

## SYNTHESIS AND CRYSTAL STRUCTURE OF LUTIDIUM AQUAFLUOROOXOVANADATE(IV)<sup>†</sup>

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### Abstract

The complex  $(\text{LutH})_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  was prepared from aqueous HF solution of  $\text{VO}^{2+}$  and lutidine. The X-ray structure revealed dimeric anions connected to the chain by hydrogen bonds. The effect of the cation and intraionic hydrogen bonds on the stability of the bioctahedral anion is discussed.

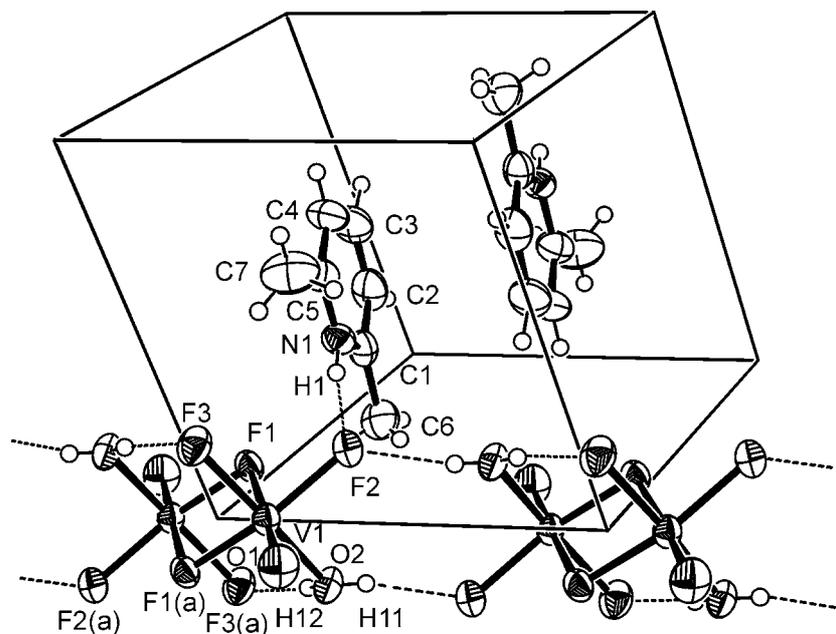
### Introduction

Structures of fluorides and fluorometallates of 3d transition metals and smaller main group metals (Li, Na, Mg, Al) relate with a few exceptions to the arrangement of octahedra. The octahedra are in most cases either isolated or connected into chains, sheets or three-dimensional networks. Fewer are oligomers built from two to five octahedra.<sup>1</sup> For example, the edge-shared bioctahedral unit was reported only recently in  $(\text{PyH})_4[\text{Al}_2\text{F}_{10}]$ .<sup>2</sup> The structures of metallic oxofluorides and oxofluorometallates as well as aquafluorometallates resemble the structures of fluorides and fluorometallates due to similar size of fluorine and oxygen atoms. The bioctahedral edge-shared unit with two metal-fluorine-metal bridges was found in structures of  $(\text{R}_4\text{N})_2[\text{M}_2\text{F}_8(\text{H}_2\text{O})_2]$  ( $\text{R} = \text{Me}$ ,  $\text{M} = \text{Fe}$ ,  $\text{Al}$ )<sup>3-5</sup> and  $(\text{R}_4\text{N})_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ).<sup>6,7</sup> The oligomeric fluorides exhibits interesting magnetic and conductive properties when compared to compounds with isolated octahedra or polymeric structures.<sup>1,8</sup> In addition, the dehydration of  $[(\text{CH}_3)_4\text{N}]_2[\text{Al}_2\text{F}_8(\text{H}_2\text{O})_2]$  afforded  $(\text{CH}_3)_4\text{N}[\text{AlF}_4]$  as the first tetrahedral fluoroaluminate.<sup>3,5</sup> Thermal decomposition of this compounds resulted in a new, porous polymorph of aluminum fluoride.<sup>9,10</sup> Herein, we report the synthesis and characterization, including X-ray structure of  $(\text{LutH})_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  **1** ( $\text{Lut} = \text{lutidine}$ ,

2,6-dimethylpyridine). The role of cation on the formation of the bioctahedral unit is discussed.

