

## The Crystal Structure of $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$

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The crystal structure of  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$  has been determined and refined on the basis of three-dimensional X-ray diffractometer data ( $\text{MoK}\alpha$  radiation). The structure is monoclinic,  $a = 7.710(2)$ ,  $b = 19.474(7)$ ,  $c = 7.216(2)$  Å,  $\beta = 116.75(1)^\circ$ ,  $V = 967.5$  Å<sup>3</sup>,  $Z = 8$ , space group  $Cc$  (No. 9). The final  $R$  and  $R_w$  were 0.0295 and 0.0300, respectively, for 1356 independent reflections and 117 variables.

The structure contains two crystallographically different  $\text{VOF}_5$  octahedra linked so as to form complex chains. Two non-equivalent octahedra share one F-F edge, forming  $\text{V}_2\text{O}_2\text{F}_8$  doublets. Two F atoms, connected to different V atoms within the doublet, form an edge in the adjacent equivalent  $\text{V}_2\text{O}_2\text{F}_8$  unit thus continuing the chain. The V-O distances are 1.583(7) and 1.595(7) Å. The V-F distances are in the range 1.881-2.205 Å, mean value: 1.989 Å. The  $\text{H}_2\text{O}$  group is a crystal water molecule.

### Introduction

The only compound Pausewang observed when investigating the system  $\text{CsF}-\text{VO}_2-\text{HF}(\text{aq})$  was  $\text{Cs}_3[\text{V}_2\text{O}_2\text{F}_7]$  (1) ( $=3\text{CsF} \cdot 2\text{VOF}_2$ ). Recently the present author has reported the crystal structure of  $\text{Cs}_3[\text{V}_2\text{O}_2\text{F}_7]$  (2) and the preparation and structure determination of  $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$  ( $=2\text{CsF} \cdot \text{VOF}_2 \cdot \text{H}_2\text{O}$ ) (3, 4, 5). The latter compound was at first erroneously given the formula  $\text{Cs}_2\text{VF}_6$ . The structure contains, according to a single crystal neutron diffraction study (3), strongly deformed octahedral complex ions:  $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ .

A careful study of the system has now revealed the presence of a third compound, which has proved to have the composition  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$  ( $=\text{CsF} \cdot \text{VOF}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ ). This paper is a report on the structure determination of the new compound.

### Experimental

#### Preparation

The starting materials were cesium carbonate, divanadium pentoxide (*p.a.* LKB-Produkter, Stockholm, Sweden), pure divanadium trioxide, obtained by reduction of  $\text{V}_2\text{O}_5$  with hydrogen, and 40% HF. The  $\text{Cs}_2\text{CO}_3$  was added to HF-solutions containing  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_3$  in the ratio 1:1. After the addition of the carbonate the pH value was always adjusted with  $\text{HF}(\text{aq})$  so as to be less than 2. When the Cs/V ratio was larger than 4 the product was  $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ , and for  $\text{Cs}/\text{V} \sim 2$  the compound  $\text{Cs}_3[\text{V}_2\text{O}_2\text{F}_7]$  appeared. When the Cs/V ratio was equal to or just below 1.5 a new, blue, crystalline compound was formed. The crystalline product, consisting of thin transparent blue plates, is insoluble in methanol.

### Analysis

The Cs/V ratio was determined with atomic absorption methods, and was close to one.

The fluorine content was analyzed by the method described by Willard and Winter (6). In order to test the method a pure sample of  $\text{Cs}_3[\text{V}_2\text{O}_2\text{F}_7]$  was analyzed for reference. The observed fluorine content of 20.1 weight-% was obtained in excellent agreement with the theoretical value of 20.0 weight-%. The analysis of the new compound gave a fluorine content of 22.6%.

In a thermogravimetric study a weight-loss of 3.35% was observed at 160°C. When a sample was carefully heated in a dry glass tube small drops of water appeared at the cool part: this experiment established the nature of the volatile product.

The oxidation number of the vanadium atoms was found from magnetic susceptibility measurements, by the Faraday method, over the range 78 to 300°K (Fig. 1) with a polycrystalline sample. The magnetic moment was found to be  $1.79 \mu_B$ , in fair agreement with the value  $1.73 \mu_B$ , for  $\text{V}^{4+}$ .

The results from the analysis are summarized in Table I. They are in agreement with the formula  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$ .

