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Dinuclear and Polynuclear Oxovanadium(IV) Compounds. 2. A Complicated Sodium Oxovanadium(IV) Trifluoroacetate Compound, $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$

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After the solid products obtained anaerobically from the reaction of $VCl_2 \cdot 2THF$ with CF_3CO_2Na in a CH_2Cl_2/THF mixture have been separated, the mother liquor can be evaporated under moist air to yield the title compound, as light blue crystals. By X-ray crystallography the formula was established and the structure determined. The structure consists of cyclic, centrosymmetric $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$ units. Each V^{IV} atom forms a very short bond, 1.591 (2) Å, to an oxygen atom ($\nu_{V=O}$ = 981 cm^{-1}) and trans to this binds a THF molecule, V–O = 2.290 (2) Å. Four oxygen atoms, one from each of four $CF_3CO_2^-$ ions, complete a distorted octahedron with V–O(av) = 2.004 [2] Å. These $V(O)(THF)(CF_3CO_2)_4$ units then embrace, and are linked together by, four Na^+ ions, using the other carboxyl oxygen atoms. The Na^+ ions are also coordinated by the remaining THF molecules and the water molecules. The coordination about the Na^+ ions is irregular. The compound crystallizes in space group $P\bar{1}$ with the following unit cell parameters: a = 13.367 (5) Å; b = 14.686 (4) Å; c = 9.684 (5) Å; α = 102.70 (3)°; β = 93.88 (3)°; γ = 110.57 (2)°; V = 1714 (3) Å^3; Z = 1.

Introduction

We have been engaged in a comprehensive study of the chemistry of vanadium in its lower (ca. +3) oxidation states and, particularly, in the reactions of $VCl_2 \cdot 2THF$ and $VCl_3 \cdot 3THF$ with various reagents such as carboxylic acids.[1-3] In this report we describe a secondary product, obtained after the initial lower valent vanadium compounds have been separated, that can be obtained from the reaction of $VCl_2 \cdot 2THF$ with CF_3CO_2Na in a CH_2Cl_2/THF solvent mixture.

Experimental Section

All chemical operations were conducted under an atmosphere of dry argon, except where stated otherwise, with use of standard Schlenk techniques. Dichloromethane was dried over P_2O_5 and THF over sodium/potassium amalgam. Each solvent was purged with argon, distilled immediately before use, and transferred by syringe.

Synthesis and Crystallization of $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$. $VCl_2 \cdot 2THF$[4] (1 equiv) and sodium trifluoroacetate (2 equiv) were placed in an air-free, three-necked flask. Dichloromethane and THF (3:1) were added, and the mixture was stirred overnight. The resulting red/green solution on filtration (i.e., removal of NaCl), evaporation, and cooling yields green $[V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3]$,[2] black $[V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3 \cdot 0.5THF \cdot 0.5CH_2Cl_2]$,[3] and an as yet unidentified red-orange crystalline product, under varying conditions.[2,3] In addition, slow evaporation of the filtered reaction mixture under moist air affords large quantities of light blue crystals as the sole isolable product under these conditions. The composition and structure of this latter compound have now been determined by X-ray crystallography, showing it to be $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$. IR (2% KBr disk): $\nu_{O\text{-}H}$ 3600 (br), $\nu_{V=O}$ 981 (s) cm^{-1}.

X-ray Structure Determination. A single well-formed, regularly shaped, light blue crystal was sealed in a glass capillary with epoxy cement and transferred to a Syntex $P\bar{1}$ automated diffractometer. Least-squares refinement of 15 intense reflections in the range 20° ≤ 2θ ≤ 30° gave an orientation matrix for calculation of setting angles and cell parameters. A triclinic cell was used with the parameters presented in Table I. A total of 6063 unique reflections were measured at room temperature, of which 4023 had intensity, I, exceeding $3\sigma(I)$ and were considered observed. The data set was corrected for Lorentz and polarization effects; with μ(Mo Kα) as 4.184 cm^{-1} no absorption correction was deemed necessary.

