

(NMe<sub>2</sub>)<sub>4</sub> and intermolecular interactions in solid Mo(NMe<sub>2</sub>)<sub>4</sub>.

The planarity around the nitrogen atoms is caused by the N to Zr p<sub>π</sub> to d<sub>π</sub> donation, which reduces the Lewis acidity of the metal. Therefore the Zr-N bonds have some multiple bond character that is not changed by rotation of the C<sub>2</sub>-N groups around the N-Zr bonds as the ZrN<sub>4</sub> group retains its D<sub>2d</sub> or higher T<sub>d</sub> symmetry irrespective of the value of ∠C(1)-N(1)-Zr-N(2) torsion angle.

The results do not give an unambiguous geometry for the ZrN<sub>4</sub> fragment. In Sn(NMe<sub>2</sub>)<sub>4</sub> a tetrahedral geometry was assumed for the co-ordination sphere of the tin atom,<sup>5</sup> while in Mo(NMe<sub>2</sub>)<sub>4</sub>, the N-Mo-N angles covered the range 107.3 (2)-112.5 (2)° with the average being 109.5 (1.9)°. If nonbonded d electrons exert any steric effect, the MoN<sub>4</sub> fragment is more likely than the ZrN<sub>4</sub> fragment to exhibit D<sub>2d</sub> symmetry. This is because in Mo(NMe<sub>2</sub>)<sub>4</sub> the two d electrons occupy the nonbonding d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital that is in the xy plane which bisects the four equivalent N-Mo-N angles of the D<sub>2d</sub> fragment. It may be, as stated in the introduction, that this effect is masked in the solid state for Mo(NMe<sub>2</sub>)<sub>4</sub>.

It would appear from our study that the covalent radius of Zr (1.45 Å) is so large that it readily allows deformation of the ZrN<sub>4</sub> moiety, deviation of the ∠C(1)-N(1)-Zr-N(2) torsion angle from 90°, and out of plane bending of the C<sub>2</sub>-N fragments. It would therefore be interesting to determine the structures of Ti(NMe<sub>2</sub>)<sub>4</sub> and V(NMe<sub>2</sub>)<sub>4</sub>, where the metal atoms have smaller covalent radii [r<sub>Ti</sub> = 1.32 Å and r<sub>V</sub> = 1.22 Å] than zirconium and vanadium has a d<sup>1</sup> configuration. The difference between the covalent radii of titanium and zirconium is known to have a profound influence upon structure. For example at room temperature titanium(IV) chloride consists of monomeric tetrahedral molecules while zir-

conium(IV) has a chain structure with octahedrally coordinated metal centers. Some differences between Ti(NMe<sub>2</sub>)<sub>4</sub> and Zr(NMe<sub>2</sub>)<sub>4</sub> attributable to changes in covalent radius have been reported. Measurements on benzene solutions have shown that while Ti(NMe<sub>2</sub>)<sub>4</sub> is monomeric, Zr(NMe<sub>2</sub>)<sub>4</sub> exists as a monomer-dimer equilibrium.<sup>3,6</sup> We thus believe that a more rigid gas-phase structure is to be expected for Ti(NMe<sub>2</sub>)<sub>4</sub> than is reported here for the zirconium analogue.

The metal-nitrogen distance in Zr(NMe<sub>2</sub>)<sub>4</sub> [2.071 (11) Å] is as expected slightly longer than that observed in Mo(NMe<sub>2</sub>)<sub>4</sub> [1.926 (6) Å],<sup>4</sup> while that in Sn(NMe<sub>2</sub>)<sub>4</sub> is 2.045 (7) Å.<sup>5</sup> The values obtained for r(C(1)-N(1)) [1.461 (4) Å], r(C(1)-H(1)) [1.118 (12) Å], ∠C(1)-N(1)-C(1') [111.2 (11)°], and ∠N(1)-C(1)-H(1) [108.7 (30)°] are in accord with related data previously determined by electron diffraction.<sup>5,18,19</sup>

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## A Series of Tris(μ-fluoro)divanadates(III, IV, V) Containing the Bioctahedral [V<sub>2</sub>(O,F)<sub>9</sub>]<sup>3-</sup> Unit. Synthesis, Characterization, and Structures of (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>F<sub>9</sub>, (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>2</sub>F<sub>7</sub>, (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>, and (NMe<sub>4</sub>)<sub>2</sub>KV<sub>2</sub>O<sub>4</sub>F<sub>5</sub>·H<sub>2</sub>O

