

The Structure of the $\text{VO}_2\text{F}_4^{3-}$ Ion: Crystal Structure of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$

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The $\text{VO}_2\text{F}_4^{3-}$ ion has a *cis* octahedral structure, as is shown by single crystal structure analysis of the title compound. The unit cell of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ (space group *Immm* or *I222*, $a = 912.6(2)$, $b = 1881.8(4)$, $c = 626.4(1)$ pm, $Z = 6$) contains two symmetrically independent anions. One is rotationally disordered. Oxo and fluoro ligands cannot be distinguished. But the second one has a distorted *cis* octahedral structure with the lengths 170.0(4), 186.1(4), and 202.3(4) pm for the V—O, V—F (axial), and V—F (equatorial) bonds. Infrared and Raman spectra as well as theoretical considerations support the crystallographic results. The phase transitions at 418 and 215 K were confirmed by variable temperature X-ray powder diffraction. Above 418 K the cubic cryolite type structure is adopted with $a = 902.6(2)$ pm. Plausible mechanisms for the phase transitions are suggested. © 1986 Academic Press, Inc.

Introduction

$(\text{NH}_4)_3\text{VO}_2\text{F}_4$ was prepared for the first time in 1889 by Petersen (1). Based on IR spectroscopic evidence Davidovich and co-workers (2) assigned to the $\text{VO}_2\text{F}_4^{3-}$ ion an octahedral structure with a *cis*-dioxo group. The IR spectrum of $\text{Na}_3\text{VO}_2\text{F}_4$ was similarly interpreted by Pausewang and Dehnicke with respect to the symmetry of the $\text{VO}_2\text{F}_4^{3-}$ ion (3). Recently Rao and co-workers stated that "electron paramagnetic resonance of γ -irradiated polycrystalline $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ has given clear indication of the existence of (less than 1%) *trans*- $\text{VO}_2\text{F}_4^{3-}$ species in the solid" and that "the conclusions drawn about the stereochemistry

of $\text{VO}_2\text{F}_4^{3-}$ in the matrix of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ equally hold good for the parent anion $\text{VO}_2\text{F}_4^{3-}$ " (4). In a subsequent paper Gillespie and Rao (5) postulated, based on ^{51}V and ^{19}F nuclear magnetic resonance spectra, the *trans*-dioxo $\text{VO}_2\text{F}_4^{3-}$ species to be present in aqueous solutions of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$. The D_{4h} symmetry of this species in solution and in the solid state was related by the authors mentioned to the VSEPR theory.

These recent results are contradictory to our ideas on the structures and the chemical bonding in oxofluoro anions of the transition elements with d^0 configuration (6). In an octahedral species with two terminal oxygen atoms, the oxygen atoms occupy mutual *cis* positions, because then all three $t_{2g}(d)$ -orbitals of the transition element are available for π -back-donation from the oxygen atoms by reasons of symmetry. To prove this hypothesis for the anion under discussion, we undertook a single crystal

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structure determination of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$. Its results are presented in this paper. So far no structural determination of a $\text{VO}_2\text{F}_4^{3-}$ salt is known.

Experimental

$(\text{NH}_4)_3\text{VO}_2\text{F}_4$ can be prepared from V_2O_5 , HF (40%), and NH_3 (1) or from hot aqueous solutions of NH_4HF_2 and NH_4VO_3 (7). Both methods give identical products with very satisfactory elemental analyses. $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ is yellow to orange, depending on the size of the octahedrally shaped crystals, and stable in air. A crystal with the approximate dimensions $0.2 \times 0.2 \times 0.2$ mm was used to collect the intensities of 1287 reflexions on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator $\vartheta/2\vartheta$ -scan, $2\vartheta_{\text{max}} = 54^\circ$).

They were reduced to 702 independent reflexions, of which 590 had intensities I greater than 1.96 (I). An empirical absorption correction (ψ -scan), Lorentz and polarization corrections were applied to the data. All reflexions hkl with $h + k + l = 2n + 1$ were absent. Therefore, the following space groups had to be considered: $I222$, $Immm$, $Imm2$, $Im2m$, and $I2mm$. E -Statistics gave no preference to any of these. Long-exposed rotation- and Weissenberg-films were checked for superstructure reflexions.

Two vanadium atoms were located by Patterson's methods on special positions of the space groups mentioned. Subsequent refinements was tried in the space groups $Immm$ and $I222$. Both refinements led to essentially identical structures.

