

dation state of As may therefore be taken as +5, *i.e.* the description of the structure with a single net positive charge on As and a single negative charge on Sb should be given most weight. The Sb atom is coordinated by four O atoms in a markedly one-sided manner, similar to the Sb^{III} site in β -Sb₂O₄ (Rogers & Skapski, 1964). This is consistent with the stereochemical influence of an electron lone-pair, *i.e.* with the above description. All O atoms bridge As and Sb.

The extended structure consists of layers parallel to the *xy* plane (Fig. 1); there is one such layer per unit *z* translation. Short Sb...O contacts are 3.06 Å to O(1) at *x, y, z*; 3.04 Å to O(3) at $-1 + x, y, z$; and 3.04 Å to O(3) at $-1 + x, \frac{1}{2} - y, z$ (*e.s.d.*'s 0.02 Å). The latter two (symmetry-related) contacts are between neighbouring layers.

The structure is not closely related to any other mixed-valence Group Vb oxide (Table 3).

We thank the Verband der Chemischen Industrie for financial support.

References

- AURIVILLIUS, B. (1952). *Ark. Kemi*, **3**, 153–161.
 JANSEN, M. (1977). *Angew. Chem.* **89**, 326–327.
 JANSEN, M. (1978). *Z. Anorg. Allg. Chem.* **441**, 5–12.
 JANSEN, M. (1979). *Z. Naturforsch. Teil B*, **34**, 10–13.
 JONES, P. G., BEESK, W., SHELDRIK, G. M. & SCHWARZMANN, E. (1980). *Acta Cryst.* **B36**, 439–440.
 ROGERS, D. & SKAPSKI, A. C. (1964). *Proc. Chem. Soc.* pp. 400–401.
 SKAPSKI, A. C. & ROGERS, D. (1965). *Chem. Commun.* pp. 611–613.

Acta Cryst. (1980). **B36**, 1925–1927

Ammonium Tetrafluorooxovanadate(IV)

BY PETER BUKOVEC AND LJUBO GOLIČ

Department of Chemistry, University of Ljubljana, Murnikova 6, 61000 Ljubljana, Yugoslavia

(Received 9 October 1978; accepted 9 April 1980)

Abstract. (NH₄)₂[VF₄O], orthorhombic, *Pna*2₁, *a* = 7.596 (1), *b* = 12.043 (2), *c* = 5.770 (1) Å, *Z* = 4, *D_m* = 2.25, *D_c* = 2.248 Mg m⁻³, *V* = 527.832 Å³, Mo *K*α (*μ* = 1.9934 mm⁻¹). The V atom is octahedrally coordinated by five F atoms at V–F distances of 1.910–2.224 Å and one O atom at 1.612 Å. The octahedra are connected through *cis* F atoms to give infinite chains parallel to the *c* axis. There are weak hydrogen bonds between the ammonium ions and the anionic chains with a shortest N...F distance of 2.825 Å. The final *R_i* value is 0.050.

Introduction. There are three ammonium fluorooxovanadates(IV) described in the literature: (NH₄)₃[VF₅O], (NH₄)₂[VF₄O] and (NH₄)₂[VF₄O]·H₂O (Davidovič, Harlamova & Samarec, 1977). They have been characterized by X-ray powder spectra; however, no complete crystal structure determination has been reported.

Crystals of the title compound were prepared in 5% HF solution with a VF₂O:NH₄F molar ratio of 1:3. The space group and preliminary cell dimensions were deduced from oscillation and Weissenberg photographs. Data were collected with an Enraf–Nonius CAD-4 automatic diffractometer in the ω–2θ mode using Mo *K*α radiation and a graphite mono-

chromator. Accurate cell constants were determined from least-squares analysis of the positions of 30 high-angle reflections. 2082 reflections, measured in the range 1.5 < θ < 30.0°, were merged into a unique set of 832 reflections. Of these, 641 were observed with *I_o* > 3σ(*I_o*) (from counting statistics) and used for the structure analysis. Lorentz–polarization corrections were applied, but no absorption corrections were made.

