), $b = 13.588$ (3), $c = 10.937$ (2) Å, $Z = 4$, $D_o = 2.17$ (3), $D_c = 2.185$ Mg m⁻³, $V = 814.54$ Å³; $R = 0.023$, $R_w = 0.021$ for 625 observed reflections. The structure consists of $\text{N}_2\text{H}_6^{2+}$ cations, discrete $[\text{TiF}_6]^{2-}$ octahedral anions and F^- anions. These units are connected by $\text{N}-\text{H}\cdots\text{F}$ hydrogen bonds.

Introduction. Some hydrazinium(1+) and hydrazinium(2+) fluoro complexes of transition metals have been prepared at the Institute 'Jožef Stefan', Ljubljana, Yugoslavia (Slivnik & Volavšek, 1968; Slivnik, Šmalc, Sedej & Vilhar, 1964). The structures of $\text{N}_2\text{H}_6[\text{TiF}_6]$ (Kojić-Prodić, Matković & Ščavničar, 1971) and $\text{N}_2\text{H}_6[\text{ZrF}_6]$ (Kojić-Prodić, Ščavničar & Matković, 1971) have been solved. For the compound with the stoichiometry $(\text{N}_2\text{H}_6)_2\text{TiF}_8$ two different formulae, $(\text{N}_2\text{H}_5)_2\text{F}_2[\text{TiF}_6]$ and $(\text{N}_2\text{H}_6)_2[\text{TiF}_8]$, were postulated (Slivnik, Maček, Orel & Sedej, 1973; Slivnik & Volavšek, 1968). The structure determination of this compound was carried out in order to determine the coordination polyhedron around Ti, as well as the presence of N_2H_5^+ or $\text{N}_2\text{H}_6^{2+}$ cations in the structure. The analysis clearly shows that the correct structural formula for the compound is $(\text{N}_2\text{H}_6)_2\text{F}_2[\text{TiF}_6]$.

Oscillation, Weissenberg (Cu *Kα* radiation) and precession photographs (Mo *Kα* radiation) gave preliminary cell dimensions and showed *mmm* symmetry. Systematic absences indicated the space group *Pccn*. Cell dimensions were determined from a least-squares fit of fifteen reflections. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer in the ω - 2θ mode, with a graphite monochromator and Mo *Kα* radiation.

One quarter of the sphere of reflections (2431 intensities in all) in the range $1.5 < \theta < 30.0^\circ$ was measured. Symmetry-equivalent reflections (*hkl* and *h \bar{k} l*) were averaged (mean discrepancy on *I* was 2.1%) to yield 1186 independent reflections of which 625 with $I_o \geq 3\sigma(I_o)$ (calculated from counting statistics) were considered as observed and used for the analysis. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the heavy-atom method and refined by full-matrix least squares with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). A difference map revealed the coordinates of all H atoms, which were included in the refinement as invariants with isotropic thermal parameters ($B = 1.5$ Å²). Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms terminated at $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.023$

* To whom correspondence should be addressed.

and $R_2 = [\sum w(F_o - F_c)^2 / \sum wF_c^2]^{1/2} = 0.021$. The following weighting scheme [weight (F_o) = $wF \times wS$] was used: $F_o < 30$: $wF = (F_o/30)^{1.5}$; $F_o > 60$: $wF = (60/F_o)^{3.0}$; $30 \leq F_o \leq 60$: $wF = 1.0$; $\sin \theta < 0.34$: $wS = (\sin \theta / 0.34)^{3.0}$; $\sin \theta > 0.44$: $wS = (0.44 / \sin \theta)^{1.5}$; $0.34 \leq \sin \theta \leq 0.44$: $wS = 1.0$.

Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for other atoms from Cromer & Mann (1968), those of non-hydrogen atoms being corrected for the effects of anomalous scattering (Cromer & Liberman, 1970). All the calculations were made on the CDC Cyber 72 computer at RRC Ljubljana.*

Discussion. The final positional parameters are presented in Table 1, interatomic distances and angles in Table 2. A view of the unit cell down *a* and the atom numbering are shown in Fig. 1. The structure contains

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34889 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Ti	2500	2500	1255 (7)
F(1)	1647 (3)	1182 (1)	1259 (3)
F(2)	4836 (7)	2262 (3)	48 (2)
F(3)	4847 (7)	2267 (3)	2458 (3)
F(4)	2270 (3)	10 (1)	3785 (10)
N(1)	8337 (7)	947 (2)	3262 (3)
N(2)	6517 (7)	956 (2)	4212 (3)
H(1)	8744	1689	3042
H(2)	9968	572	3497
H(3)	7749	571	2464
H(4)	5952	1692	4385
H(5)	7296	609	4981
H(6)	4919	591	3916

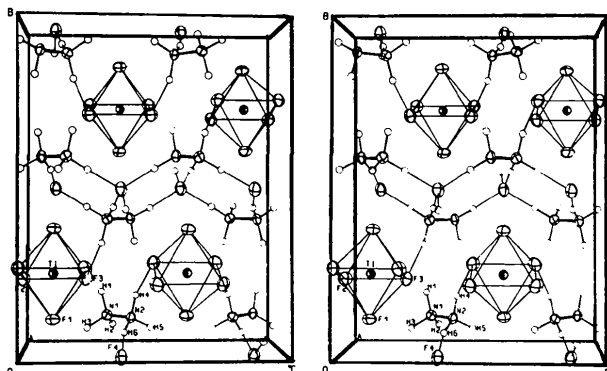


Fig. 1. Stereoscopic view of the structure down *a* and the numbering of the atoms. The atoms are represented by thermal ellipsoids drawn at the 65% probability level (Johnson, 1965).

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(a) Ti octahedron

Ti—F(1)	1.851 (1)	F(1)—Ti—F(2)	90.4 (2)
Ti—F(2)	1.867 (6)	F(1)—Ti—F(3)	90.5 (2)
Ti—F(3)	1.867 (6)	F(2)—Ti—F(3)	89.8 (1)
		F(1)—Ti—F(2')	89.8 (2)
		F(1)—Ti—F(3')	89.3 (2)
		F(2)—Ti—F(2')	90.0 (4)
		F(3)—Ti—F(3')	90.4 (4)
		F(1)—Ti—F(1')	179.8 (5)
		F(2)—Ti—F(3')	179.7 (2)

(b) N—N distance in $N_2H_6^{2+}$ ion

N(1)—N(2)	1.441 (5)
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(c) Hydrogen bonds

N(1)—H(1)···F(3 ⁱⁱ)	2.765 (5)	N(2)—H(4)···F(2 ^v)	2.747 (5)
N(1)—H(2)···F(4 ⁱⁱⁱ)	2.568 (5)	N(2)—H(5)···F(4 ^{vi})	2.639 (10)
N(1)—H(3)···F(4 ^{iv})	2.654 (10)	N(2)—H(6)···F(4)	2.700 (4)

Roman numeral superscripts refer to the following coordinate transformations:

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

nearly regular $[TiF_6]^{2-}$ octahedra, $N_2H_6^{2+}$ ions and F^- ions, held together by a three-dimensional system of hydrogen bonds. Each $N_2H_6^{2+}$ cation forms six hydrogen bonds of the type $N-H \cdots F$. The values of the hydrogen-bond distances are in the usual range of 2.639 (10) to 2.765 (5) Å (Table 2) (Anderson, Vilminot & Brown, 1973; Kojić-Prodić, Ščavničar & Matković, 1971; Golić & Lazarini, 1974), apart from the bond N(1)—H(2)···F(4), 2.568 (5) Å, which is the shortest $N \cdots F$ hydrogen bond known by the authors. Two of the six H atoms of the $N_2H_6^{2+}$ ion are linked to two F atoms of the two different $[TiF_6]^{2-}$ octahedra, while the other four are linked to four different F^- ions. There are some more $N \cdots F$ contact distances of about 2.8 Å which may suggest bifurcated or even trifurcated hydrogen bonds. The positions of the H atoms, which will be discussed later, seem to be reliable and do not support such a prediction. The reason for such relatively short contacts is probably in the orientation of the $[TiF_6]^{2-}$ octahedra in three-dimensional packing.