Electron density difference maps showed

TABLE I
FINAL POSITIONAL AND THERMAL PARAMETERS (SPACE GROUP $Immm$)

Atom	Site	S.O.F.	x	y	z	B
V(1)	2a	1.00	0.0	0.0	0.0	
V(2)	4g	1.00	0.0	0.3146(1)	0.0	
O(1)	8l	1.00	0.0	0.2569(2)	0.2090(7)	
F(1)	8n	1.00	0.2027(5)	0.3254(3)	0.0	
F(2)	8l	1.00	0.0	0.3965(2)	0.2090(6)	
O/F(3)	4g	0.50	0.0	0.0992(6)	0.0	2.8(2)
O/F(4)	16o	0.125	0.0347(19)	0.0949(10)	0.1005(20)	3.3(4)
O/F(5)	4e	0.50	0.2090(12)	0.0	0.0	3.6(2)
O/F(6)	8m	0.25	0.1454(24)	0.0	0.2063(37)	5.8(5)
O/F(7)	4i	0.50	0.0	0.0	0.2948(17)	3.3(2)
O/F(8)	16o	0.125	0.1425(24)	0.0362(11)	0.1868(36)	3.2(4)
N(1)	4h	1.00	0.0	0.1357(5)	0.5	3.6(2)
N(2)	8n	1.00	0.2710(6)	0.1702(3)	0.0	3.4(1)
N(3)	16o	0.25	0.2009(9)	0.5	0.0607(14)	2.8(2)
N(4)	4e	0.50	0.4287(17)	0.0	0.0	3.6(3)
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V(1)	5.8(2)	3.1(1)	4.7(1)	0.0	0.0	0.0
V(2)	5.3(1)	1.8(1)	3.5(1)	0.0	0.0	0.0
O(1)	5.9(3)	2.5(2)	2.4(2)	0.0	0.0	1.0(1)
F(1)	2.7(2)	6.0(2)	6.7(3)	-0.2(2)	0.0	0.0
F(2)	6.7(2)	2.8(1)	3.4(2)	0.0	0.0	-1.5(1)

B_{ij} defined as $\exp[-\frac{1}{4}(B_{11}a^*h^2 + \dots + 2B_{12} \cdot a^* \cdot b^* \cdot hk + \dots)]$

the $\text{VO}_2\text{F}_4^{3-}$ octahedron located at the origin, and also that one third of the NH_4^+ ions were disordered. To account for this, partial occupancy factors were introduced. Due to their strong correlation with the temperature factors they were not refined further. By refining 66 parameters in the space group *I222* a final *R*-value of 0.069 ($R_w = 0.083$) was obtained. Refinement of 52 parameters in the space group *Immm* gave $R = 0.072$ ($R_w = 0.088$). The data given in Tables I and II refer to the refinement in the more symmetrical space group *Immm*.

For the DSC measurements a DSC-4 Perkin-Elmer differential scanning calorimeter and for the powder diagrams a variable temperature Enraf-Nonius Simon-Guinier camera were used.

Results and Discussion

$(\text{NH}_4)_3\text{VO}_2\text{F}_4$ crystallizes in the space group *Immm* (or *I222*) with $a = 912.6(2)$, $b = 1881.8(4)$, $c = 626.4(1)$ pm, $V = 1.076$ nm³, $Z = 6$, $D_m = 1.96$, $D_c = 1.97$ g cm⁻³. The unit cell contains two symmetrically independent kinds of $\text{VO}_2\text{F}_4^{3-}$ ions, as anticipated from the unusual number of six formula units in the unit cell. The anion, containing V(1), is located at the origin of the space group (twofold positions for *Immm* or *I222*). This implies D_{2h} (or D_2) symmetry for the $\text{VO}_2\text{F}_4^{3-}$ octahedron, and hence a *trans*-octahedral structure. But during the refinement it became clear that this octahedral unit is severely disordered over (at least) 5 positions: one octahedron, consisting of the oxo and fluoro ligands O/F(3), O/F(5), and O/F(7), is oriented along the crystallographic axes. Its occupancy factor is approximately 0.5. The ligands O/F(4), O/F(6), and O/F(8) form a second octahedron. The symmetry elements of the space group generate four different orientations of this polyhedron, each with an occupancy factor of 0.125. The disorder de-

TABLE II
BOND DISTANCES (pm) AND BOND ANGLES (DEG) IN
 $(\text{NH}_4)_3\text{VO}_2\text{F}_4$

