CROATICA CHEMICA ACTA CCACAA 57 (4) 673—677 (1984)

YU ISSN 0011—1643
CCA-1482 UDC 546.881
Original Scientific Paper

Synthesis and Crystal Structure of Tetraethylammonium Di-μ-fluoro-bis[aquadifluoro-oxovanadate(IV)]*

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Received November 27, 1983

The title complex, $[NEt_4]_2[V_2O_2F_6(H_2O)_2]$, has been isolated from an aqueous solution of VOF_2 and $[NEt_4]F$. The crystal structure has been determined from threedimensional counter X-ray data. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 708.8(1)$, $b = 1316.6(2)$, $c = 1362.4(2)$ pm, $\beta = 97.58(1)°$ and $Z = 2$. Least-squares refinement of the structure based on 1523 observations led to final discrepancy indices of $R = 0.058$ and $R_w = 0.067$. The structure consists of discrete dinuclear units $[V_2O_2F_6(H_2O)_2]^{2-}$ with a crystallographic centre of inversion. Dimeric units are linked into chains by hydrogen bonds [O—H ... F 259.1(5) and 267.9(5) pm]. The geometry around vanadium is distorted octahedral with V—F distances from 192.0(4) to 220.9(3) pm, V—O 159.4(4) pm, V—OH_2 208.3(4) pm, V—V 332.8(1) pm, and V—F—V 106.0(2)°.

INTRODUCTION

There is a wide interest in the study of oxovanadium(IV) complexes.[1] Fluorooxovanadates(IV) were manly prepared with alkali and ammonium ions[2,3] and show different stoichiometries. Isolated $[VOF_5]^{3-}$ octahedra were found in $M_3^I[VOF_5]$[2] and $[M^{III}(NH_3)_6][VOF_5]$[4], connected to cis-chains in $K_2[VOF_4]$[5] and $(NH_4)_2[VOF_4]$[6], or to complex chains in $Cs[VOF_3] \cdot 0.5\,H_2O$.[7] Recently a new type of complex, $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$, with a dinuclear anion has been reported.[8]

In this paper we describe the synthesis and X-ray crystallographic characterization of $[NEt_4]_2[V_2O_2F_6(H_2O)_2]$, another dinuclear oxofluorovanadate.

EXPERIMENTAL

Preparation

Tetraethylammonium fluoride solution was obtained by neutralization of the corresponding hydroxide (25% B. D. H. Chemicals) with 20% hydrogen fluoride to pH 5.

0.01 mol of vanadium pentoxide in 40 ml hydrogen fluoride (10%) was reduced with sulphur dioxide and the excess of SO_2 driven off in a water bath. A solution of tetraethylammonium fluoride (0.20 mol) was added. In a few days blue crystals were formed which were filtered off, washed with ethanol and dried over KOH. Found: 18.81% V; 21.81% F; 5.08% N; 6.30% H_2O. $[N(C_2H_5)_4]_2[V_2O_2F_6(H_2O)_2]$, requires: 18.71% V; 20.94% F; 5.14% N; 6.62% H_2O.

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

Crystal Data

$[N(C_2H_5)_4]_2[V_2O_2F_6(H_2O)_2]$, M = 544.40, Monoclinic, $P2_1/n$, $a = 708.8(1)$, $b = 1316.6(2)$, $c = 1362.4(2)$ pm, $\beta = 97.58(1)°$, $Z = 2$, D_m (by flotation) 1.42, $D_c = 1.434$ g cm^{-3}, μ (Mo-Kα) = 8.6 cm^{-1}, $\lambda = 0.71069$ Å.

Preliminary cell dimensions and space-group symmetry were determined from oscillation and Weissenberg photographs taken with Cu-Kα radiation. Accurate cell parameters were obtained by least-squares treatment of 60 high-angle reflections, collected on an Enraf-Nonius CAD-4 automatic diffractometer, using graphite-monochromated Mo-Kα radiation. Intensity data were collected from a crystal of dimensions $0.3 \times 0.2 \times 0.1$ mm with the $\omega - 2\Theta$ scan technique. A total of 3057 reflections were measured in the interval $1.0 < \Theta < 27.0°$. The symmetry related reflections were averaged giving a mean discrepancy of I = 1.3%. The final set contains 2739 independent reflections of which 1523 with $I_o > 2\sigma(I_o)$ (obtained from counting statistics) were considered observed and used for the structure analysis. The data were corrected for Lorenz and polarization effects, but no absorption corrections were applied.