The IR spectrum between 1200 and 3800  $\text{cm}^{-1}$  was recorded by a double beam instrument. Finely powdered crystals of the compound were milled with KBr and pressed to a disk. The absorption bands at

TABLE I  
ANALYSIS OF  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$

	Observed	Theoretical
Cs/V ratio	0.98	1
F (weight %)	22.6	21.44
$\text{H}_2\text{O}$ (weight %)	3.35	3.39
$\mu_{\text{eff}}$	$1.79 \mu_B$	$1.73 \mu_B$
Density ( $\text{g cm}^{-3}$ )	3.62	3.65

$\sim 3500 \text{ cm}^{-1}$  and  $\sim 1550 \text{ cm}^{-1}$  were assumed to originate from  $\text{H}_2\text{O}$  in the structure.

### Unit Cell Dimensions and Space Group

The powder photographs were taken with a Guinier-Hägg camera at 20°C, using  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54051 \text{ \AA}$ ) and with KCl ( $a = 6.2930 \text{ \AA}$ ) as an internal standard. The powder pattern, listed in Table II, was indexed with the aid of Weissenberg photographs. The compound belongs to the monoclinic system. Least squares refinement of the cell parameters gave:  $a = 7.710(2)$ ,  $b = 19.474(7)$ ,  $c = 7.216(2) \text{ \AA}$  and  $\beta = 116.75(1)^\circ$ , (Table III(a)). No extra reflections were observed. The density of  $3.62 \text{ g cm}^{-3}$  determined from the loss of weight in benzene gives a unit cell content of 8 units of  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$ , calculated value  $3.65 \text{ g cm}^{-3}$ .

### Data Collection and Structure Determination

A crystal with the dimensions  $0.172 \times 0.025 \times 0.185 \text{ mm}^3$  was selected and mounted along the unique  $b$  axis. Preliminary investigations by means of polarization microscopy, oscillation and Weissenberg photographs proved it to be suitable for diffraction work. A Siemens AED diffractometer with niobium-filtered  $\text{MoK}\alpha$  radiation was used for the data collection. The  $\theta$ - $2\theta$  scan technique was employed, with the five-point measuring procedure. The scan range for the individual

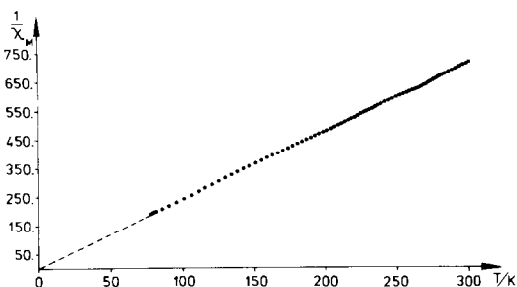


FIG. 1. The reciprocal magnetic susceptibility of  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$  versus the temperature.

TABLE II

POWDER PATTERN OF Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O. CuKα<sub>1</sub> RADIATION (λ = 1.54051 Å)

<i>h k l</i>	<i>d</i> <sub>0</sub>	10 <sup>5</sup> sin <sup>2</sup> θ <sub>0</sub>	10 <sup>5</sup> sin <sup>2</sup> θ <sub>c</sub>	<i>I</i> <sub>0</sub>
0 2 0	9.76	623	626	w
1 1 0	6.489	1409	1408	vw
1 1 $\bar{1}$	6.037	1628	1633	w
0 2 1	5.375	2054	2055	m
1 3 0	4.703	2683	2660	w
1 3 $\bar{1}$	4.535	2885	2884	vs
0 4 1	3.885	3930	3932	m
1 1 1	3.833	4039	4041	vvs
2 2 $\bar{1}$	3.572	4651	4653	s
1 1 $\bar{2}$	3.548	4714	4716	m
2 0 0	3.445	4998	5007	vwv
1 5 0	3.390	5163	5163	s
1 3 1	3.348	5294	5293	w
1 5 $\bar{1}$	3.317	5391	5388	vw
2 2 0	3.245	5633	5633	vw
2 0 $\bar{2}$	3.169	5906	5906	w
0 2 2	3.059	6340	6341	s
2 4 $\bar{1}$	3.013	6534	6531	m
2 2 $\bar{2}$			6532	
0 4 2	2.686	8223	8219	vwv
1 5 $\bar{2}$	2.646	8477	8470	vw
1 7 $\bar{1}$	2.549	9129	9142	m
1 1 2	2.494	9539	9532	vw
3 1 $\bar{2}$	2.446	9913	9913	vw
3 3 $\bar{1}$	2.3784	10488	10490	w
2 6 0	2.3592	10660	10639	w
1 1 $\bar{3}$			10656	
1 3 2	2.3459	10781	10783	w
2 4 1	2.2874	11339	11347	v
0 6 2			11348	
3 1 $\bar{3}$	2.1006	13446	13445	s
2 0 2	1.9539	15540	15538	w

lattice points was  $\Delta\theta = \pm 0.95^\circ$ , in steps of  $0.01^\circ$  with the maximum step time 0.6 s.