The position of the V atom was found from a three-dimensional Patterson map. The positions of all non-hydrogen atoms were located from a partially phased Fourier synthesis. All atomic positions, together with individual isotropic temperature factors, were refined by a number of full-matrix least-squares cycles, with all the collected data included, to *R* = 0.067. The structure was then refined with anisotropic temperature factors to *R* = 0.050. H atoms were found in a difference electron-density map. These atoms were included with fixed positional and isotropic thermal parameters (*U_H* = 0.07 Å²). Atomic scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and for other atoms from Cromer & Mann (1968), those for V, F, O, and N being corrected for the effects of anomalous scattering (Cromer & Liberman, 1970).

The weighting function was determined empirically from:

$$\begin{aligned}
 F_{\text{obs}} < 11; \text{WF} &= (F_{\text{obs}}/11)^{3.0} \\
 F_{\text{obs}} > 24; \text{WF} &= (24/F_{\text{obs}})^{2.0} \\
 11 < F_{\text{obs}} < 24; \text{WF} &= 1.0 \\
 \sin \theta < 0.35; \text{WS} &= (\sin \theta/0.35)^{3.0} \\
 \sin \theta > 0.45; \text{WS} &= (0.45/\sin \theta)^{2.0} \\
 0.35 < \sin \theta < 0.45; \text{WS} &= 1.0 \\
 \text{Weight } (F_{\text{obs}}) &= \text{WF} \times \text{WS}.
 \end{aligned}$$

The final agreement indices are

$$\begin{aligned}
 R_1 &= \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}| = 0.050 \\
 R_2 &= [\sum w(F_{\text{obs}} - F_{\text{calc}})^2 / \sum wF_{\text{obs}}^2]^{1/2} = 0.056.
 \end{aligned}$$

All the calculations were made on the CDC Cyber 72 computer at RRC Ljubljana using the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35115 (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 ($\times 10^4$)

	x	y	z	B (\AA^2)
V	1700 (1)	671 (1)	2520*	1.09 (3)
O	3020 (11)	1158 (7)	4456 (12)	2.13 (20)
F(1)	5070 (6)	3102 (3)	2321 (14)	1.77 (12)
F(2)	2200 (6)	4234 (4)	7181 (9)	1.92 (14)
F(3)	19 (13)	-33 (9)	4699 (9)	1.72 (12)
F(4)	2930 (10)	1194 (7)	-153 (10)	2.18 (17)
N(1)	64 (8)	2283 (4)	7403 (20)	1.98 (16)
N(2)	1645 (9)	4050 (5)	2261 (18)	1.91 (19)
H(1)	2851	3655	2410	5.53
H(2)	646	3477	2476	5.53
H(3)	1156	4667	1193	5.53
H(4)	1161	4661	3324	5.53
H(5)	5810	7924	2129	5.53
H(6)	5133	6785	3842	5.53
H(7)	4798	6755	1002	5.53
H(8)	3686	7621	2498	5.53

* The z coordinate of V was fixed for origin definition.

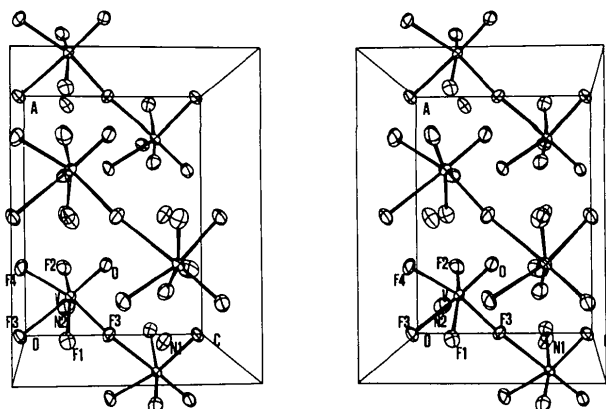


Fig. 1. Stereoscopic view of the structure down *b*.

Discussion. The final positional parameters are given in Table 1. The structural arrangement as viewed along the *b* direction is illustrated in Fig. 1. The V atom is octahedrally coordinated by one O and five F atoms. The octahedra are joined together through the F(3) atoms to give infinite *cis* chains parallel to the *c* axis.