The position of the vanadium atom was determined from a three-dimensional Patterson map. Positions for the other non-hydrogen atoms were established from F_o Fourier synthesis. At this stage there were three possibilities for placing the oxygen atom of the water molecule. By choosing the same position in the dinuclear anion as in $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$[8] the best agreement was obtained (R = 0.090). Calculated positions of methylene hydrogen atoms improved the R value to 0.084. After refinement with anisotropic temperature factors (R = 0.065) the difference electron-density map revealed hydrogen atoms of the water molecule as well as 8 od 12 methyl hydrogens. Hydrogen atoms were included in the final refinement as invariants with isotropic thermal parameters, $U = 0.06$ Å^2. Refinement terminated at R 0.058 $(= \Sigma|\Delta F|/\Sigma|F_o|)$ and R_w $0.067 = |\Sigma w(\Delta F)^2/\Sigma w(F_o)^2|^{1/2}$. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weighting function $w = W_F W_S$ was determined empirically from $W_F(|F_o| < 12.0) = (|F_o|/12.0)^{5.0}$, $W_F(F_o > 35.0) = (35.0/|F_o|)^{2.0}$, and $W_F(12.0 < |F_o| < 35.0) = 1.0$, and $W_S(\sin\Theta < 0.25) = (\sin\Theta/0.25)^{2.0}$, $W_S(\sin\Theta > 0.40) = (0.40/\sin\Theta)^{4.0}$, and $W_S(0.25 < \sin\Theta < 0.40) = 1.0$.

The atomic scattering factors for H atoms were taken from ref. 9 and for the other atoms from ref. 10, with those of non-hydrogen atoms corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 11. All the calculations were carried out on the CDC CYBER 72 computer at RRC Ljubljana using »X-Ray 72« systems of crystallographic programs.[12]

RESULTS AND DISCUSSION

Positional parameters for the structure are given in Table I*. Interatomic distances and angles are given in Table II. The structure, illustrated in Figure 1, consists of dinuclear $[V_2O_2F_6(H_2O)_2]^{2-}$ anions and $[NEt_4]^+$ cations. Vanadium is octahedrally coordinated by four fluorine atoms, the oxygen atom of the vanadyl group and the water molecule. The structure bears a close resemblance to triclinic $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$[8], where the same anion is present. The anion in $[NEt_4]_2[V_2O_2F_6(H_2O)_2]$ is centrosymmetric with a V—V bond distance of 332.8(1) pm in comparison with 329.2(1) pm in $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$[8]. The four V—F bonds and the V—OH$_2$ distance in the »tetraethyl« compound are also longer (4—8 pm) in comparison to the »tetramethyl« one. In contrast the V = O distance of 159.4(4) pm in $[NEt_4]_2[V_2O_2F_6(H_2O)_2]$ is 1.3 pm shorter than the corresponding one in $[NMe_4]_2[V_2O_2F_6(H_2O)_2]$; this means that »$VF_4O_2$« octahedra become more distorted with larger cations. The difference in V—F(1) bond distances could be explained by the trans influence of vanadyl oxygen. This effect has already been observed in fluorooxovanadates(IV).[8] The close

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* The atomic thermal parameters and observed and calculated structure amplitudes are available from the authors.