Three standard reflections (4 0 0, 0 18 0, and 2 2 1) were automatically monitored throughout the data collection. No significant change in their net intensities was observed.

All the 1410 possible lattice points, systematic extinctions excluded, up to  $\theta = 30^\circ$ , were measured.

The net intensity  $I_n$  was calculated as  $I_i - I_b$ , and the estimated standard deviation was obtained by  $\sigma(I_n) = (I_i + I_b)^{1/2}$ . Altogether

TABLE III(a)

THE CRYSTAL STRUCTURE OF Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O  
Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O: M.W. = 265.85  
SPACE GROUP: *Cc* (No. 9)<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cs(1)	0 <sup>b</sup>	0.18897(2)	0 <sup>b</sup>
Cs(2)	0.11663(11)	0.58784(2)	0.25694(12)
V(1)	0.35210(20)	0.12816(4)	0.61625(20)
V(2)	0.11590(18)	-0.00175(4)	0.31806(18)
O(1)	0.06299(111)	0.35770(30)	0.29630(106)
O(2)	0.39712(96)	0.47268(26)	0.19024(96)
F(1)	0.15327(72)	0.03825(16)	0.09091(62)
F(2)	0.39443(61)	0.03874(16)	0.51518(66)
F(3)	0.06660(65)	0.08944(16)	0.38804(68)
F(4)	0.26068(79)	0.08120(18)	0.80425(69)
F(5)	0.36608(78)	0.16862(20)	0.38670(72)
F(6)	0.21524(102)	0.20734(22)	0.62875(105)
O <sub>w</sub>	0.34950(149)	0.27942(45)	0.00612(171)

<sup>a</sup> Cell dimensions:  $a = 7.710(2)$ ,  $b = 19.474(7)$ ,  $c = 7.216(2)$  Å,  $\beta = 116.75(1)^\circ$  and  $V = 967.5$  Å<sup>3</sup>. Cell content: 8 Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O.

<sup>b</sup> Defines the origin.

1356 reflections were judged significant from the criterion  $\sigma(I_n)/I_n \leq 0.40$ .

The reflections  $hkl$ :  $h + k = 2n + 1$  and  $h0l$ :  $l = 2n + 1$  were systematically absent, indicating the space group to be *C2/c* (No. 15) or *Cc* (No. 9).

A tentative structure was derived from a data set corrected for Lorentz and polarization effects. The structure was solved with three-dimensional Patterson and Fourier methods. The determination was not successful until the symmetry of the trial structure was lowered to the acentric space group *Cc*. All the prominent peaks in the Patterson function were explained by two Cs, and two V atom positions. The metal positions were refined with least-squares methods, and the new coordinates were used for a further ( $F_0 - F_{\text{metal}}$ ) synthesis. At this stage eight ligand positions were derived and included in the least-squares calculations. The *R* value then dropped to 0.08. In a difference Fourier synthesis a further atom was located, too far ( $>4$  Å) from the vanadium atoms to belong

TABLE III(b)  
FINAL ANISOTROPIC TEMPERATURE FACTORS DEFINED AS  
 $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot hk + 2\beta_{13} \cdot hl + 2\beta_{23} \cdot kl)]^a$

Atom ( <i>n</i> )	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1$ (Å)	$R_2$ (Å)	$R_3$ (Å)	$R$ (Å)
Cs(1)	1319(11)	133(1)	2238(15)	39(2)	150(10)	137(3)	0.143	0.177	0.262	0.347
Cs(2)	910(9)	206(1)	1165(10)	-4(2)	300(8)	-63(2)	0.142	0.170	0.203	0.300
V(1)	883(24)	97(2)	854(23)	-73(5)	290(20)	-21(5)	0.120	0.138	0.164	0.246
V(2)	720(21)	90(2)	550(19)	6(4)	232(17)	-7(4)	0.108	0.131	0.138	0.218
O(1)	1273(147)	249(14)	1442(153)	232(34)	162(123)	80(34)	0.134	0.204	0.246	0.346
O(2)	936(122)	198(12)	1268(130)	-143(28)	240(103)	-166(30)	0.120	0.186	0.211	0.306
F(1)	1502(108)	97(6)	750(87)	25(19)	608(80)	30(16)	0.113	0.137	0.191	0.261
F(2)	716(85)	101(6)	1079(95)	2(17)	250(74)	-26(18)	0.129	0.138	0.166	0.251
F(3)	694(82)	106(6)	968(88)	-4(16)	221(70)	-40(17)	0.124	0.140	0.162	0.247
F(4)	1469(111)	129(7)	948(98)	-179(21)	558(86)	-46(20)	0.129	0.138	0.210	0.282
F(5)	1450(116)	139(8)	1220(106)	-94(22)	500(92)	98(21)	0.130	0.168	0.211	0.299
F(6)	2240(161)	128(9)	2798(175)	10(27)	1356(140)	-170(30)	0.144	0.222	0.250	0.362
O <sub>w</sub>	1747(213)	394(24)	3233(303)	-60(54)	1369(216)	139(64)	0.182	0.251	0.288	0.424