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Tetramethylammonium salts of the anions [V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>]<sup>3-</sup>, [V<sub>2</sub>O<sub>2</sub>F<sub>7</sub>]<sup>3-</sup>, and [V<sub>2</sub>F<sub>9</sub>]<sup>3-</sup>, each consisting of face-sharing double octahedra, have been prepared and their structural chemistries investigated. (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>, (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>2</sub>F<sub>7</sub>, and (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>F<sub>9</sub> crystallize in the hexagonal Cs<sub>3</sub>Cr<sub>2</sub>Cl<sub>9</sub> type structure, space group P6<sub>3</sub>/m, with Z = 2. (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>: a = 8.076 (4) Å, c = 18.703 (8) Å. (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>2</sub>F<sub>7</sub>: a = 8.031 (5) Å, c = 18.571 (7) Å. (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>F<sub>9</sub>: a = 8.050 (9) Å, c = 18.671 (11) Å. With use of 647, 591, and 477 unique data (I ≥ 1.96σ(I)), the three structures were refined to R = 0.044, 0.055, and 0.055, respectively. In [V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>]<sup>3-</sup> and [V<sub>2</sub>O<sub>2</sub>F<sub>7</sub>]<sup>3-</sup> the oxo ligands are bonded terminally. Both anions are disordered in the solid state to adopt the symmetry of the space group. The vanadium-vanadium distances decrease with oxidation state in the order [V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>]<sup>3-</sup>, [V<sub>2</sub>O<sub>2</sub>F<sub>7</sub>]<sup>3-</sup>, [V<sub>2</sub>F<sub>9</sub>]<sup>3-</sup> from 3.138 (1) and 2.977 (2) to 2.894 (3) Å. The V-F (bridging) distances decrease in the same order from 2.114 (2) and 2.071 (3) to 2.044 (3) Å. The repulsion between the metal atoms is diminished by these ligands, which have very short nonbonding contacts. (NMe<sub>4</sub>)<sub>2</sub>KV<sub>2</sub>O<sub>4</sub>F<sub>5</sub>·H<sub>2</sub>O crystallizes in orthorhombic space group Pnma with a = 10.724 (2) Å, b = 18.796 (4) Å, c = 8.658 (2) Å, and Z = 4. The structure was refined to R = 0.036 with use of 1485 unique data. The dimensions of the [V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>]<sup>3-</sup> ion here and in (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>O<sub>4</sub>F<sub>5</sub> are very similar. The magnetic moment of (NMe<sub>4</sub>)<sub>3</sub>V<sub>2</sub>F<sub>9</sub> at room temperature is 2.65 μ<sub>B</sub> per vanadium.

### Introduction

Compounds containing the binuclear anion [M<sub>2</sub>X<sub>9</sub>]<sup>3-</sup> (X = Cl, Br, I) are well-known.<sup>1</sup> Recently oxo compounds like Ba<sub>3</sub>M<sub>2</sub>O<sub>9</sub> (M = Te(VI),<sup>2</sup> W(VI)<sup>3</sup>) and oxo fluoro compounds like Cs<sub>3</sub>-

Mo<sub>2</sub>O<sub>6</sub>F<sub>3</sub>,<sup>4</sup> Cs<sub>3</sub>V<sub>2</sub>O<sub>4</sub>F<sub>5</sub>,<sup>5,6</sup> and Cs<sub>3</sub>V<sub>2</sub>O<sub>2</sub>F<sub>7</sub><sup>5-7</sup> containing face-sharing bioctahedral units have been characterized. The A<sub>3</sub>M<sub>2</sub>X<sub>9</sub> compounds crystallize in three types of structures that consist of hexagonal AX<sub>3</sub> layers but have different stacking modes and

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different arrangements of the M atoms. The  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  and the  $\text{Cs}_3\text{Fe}_2\text{F}_9$  types have a purely hexagonal (h6) sequence of six layers. In  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  two-thirds of all octahedral sites between all layers are filled, whereas in  $\text{Cs}_3\text{Fe}_2\text{F}_9$  two filled layers alternate with one vacant layer. The  $\text{Cs}_3\text{Cr}_2\text{Cl}_9$  structure has a chchc sequence of six layers. The M atoms fill these octahedra of X atoms, which share a common face. The  $\text{Cs}_3\text{Fe}_2\text{F}_9$  type and the  $\text{Cs}_3\text{Cr}_2\text{Cl}_9$  type structures have hexagonal unit cells with similar lattice constants, but the double octahedra are located in the former at 0, 0,  $1/4$  and 0, 0,  $3/4$  and in the latter at  $1/3, 2/3, 3/4$  and  $2/3, 1/3, 1/4$ . The site symmetries of these special positions are  $\bar{6}m2$  in space group  $P6_3/mmc$  and  $\bar{6}$  in  $P6_3/m$ .

We ascribed earlier the stability of the oxo fluoro anions  $[\text{Mo}_2\text{O}_6\text{F}_3]^{2-}$ ,  $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ , and others to their integration into the densely packed layer structures. Slight displacements of cations, metal atoms, and ligands and also  $\text{O} \rightarrow \text{M}$   $\pi$ -bonding compensate for the buildup of positive charge between the metal atoms and of negative charge on the ligands around the octahedral voids.<sup>5</sup> If the bioctahedral oxo fluoro anions would be stable also as salts with large (organic) cations, their inherent stability would be proved despite their electrostatically unfavorable structures. Only a limited number of  $[\text{M}_2\text{X}_9]^{3-}$  compounds with large organic counterions, mainly restricted to  $[\text{Mo}_2\text{Cl}_9]^{3-}$ , have been structurally characterized so far.<sup>8,9</sup> According to this work the cations have a marked influence upon the overall parameters of the  $[\text{Mo}_2\text{Cl}_9]^{3-}$  group, especially on the M-M distance.

In this paper we report the successful preparation of tetramethylammonium salts of the  $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ ,  $[\text{V}_2\text{O}_2\text{F}_7]^{3-}$ , and  $[\text{V}_2\text{F}_9]^{3-}$  anions. We investigated their structures using single crystals and determined the distribution of oxo and fluoro ligands on the terminal and bridging ligand positions using vibrational spectroscopy. The metal to metal distances and the magnetic behavior are of special interest in this series of compounds, in which vanadium has the oxidation states +V, +IV, and +III. Only one fluoride with a  $[\text{M}_2\text{X}_9]^{3-}$  structure, i.e.  $\text{Cs}_3\text{Fe}_2\text{F}_9$ , has been known so far.<sup>6,10</sup>

## Experimental Section

**Materials and Methods.** All preparative reactions were performed in freshly distilled, dry solvents. HF solutions were kept in Teflon vessels. Unless otherwise noted, no special precautions were taken to eliminate atmospheric oxygen or moisture.  $\text{VCl}_4$  and  $(\text{NMe}_4)_2[\text{V}_2\text{O}_6(\text{H}_2\text{O})_2]^{12}$  were prepared by literature methods. A 20% ethanol solution of tetramethylammonium fluoride was prepared as follows: A 100-g portion of commercial 25% methanolic tetramethylammonium hydroxide was neutralized with 40% HF, and the solution was concentrated to approximately 30 mL. After addition of 200 mL of ethanol, half of the solvents were distilled off. This procedure was repeated several times to remove traces of water. In order to obtain a 20% solution, the appropriate amount of ethanol was added. All other reagents were obtained from standard commercial sources and used without further purification.

