JOURNAL OF SOLID STATE CHEMISTRY **29**, 195–204 (1979)

Neutron and X-Ray Diffraction Structure Determination of $Cs_2[VOF_4(H_2O)]$, a Compound Previously Assigned Cs_2VF_6 Composition

KJELL WALTERSSON

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

Received May 17, 1978, in revised form October 12, 1978

The crystal structure of $Cs_2[VOF_4(H_2O)]$ has been studied on the basis of three-dimensional neutron and X-ray diffraction data. The structure is orthorhombic; $a = 15.251(2)$, $b = 6.486(1)$, and $c = 7.010(1)$ Å; $Z = 4$; $V = 693.46$ Å^3; space group *Ccmm* (No. 63). From the neutron data the positions of all atomic species except vanadium were refined. The final R_w value was 0.030 for 427 independent reflections with $\sigma(I)/I \leq 0.60$. In the X-ray case the positions of nonhydrogen atoms were refined. The final R_w value was 0.022 for 509 observations with $\sigma(I)/I \leq 0.40$. The structure contains strongly deformed octahedral complex ions $[VOF_4(H_2O)]^{2-}$, held together by hydrogen bonds O–H---F (forming chains in the *c* direction) with cesium atoms inserted between them. The vanadyl ion VO^{2+} (V–O) bond distance 1.602(8) Å; X-ray value) is coordinated to four fluorine ligands and to one H_2O molecule in *trans* position to the vanadyl oxygen. The V–F and the V–O_w distances are 4 × 1.919(4) and 2.268(8) Å, respectively; all are X-ray values. The O–H distance is 0.987(7) Å and the H–O_w–H angle 105.1(9)°. The coordination numbers of the two crystallographically independent cesium atoms are 13 and 11, respectively.

Introduction

The crystal structure of a compound given the formula Cs_2VF_6 was reported a few years ago (*1*, *2*). The structure was determined and refined from three-dimensional X-ray diffractometer data (Mo*Kα* radiation). The evidence for the stoichiometry Cs_2VF_6 of the compound, a fluorine analysis with a specific ion electrode and the crystal structure refined to $R_w = 0.030$, was, however, not conclusive, and a fluorine analysis with another method was deemed desirable. This gave a fluorine content markedly different from the previous one, viz., 17.5 wt% instead of 26.46 wt% calculated for Cs_2VF_6. A thermogravimetric study of the compound and new ir data gave support for revision of the formula of the compound to $Cs_2[VOF_4(H_2O)]$.

The single-crystal neutron diffraction study of the compound reported in this paper has proved the revision of the stoichiometry to be correct.

Experimental

Preparation and Characterization

Mixtures of divanadium pentoxide (Fisher p.a.) and pure divanadium trioxide (obtained by reduction of V_2O_5 with hydrogen) in the mole ratio 1:1 were added to different amounts of cesium carbonate (Merck p.a.) and dissolved in 40% HF. In all preparations, the pH value of the resulting solution was less than 2. When the Cs/V ratio was 2 the crystallization produced $Cs_3V_2O_2F_7$ (*3*, *4*, *19*), and for Cs/V ≥ 4 the blue crystalline product was the compound previously given the formula Cs_2VF_6.

0022-4596/79/080195-10$02.00/0

The cesium and vanadium contents of the latter compound were determined with an atomic absorption instrument. The Cs/V ratio was found to be close to 2.

The amount of fluorine in the sample was determined with the method described by Willard and Winter (*5*). The fluorine content was found to be 17.5 wt% instead of 26.46 wt% calculated for Cs_2VF_6. Furthermore, a thermogravimetric study of the compound was performed. At 115°C a weight loss of 4.1% was observed. A sample was also heated carefully in a dry glass tube. Small drops of water appeared in the cold part of the tube, which established the nature of the volatile product.