<sup>a</sup>  $\beta_{ij}$  values are given in Å<sup>2</sup> × 10<sup>5</sup>. E.s.d. in parentheses. The r.m.s. components ( $R_i$ ) of thermal displacements along the ellipsoid axes and the r.m.s. radial ( $R$ ) thermal displacements are included.

to their coordination spheres. It seemed reasonable to assume that the atom was an oxygen belonging to an H<sub>2</sub>O molecule.

The two V atoms were both in octahedral coordination. It turned out that both the V(1) and V(2) atoms have one vanadium–ligand distance shorter than 1.60 Å. Therefore it was assumed that those two ligands were oxygens. All other vanadium–ligand distances were in the range 1.9–2.2 Å and assumed to be V–F contacts.

With these assumptions the formula of the compound is Cs[V(VOF<sub>3</sub>)<sub>2</sub> · ½H<sub>2</sub>O], in good agreement with the analytical results (see Table 1).

### Refinement

New absorption and preparatory extinction corrections were applied to the data set. The calculated linear absorption coefficient  $\mu(\text{MoK}\alpha) = 96.4 \text{ cm}^{-1}$  was used in calculating a transmission factor for each reflection (7). The absorption was estimated by the Gaussian integration method with  $10 \times 6 \times$

12 grid points. The factor ( $t$ ) in the formula  $I = L_p I_n/t$  ranged from 0.182 to 0.652.

The least-squares refinements were now continued with a full-matrix program. In the final cycles of refinement there were 37 positional parameters, 78 anisotropic temperature factors, one scale factor, and one isotropic extinction coefficient—altogether 117 variables. Scattering factors for neutral atoms were used (8). The quantity minimized was  $w(|F_0| - |F_c|)^2$ . The final  $R$  and  $R_w$  were 0.0295 and 0.0300, respectively. Statistical weights were applied to the structure factors.

In a final three-dimensional ( $F_0 - F_c$ ) synthesis the maximum residual peak showed a height of 13% of the H<sub>2</sub>O peak in the corresponding  $F_0$  synthesis.

The calculations were performed on IBM 1800 and IBM 360/75 computers.

### Description and Discussion of the Structure

The final positional and thermal parameters together with their estimated

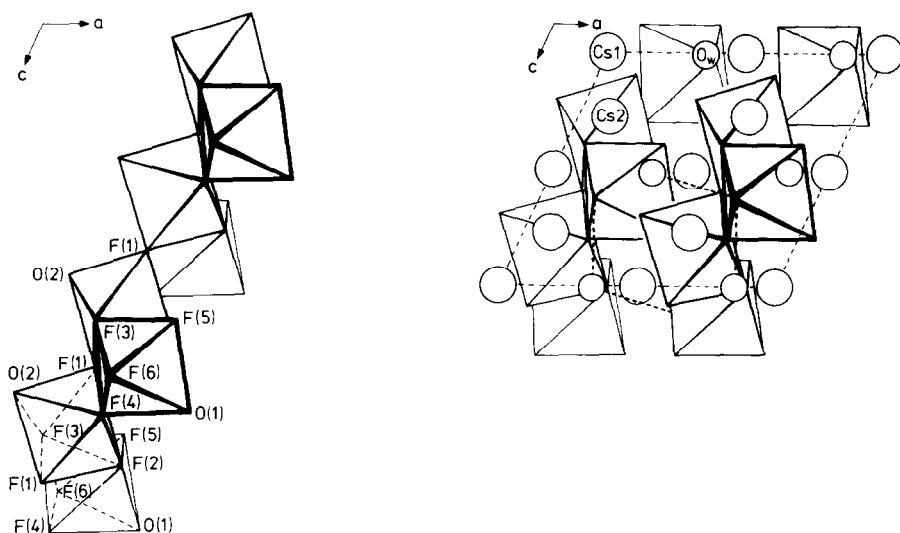


FIG. 2. The structure of  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$  projected on (010) (right) and the  $\text{VOF}_3$  chains in the same projection (left). The possible hydrogen-bond system  $\cdots\text{O}_w \cdots \text{F}(6) \cdots \text{O}_w \cdots \text{F}(6) \cdots$  is indicated by dashed lines (right).

standard deviations, as well as the numerical values of the root mean square displacements, are given in Table III.

The space group  $Cc$  is unambiguously determined by, for instance, the two Cs atom positions.