The following instruments were used in this work: IR, Perkin-Elmer 457 infrared spectrometer and Bruker IFS 113 Fourier transform spectrometer; Raman spectra, Coderg T-800 spectrometer,  $\text{Kr}^+$  laser (647.1 nm) or  $\text{Ar}^+$  laser (514.5 nm); X-ray crystallography, Syntex P2<sub>1</sub> diffractometer. Vanadium was analyzed volumetrically with  $\text{Fe}(\text{II})$ ; tetramethylammonium, by gravimetric methods as tetraphenylborate or by microanalysis. All new compounds gave satisfactory elemental analyses.

**Preparations.**  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$ . To a solution of vanadium(V) oxide in 40% HF ( $\text{V}_2\text{O}_5:\text{HF} = 1:8$ ) was added the stoichiometric amount of

25% methanolic tetramethylammonium hydroxide.  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  crystallized in well-shaped yellow hexagonal prisms from the clear solution. The product was washed with ethanol and dried at 60 °C.

$(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5 \cdot \text{H}_2\text{O}$ . Slow addition of a methanol solution containing potassium bromide to a saturated solution of  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  in methanol/water (20:1) in the ratio 1:1 precipitated a microcrystalline product. To obtain single crystals, separate pellets of KBr and of  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  were pressed and kept tightly together in a methanol/water (20:1) mixture for several days. Well-formed yellow prismatic single crystals developed in the region between the pellets.

$(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$ . **Method A.** Vanadium dioxide (1 g, 12 mmol) dissolved in 40% HF (20 mL) was added under nitrogen to a methanol solution containing 25% tetra-*n*-butylammonium hydroxide (2.08 g, 18 mmol). The solvent was removed, and the dark green residue was dried with  $\text{P}_2\text{O}_5$  and KOH for several days under nitrogen and then dissolved in DMF (50 mL). A microcrystalline product was precipitated by addition of ethanol solution containing tetramethylammonium chloride. Single crystals could be obtained by slow interdiffusion of these solutions as turquoise green hexagonal plates.

**Method B.**  $(\text{NMe}_4)_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$  (500 mg, 1.26 mmol) was dissolved under nitrogen in refluxing methanol (100 mL). Then an ethanol solution of tetramethylammonium fluoride (20%, 11.6 mmol) was added ( $\text{V}:\text{F} = 1:1$ ). After the mixture was cooled to -10 °C, microcrystalline  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$  was obtained.

$(\text{NMe}_4)_3\text{V}_2\text{F}_9$ . To 100 mL of DMF solution containing vanadium trichloride (4–8 mmol) was added, at 100 °C under nitrogen, the stoichiometric amount of tetramethylammonium fluoride dissolved in ethanol (20% solution). The preparation was carried out in a three-necked bottle, fitted with a dropping funnel and a still-head connected to a condenser. The volume of the solution was kept constant by adjusting properly both the dropping and distilling rates. Addition of tetramethylammonium fluoride should be stopped when the violet to green color of vanadium trichloride disappears and the bright yellow precipitate can be recognized. The product was filtered out by suction, washed with acetone, and dried in vacuo. The byproduct tetramethylammonium chloride was removed by several washings with cold ethanol. Single crystals could be prepared by the following diffusion technique:  $\text{VCl}_3$  was dissolved in DMF and the mixture carefully covered with an ethanol solution containing tetramethylammonium fluoride. After the mixture was allowed to stand 3–5 days at 60 °C, hexagonally shaped, intensive yellow crystals of  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  appeared at the bottom of the vessel besides yellow-green crystals of  $(\text{NMe}_4)_2[\text{V}_2\text{F}_8(\text{H}_2\text{O})_2]^{13}$  and dark green agglomerates of  $\text{VF}_3(\text{H}_2\text{O})_3$  in the upper parts.

**Collection and Reduction of X-ray Data.** Crystals were mounted in glass capillaries. Diffraction studies were performed on a Syntex (Nicolet) P2<sub>1</sub> four-circle automated diffractometer with a Mo X-ray source equipped with a graphite monochromator and a low-temperature device. The final orientation matrix and unit cell parameters were determined by least-squares treatment of 14 machine-centered reflections having  $2\theta > 20^\circ$ . The intensities of one check reflection revealed no significant change in intensity during data acquisition. The crystal parameters and details of the data collection are summarized in Table I.

**Structure Solution and Refinement.** The E-XTL program package including full-matrix least-squares refinement with the weighting scheme  $1/w = \sigma^2(F_o) + (gF_o)^2$  where  $g = 0.015$  was used throughout, with the exception of the  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  study. This structure was refined by using SHELX programs and  $g = 0.02$ . Final *R* factors and other data are included in Table I. Individual structural refinements are briefly described.

(a)  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$ ,  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$ , and  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$ . The systematic absences, only  $00l$  ( $l = 2n$ ), excluded the space group  $P6_3/mmc$  (No. 194), which is frequently observed for compounds with composition  $\text{A}_3\text{M}_2\text{X}_9$ ,<sup>4</sup> and favored space group  $P6_3/m$  (No. 176), which proved to be correct during structure solution. Heavy-atom positions of  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  were revealed by Patterson methods. All remaining non-hydrogen atoms were located with use of successive difference Fourier maps.