Interatomic distances and angles are presented in Table 2. The V—O bond length of 1.612 Å is characteristic of octahedral oxovanadium(IV) complexes, e.g. 1.606 Å in $\text{Na}_3[\text{V}(\text{C}_2\text{O}_4)_2\text{FO}].6\text{H}_2\text{O}$ (Rieskamp & Mattes, 1976), 1.594 Å in $(\text{NH}_4)_2[\text{V}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})].\text{H}_2\text{O}$ (Oughtred, Raper & Shearer, 1976) or 1.62 Å in square-pyramidal $(\text{NH}_4)_2[\text{V}(\text{NCS})_4\text{O}].5\text{H}_2\text{O}$ (Hazell, 1963).

The terminal F atoms are all *cis* to the O atom. Two of them [F(1) and F(2)] have nearly the same V—F bond lengths. This can be explained by the very similar contact distances between these two F atoms and the two N atoms. The third terminal fluorine, F(4), exhibits the shortest V—F bond length because the interaction with the ammonium ions is weaker in this case (see Table 2).

There is a great difference between the lengths of the two bridging V—F bonds, one of which is *cis* and the other *trans* with respect to the O atom. This can be

Table 2. Interatomic distances (Å) and angles ($^\circ$)

Distances and angles of the $[\text{VF}_5\text{O}]$ octahedron			
V—O	1.612 (8)	V—F(3)	1.982 (9)
V—F(1 ^l)	1.930 (4)	V—F(3 ^{lll})	2.224 (8)
V—F(2 ^{ll})	1.933 (5)	V—F(4)	1.910 (7)
O—V—F(3)	96.7 (4)	F(3)—V—F(1 ^l)	87.3 (4)
O—V—F(4)	97.8 (4)	F(4)—V—F(3 ^{lll})	79.1 (3)
O—V—F(3 ^{lll})	176.8 (4)	F(4)—V—F(2 ^{ll})	90.1 (3)
O—V—F(2 ^{ll})	97.3 (3)	F(4)—V—F(1 ^l)	90.8 (3)
O—V—F(1 ^l)	99.3 (4)	F(3 ^{lll})—V—F(2 ^{ll})	82.5 (3)
F(3)—V—F(4)	165.5 (3)	F(3 ^{lll})—V—F(1 ^l)	81.1 (3)
F(3)—V—F(3 ^{lll})	86.5 (3)	F(2 ^{ll})—V—F(1 ^l)	163.1 (2)
F(3)—V—F(2 ^{ll})	87.7 (3)		

Contact distances

N(1)—F(1 ^{lx})	2.875 (14)	N(1)—F(2 ^{lll})	2.843 (8)
N(1)—F(1 ^{lll})	2.969 (14)	N(1)—F(2)	2.859 (7)
N(2)—F(1)	2.841 (8)	N(2)—F(2)	2.879 (12)
N(2)—F(1 ^{lll})	2.855 (8)	N(2)—F(2 ^v)	2.970 (12)
N(1)—F(3 ^{vii})	3.016 (12)	N(1)—F(4 ^{lx})	2.825 (11)
N(1)—F(3)	3.196 (12)	N(1)—F(4 ^{lv})	2.906 (11)
N(2)—F(3 ^{vii})	3.134 (12)	N(2)—F(4 ^{vii})	3.000 (11)
N(2)—F(3 ^x)	3.155 (13)	N(2)—F(4 ^{lll})	3.161 (11)
N(1)—O(1 ^{lll})	2.971 (12)		
N(1)—O(1)	3.126 (12)		
N(2)—O(1 ^{viii})	3.021 (11)		
N(2)—O(1 ^{lll})	3.041 (12)		

Equivalent positions

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

attributed to a strong *trans* effect, which has already been observed in this type of compound (Rieskamp & Mattes, 1976).

Ammonium ions bind the anionic chains together with the contact distances given in Table 2. Each ammonium ion is coordinated by eight F and two O atoms.

The financial support by the Research Council of Slovenia is gratefully acknowledged.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

DAVIDOVIČ, R. L., HARLAMOVA, L. G. & SAMAREC, L. V. (1977). *Koord. Khim.* **3**, 850–856.