### Results and discussion

The compound **1** crystallizes as blue crystals from the solution of  $\text{VO}^{2+}$  in 10% aqueous HF after addition of lutidine (lutidine :  $\text{VO}^{2+}$  mol ratio was 5:1). The X-ray structure determination shows bioctahedral anions  $[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]^{2-}$  connected into chains by fluorine–water hydrogen bonds (Figure 1, Tables 1 and 2). Lutidinium cation is hydrogen-bonded to the terminal fluorine atom of the anion. The structure of anion is similar to the structure of anion found in  $(\text{R}_4\text{N})_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  ( $\text{R} = \text{Me}, \text{Et}$ ).<sup>6,7</sup> Vanadium atom is six-coordinated by two terminal and two bridging fluorine atoms, oxygen atom (oxo ligand) and water molecule. Two bridging fluorine atoms are at distances of 1.938(1) and 2.189(1) Å with the longer distance in trans position to oxo ligand. All water hydrogen atoms form strong hydrogen bonds. There are two intraionic hydrogen bonds within  $[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]^{2-}$  with the distance  $\text{F}(3)\cdots\text{H}(12)\text{--}\text{O}(2)$  2.670(2) Å and angle 158(3)°. The distances  $\text{F}(3)\cdots\text{H}(12)$  and  $\text{H}(12)\text{--}\text{O}(2)$  are 1.80(4) and 0.91(4) Å, respectively. The hydrogen bond energy of 29 kJ mol<sup>-1</sup> was estimated from IR spectra for analogous hydrogen bond (distance 2.686 Å) in  $[(\text{CH}_3)_4\text{N}]_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$ .<sup>6</sup> The dissociation of  $[(\text{C}_5\text{Me}_5)_4\text{Ti}_4\text{F}_{13}\text{Li}]$  with the cleavage



**Figure 1.** Molecular structure of  $(\text{LutH})_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  **1**.

of two Ti(IV)–F–Ti(IV) bridging bonds is endothermic at  $75 \text{ kJ mol}^{-1}$ .<sup>11</sup> We used these values for a rough evaluation of bonding energies within bioctahedral anion in **1**. The contribution of two hydrogen bonds ( $58 \text{ kJ mol}^{-1}$ ) seems comparable to the contribution of two V(IV)–F–V(IV) bridging bonds ( $75 \text{ kJ mol}^{-1}$ ). Therefore the intraionic hydrogen bonds in  $[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]^{2-}$  are likely important for stability of this bioctahedral anion. However, the dehydration of  $[(\text{CH}_3)_4\text{N}]_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  leaves anhydrous product with  $[\text{VOF}_3]^-$  anions coupled to some extent and with no center of symmetry.<sup>6</sup> On the other hand, the dehydration of  $[(\text{CH}_3)_4\text{N}]_2[\text{Al}_2\text{F}_8(\text{H}_2\text{O})_2]$  resulted in free tetrahedral  $[\text{AlF}_4]^-$  anions.<sup>3,5</sup> This anion was also observed by  $^{19}\text{F}$  NMR spectroscopy in acetonitrile solution of  $[(\text{CH}_3)_4\text{N}]_2[\text{Al}_2\text{F}_8(\text{H}_2\text{O})_2]$ .<sup>5</sup>