The structure was solved by Patterson and Fourier methods and refined[5] by the full-matrix least-squares procedure. A Patterson synthesis provided the unique vanadium atom position, and three cycles of isotropic refinement produced values of R_1 = 0.54 and R_2 = 0.60 where the R_i values are defined as

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$
$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

At this stage a difference Fourier map indicated the presence of two sodium atoms per asymmetric unit and the molecule therefore appeared to contain an array of four sodium and two vanadium atoms located around a center of inversion at 0, 0, 0. Successive difference Fourier syntheses revealed a total of eight crystallographically distinct coordinated ligands (four trifluoroacetate groups, three THF molecules, and one molecule of water) in the asymmetric unit. The presence of coordinated water was later confirmed by observations of the expected broad $\nu_{O\text{-}H}$ absorption in the infrared spectrum of the compound. The fluorine atoms of three trifluoroacetate groups were found to be subject to twofold disorder (all equal occupancies) while the fourth showed a well-defined (equal occupancy) fourfold disorder. One THF molecule was refined with use of a 70:30 disordered model. Attempts at refining probable disorder of the remaining THF ligands proved unsuccessful, however, and they were each treated in only one

Table I. Crystallographic Data and Syntex $P\bar{1}$ Data Collection Parameters

formula	$V_2Na_4F_{24}O_{26}C_{40}H_{52}$
space group	$P\bar{1}$
a, Å	13.367 (5)
b, Å	14.686 (4)
c, Å	9.684 (5)
α, deg	102.70 (3)
β, deg	93.88 (3)
γ, deg	110.57 (2)
V, Å^3	1714 (3)
d_{calcd}, g/cm^3	1.550
Z	1
radiation	graphite-monochromated Mo Kα (λ_α = 0.710 73 Å)
fw	1598.67
cryst size, mm	0.5 × 0.5 × 0.4
μ(Mo Kα), cm^{-1}	4.184
range 2θ, deg	$+h, \pm k, \pm l$; $0 \leq 2\theta \leq 50$
scan type	θ–2θ
no. of unique data	6063
no. of data, $F_o^2 > 3\sigma(F_o^2)$	4023
no. of variables	551
p	0.07
R_1[a]	0.067
R_2[b]	0.093
goodness of fit	2.088
largest shift[a]	0.18
largest peak,[b] e/Å^3	0.41

[a] Largest parameter shift in final refinement cycle. [b] Largest peak in a final difference Fourier.

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(1) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3127.

(2) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316.

(3) Cotton, F. A.; Lewis, G. E.; Mott, G. N., papers in preparation.

(4) Hall, V. M.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69.

(5) Calculations were performed with a PDP 11/60 computer and the Enraf-Nonius Structure Determination Package with programs written chiefly by Frenz and Okaya.