The structure of  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$  and  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  could be refined straightforwardly by using the final parameters of  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$ . The  $\text{NMe}_4^+$  ion, located at  $z = 1/4$ , is disordered by reflection across the mirror to adapt  $\bar{6}$  symmetry. Refinement converged best when half-occupancy was assumed for N2 (site 4e) and also C4 (site 4e) and when C3 was restricted to the mirror plane at  $z = 1/4$  (site 6h). The terminal ligand positions in the double octahedron  $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$  or  $[\text{V}_2\text{O}_2\text{F}_7]^{3-}$  were assumed to be occupied statistically by four oxygen and two fluorine atoms or by two oxygen and four fluorine atoms, respectively (see below). The oxygen scattering factor was used in the former case, and the fluorine scattering factor, in the latter one. Hydrogen atoms at C1 and C2 (and

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- (13)  $(\text{NMe}_4)_2[\text{V}_2\text{F}_8(\text{H}_2\text{O})_2]$  is isostructural with  $(\text{NMe}_4)_2[\text{V}_2\text{O}_6(\text{H}_2\text{O})_2]$  according to Guinier powder diagrams.

Table I. Crystal Data and Details of Data Collection

formula	$C_{12}H_{36}F_3N_3O_4V_2$	$C_8H_{26}F_3KN_2O_5V_2$	$C_{12}H_{36}F_7N_3O_2V_2$	$C_{12}H_{36}F_9N_3V_2$
mol wt	483.3	466.3	489.3	490.3
$a$ , Å	8.076 (4)	10.724 (2)	8.031 (5)	8.050 (9)
$b$ , Å		18.796 (4)		
$c$ , Å	18.703 (8)	8.658 (2)	18.571 (7)	18.671 (11)
$V$ , Å <sup>3</sup>	1056	1745	1037	1056
cryst syst	hexagonal	orthorhombic	hexagonal	hexagonal
$Z$	2	4	2	2
$d_{\text{calcd}}$ ( $d_{\text{obsd}}$ ), g/cm <sup>3</sup>	1.52 (1.50)	1.77 (1.72)	1.57 (1.50)	1.57 (1.51)
space group	$P6_3/m$	$Pnma$	$P6_3/m$	$P6_3/m$
cryst dimens, mm	$0.1 \times 0.1 \times 0.25$	$0.1 \times 0.1 \times 0.2$	$0.2 \times 0.2 \times 0.1$	$0.1 \times 0.075 \times 0.025$
radiation ( $\lambda$ , Å)	Mo $K\alpha$ (0.71069)	Mo $K\alpha$ (0.71069)	Mo $K\alpha$ (0.71069)	Mo $K\alpha$ (0.71069)
abs coeff, $\mu$ , cm <sup>-1</sup>	10.0	14.4	10.2	10.3
abs cor	$\psi$ scan	$\psi$ scan	$\psi$ scan	$\psi$ scan
scan (max $2\theta$ , deg)	$\theta/2\theta$ (54)	$\theta/2\theta$ (54)	$\theta/2\theta$ (54)	$\theta/2\theta$ (54)
scan speed, deg/min	4.88–29.3	3.91–29.3	4.88–29.3	4.88–29.3
bkgd/scan time	0.75	0.75	0.75	0.75
temp, K	$295 \pm 5$	$140 \pm 5$	$140 \pm 5$	$140 \pm 5$
no. of data collected	1887 (+ $h$ , + $k$ , $\pm l$ )	2244 (+ $h$ , + $k$ , + $l$ )	1835 (+ $h$ , + $k$ , $\pm l$ )	967 (+ $h$ , + $k$ , $\pm l$ )
no. of unique data ( $I \geq 1.96\sigma(I)$ )	647	1485	591	478
no. of variables	62	166	62	68
goodness of fit	2.56	1.37	2.52	1.32
$R$ ( $R_w$ )	0.044 (0.059)	0.036 (0.038)	0.055 (0.062)	0.055 (0.047)

Table II. Atom Positional Parameters ( $\times 10^4$ ) in the Order  $(NMe_4)_3V_2O_4F_5$ ,  $(NMe_4)_3V_2O_2F_7$ , and  $(NMe_4)_3V_2F_9$  (Refined Hydrogen Atoms Omitted)

atom	site	$x$	$y$	$z$
V	4f	3333	6667	1661.0 (4) 1698.9 (6) 1725.0 (8)
O/F	12i	1969 (3) 2585 (4) 2614 (5)	4531 (3) 4464 (4) 4442 (5)	1249 (1) 1231 (1) 1216 (2)
F	6h	1322 (4) 1284 (4) 1290 (6)	5874 (4) 5385 (4) 5354 (6)	2500
N1	4f	3333	6667	5817 (2) 5817 (3) 5806 (4)
C1	4f	6667	3333	1618 (3) 1618 (4) 1604 (4)
C2	12i	4681 (5) 4663 (6) 4652 (9)	2592 (6) 2042 (6) 2037 (9)	559 (2) 551 (2) 548 (3)
N2	4e	0	0	2351 (5) 2304 (6) 2309 (9)
C3	6h	2034 (7) 2035 (8) 2000 (13)	894 (7) 1177 (9) 1203 (15)	2500
C4	4e	0	0	1547 (7) 1503 (8) 1504 (10)

for  $(NMe_4)_3V_2F_9$  two of three hydrogen atoms at C3) were located from difference Fourier maps and refined isotropically. The remaining hydrogen atoms were not included in the calculations. Fourier maps revealed for  $(NMe_4)_3V_2O_4F_5$  and  $(NMe_4)_3V_2F_9$  several random features ( $<0.59$  and  $<0.55$  e/Å<sup>3</sup>, respectively) and for  $(NMe_4)_3V_2O_2F_7$  one peak near C3 (0.8 e/Å<sup>3</sup>, probably to be assigned to a hydrogen atom) and several random features ( $<0.60$  e/Å<sup>3</sup>).