The hydrogen bonds connecting anions  $[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]^{2-}$  to the chain are very short and nearly linear. The distance  $\text{F}(2)\cdots\text{H}(11)\text{--}\text{O}(2)$  is  $2.607(2) \text{ \AA}$  and the angle is  $167(3)^\circ$ . The hydrogen atom is at distances  $\text{F}(2)\cdots\text{H}(11)$   $1.93(3) \text{ \AA}$  and  $\text{H}(11)\text{--}\text{O}(2)$   $0.69(4) \text{ \AA}$ . However much shorter intraionic hydrogen bond of coordinated fluorine to water of  $2.437 \text{ \AA}$  was found in dicobalt pyrazolate complex.<sup>12</sup> The lutidinium cation forms a hydrogen bond to terminal fluorine with distance of  $2.775(2) \text{ \AA}$ . The lutidinium–fluorine hydrogen bond does not alter the pattern of intra- and interionic hydrogen bonding in **1** in comparison to bioctahedral aquafluorometallates with tetraalkylammonium cations.<sup>6,7</sup> We can conclude that interaction of coordinated fluorines and cations are very weak in aquafluorometallates with large tetraalkylammonium and lutidinium cations. Consequently all the coordinated fluorines could be strong acceptors of hydrogen bonds from coordinated water molecules. This intra- and interionic hydrogen bond network likely stabilizes the bioctahedral unit in **1** and in related aquafluorometalates.

The IR spectrum of **1** shows very broad absorption of stretching vibrations of the N–H and O–H bonds from  $3000$  to  $3300 \text{ cm}^{-1}$  and terminal fluorine stretching vibrations at  $500 \text{ cm}^{-1}$ . The V=O stretching appears at  $976 \text{ cm}^{-1}$  characteristic for oxo ligand not involved in hydrogen bond.<sup>6, 13</sup> The absorptions of lutidinium cation are at expected frequencies.

**Table 1.** Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms for **1**

	x/a	y/b	z/c	U <sub>eq</sub>
V1	0.20690(4)	0.94195(3)	0.90077(3)	0.0304(1)
F1	0.04028(13)	0.91761(12)	1.13053(10)	0.0340(3)
F2	0.40124(14)	0.80220(13)	1.02156(12)	0.0393(3)
F3	0.09366(16)	0.74797(13)	0.91117(13)	0.0457(3)
O1	0.3213(2)	0.9753(2)	0.73121(15)	0.0513(4)
O2	0.2586(2)	1.15640(18)	0.95100(17)	0.0405(4)
N1	0.7279(2)	0.35434(19)	0.67548(17)	0.0375(4)
C1	0.7526(3)	0.2760(2)	0.5609(2)	0.0402(5)
C2	0.7762(3)	0.3776(3)	0.4122(2)	0.0547(7)
C3	0.7731(4)	0.5509(3)	0.3869(3)	0.0636(8)
C4	0.7473(4)	0.6234(3)	0.5077(3)	0.0588(7)
C5	0.7254(3)	0.5227(2)	0.6557(2)	0.0465(6)
C6	0.7515(5)	0.0893(3)	0.6028(3)	0.0554(8)
C7	0.7008(6)	0.5868(4)	0.7960(4)	0.0756(12)

U<sub>eq</sub> = 1/3 of the trace of the orthogonalized U Tensor

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**

V1-F1	2.1893(11)	F2-V1-F3	92.22(6)
V1-F2	1.9339(12)	F2-V1-O1	102.47(7)
V1-F3	1.9103(12)	F2-V1-O2	89.60(6)
V1-O1	1.5883(14)	F1(a)-V1-F2	155.05(5)
V1-O2	2.0708(16)	F3-V1-O1	101.14(7)
V1-F1(a)	1.9380(11)	F3-V1-O2	160.91(6)
N1-H1	0.78(3)	F1(a)-V1-F3	88.01(6)
F1-V1-F2	80.64(5)	O1-V1-O2	97.01(8)
F1-V1-F3	81.91(5)	F1(a)-V1-O1	101.96(7)
F1-V1-O1	175.48(7)	F1(a)-V1-O2	82.45(6)
F1-V1-O2	79.64(6)	V1-F1-V1(a)	105.31(5)
F1-V1-F1(a)	74.69(5)		

The thermal decomposition proceeds in four overlapping steps with mass loss 15.2, 25.9, 8.6 and 16.6% in corresponding temperature ranges 100–160 °C, 160–220 °C, 220–330 °C and 330–580 °C. No stable intermediate was observed in thermogravimetric curve and no stoichiometry of decomposition could be proposed from mass loss.