H atoms in the $N_2H_6^{2+}$ ion (a projection down the N—N bond is shown in Fig. 2) are in the rather unexpected *cis* conformation, the maximum H—N—N torsion angle being 5.0°. From a difference map all the H atoms were located as the highest six peaks of density 0.55 to 0.64 e Å⁻³ (all other peaks were below 0.34 e Å⁻³) at distances in the range 0.88 to 1.07 Å from the N atoms and with N—N—H and H—N—H tetrahedral angles between 103 and 114°. These atoms were placed at calculated positions 1.06 Å from the N atoms.

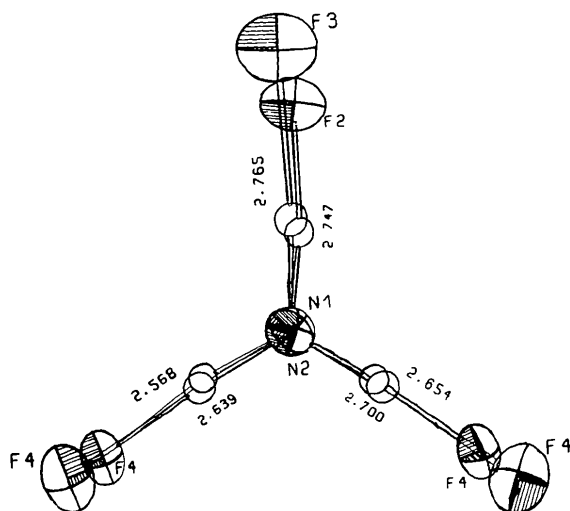


Fig. 2. Projection of the $N_2H_6^{2+}$ ion down the N-N bond, and hydrogen bonds.

In the $[TiF_6]^{2-}$ ion the F atoms are octahedrally disposed round the Ti atom. The Ti-F bond lengths (Table 2) are close to reported values (Kojić-Prodić, Matković & Ščavničar, 1971; Weiss, Fischer & Chevrier, 1966; Fischer, de Cian & Weiss, 1967).

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The Structure of the Hexamolybdoperiodate Anion in Its Potassium Salt

BY HIDETAKA KONDO, AKIKO KOBAYASHI AND YUKIYOSHI SASAKI

Department of Chemistry and The Research Centre for Spectrochemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

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Abstract. $K_5[IMo_6O_{24}] \cdot 5H_2O, P\bar{1}$, $a = 10.084$ (1), $b = 17.593$ (2), $c = 7.692$ (1) Å, $\alpha = 95.07$ (1), $\beta = 91.38$ (1), $\gamma = 82.45$ (1)°, $U = 1347.5$ (2) Å³, FW = 1372.10, $Z = 2$, $D_m = 3.37$, $D_x = 3.42$ Mg m⁻³, $\mu = 4.375$ mm⁻¹ (for Mo $K\alpha$). The $[IMo_6O_{24}]^{5-}$ anion has been found to be a typical Anderson-type heteropolyanion and has approximate $\bar{3}m$ symmetry. The metal-oxygen bond lengths in this anion and in $[TeMo_6O_{24}]^{6-}$ show the difference between the $I^{7+}-O$ and $Te^{6+}-O$ bond strengths.

Introduction. Many Keggin-type heteropolyanions have been studied; there is also another group of heteropolyanions called the Anderson type (Anderson, 1937). The latter type of polyanion consists of seven octahedra sharing edges with one another. Six Mo octahedra are arranged hexagonally around the octahedron containing the heteroatom.

A number of examples of the preparations of Anderson-type polyanions have been reported (*Gmelins Handbuch der Anorganischen Chemie*,