(b)  $(NMe_4)_2KV_2O_4F_5 \cdot H_2O$ . The systematic absences  $OkI$  ( $k + l = 2n$ ) and  $hk0$  ( $h = 2n$ ) define space groups  $Pnma$  (No. 62, centrosymmetric) and  $Pn2_1a$  (nonstandard setting of No. 33, acentric). Statistical tests indicated an inversion center to be present. The choice of space group  $Pnma$  was confirmed by successful solution and refinement of the structure. Heavy-atom positions were revealed by Patterson methods. All remaining atoms (including hydrogen atoms) were located with use of successive difference Fourier maps. The final map contained several random features ( $<0.49$  e/Å<sup>3</sup>). The oxygen scattering factors were used for atoms O1 and O2, and the fluorine scattering factor was used for atom F4 (see below).

Table III. Atom Positional Parameters ( $\times 10^4$ ) for  $(NMe_4)_2KV_2O_4F_5 \cdot H_2O$  (Refined Hydrogen Atoms Omitted)

atom	$x$	$y$	$z$
V	3022.7 (5)	3322.9 (2)	4492.3 (6)
O1	3680 (2)	1262 (1)	5975 (2)
O2	1587 (2)	1294 (1)	4373 (2)
F1	2288 (2)	2500	5847 (3)
F2	2456 (2)	2500	2991 (2)
F3	4350 (2)	2500	4574 (3)
F4	3796 (2)	1301 (1)	2926 (2)
K	0022 (1)	2500	3419 (1)
N	2047 (2)	0827 (1)	9492 (3)
C1	2007 (3)	1624 (1)	9515 (4)
C2	1385 (3)	0554 (2)	0885 (3)
C3	1405 (3)	0564 (2)	8070 (4)
C4	3368 (3)	0583 (2)	9495 (4)
O3	4739 (4)	2500	8423 (5)
H1	5558 (61)	2500	8440 (71)
H2	4445 (64)	2500	7648 (88)

## Results and Discussion

**Syntheses and Properties.**  $(NMe_4)_3V_2O_4F_5$  was prepared in weakly acid aqueous solution by a method similar to the preparation of the alkali-metal salts of this anion.<sup>6</sup>  $NMe_4^+$  was added as a 25% methanolic solution of its hydroxide.  $(NMe_4)_3V_2O_4F_5$  is quite soluble in water and rather stable in air. To prepare  $(NMe_4)_3V_2O_2F_7$ ,  $(n-Bu_4N)_3V_2O_2F_7$  or  $(NMe_4)_2V_2O_2F_6(H_2O)_2$  was used as the precursor. Vanadium(III) fluoride cannot be prepared in aqueous solution. Therefore, a nonaqueous procedure had to be developed: vanadium trichloride, very soluble in DMF, was fluorinated with a solution of tetramethylammonium fluoride in ethanol. Traces of water were continuously removed by distillation of the ethanol/water azeotrope.  $(NMe_4)_3V_2F_9$  is very hygroscopic, its oxidation under air is slow, and its color is light yellow.

**Vibrational Spectra.** Vibrational spectroscopy is an excellent tool to distinguish between oxo and fluoro ligands, especially in cases where X-ray crystallography gives ambiguous results.<sup>4,5</sup> No bands were observed in the spectra of  $[V_2O_4F_5]^{3-}$  and  $[V_2O_2F_7]^{3-}$  in the region 560–880 cm<sup>-1</sup>. Bridging V–O–V stretching modes are usually attributed to this region.<sup>14,15</sup> Obviously, as in  $Cs_3V_2O_4F_5$  and  $Cs_3V_2O_2F_7$ , the oxo ligands are bonded exclusively in terminal positions.<sup>5,7,16</sup>  $\nu_{as}$ ,  $\nu_{as}(VO_2)$ , and  $\nu(VO)$  were observed at 926–930, 884–914, and 970–980 cm<sup>-1</sup>, respectively. Bands at 500–550 cm<sup>-1</sup> have to be assigned to V–F (terminal) stretching modes.<sup>17</sup> In the region 400 cm<sup>-1</sup> and lower, bands due to  $NMe_4^+$

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(15) Beattie, I. R.; Gilson, T. R. *J. Chem. Soc. A* **1969**, 2322.

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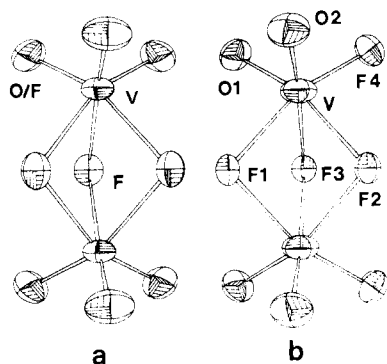


Figure 1. ORTEP view of the  $[V_2O_4F_5]^{3-}$  ion in (a)  $(NMe_4)_3V_2O_4F_5$  and (b)  $(NMe_4)_2KV_2O_4F_5 \cdot H_2O$ .

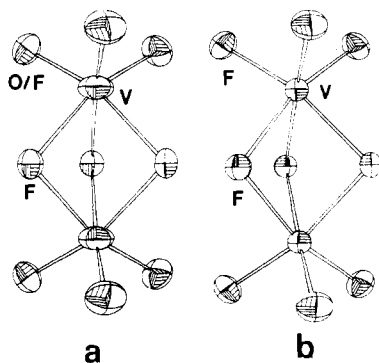


Figure 2. ORTEP view of (a) the  $[V_2O_2F_7]^{3-}$  ion and (b) the  $[V_2F_9]^{3-}$  ion in their  $NMe_4^+$  salts.

interfere with  $V=O$  deformation and  $F-V-F$  stretching modes. Therefore, no detailed assignment is possible in this region. From the spectra no conclusions can be drawn with respect to the point group symmetry ( $C_{2v}$  or  $C_2$ ) of the individual  $[V_2O_4F_5]^{3-}$  and  $[V_2O_2F_7]^{3-}$  polyhedra.