The most important distances and angles are given in Table IV. The V–O and V–F distances, corrected for thermal motions according to the riding-motion model, are included.

The structure is projected on (010) in Fig. 2. The unit cell contains eight Cs atoms, eight V atoms, eight O atoms, 24 F atoms and four water molecules.

The two crystallographically non-equivalent V(1) and V(2) atoms are each coordinated to six ligands forming somewhat deformed octahedra. The vanadium atoms are considerably closer to one ligand in each octahedron, however the short distances being 1.583(7) and 1.595(7) Å, respectively. It was assumed at an early stage of the refinement that these two ligands are oxygens and consequently the other ligands at

distances of 1.881–2.205 Å from the V atoms are all fluorines. This is confirmed by a comparison with observed V–O and V–F distances in several closely related V(V) and V(IV) compounds, summarized in Table V. The terminal V–O distances found in oxofluorovanadates (all in the range 1.53–1.65 Å) are much shorter than the sum of the effective ionic radii of vanadium and oxygen (9). Therefore these distances have been associated with multiple V=O bonds. When two terminal oxygens are situated at the same vanadium atom, the V–O bond lengths are at the upper limit of the distance range mentioned above. Although the V(IV) compounds might be expected to give slightly longer V=O bonds, the difference is not obvious. The V=O distances in bis(acetylacetonato)4-phenylpyridine-oxovanadium(IV) and bis(acetylacetonato)-oxovanadium(IV) are in the range of 1.56–1.58 Å (10, 11).

The structure of  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$  contains complex  $\text{VOF}_3$ -chains (see Fig. 3) composed of two crystallographically

TABLE IV  
 INTERATOMIC DISTANCES (Å) AND BOND ANGLES IN Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O

(a) V(1) <i>octahedron</i>		Corrected
<b>Metal ligand distances</b>		
V(1)–O(1)	1.583(7)	1.601
–F(5)	1.881(5)	1.888
–F(6)	1.893(5)	1.912
–F(2)	1.971(4)	1.972
–F(4)	2.009(5)	2.014
–F(3)	2.205(5)	2.206
		<b>Distances between the ligands</b>
O(1)–V(1)–F(2)	<b>Bond angles</b> 100.2(3)	2.738(7)
–F(3)	169.6(2)	3.773(9)
–F(4)	93.9(3)	2.641(9)
–F(5)	101.8(3)	2.695(8)
–F(6)	102.0(3)	2.709(10)
F(2)–V(1)–F(3)	72.4(2)	2.473(6)
–F(4)	90.8(2)	2.835(6)
–F(5)	87.7(2)	2.669(5)
–F(6)	157.8(3)	3.792(6)
F(3)–V(1)–F(4)	79.2(2)	2.691(6)
–F(5)	85.4(2)	2.780(6)
–F(6)	85.6(2)	2.795(6)
F(4)–V(1)–F(5)	164.2(2)	3.852(6)
–F(6)	88.1(2)	2.713(6)
F(5)–V(1)–F(6)	87.4(2)	2.608(8)
V(1)–F(4)–V(2)	141.6(2)	—
<b>Metal–metal separations (&lt;3.65 Å)</b>		
V(1)–V(2)	3.289(2)	
(b) V(2) <i>octahedron</i>		Corrected
<b>Metal ligand distances</b>		
V(2)–O(2)	1.595(7)	1.609
–F(3)	1.930(4)	1.933
–F(4)	1.936(4)	1.945
–F(1)	1.950(4)	1.955
–F(1)'	1.988(4)	1.993
–F(2)	2.123(4)	2.126
		<b>Distances between the ligands</b>
O(2)–V(2)–F(1)	<b>Bond angles</b> 99.0(3)	2.705(8)
–F(1)'	96.0(3)	2.677(8)
–F(2)	172.3(3)	3.710(8)
–F(3)	99.0(2)	2.690(7)
–F(4)	101.8(3)	2.749(8)
F(1)–V(2)–F(1)'	164.8(3)	3.903(3)
–F(2)	85.8(2)	2.776(6)
–F(3)	88.5(2)	2.707(6)
–F(4)	88.2(2)	2.705(5)