V(1)-O/F(3)	186.6(11)	V(2)-O(1)	170.0(4)
-O/F(4)	192.0(19)	-F(1)	186.1(4)
-O/F(5)	190.7(11)	-F(2)	202.3(4)
-O/F(6)	185.2(23)		
-O/F(7)	184.6(11)		
-O/F(8)	187.7(22)		
N(1)-F(1)	281.1(5)	N(3)-F(1)	330.7(5)
-O(1)	292.0(8)	-F(2)	283.1(7)
-O/F(4)	263.6(19)	-F(2)	316.4(7)
-O/F(3)	320.6(3)	-O/F(5)	287.2(9)
-O/F(7)	285.8(9)	-O/F(6)	262.7(24)
N(2)-F(1)	298.6(7)	-O/F(6)	202.5(24)
-F(1)	314.2(1)	-O/F(7)	319.8(10)
-F(2)	304.4(5)	-O/F(7)	287.6(9)
-O(1)	323.9(6)	-O/F(8)	223.8(23)
-O(1)	309.4(6)	N(4)-F(2)	274.6(5)
-O/F(4)	265.6(19)	-O/F(5)	200.6(19)
-O/F(4)	319.1(19)	-O/F(5)	330.6(19)
-O/F(8)	301.8(22)	-O/F(6)	289.1(26)
-O/F(3)	281.1(8)	-O/F(8)	294.2(26)
F(4)-V(1)-F(4)'	179.9(8)	O(1)-V(2)-O(1)'	100.7(2)
-F(6)	96.4(8)	-F(1)	94.0(2)
-F(6)'	83.6(8)	-F(2)	89.3(2)
-F(8)	91.1(9)	-F(2)'	170.0(2)
-F(8)'	88.9(7)	F(1)-V(2)-F(1)'	167.4(2)
F(6)-V(1)-F(6)	180.0(8)	-F(2)	85.2(2)
-F(8)	86.5(8)	F(3)-V(2)-F(2)'	80.7(1)
-F(8)'	93.5(8)		
F(8)-V(1)-F(8)'	179.9(8)		

scribed does not allow us to assign individual positions on the octahedra to the oxo and fluoro ligands. The ligand bond distances vary between 184.6(11) and 190.7(11) pm in the octahedron containing O/F(3), O/F(5), and O/F(7), and between 185.2(23) and 192.0(19) pm in the octahedron containing O/F(4), O/F(6), and O/F(8). The mean bond lengths are equal within the standard deviations and are very close to the mean bond distance of 186.1 pm in the undisturbed octahedron around V(2) (see below). Therefore identical structures can be postulated for both the octahedra around V(1) and V(2).

The structure in question is the *cis*-octahedral structure, as unambiguously shown by the V(2), O(1), F(1), F(2) octahedron (see Fig. 1). The $\text{VO}_2\text{F}_4^{3-}$ anion is situated on mirror planes intersecting the O(1)-V-

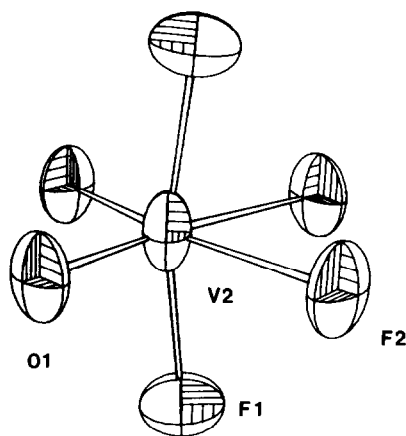


FIG. 1. ORTEP-Plot (50% probability) of the $\text{VO}_2\text{F}_4^{3-}$ ion with V(2) as central atom.