**Description of the Structures.**  $(NMe_4)_3V_2O_4F_5$ ,  $(NMe_4)_3V_2O_2F_7$ , and  $(NMe_4)_3V_2F_9$  are isostructural and crystallize in the hexagonal  $Cs_2Cr_2Cl_9$  type structure, whereas the alkali-metal salts  $Cs_3V_2O_4F_5$  and  $Cs_3V_2O_2F_7$  adopt the  $Cs_2Fe_2F_9$  structure. The former structure can accommodate the spacious tetramethylammonium cations more favorably due to the alternate stacking of the double octahedra (see the Introduction). The latter seems to be preferred if small anions, like oxide and fluoride, and slightly larger cations, like  $K^+$ ,  $Cs^+$ , and  $Ba^{2+}$ , form the layers. The  $NMe_4^+$  salts crystallize in space group  $P6_3/m$ , a lower symmetry subgroup of  $P6_3/mmc$ , the space group of the prototype. The double octahedra are rotated in the unit cell by  $8-10^\circ$  with respect to the  $a$  and  $b$  axes. The tetramethylammonium ions above and below the double octahedra follow this rotation, but the tetramethylammonium ions along  $0, 0, z$  are rotated by approximately  $10^\circ$  in the opposite direction. These rotations relax intermolecular contacts between the methyl groups of different cations and between the methyl groups and the bridging ligands. Deviation of the double octahedra from point group symmetry  $\bar{6}m2$  is very small: the triangles of the bridging ligands are rotated from the ideal angle by less than  $1^\circ$ . The structures of the individual double octahedra are shown in Figures 1 and 2; the dimensional data are collected in Tables IV and V.

$[V_2O_4F_5]^{3-}$  and  $[V_2O_2F_7]^{3-}$  can reach the observed crystallographic symmetry  $\bar{6}$  only if oxo and fluoro ligands are statistically distributed. According to the vibrational spectra, oxygen occupies only terminal positions in  $(NMe_4)_3V_2O_4F_5$  and  $(NMe_4)_3V_2O_2F_7$ . The former compound contains  $VO_2$ , and the latter,  $VO$  groups only. Therefore, the individual units present in solid state are

Table IV. Interatomic Distances (Å) and Angles (deg) in  $(NMe_4)_3V_2O_4F_5$ ,  $(NMe_4)_3V_2O_2F_7$ , and  $(NMe_4)_3V_2F_9$

	$[V_2O_4F_5]^{3-}$	$[V_2O_2F_7]^{3-}$	$[V_2F_9]^{3-}$
V...V	3.138 (1)	2.977 (2)	2.894 (3)
V-O/F	1.698 (3)	1.783 (3)	1.847 (3)
V-F	2.114 (2)	2.071 (3)	2.044 (3)
O/F...O/F	2.620 (3)	2.698 (4)	2.742 (4)
O/F...F	2.736 (3)	2.768 (3)	2.811 (4)
O/F...F'	2.786 (3)	2.822 (3)	2.864 (5)
F...F	2.454 (5)	2.494 (4)	2.500 (7)
N1-C1	1.497 (6)	1.488 (8)	1.490 (10)
N1-C2	1.485 (5)	1.497 (4)	1.494 (8)
N2-C3	1.453 (6)	1.467 (7)	1.448 (9)
N2-C4	1.505 (16)	1.487 (18)	1.501 (25)
O/F-V-O/F	101.1 (1)	98.3 (1)	95.9 (1)
O/F-V-F	91.1 (1)	91.5 (1)	92.4 (2)
O/F-V-F'	93.3 (1)	93.8 (1)	94.7 (1)
O/F-V-F''	159.0 (1)	163.1 (1)	165.8 (1)
F-V-F	70.1 (1)	74.1 (1)	75.4 (2)
V-F-V	95.8 (1)	91.9 (1)	90.1 (2)
C1-N1-C2	109.0 (2)	109.6 (3)	108.8 (3)
C2-N1-C2	109.9 (3)	109.3 (3)	110.2 (3)
C3-N2-C3	116.4 (4)	114.0 (5)	114.2 (5)
C3-N2-C4	101.0 (5)	104.4 (5)	104.2 (6)

Table V. Interatomic Distances (Å) and Angles (deg) in  $(NMe_4)_2KV_2O_4F_5 \cdot H_2O$

V...V	3.093 (1)	O1-V-O2	103.5 (1)
V-O1	1.659 (2)	O1-V-F4	102.1 (1)
V-O2	1.702 (2)	O2-V-F4	102.2 (2)
V-F4	1.740 (2)	F1-V-F2	72.3 (1)
V-F1	2.095 (2)	F1-V-F3	72.1 (1)
V-F2	2.110 (2)	F2-V-F3	71.1 (1)
V-F3	2.103 (2)	O1-V-F1	94.2 (1)
K-O2	2.939 (2)	O1-V-F2	91.8 (1)
K-F4	2.858 (2)	O2-V-F1	90.4 (1)
K-F2	2.637 (2)	O2-V-F2	90.7 (1)
K-F3	2.690 (2)	F4-V-F2	87.4 (1)
K-O3	2.751 (4)	F4-V-F3	90.2 (1)
K...O1	4.685 (2)	V-F1-V'	95.1 (1)
F1...F2	2.480 (3)	V-F2-V'	94.2 (1)
F1...F3	2.470 (3)	V-F3-V'	94.7 (1)
F2...F3	2.450 (3)	C1-N-C2	108.6 (2)
N-C1	1.500 (3)	C1-N-C3	109.2 (2)
N-C2	1.490 (4)	C1-N-C4	109.5 (2)
N-C3	1.494 (4)	C2-N-C3	109.5 (2)
N-C4	1.489 (4)	C2-N-C4	110.2 (2)
		C3-N-C4	109.8 (2)