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Table II. Positional Parameters and Their Estimated Standard Deviations for $Na_4(VO)_2[CF_3CO_2]_8[THF]_6[H_2O]_2$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
V(1)	0.21858 (6)	0.18451 (6)	0.08323 (8)	O(3)	0.1557 (2)	0.0530 (3)	−0.2763 (4)
Na(1)	−0.0187 (1)	0.0235 (1)	−0.2097 (2)	O(4)	0.1746 (3)	0.2902 (2)	0.0273 (4)
Na(2)	−0.1484 (1)	0.1743 (1)	−0.2542 (2)	O(5)	0.0243 (2)	0.2065 (2)	−0.1350 (3)
F(1A)	0.3008 (6)	0.0746 (11)	−0.4456 (10)	O(6)	0.2079 (3)	0.2483 (3)	0.2844 (3)
F(1B)	0.4202 (6)	0.1941 (8)	−0.2756 (9)	O(7)	0.0762 (3)	0.1404 (2)	0.3641 (4)
F(2A)	0.3790 (9)	0.2312 (8)	−0.3139 (11)	O(8)	0.3151 (3)	0.1238 (2)	0.1608 (4)
F(2B)	0.2999 (7)	0.1227 (8)	−0.4471 (7)	O(9)	0.2061 (2)	−0.0130 (2)	0.2164 (4)
F(3A)	0.4142 (5)	0.1096 (7)	−0.2691 (11)	O(10)	0.3801 (2)	0.3195 (2)	0.1458 (4)
F(3B)	0.3567 (8)	0.0337 (9)	−0.3309 (15)	O(11)	−0.0738 (3)	0.0829 (3)	−0.4325 (3)
F(4A)	0.0145 (5)	0.3736 (4)	−0.1730 (7)	O(12)	−0.2266 (3)	0.2735 (3)	−0.3430 (6)
F(4B)	0.0879 (8)	0.4381 (5)	0.0395 (8)	O(13)	−0.1807 (4)	0.2187 (4)	−0.0091 (6)
F(5B)	0.0122 (7)	0.3809 (6)	−0.1314 (12)	C(1)	0.2468 (3)	0.1112 (4)	−0.2223 (5)
F(5A)	0.0645 (7)	0.4248 (6)	0.0793 (8)	C(2)	0.3343 (5)	0.1231 (6)	−0.3192 (7)
F(6A)	0.1704 (8)	0.4499 (6)	−0.0650 (15)	C(3)	0.0949 (4)	0.2812 (3)	−0.0599 (5)
F(6B)	0.1901 (5)	0.4383 (4)	−0.1090 (8)	C(4)	0.0938 (5)	0.3847 (4)	−0.0660 (7)
F(7A)	0.2317 (8)	0.3786 (7)	0.5470 (11)	C(5)	0.1481 (4)	0.2203 (4)	0.3743 (5)
F(7B)	0.9165 (9)	0.7096 (9)	0.4198 (13)	C(6)	0.1678 (6)	0.3038 (5)	0.5114 (7)
F(7C)	0.7998 (13)	0.7144 (12)	0.3743 (19)	C(7)	0.2939 (3)	0.0447 (3)	0.2020 (5)
F(7D)	0.7229 (8)	0.6399 (8)	0.4520 (11)	C(8)	0.3952 (4)	0.0247 (4)	0.2406 (7)
F(8A)	0.8360 (7)	0.7442 (7)	0.3716 (10)	C(9A)	0.4858 (7)	0.3111 (9)	0.1152 (17)
F(8B)	0.1911 (9)	0.3922 (9)	0.4962 (13)	C(10A)	0.5599 (8)	0.4213 (10)	0.1642 (18)
F(8C)	0.0613 (12)	0.3212 (11)	0.5211 (16)	C(11A)	0.5193 (8)	0.4654 (9)	0.2795 (15)
F(8D)	0.0950 (14)	0.3703 (12)	0.4471 (19)	C(12A)	0.3943 (8)	0.4166 (8)	0.2110 (19)
F(9A)	0.1211 (10)	0.3602 (10)	0.5085 (14)	C(9B)	0.423 (1)	0.389 (1)	0.061 (2)
F(9C)	0.7463 (9)	0.6111 (8)	0.4924 (13)	C(10B)	0.513 (2)	0.477 (1)	0.183 (2)
F(9D)	0.8731 (7)	0.7273 (6)	0.3828 (9)	C(11B)	0.563 (2)	0.410 (2)	0.247 (3)
F(9B)	0.7098 (15)	0.6826 (13)	0.4294 (21)	C(12B)	0.448 (2)	0.353 (1)	0.288 (2)
F(10A)	0.4410 (5)	−0.0016 (6)	0.1117 (8)	C(13)	−0.1743 (8)	0.3679 (7)	−0.3669 (13)
F(10B)	0.3652 (7)	−0.0567 (7)	0.2687 (13)	C(14)	−0.2581 (9)	0.4069 (7)	−0.4011 (16)
F(11A)	0.3812 (4)	−0.0454 (4)	0.3159 (7)	C(15)	−0.3531 (9)	0.3379 (8)	−0.4058 (17)
F(11B)	0.4422 (5)	0.0145 (7)	0.1572 (8)	C(16)	−0.3378 (8)	0.2450 (8)	−0.3896 (16)
F(12A)	0.4750 (6)	0.0996 (6)	0.3137 (14)	C(17)	−0.1524 (8)	0.1738 (7)	0.1016 (8)
F(12B)	0.4621 (5)	0.1026 (7)	0.3474 (9)	C(18)	−0.1740 (12)	0.2117 (11)	0.2331 (15)
O(1)	0.1063 (2)	0.0909 (2)	0.0400 (3)	C(19)	−0.2183 (13)	0.2869 (12)	0.2024 (16)
O(2)	0.2823 (2)	0.1647 (3)	−0.0977 (3)	C(20)	−0.2358 (9)	0.2794 (8)	0.0446 (13)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