$\text{O}(1')$ and $\text{F}(2)-\text{V}-\text{F}(2')$ angles and the $\text{O}(1)-\text{V}$ and $\text{F}(2)-\text{V}$ bonds. Here oxo and fluoro ligands can be distinguished clearly. The $\text{V}-\text{O}(1)$ bond distance (170.0(4) pm) shows considerable double bond character. The distance is slightly larger than in the polymeric $\text{VO}_2\text{F}_3^{2-}$ anion (163.6(2) pm) (8) with the very weakly bonded bridging fluoro ligands opposite to the terminal oxygen atoms. The bond distances for the "axial" (F(1)) and "equatorial" (F(2)) fluoro ligands are 186.1(4) and 202.3(4) pm, respectively. The $\text{V}-\text{F}(2)$ bond is rather long due to the structural "trans" effect (9). The "axial" bond length is in the range of $\text{V}(+\text{V})-\text{F}$ single bonds (10). Besides the bond distances, the bond angles in the $\text{VO}_2\text{F}_4^{3-}$ octahedron also deviate considerably from ideal symmetry. The central atom V(2) approaches the octahedral edge occupied by the oxygen atoms, widening the OVO angle to $100.7(2)^\circ$ and the $\text{F}(1)-\text{V}-\text{F}(1')$ angle to 192.6° (167.4°). The structure of the $\text{VO}_2\text{F}_4^{3-}$ ion described here agrees completely with the general pattern of the structures of neutral and ionic fluoro-oxo compounds of vanadium (+V) and molybdenum (+VI) (6, 11, 12).

As mentioned already, one third of the

NH_4^+ ions (N(3) and N(4))—like one third of the $\text{VO}_2\text{F}_4^{3-}$ ions—are disordered over two sites, which are half-filled each. This disorder can be related in detail with the disorder of the anions, and can be detected from Table II, where unreasonably short distances occur. The remaining bond distances are in the usual range of hydrogen-bridged $\text{N} \dots \text{O}$ and $\text{N} \dots \text{F}$ bonds.

The IR spectrum of $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ has already been reported (2). We can confirm these results. A Raman spectrum recorded by us contains two strong bands in the VO stretching region at 912 and 870 cm^{-1} . Their intensity ratio is 2 : 1 and reversed with respect to the intensities of the IR frequencies at 905 and 860 cm^{-1} . The bands have to be assigned to the symmetric and to the anti-symmetric stretching frequencies of a *cis*-octahedral structure and exclude a *trans*-octahedral structure.

The reversible first order phase transition at 418 ± 3 K, observed by Rao and co-workers in their EPR work, also appeared in DSC curves registered by us. The transition could easily be detected also in an X-ray powder diagram photographed with a variable temperature Guinier camera in the temperature range 293–450 K. According to this diagram, the structure becomes cubic at the transition point. A cryolite type face-centered cubic lattice with $a = 902.6(2)$ pm and $Z = 4$ could be derived from the observed ϑ -values. The relationship between the lattice constants of the high and room temperature modifications is very simple: The cubic axes are oriented with respect to the orthorhombic cell in the [100], [031], and $[0\bar{3}1]$ directions. The cryolite structure is adopted, because the hydrogen bond network, which stabilizes the orthorhombic structure at ambient temperatures, is disrupted above the transition temperature. (The sodium salt $\text{Na}_3\text{VO}_2\text{F}_4$ shows the cryolite or elpasolite structure even down to room temperatures (3).) The V(1)- and V(2)-octahedra become identical

by the onset of rotational disorder of the V(2)-octahedra. The difference between oxo and fluoro ligands disappears and the NH_4^+ ions move to their special positions in the cryolite type structure. The maximal path lengths of these motions are less than 70 pm. Whereas low temperature DSC measurements did not indicate a distinct phase transition, single crystal work and a variable temperature Guinier diagram showed a second order phase transition to occur at 210–220 K, as supposed earlier (5). From the powder diagram the following cell constants were derived: $a = 916(1)$, $b = 1871(2)$, and $c = 620.2(9)$ pm. They agree well with the low temperature single crystal data. Compared to the room temperature modification, the b and c axes lengths have decreased, but the length of the a axis has increased. We collected a set of intensities from a single crystal at approximately 150 K. But we were unable to refine the structure model, which was very similar to the structure described in this paper, to R lower than 0.25. We ascribe this failure to twinning. The crystal, cooled down from room temperature, contained obviously differently oriented domains of the low temperature modification which is formed by an ordering process from the disordered room temperature structure.

Finally some remarks on the results of the EPR work mentioned above, where different conclusions have been drawn with the respect to the structure of the $\text{VO}_2\text{F}_4^{3-}$

ion: V(IV)-compounds containing a $\text{V}=\text{O}$ group usually show independently from the remaining ligands axial or nearly axial EPR spectra. So *cis*- or *trans*-structures might not be distinguishable. The observed super hyperfine structure on the perpendicular components ascribed to splitting by ^{19}F interactions may be due as well to the presence of two or more crystallographically non equivalent $\text{VO}_2\text{F}_4^{3-}$ octahedra in the structure, as shown by us. Clear results can probably be obtained in this case only from single crystal EPR data.

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