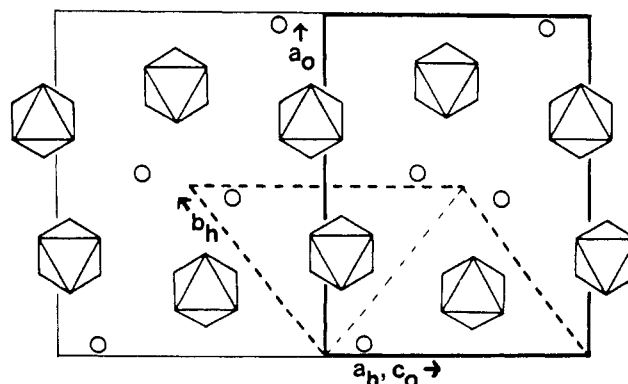


Figure 3. Relationship between the hexagonal unit cell of  $(NMe_4)_3V_2O_4F_5$  (h) and the orthorhombic cell of  $(NMe_4)_2KV_2O_4F_5 \cdot H_2O$  (o). For clarity only double octahedra and potassium ions (small circles) are shown.

$[O_2FV(\mu-F)_3VFO_2]^{3-}$  and  $[OF_2V(\mu-F)_3VF_2O]^{3-}$ . The statistical distribution makes it difficult to assign individual  $V=O$  (terminal) or  $V-F$  (terminal) bond distances. To overcome this difficulty, we tried to reduce the symmetry of the  $[V_2O_4F_5]^{3-}$  site in the crystal by synthesizing  $(NMe_4)_2KV_2O_4F_5 \cdot H_2O$ . Its orthorhombic structure is closely related to the hexagonal structure of  $(NMe_4)_3V_2O_4F_5$ : The stacking sequences of  $NMe_4^+$  and  $V_2O_4F_5^{3-}$

(17) (a) Rieskamp, H.; Mattes, R. Z. *Naturforsch., B: Anorg. Chem. Org. Chem.* **1976**, *31B*, 537, 541. (b) Rieskamp, H.; Mattes, R. Z. *Anorg. Allg. Chem.* **1976**, *419*, 193. (c) Stomberg, R. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 325.

ions along  $c$  in  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  and along  $b$  in  $(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5\cdot\text{H}_2\text{O}$  are identical in both structures (see Figure 3). The respective crystallographic axes have approximately the same lengths. The tetramethylammonium ions, located in the hexagonal structures on site 4e across the mirror planes, are replaced in  $(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5\cdot\text{H}_2\text{O}$  by potassium ions and water molecules, both again on mirror planes.

**Structure of the  $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$  Ion.** In the tetramethylammonium salt the observed distance from vanadium to the terminal ligands, 1.698 (3) Å, is the mean length of two  $\text{V}=\text{O}$  bonds and one  $\text{V}-\text{F}$  bond. One expects 1.86–1.89 Å for a terminal  $\text{V}-\text{F}$  bond and 1.62–1.64 Å for a  $\text{V}=\text{O}$  bond in a  $\text{VO}_2$  group.<sup>17</sup> The bond distances  $\text{V}-\text{O}1$ ,  $\text{V}-\text{O}2$ , and  $\text{V}-\text{F}4$ , 1.659 (2), 1.702 (2), and 1.740 (2) Å, in the tetramethylammonium-potassium salt indicate that these positions of O1, O2, and F4 are fractionally occupied by oxygen and fluorine as well. If one assumes the values of 1.620 Å for the  $\text{V}=\text{O}$  bond and of 1.860 Å for the  $\text{V}-\text{F}$  bond lengths, the observed numbers are well reproduced, taking the ratios 2:1 in the tetramethylammonium salt and 5:1, 2:1, and 1:1 for the positions O1, O2, and F4 in the tetramethylammonium-potassium compound. A calculation of valence sums for vanadium(V) with the bond length/bond strength relations of Brown and Altermatt<sup>18</sup> gives the values 4.89 and 4.92 for the compounds under discussion. The distribution of oxo and fluoro ligands in the terminal positions of the  $\text{NMe}_4-\text{K}$  salt deviates considerably from statistics. This is probably due to the different distances of O1, O2, and F4 to potassium ions in the crystal structure. The position with highest fluorine content (F4) has the shortest distance; O1 (approximately 17% fluorine occupancy) has no nearest potassium neighbor at all. The  $\text{V}-\text{F}1$ ,  $\text{V}-\text{F}2$ , and  $\text{V}-\text{F}3$  bridging bond lengths (2.095 (2)–2.114 (2) Å) fall in the usual range.<sup>17</sup> They vary slightly due to the trans effect of the oxo ligands.

**Structure of the  $[\text{V}_2\text{O}_2\text{F}_7]^{3-}$  and  $[\text{V}_2\text{F}_9]^{3-}$  Ions.** The (averaged) bond distance of the terminal ligands in  $[\text{V}_2\text{O}_2\text{F}_7]^{3-}$  is 1.783 (3) Å. One can estimate herefrom a  $\text{V}=\text{O}$  distance of 1.59 Å and a  $\text{V}-\text{F}$  (terminal) distance of 1.88 Å. The  $\text{V}-\text{F}$  (bridging) bond length is 2.071 (3) Å. Similar values have been observed in several other vanadium(IV) oxo fluoro compounds.<sup>7,12,17</sup> Valence sum calculations<sup>18</sup> gave exactly 4.0 for vanadium(IV). Despite the large difference between  $\text{V}=\text{O}$  and  $\text{V}-\text{F}$  bond distances, oxygen and fluorine atoms are not resolved in electron density maps. Also no unusual anisotropic behavior was observed for this site. Inspection of the thermal ellipsoids of the vanadium atoms in the structures of  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  and  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$  (see Figures 1 and 2) reveals that the central atoms and not the ligands move in order to control the distances to the terminal oxo or fluoro ligands.