TABLE IV—continued

F(1)–V(2)–F(2)	79.5(2)		2.630(6)
–F(3)	91.6(2)		2.809(5)
–F(4)	86.3(2)		2.684(6)
F(2)–V(2)–F(3)	75.0(2)		2.473(6)
–F(4)	84.2(2)		2.724(5)
F(3)–V(2)–F(4)	159.1(2)		3.803(5)
V(2)–F(1)–V(2)	132.8(2)		—
Metal–metal separations (<3.65 Å)			
V(2)–V(1)	3.289(2)	V(2)–V(2) (2x)	3.609(1)
(c) Cs(1) coordination sphere			
Cs(1)–F(5)	2.944(4)	Cs(1)–F(3)	3.251(4)
–F(5)	2.970(5)	–O <sub>w</sub>	3.272(11)
–F(1)	3.122(3)	–F(6)	3.405(6)
–O(1)	3.143(8)	–F(4)	3.605(5)
–O <sub>w</sub>	3.203(10)		
(d) Cs(2) coordination sphere			
Cs(2)–F(5)	2.951(5)	Cs(2)–F(2)	3.193(4)
–F(2)	3.060(4)	–O <sub>w</sub>	3.199(10)
–O(2)	3.123(6)	–O(2)	3.298(6)
–F(3)	3.159(5)	–O(1)	3.333(7)
–F(4)	3.186(5)	–F(1)	3.358(5)
(e) Distances around O <sub>w</sub> atom			
O <sub>w</sub> –F(6)	2.560(12)		
–F(6)	2.814(12)		
–Cs(2)	3.199(10)		
–Cs(1)	3.203(10)		
–Cs(1)	3.272(11)		

Estimated standard deviations in last decimal place are given in parentheses.

different kinds of  $\text{VOF}_5$ -octahedra linked by corner- and edgesharing. The chain might be regarded as containing  $\text{V}_2\text{O}_2\text{F}_8$ -doublets of  $\text{VOF}_5$  octahedra formed by sharing the F(2)–

F(3) edge. Two F atoms, F(1) and F(4), connected to different V atoms within the doublet, form an edge in the adjacent equivalent  $\text{V}_2\text{O}_2\text{F}_8$  unit.

An alternative description of the chain, which better serves the need for a discussion of the interatomic bonding scheme, is the following. The V(2)-octahedra are linked to each other by common *trans*-fluorine vertices, F(1), thus forming a zig-zag chain running in the *c* direction. The V(1) octahedra are connected to two adjacent V(2)-octahedra by an edge F(2)–F(3), and a vertex, F(4). Thus the F(1), F(2), F(3), and F(4) atoms are all shared between two V atoms, while the F(5) and F(6) atoms are terminal fluorines only bonded to one vanadium, namely the V(1) atom. This is also

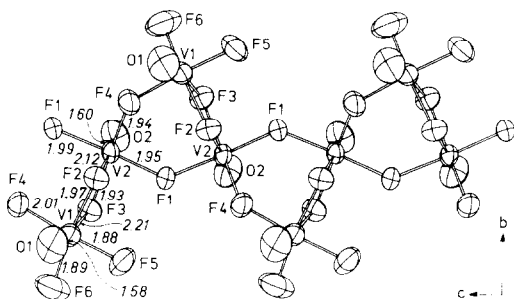


FIG. 3. The complex chain of octahedrally coordinated vanadium atoms. The vanadium–ligand distances are included.

TABLE V  
 METAL-LIGAND DISTANCES IN OXOFLUOROVANADATES

Compound (Reference)	Coordination	V=O (terminal)	V-F (terminal)	V-F (bridge, corner)	V-F (bridge, edge)	V-O (bridge)	V-X trans to a V=O bond
CsVOF <sub>3</sub> · ½H <sub>2</sub> O (this study)	VOF <sub>2</sub> F <sub>3/2</sub>	1.583	1.881 1.893	2.009	1.971 2.205	—	2.205(V-F)
	VOF <sub>5/2</sub>	1.595	—	1.936 1.950 1.988	1.930 2.123	—	2.123(V-F)
K <sub>2</sub> VO <sub>2</sub> F <sub>3</sub> (12)	VO <sub>2</sub> F <sub>2</sub> F <sub>2/2</sub>	1.636	1.862 1.914	2.187 2.187	—	—	2.187(V-F) 2.187(V-F)
		1.572	1.786 1.790	1.875 2.333	—	—	2.333(V-F)
KVOF <sub>4</sub> (16)	VOF <sub>3</sub> F <sub>2/2</sub>	1.529	1.783 1.788	1.793 2.312	—	—	2.312(V-F)
			1.788	—	—	—	—
NH <sub>4</sub> VO <sub>2</sub> F <sub>2</sub> (13)	VOFO <sub>2/2</sub> F <sub>2/2</sub>	1.56	1.87	—	1.96 2.21	1.75 1.99	2.21(V-F)
	VOFO <sub>2/2</sub> F <sub>2/2</sub>	1.54	1.85	—	1.98 2.21	1.72 1.97	2.21(V-F)
Cs <sub>2</sub> [VOF <sub>4</sub> (H <sub>2</sub> O)](3)	VOF <sub>4</sub> O <sub>w</sub>	1.602	1.919 1.919 1.919	—	—	—	2.268(V-O <sub>w</sub> )
			1.919	—	—	—	—
			1.919	—	—	—	—
			1.919	—	—	—	—
VOF <sub>3</sub> (17)	VOFF <sub>4/2</sub>	1.57	1.70	1.81 2.34	1.93 1.95	—	2.34(V-F)
			1.71	1.93 1.93	—	—	—
VF <sub>5</sub> (18)	VF <sub>4</sub> F <sub>2/2</sub>	—	1.68 1.68 1.71 1.73	1.93 1.93	—	—	—
			1.65	2.00	—	—	—
			1.65	2.00	—	—	—
			1.70	—	—	—	—
			1.71	—	—	—	—