TABLE I

Atomic Co-ordinates with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c
V	0.3173(1)	0,5336(1)	0.4169(1)
F(1)	0.559(4)	0.4618(3)	0.4255(4)
F(2)	0.1041(4)	0.6023(3)	0.4603(3)
F(3)	0.4615(5)	0.6578(3)	0.4165(2)
O(1)	0.2438(6)	0.5188(4)	0.3021(3)
O(2)	0.2182(5)	0.3977(3)	0.4694(3)
N(1)	0.7368(7)	0.2235(4)	0.3090(4)
C(1)	0.8321(10)	0.3266(5)	0.3021(5)
C(2)	0.8869(11)	0.3533(6)	0.2014(5)
C(3)	0.6655(11)	0.2213(6)	0.4094(5)
C(4)	0.5834(14)	0.1199(7)	0.4357(7)
C(5)	0.5765(10)	0.2096(6)	0.2257(6)
C(6)	0.4200(12)	0.2881(8)	0.2219(8)
C(7)	0.8784(10)	0.1384(5)	0.2989(5)
C(8)	1.0422(11)	0.1311(8)	0.3826(7)
H(1)	0.7348	0.3843	0.3220
H(2)	0.9595	0.3278	0.3557
H(3)	0.9672	0.2921	0.1744
H(4)	0.7601	0.3670	0.1493
H(5)	0.7846	0.2397	0.4663
H(6)	0.5579	0.2800	0.4111
H(7)	0.5198	0.1257	0.5032
H(8)	0.4761	0.0946	0.3763
H(9)	0.6353	0.2119	0.1557
H(10)	0.5124	0.1360	0.2330
H(11)	0.4781	0.3614	0.2049
H(12)	0.3077	0.2680	0.1636
H(13)	0.8004	0.0666	0.2961
H(14)	0.9359	0.1481	0.2301
H(15)	1.1349	0.0686	0.3695
H(16)	1.1246	0.2012	0.3865
H(17)	0.3246	0.3785	0.5138
H(18)	0.1224	0.4019	0.5020

TABLE II

Interatomic Distances (pm) and Angles (°) with Estimated Standard Deviations in Parentheses

a) Intramolecular distances and angles in $[V_2O_2F_6(OH_2)_2]^{2-}$

V — F(1)	195.2(3)	F(2) — V — O(1)	101.03(19)
V — F(2)	192.0(4)	F(2) — V — O(2)	89.06(16)
V — F(3)	192.8(3)	F(3) — V — O(1)	101.89(20)
V — F(1^{I})	220.9(3)	F(3) — V — O(2)	158.73(15)
V — O(1)	159.4(4)	O(1) — V — O(2)	98.66(21)
V — O(2)	208.3(4)	F(1^{I}) — V — F(1)	73.96(14)
F(1) — V — F(2)	158.80(13)	F(1^{I}) — V — F(2)	85.01(13)
F(1) — V — F(3)	87.03(14)	F(1^{I}) — V — F(3)	80.69(14)
F(1) — V — O(1)	99.84(19)	F(1^{I}) — V — O(1)	173.26(19)
F(1) — V — O(2)	84.11(15)	F(1^{I}) — V — O(2)	78.29(15)
F(2) — V — F(3)	92.33(15)		

b) Intramolecular distances and angles in $(C_2H_5)_4N^+$

N(1) — C(1)	152.4(8)	C(1) — N(1) — C(5)	110.90(49)
N(1) — C(3)	152.0(9)	C(1) — N(1) — C(7)	110.32(49)
N(1) — C(5)	150.8(8)	C(3) — N(1) — C(5)	111.61(52)
N(1) — C(7)	152.3(9)	C(3) — N(1) — C(7)	111.52(51)
C(1) — C(2)	151.5(11)	C(5) — N(1) — C(7)	106.45(50)
C(3) — C(4)	151.7(13)	N(5) — C(1) — C(2)	115.58(54)
C(5) — C(6)	151.1(12)	N(1) — C(3) — C(4)	114.36(63)
C(7) — C(8)	151.9(11)	N(1) — C(5) — C(6)	114.82(66)
C(1) — N(1) — C(3)	106.02(50)	N(1) — C(7) — C(8)	115.19(62)

Atomic contacts

O(2) — F(3^{I})	267.9(5)
O(2) — F(2^{II})	259.1(5)
F(2) — C(5^{III})	303.3(8)
F(3) — C(3^{I})	308.7(8)
V — V(^{I})	328.8(1)

Symmetry code

I: 1 — x, 1 — y, 1 — z
II: —x, 1 — y, 1 — z
III: 1/2 — x, 1/2 + y, 1/2 — z

similarity of the dimeric units in both compounds is also shown by the V—F—V bond angles of 105.5(1)° in $[NMe_4]_2 [V_2O_2F_6(H_2O)_2]$ and 106.0(2)° in $[NEt_4]_2 [V_2O_2F_6(H_2O)_2]$. The anions are linked together by short hydrogen bonds, O(2) — H(1) . . . F(2) = 259.1(5) pm, to form chains parallel to the *a* axis. The same situation was found in $[NMe_4]_2 [V_2O_2F_6(H_2O)_2]$ but the position of the chains relative to each other is different due to different cations and different space groups. Additionally there is an intramolecular hydrogen bond O(2) — — H(2) . . . F(3) of 267.9(5) pm.