orientation with anisotropic thermal parameters. No disorder of the V, Na, or O–C–O (carboxylate) groups was observed, and we have no reason to suspect macroscopic crystal twinning. The refined isotropic model gave $R_1 = 0.18$ and $R_2 = 0.21$, and with anisotropic thermal parameters assigned to all atoms except the fourfold disordered fluorine atoms and the lower occupancy disordered THF carbon atoms, convergence was reached at $R_1 = 0.067$ and $R_2 = 0.093$. The error in an observation of unit weight was 2.088, and the largest shift/error in the final cycle was 0.18. A final difference synthesis exhibited random peaks as high as 0.41 e/Å^3. Final positional parameters are given in Table II. A table of thermal parameters is available as supplementary material as are values of observed and calculated structure factor amplitudes.

Results and Discussion

The entire formula unit, $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$, forms a large cyclic molecule centered at the origin of the unit cell. Since the unit cell origin is a crystallographic inversion center, the molecule itself is rigorously centrosymmetric. It is depicted in Figure 1, and a set of atoms constituting one asymmetric unit are labeled. The bond lengths and angles are listed in Table III.

The vanadium atom and its surroundings constitute a rather conventional structural moiety. The V–O(1) unit, with a bond length of 1.591 (2) Å, is a typical oxovanadium(IV) group. The infrared spectrum of the compound has a strong band at 981 cm^{-1}, which is quite typical, as is the blue color of the compound. In addition, as is usually the case, there are five additional atoms in the coordination sphere, with the bond trans to the V═O bond elongated and the angles between V═O and the other four bonds >90°. In this case the trans ligand is a tetrahydrofuran molecule, with a V–O(10) distance of 2.290 (2) Å. This THF molecule was refined with a twofold disorder (70:30 for the A and B sets of carbon atoms). The O(1)–V–O(10) group is essentially linear, 179.8 (1)°. In the equatorial plane are four carboxylato oxygen atoms, each from a different $CF_3CO_2^-$ ion, with V–O distances ranging from 1.999 (3) to 2.008 (2) Å and averaging 2.004 [2] Å. The O(1)–V–O(carboxylate) angles range 100.5 (1)–101.2 (1)° and average 100.8 [1]°.

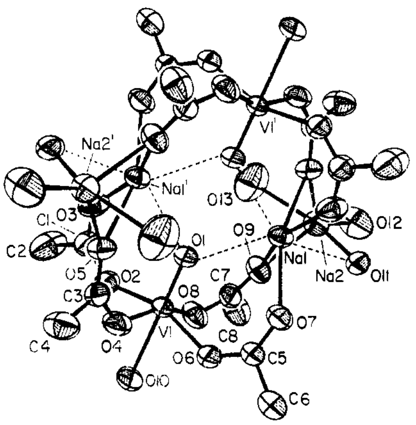

Figure 1. The $Na_4(VO)_2[CF_3CO_2]_8[THF]_6[H_2O]_2$ unit, showing the atom-labeling scheme. There is a crystallographic inversion center at the center of the ring. The fluorine atoms of the CF_3 groups and the carbon atoms of the THF molecules (whose oxygen atoms are O(10), O(12), and O(13)) are omitted.