demonstrated by the data given in Table VI, which shows the functions of the O and F atoms in Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O.

The terminal V(1)-F(5) and V(1)-F(6) bond distances, being 1.881(5) and 1.893(5) Å respectively, approximately equal the sum of the effective ionic radii. These distances are in fair agreement with average terminal V-F distances found in K<sub>2</sub>VO<sub>2</sub>F<sub>3</sub> (12), NH<sub>4</sub>VO<sub>2</sub>F<sub>2</sub> (13), Cs<sub>2</sub>[VOF<sub>4</sub>(H<sub>2</sub>O)] (3), and (NH<sub>4</sub>)<sub>2</sub>VO<sub>2</sub>F(C<sub>2</sub>O<sub>4</sub>) (14). Considerably

shorter values have been reported for CsVOF<sub>4</sub> (15), KVOF<sub>4</sub> (16), VOF<sub>3</sub> (17) and VF<sub>5</sub> (18), though.

The VOF<sub>3</sub>-chain is somewhat more complicated than the chains with VO<sub>2</sub>F<sub>3</sub>-, VO<sub>2</sub>F<sub>2</sub>- or VOF<sub>4</sub>-stoichiometry, referred to in Table V, formed by corner- or edgesharing between similar vanadium polyhedra. A feature common to Cs[VOF<sub>3</sub>] · ½H<sub>2</sub>O and the chain structures referred to in Table V is that the bridging atoms are fluorines. The only reported exception is NH<sub>4</sub>VO<sub>2</sub>F<sub>2</sub>,



TABLE VI  
THE FUNCTIONS OF THE O AND F ATOMS IN  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$ . (X = O, or F)

X-V distances	(Å)	Mean values	X-Cs distances	(Å)	Hydrogen bond distances	(Å)
O(1)-V(1)	1.583(7)	—	O(1)-Cs(1)	3.143(8)		
			-Cs(2)	3.333(7)		
O(2)-V(2)	1.595(7)	—	O(2)-Cs(2)	3.123(6)		
			-Cs(2)	3.298(6)		
F(1)-V(2)	1.950(4)		F(1)-Cs(1)	3.122(3)		
-V(2)	1.988(4)	1.969	-Cs(2)	3.358(5)		
F(2)-V(1)	1.971(4)		F(2)-Cs(2)	3.060(4)		
-V(2)	2.123(4)	2.047	-Cs(2)	3.193(4)		
F(3)-V(2)	1.930(4)		F(3)-Cs(2)	3.159(5)		
-V(1)	2.205(5)	2.068	-Cs(1)	3.251(4)		
F(4)-V(2)	1.936(4)		F(4)-Cs(2)	3.186(5)		
-V(1)	2.009(5)	1.973	-Cs(1)	3.605(5)		
F(5)-V(1)	1.881(5)	—	F(5)-Cs(1)	2.944(4)		
			-Cs(2)	2.951(5)		
			-Cs(1)	2.970(5)		
F(6)-V(1)	1.893(5)	—	F(6)-Cs(1)	3.405(6)	F(6)-O <sub>w</sub>	2.560(12)
			O <sub>w</sub> -Cs(2)	3.199(10)	-O <sub>w</sub>	2.814(12)
			-Cs(1)	3.203(10)	O <sub>w</sub> -F(6)	2.560(12)
			-Cs(1)	3.272(11)	-F(6)	2.814(12)

which supposedly contains double bridges of O and F atoms.

The bridging V-F bonds in  $\text{Cs}[\text{VOF}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$  exhibit a variety of distances in the range of 1.930–2.205 Å. These V-F distances can be rationalized by division into two groups. The bridges constituting corner-sharings have two bridge arms nearly equal in length with the V-F distances in the narrow range 1.94–2.01 Å, *viz.* the V(2)-F(1)-V(2) and V(2)-F(4)-V(1) bridges. The double bridges formed by the F(2) and F(3) atoms constituting edge-sharings have two bridge arms in *trans* positions to short V=O bonds. These latter V-F distances are in the wide range 1.93–2.21 Å, with two long V-F bonds *trans* to V=O bonds, *viz.* V(1)-F(3) and V(2)-F(2) which are 2.205 and 2.123 Å, respectively (*cf.* also Table VI). The *trans* effect for other oxofluorovanadates is demonstrated in Table V. In  $\text{K}_2\text{VO}_2\text{F}_3$  (12) each bridging F atom is *trans* to two V=O

bonds, and therefore the two bridge arms are of equal length.