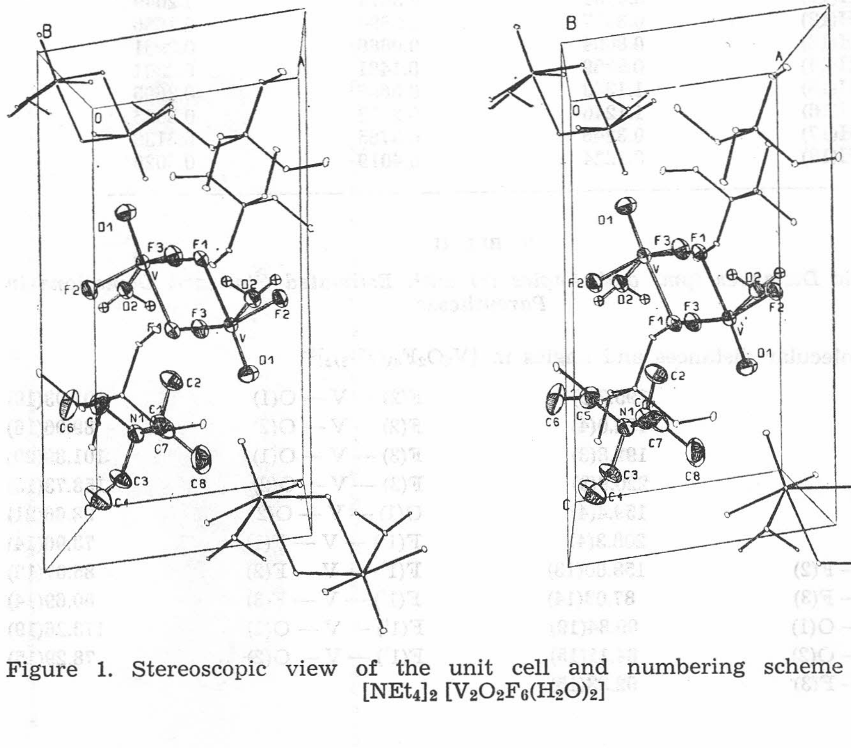

Figure 1. Stereoscopic view of the unit cell and numbering scheme used for $[NEt_4]_2 [V_2O_2F_6(H_2O)_2]$

Tetraethylammonium cations, which are located between the anionic chains, have bond lengths and angles close to the reported values.[13] The shortest $CH_2 \ldots F$ and $CH_3 \ldots F$ distances are 303.3 and 328.9 pm, respectively.

Acknowledgement. — Thanks are due to Prof. L. Golič for the collection of diffraction data.

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POVZETEK

Sinteza in kristalna struktura tetraetilamonijevega di-μ-fluoro-bis[akvadifluorooxovanadat(IV)]

Alojz Demšar in Peter Bukovec

Spojina $[Et_4N]_2\,[V_2O_2F_6(H_2O)_2]$ je bila izolirana iz vodne raztopine VOF_2 in $Et_4N\,F$. Kompleks kristalizira v monoklinski prostorski skupini $P2_1/n$, $a = 708{,}8(1)$, $b = 1316.6(2)$, $c = 1362.4(2)$ pm, $\beta = 97.58(1)^\circ$, $Z = 2$. Piljenje strukture s 1523 podatki se je končalo s faktorji ujemanja $R = 0.058$ in $R_w = 0.067$.

Struktura je sestavljena iz dvojedrnih enot $[V_2O_2F_6(H_2O)_2]^{2-}$, ki imajo center inverzije. Dimerni anioni so povezani v verige z vodikovimi vezmi [O—H ... F 259.1(5) in 267.9(5) pm]. Geometrija okrog vanadija je deformiran oktaeder z V—F razdaljami od 192.0(4) do 220.9(3) pm, V—O 159.4(4) pm, V—OH_2 208.3(4) pm, V—V 332.8(1) pm in V—F—V 106.0(2)°.