The sodium ions occupy two crystallographically distinct positions. Na(1) has two short contacts to carboxylate oxygen atoms, O(3) and O(7), that are not coordinated to Na(2) and two longer contacts to O(5) and O(9), which are also coordinated to Na(2). There are then three other quite long Na(1) to oxygen contacts, in the range 2.62–2.65 Å, to the two vanadyl oxygen atoms, O(1) and O(1′), and to the water oxygen atom O(11), which is primarily bonded to Na(2). As can be

Table III. Bond Distances (Å) and Angles (deg) in $Na_4(VO)_2[CF_3CO_2]_8[THF]_6(H_2O)_2$

Distances

V(1)–O(1)	1.591 (2)	O(7)–C(5)	1.205 (4)	C(4)–F(4A)	1.37 (2)	C(7)–C(8)	1.524 (6)
–O(2)	2.008 (2)	O(8)–C(7)	1.255 (4)	–F(4B)	1.17 (2)	C(8)–F(10A)	1.46 (2)
–O(4)	2.004 (3)	O(9)–C(7)	1.221 (4)	–F(5A)	1.53 (2)	–F(10B)	1.22 (2)
–O(6)	2.005 (3)	O(10)–C(9A)	1.506 (8)	C(4)–F(5B)	1.20 (2)	–F(11A)	1.36 (1)
–O(8)	1.999 (3)	–C(9B)	1.43 (1)	–F(6A)	1.13 (2)	–F(11B)	1.07 (2)
–O(10)	2.290 (2)	–C(12A)	1.366 (8)	–F(6B)	1.40 (2)	–F(12A)	1.26 (2)
Na(1)–O(3)	2.378 (3)	–C(12B)	1.48 (2)	C(5)–C(6)	1.532 (7)	–F(12B)	1.35 (1)
–O(5)	2.465 (3)	O(12)–C(13)	1.395 (9)	C(6)–F(7A)	1.09 (1)	C(9A)–C(10A)	1.52 (2)
–O(7)	2.363 (3)	–C(16)	1.406 (9)	–F(7B)	1.33 (1)	C(9B)–C(10B)	1.60 (2)
–O(9)	2.450 (3)	O(13)–C(17)	1.470 (8)	–F(7C)	1.28 (2)	C(10A)–C(11A)	1.41 (2)
Na(2)–O(5)	2.348 (3)	–C(20)	1.383 (9)	–F(7D)	1.38 (1)	C(10B)–C(11B)	1.57 (4)
–O(9)	2.340 (3)	C(1)–C(2)	1.535 (6)	–F(8A)	1.46 (1)	C(11A)–C(12A)	1.60 (1)
–O(11)	2.435 (3)	C(2)–F(1A)	1.23 (2)	–F(8B)	1.27 (1)	C(11B)–C(12B)	1.59 (4)
–O(12)	2.337 (4)	–F(1B)	1.22 (1)	–F(8C)	1.54 (2)	C(13)–C(14)	1.48 (1)
–O(13)	2.429 (4)	–F(2A)	1.47 (2)	–F(8D)	1.77 (2)	C(14)–C(15)	1.31 (1)
O(2)–C(1)	1.242 (4)	–F(2B)	1.29 (1)	–F(9A)	1.20 (2)	C(15)–C(16)	1.49 (1)
O(3)–C(1)	1.214 (4)	–F(3A)	1.24 (1)	–F(9B)	1.63 (2)	C(17)–C(18)	1.37 (1)
O(4)–C(3)	1.263 (4)	–F(3B)	1.43 (2)	–F(9C)	1.38 (1)	C(18)–C(19)	1.50 (2)
O(5)–C(3)	1.204 (4)	C(3)–C(4)	1.540 (6)	–F(9D)	1.29 (1)	C(19)–C(20)	1.50 (2)
O(6)–C(5)	1.260 (4)						