### Experimental

**General Considerations.** Infrared spectra (Nujol) were recorded on a Perkin-Elmer FT-1720X spectrometer. Elemental analyses were carried out on Perkin-Elmer 2400 CHN analyser at the University of Ljubljana (Department of Organic Chemistry). Thermogravimetric analysis was done on a Mettler 2000C in the atmosphere of argon.

**Table 3.** Crystallographic Data for **1**

Chemical formula	C <sub>14</sub> H <sub>24</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> V <sub>2</sub>
Molecular weight	500.23
Crystal system	Triclinic
Space group	P1-(No. 2)
a(Å)	7.1910(10)
b(Å)	8.253(2)
c(Å)	9.195(2)
α(°)	73.38(3)
β(°)	78.59(3)
γ(°)	78.22(3)
V(Å <sup>3</sup> )	506.2(2)
Z	1
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.641
μ (cm <sup>-1</sup> )	0.998
Crystal size (mm)	0.2 x 0.15 x 0.15
θ Range (°)	2.6, 28.3
Tot. no. coll. data	4072
No. of unique data	2054
R(int)	0.010
No. of obs. data	1945
Threshold	[I>2.0σ(I)]
Numbers of par.	176
R (observed)	0.0279
wR <sub>2</sub> (obs.)	0.0760
S	1.08
Largest difference peak and hole(eÅ <sup>-3</sup> )	-0.35, 0.26

$$R=3(|F_o|-|F_c|)/3|F_o|. \quad wR_2=(3[w(F_o^2-F_c^2)^2]/3(wF_o^2)^2)^{1/2}.$$

**(LutH)<sub>2</sub>[V<sub>2</sub>F<sub>6</sub>O<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] 1.** Vanadium pentaoxide (5 mmol, 0.94 g) was dissolved in 40 mL of 10 % HF in Teflon becher. Gaseous SO<sub>2</sub> was bubbled into solution for 20 min. The solution was heated on a water bath for 0.5 h, cooled to room temperature and 2,6-dimethylpyridine (50 mmol, 5.3 g) was added. The blue crystals of **1** appeared in 5 days. The crystals were filtered and washed with acetone. Yield 2.3 g (46%). *Anal.*

Calculated for  $C_{14}H_{24}F_6N_2O_4V_2$ : C, 33.62; H, 4.84; N, 5.60, V, 20.37. Found: C, 33.27; H, 4.75; N, 5.39; V, 21.0. IR ( $cm^{-1}$ , Nujol): 3284, 3180, 3077, 1643, 1625, 1550, 1274, 1180, 1056, 976, 811, 561, 502.

**X-ray Crystallography.** The details of crystal data collection and refinement parameters for  $(LutH)_2[V_2F_6O_2(H_2O)_2]$  **1** are listed in Table 1. Data were collected with an Kappa-CCD Nonius diffractometer using graphite monochromated  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods implemented in SHELXS86<sup>14</sup> and refined with SHELX97.<sup>15</sup> All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were refined isotropically having isotropic displacement parameters taken from those of attached heavy atoms and multiplied by 1.2. Supplementary data (X-ray crystallographic files, in CIF format) are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition number CCDC 184130 for the structure **1**.

### Acknowledgements

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**Povzetek**

Akvaoksofluorovanadat(IV)  $(\text{LutH})_2[\text{V}_2\text{F}_6\text{O}_2(\text{H}_2\text{O})_2]$  (Lut = lutidin; 2,6-dimethylpiridin) kristalizira iz raztopine  $\text{VO}^{2+}$  in lutidina v 10 % HF. V kristalni strukturi so anioni kot dvojni oktaedri, povezani preko skupnega roba in z dvema vodikovima vezema. Vodikove vezi povezujejo anione v verigo.