In the  $[\text{V}_2\text{F}_9]^{3-}$  ion the  $\text{V}-\text{F}$  (terminal) and  $\text{V}-\text{F}$  (bridging) bond lengths are 1.847 (3) and 2.044 (3) Å, respectively. For comparison, the  $\text{V}-\text{F}$  bond distances in the elpasolite type compounds  $\text{M}'\text{M}_2''\text{VF}_6$  ( $\text{M}'$ ,  $\text{M}'' = \text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ ) are 1.94–1.95 Å.<sup>19</sup>

The main points of interest are the dimensions and the structural changes within the  $\text{V}_2(\text{O},\text{F})_9$  double octahedra. Their geometry is mainly determined by the repulsion between the positively charged metal atoms, which varies with the oxidation state of

vanadium. The metal-metal distances decrease from 3.138 (1) (3.093 (1) Å in the  $\text{NMe}_4-\text{K}$  salt) to 2.977 (2) and finally to 2.894 (3) Å in the series  $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ ,  $[\text{V}_2\text{O}_2\text{F}_7]^{3-}$ ,  $[\text{V}_2\text{F}_9]^{3-}$ . Slightly different distances have been observed for  $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$  (3.07 (7) Å, 5) and  $\text{Cs}_3\text{V}_2\text{O}_2\text{F}_7$  (2.99 (4) Å<sup>7</sup>).  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  is the first  $\text{A}_3\text{M}_2\text{X}_9$  type compound of vanadium(III), where the  $\text{V}-\text{V}$  distance has been determined exactly. The negatively charged  $(\mu-\text{F})_3$  groups of the compounds under discussion have remarkably short nonbonding  $\text{F}\cdots\text{F}$  contacts (2.454 (5) to 2.500 (6) Å). They diminish therefore the repulsion between the metal atoms considerably. The  $\text{V}-\text{F}$  (bridging) bond distances increase with oxidation number from 2.044 (3) to 2.114 (2) Å due to the increasing metal-metal distance and due to the trans effect of the terminal  $\text{V}=\text{O}$  bonds in  $[\text{V}_2\text{O}_2\text{F}_7]^{3-}$  and  $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ . The combined effects lead to a drastic change in the ratio  $d':d''$  in Cotton and Ucko's notation,<sup>20</sup> from 1.52 in  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  to 2.04 and 2.10 in  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$  and  $(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5\cdot\text{H}_2\text{O}$ , respectively. Two further structures,  $\text{V}_4(\text{P}_2\text{O}_7)_3$ <sup>21</sup> and  $(\text{PPh}_4)_2[\text{V}_2\text{Cl}_9][\text{VCl}_3]\cdot\text{CH}_2\text{Cl}_2$ <sup>22</sup> containing vanadium-centered double octahedra, were characterized recently. In the former compound two types of  $[\text{V}_2\text{O}_9]$  groups are present, with vanadium(III)-vanadium(III) distances of 2.774 (8) and 3.026 (7) Å. The vanadium(IV)-vanadium(IV) distance in the  $[\text{V}_2\text{Cl}_9]^-$  ion of the latter compound is 3.325 (3) Å.

$\text{A}_3\text{M}_2\text{X}_9$  type compounds show interesting magnetic properties, as revealed by careful studies on  $\text{Cs}_3\text{Fe}_2\text{F}_9$ ,<sup>10</sup>  $\text{Cs}_3\text{V}_2\text{O}_2\text{F}_7$ ,<sup>23</sup>  $\text{A}_3\text{Cr}_2\text{X}_9$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}^{24}$ ),  $\text{Cs}_3\text{V}_2\text{Cl}_9$ , and  $\text{Rb}_3\text{V}_2\text{Br}_9$ .<sup>1b</sup> No detailed studies of  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$  and  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  have been performed so far. But here the interdimer interaction may well be separated from intradimer interactions.<sup>10</sup> Measurement of the magnetic moment of  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$  at varying fields at room temperature gives  $\mu_{\text{eff}} = 2.65 \mu_{\text{B}}$  per vanadium atom.

A more general discussion of the structural and magnetic properties of  $\text{A}_3\text{M}_2(\text{O},\text{F})_9$  compounds including  $(\text{NMe}_4)_3\text{Cr}_2\text{F}_9$  and  $(\text{NMe}_4)_3\text{Fe}_2\text{F}_9$ <sup>25</sup> will be presented elsewhere.

**Acknowledgment.** We thank the Fonds der Deutschen Chemischen Industrie for support.

**Registry No.**  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$ , 114397-63-6;  $(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5\cdot\text{H}_2\text{O}$ , 114397-65-8;  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$ , 114397-67-0;  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$ , 114397-69-2;  $(\text{NMe}_4)_2[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]$ , 79776-23-1.

**Supplementary Material Available:** For  $(\text{NMe}_4)_3\text{V}_2\text{F}_9$ ,  $(\text{NMe}_4)_3\text{V}_2\text{O}_2\text{F}_7$ ,  $(\text{NMe}_4)_3\text{V}_2\text{O}_4\text{F}_5$ , and  $(\text{NMe}_4)_2\text{KV}_2\text{O}_4\text{F}_5\cdot\text{H}_2\text{O}$ , tables of thermal parameters for the non-hydrogen atoms and hydrogen atom parameters (4 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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