HAZELL, A. C. (1963). *J. Chem. Soc.* pp. 5745–5752.

OUGHTRIED, R. E., RAPER, E. S. & SHEARER, H. M. M. (1976). *Acta Cryst.* **B32**, 82–87.

RIESKAMP, H. & MATTES, R. (1976). *Z. Naturforsch. Teil B*, **31**, 537–540.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1980). **B36**, 1927–1929

Structure of and Hydrogen Bonding in Dicaesium Aquapentachloroferrate(III)

By J. E. GREEDAN, DANIEL C. HEWITT, ROMOLO FAGGIANI AND I. D. BROWN

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(Received 24 August 1979; accepted 8 April 1980)

Abstract. $\text{Cs}_2[\text{FeCl}_5(\text{H}_2\text{O})]$, orthorhombic, *Cmcm*, $a = 7.426$ (4), $b = 17.306$ (7), $c = 8.064$ (2) Å, $Z = 4$, $D_x = 3.301$ Mg m⁻³. 539 observed reflections at $T = 243$ K using Mo $K\alpha$ radiation were used to refine the structure to $R_w = 0.027$. H atoms were located and their positions refined. The compound is isostructural with $\text{Cs}_2[\text{RuCl}_5(\text{H}_2\text{O})]$.

Introduction. During attempts to prepare crystals of $\text{Cs}_2\text{Na}[\text{FeCl}_6]$ by slow evaporation of a 2M HCl solution of NaCl, CsCl, and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in appropriate amounts (Morss, Siegal, Stenger & Edelstein, 1970), we noted the presence of three crystalline phases: colourless cubes of NaCl, small (~1 mm) orange octahedra of $\text{Cs}_2\text{Na}[\text{FeCl}_6]$, and large (several mm) red-orange acicular crystals of a hitherto unknown composition. These acicular crystals were found to contain Cs, Cl and Fe but no Na by emission spectrographic analysis. Subsequently, Cl was determined by Mohr titration, Fe by atomic absorption, and Cs by neutron activation analysis, giving Cl 35.0, Fe 10.0 and Cs 53.2% compared to expected values for $\text{Cs}_2[\text{FeCl}_5(\text{H}_2\text{O})]$ of Cl 34.28, Fe 10.80, Cs 51.37%. Water was detected from characteristic bands in the infrared spectrum of powdered crystals.

Precession photographs showed orthorhombic symmetry with systematic absences $hkl: h + k = 2n + 1; h0l: l = 2n + 1$ suggesting space groups *Cmcm*, *C2cm* or *Cmc2*. Structure refinement confirms the

choice of *Cmcm*. An acicular crystal elongated along [010] of approximately cylindrical cross section and dimensions 0.125 mm in diameter × 1 mm in length was chosen for diffraction measurements on a Syntex $P2_1$ diffractometer. The crystal was cooled to 243 K in a stream of nitrogen in order to obtain accurate parameters. Cell dimensions were obtained by least-squares refinement of 15 well centred reflections with $2\theta > 20^\circ$ using monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities of 1330 reflections with $0 \leq h \leq 9, 0 \leq k \leq 22, 0 \geq l \geq -10$ were measured using a $\theta/2\theta$ scan mode. Two standard reflections (131 and 042) measured at regular intervals showed no significant variation. Equivalent reflections were averaged to give 669 unique reflections. Of these, 539 had $I > 3\sigma(I)$ and were classed as observed. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were not considered necessary ($\mu R = 0.52$ for the cylinder; maximum transmission coefficient = 0.45, minimum = 0.37).

The structure was assumed to be similar to $\text{Cs}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ (Hopkins, Zalkin, Templeton & Adamson, 1966) which has the same space group and similar lattice constants: $a = 7.400$ (4), $b = 17.289$ (8), $c = 7.986$ (5) Å. Least-squares refinement of positional and anisotropic temperature parameters of the non-hydrogen atoms and a secondary-extinction coefficient (Larson, 1967) resulted in $R_1 = \sum (|F_o| - k|F_c|) / \sum |F_o| = 0.023$. Atomic scattering factors, corrected