Angles

O(1)-V(1)-O(2)	100.8 (1)	O(11)–Na(2)–O(12)	113.6 (2)	C(1)–C(2)–F(1B)	117.7 (7)	C(5)–C(6)–F(9C)	109.9 (7)
–O(4)	100.5 (1)	–O(13)	149.6 (2)	–F(2A)	105.4 (9)	–F(9D)	114.6 (6)
–O(6)	100.7 (1)	O(12)–Na(2)–O(13)	96.8 (2)	–F(2B)	112.9 (8)	O(8)–C(7)–O(9)	128.5 (4)
–O(8)	101.2 (1)	V(1)–O(2)–C(1)	134.9 (2)	–F(3A)	113.0 (8)	–C(8)	112.1 (3)
–O(10)	179.8 (1)	Na(1)–O(3)–C(1)	134.7 (3)	–F(3B)	103.4 (9)	O(9)–C(7)–C(8)	119.3 (4)
O(2)–V(1)–O(4)	90.1 (1)	V(1)–O(4)–C(3)	130.2 (2)	O(4)–C(3)–O(5)	130.1 (4)	C(7)–C(8)–F(10A)	110 (1)
–O(6)	158.5 (1)	Na(1)–O(5)–Na(2)	87.57 (9)	–C(4)	111.4 (3)	–F(10B)	107 (1)
–O(8)	86.3 (1)	–C(3)	138.5 (3)	O(5)–C(3)–C(4)	118.6 (4)	–F(11A)	114.6 (6)
–O(10)	79.3 (1)	Na(2)–O(5)–C(3)	133.6 (3)	C(3)–C(4)–F(4A)	110.4 (8)	–F(11B)	117 (2)
O(4)–V(1)–O(6)	86.1 (1)	V(1)–O(6)–C(5)	134.7 (2)	–F(4B)	118 (1)	–F(12A)	115.9 (9)
–O(8)	158.3 (1)	Na(1)–O(7)–C(5)	135.8 (3)	–F(5A)	104 (1)	–F(12B)	108.9 (8)
–O(10)	79.4 (1)	V(1)–O(8)–C(7)	131.3 (2)	–F(5B)	114 (1)	O(10)–C(9A)–C(10A)	99.9 (9)
O(6)–V(1)–O(8)	89.5 (1)	Na(1)–O(9)–Na(2)	88.13 (9)	–F(6A)	122 (1)	–C(9B)–C(10B)	99 (1)
–O(10)	79.13 (9)	–C(7)	139.2 (3)	–F(6B)	108.2 (8)	C(9A)–C(10A)–C(11A)	106.4 (9)
O(8)–V(1)–O(10)	78.9 (1)	Na(2)–O(9)–C(7)	132.7 (3)	O(6)–C(5)–O(7)	129.4 (4)	C(9B)–C(10B)–C(11B)	98 (2)
O(3)–Na(1)–O(5)	90.3 (1)	V(1)–O(10)–C(9A)	122.8 (4)	–C(6)	113.3 (3)	C(10A)–C(11A)–C(12A)	98 (1)
–O(7)	87.7 (1)	–C(9B)	125.4 (6)	O(7)–C(5)–C(6)	117.2 (4)	C(10B)–C(11B)–C(12B)	89 (2)
–O(9)	159.9 (1)	–C(12A)	126.0 (4)	C(5)–C(6)–F(7A)	129.5 (8)	O(10)–C(12A)–C(11A)	102.9 (8)
O(5)–Na(1)–O(7)	158.5 (1)	–C(12B)	123.4 (6)	–F(7B)	113.7 (6)	O(10)–C(12B)–C(11B)	100 (1)
–O(9)	83.53 (9)	C(9A)–O(10)–C(12A)	111.2 (5)	–F(7C)	115 (1)	O(12)–C(13)–C(14)	107.5 (8)
O(7)–Na(1)–O(9)	91.1 (1)	C(9B)–O(10)–C(12B)	110.9 (8)	–F(7D)	109.0 (7)	C(13)–C(14)–C(15)	108.5 (9)
O(5)–Na(2)–O(9)	88.6 (1)	C(13)–O(12)–C(16)	107.1 (6)	–F(8A)	105.5 (6)	C(14)–C(15)–C(16)	108.5 (9)
–O(11)	76.8 (1)	Na(2)–O(13)–C(17)	122.6 (4)	–F(8B)	116.2 (7)	O(12)–C(16)–C(15)	106.2 (9)
–O(12)	133.7 (1)	–C(20)	127.2 (6)	–F(8C)	106.8 (6)	O(13)–C(17)–C(18)	113.2 (8)
–O(13)	81.5 (1)	O(2)–C(1)–O(3)	130.0 (3)	–F(8D)	99.0 (6)	C(17)–C(18)–C(19)	101 (1)
O(9)–Na(2)–O(11)	76.4 (1)	–C(2)	112.9 (3)	–F(9A)	116.7 (9)	C(18)–C(19)–C(20)	112 (1)
–O(12)	137.3 (1)	O(3)–C(1)–C(2)	117.1 (4)	–F(9B)	97.9 (8)	O(13)–C(20)–C(19)	102.0 (8)
–O(13)	82.0 (1)	C(1)–C(2)–F(1A)	114.6 (7)				