The ir spectrum between 500 and 3800 cm^{-1} was recorded by a double-beam instrument. The spectrum is presented in Fig. 1. The broad absorption band at ~3500 cm^{-1} is interpreted as belonging to the stretching vibration of an OH group or H_2O molecule. A sharp absorption band at

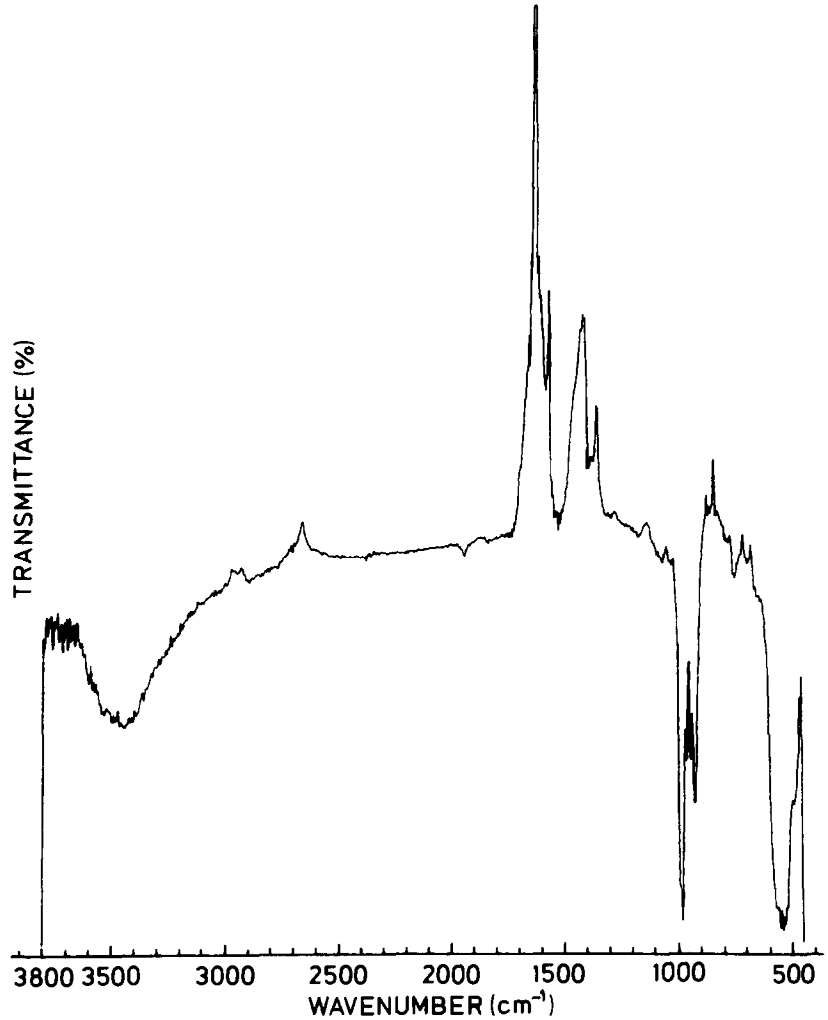

FIG. 1. The ir spectrum of $Cs_2[VOF_4(H_2O)]$ between 500 and 3800 cm^{-1}, recorded by a double-beam instrument.

1630 cm^{-1} is assigned to the bending mode of H_2O.

The magnetic susceptibility measurements, carried out by the Faraday method over the range 78 to 270°K, confirmed the oxidation number of the vanadium atoms to be +4. The observed magnetic moment, 1.67 μ_B, was in fair agreement with the expected value, 1.73 μ_B, for V^{4+} (see Fig. 2).

Thus the observed fluorine content, the magnetic susceptibility measurements, and the TGA analysis are in accord with the formula $Cs_2[VOF_4(H_2O)]$: F observed 17.5 wt%, calculated 17.8 wt%; H_2O observed 4.1 wt%, calculated 4.22 wt%.

Crystal Data and Data Collection

X-Ray Data

X-Ray powder patterns of the compound were recorded by means of a Guinier–Hägg focusing camera using $CuK\alpha_1$ radiation (λ = 1.54051 Å) and KCl (a = 6.2930 Å) as internal standard (*7*). Least-squares refinement of the lattice constants led to excellent agreement with the results published earlier, viz., $a = 15.251(2)$, $b = 6.486(1)$, and $c = 7.010(1)$ Å. No extra reflection lines were detected. The powder pattern is given in Table I.