The coordination spheres of the two Cs atoms, visualized in Fig. 4(a)-(b), are complex with no directional character. Only distances less than 4.0 Å have been considered. Cs(1) has nine neighbours: one O atom, six F atoms, and two H<sub>2</sub>O molecules. The distance range is 2.94–3.61 Å. The ten-coordinated Cs(2) atoms are in contact with three O atoms, six F atoms, and one H<sub>2</sub>O molecule. The distances are in the range 2.95–3.36 Å.

The O<sub>w</sub> atom is a crystal water molecule. The V-O<sub>w</sub> distances are longer than 4.0 Å. There are two F(6) atoms in contact with the O<sub>w</sub> atom, the distances being 2.560(12) and 2.814(12) Å. Both these separations may be associated with hydrogen bonds (O<sub>w</sub>...F). This assumption is also supported by the data given in Table VI. The possible hydrogen-bond system ...O<sub>w</sub>...F(6)...O<sub>w</sub>...F(6)... is

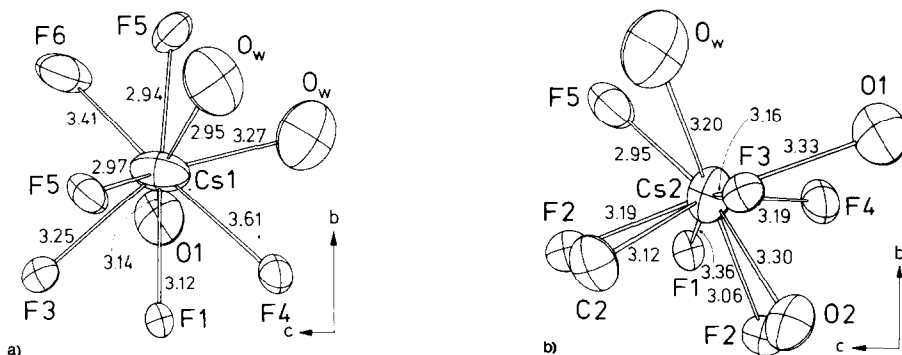


FIG. 4. The cesium coordination polyhedra: (a) Cs(1) coordination sphere, (b) Cs(2) coordination sphere.

indicated in Fig. 2. The geometry of O-H...F hydrogen bonds has been discussed recently by Simonov and Butvetsky (19). In their data the  $O_w \cdots F$  hydrogen-bond lengths varied between 2.56 and 2.86 Å (average 2.68 Å) for a total of 46 hydrogen bonds observed in metal fluoride hydrates.

The IR spectrum of  $Cs[VOF_3] \cdot \frac{1}{2}H_2O$  in the region 400–1300  $cm^{-1}$ , reproduced in Fig. 5, was recorded by a single beam instrument. The two absorption bands at 990 and 975  $cm^{-1}$  probably arise from  $\nu(V=O)$  vibrations. The medium band at 700  $cm^{-1}$  and the very strong and broad absorption band at 525  $cm^{-1}$  are both assigned to  $\nu(V-F)$  vibrations. The band assign-

ments are based upon those made for oxovanadium(IV) complexes reported by Piovesana and Selbin (20).

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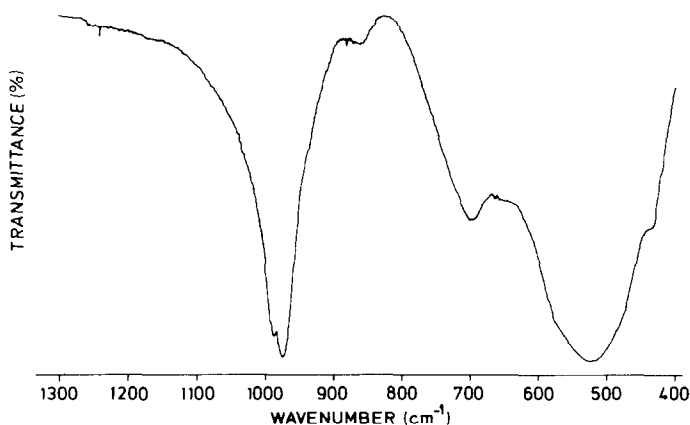


FIG. 5. The IR spectrum of  $Cs[VOF_3] \cdot \frac{1}{2}H_2O$  in the region 400–1300  $cm^{-1}$ .

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