Other Distances and Angles to Sodium Ions

Na(1)–O(1)	2.619 (2)	Na(1)–O(1′)	2.644 (3)	Na(1)–O(11)	2.649 (3)

O(1)–Na(1)–O(1′)	70.67 (8)	O(1)–Na(1)–O(9)	118.1 (1)	O(1)–Na(1)–O(7′)	77.68 (9)	V(1)–O(1)–Na(1′)	124.9 (1)
–O(3)	77.96 (9)	–O(11)	143.05 (9)	–O(9′)	73.42 (9)	Na(1)–O(1)–Na(1′)	109.33 (8)
–O(5)	73.53 (8)	–O(3′)	125.7 (1)	–O(11′)	140.78 (9)	Na(1)–O(11)–Na(2)	81.78 (8)
–O(7)	126.7 (1)	–O(5′)	120.09 (9)	V(1)–O(1)–Na(1)	125.8 (1)		

seen from the O–Na(1)–O angles listed in Table III, the oxygen atoms are arranged in a very irregular fashion about Na(1).

The other sodium ion, Na(2), has five oxygen atoms coordinated to it, at distances in the relatively narrow range of 2.34–2.44 Å. The angular distribution does not clearly describe any symmetrical polyhedron but can be considered very crudely as a distorted square pyramid, with O(12) as the apical ligand.

The trifluoroacetate ions play two structural roles. One is that of a conventional, simple bridging group, in which one oxygen atom is coordinated to a vanadium atom and the other to one sodium ion, Na(1). The other trifluoroacetate ion is in a much less common situation. One of its oxygen atoms is bound to one vanadium atom, but the other is bound to two sodium ions. This latter η^3 behavior has been reported in $Mn(CH_3CO_2)_2 \cdot 4H_2O$[6] and in $Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$.[7]

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Registry No. $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$, 85421-79-0.

Supplementary Material Available: Tables of thermal vibration parameters and structure factors (22 pages). Ordering information is given on any current masthead page.

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(6) Bertaut, E. F.; Duc, T. Q.; Burlet, P.; Burlet, P.; Thomas, M.; Moreau, J. M. *Acta. Crystallogr., Sect. B* **1974**, *B30*, 2234.

(7) Kraihanzel, C. S., private communication.