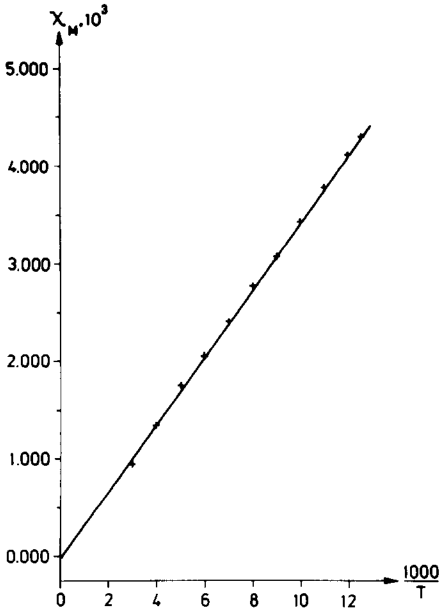

FIG. 2. The magnetic susceptibility measured by the Faraday method. Slope $c = 0.344$; $\mu_{eff} = 2.84c^{1/2}\mu_B$; $\mu_{eff} = 1.67\ \mu_B$.

TABLE I

POWDER PATTERN OF $Cs_2[VOF_4(H_2O)]^a$

h	k	l	d_{obs}	$10^5 \times \sin^2 \theta_{obs}$	$10^5 \times \sin^2 \theta_{calc}$	I_{obs}
1	1	0	5.978	1660	1665	m
1	1	1	4.548	2869	2872	w
3	1	0	4.002	3705	3706	s
4	0	0	3.809	4090	4081	vw
0	0	2	3.508	4822	4829	vs
3	1	1	3.477	4908	4913	vs
4	0	1	3.350	5286	5288	s
0	2	0	3.246	5631	5641	s
1	1	2	3.021	6501	6494	m
2	2	1	2.746	7868	7868	vw
3	1	2	2.635	8546	8535	m
4	0	2	2.581	8906	8910	s
6	0	0	2.542	9183	9183	m
4	2	0	2.470	9722	9722	s
6	0	1	2.3880	10404	10390	m
0	2	2	2.3801	10473	10470	vs
4	2	1	2.3291	10937	10929	m
1	3	0	2.1403	12951	12946	vw
6	0	2	2.0571	14020	14012	vw
3	1	3	2.0184	14563	14572	s
4	0	3	1.9915	14959	14947	m
7	1	1	1.9812	15115	15116	m
6	2	1	1.9242	16024	16031	w
3	3	1	1.9144	16189	16194	m
8	0	1	1.8399	17525	17532	vw
7	1	2	1.7790	18746	18738	vw
0	0	4	1.7517	19336	19317	m
6	2	2	1.7386	19628	19652	w
4	2	3	1.6980	20577	20588	vw
9	1	0	1.6387	22095	22071	vw
7	1	3	1.5479	24762	24775	w
0	2	4	1.5420	24951	24958	w
6	2	3	1.5199	25681	25689	w
3	3	3	1.5151	25845	25852	w
7	3	1	1.4991	26401	26397	vw
0	4	2	1.4712	27411	27392	vw
10	0	2	1.3984	30338	30337	w
10	2	0	1.3803	31141	31148	vw
3	1	5	1.3231	33892	33888	m

[a] $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å); internal standard KCl ($a = 6.2930$ Å).

A crystal with 3.8×10^{-4} mm^3 volume was selected and mounted along the b axis on a Siemens AED diffractometer. Nb-filtered Mo$K\alpha$ radiation, the θ–2θ scan technique, and the five-point measuring procedure were used for the X-ray data collection. All the 588 possible lattice points, systematic extinctions excluded, up to 30° were measured. Of these, 509 were judged significant from the criterion $\sigma(I)/I \leq 0.40$, where $\sigma(I) = (I_t + I_b)^{1/2}$ and $I = I_t - I_b$. Lorentz polarization and absorption corrections ($\mu = 119$ cm^{-1}) were applied to the data.

Neutron Data

A well-shaped prismatic crystal with the volume 9.4 mm^3 was selected. Preliminary investigations by means of polarization microscopy, oscillation, and Weissenberg photographs proved it to be useful for neutron diffraction work. The neutron data were collected at ~25°C at the Studsvik R2 reactor.

The procedure of the data collection is described in detail by Tellgren *et al.* (*8*). The crystal was mounted along the prism axis (b).

The ω-scan technique was applied. The neutron wavelength was 1.210 Å. The integrated intensities were measured for all the 1164 independent lattice points with $\theta \leq 57°$ within one octant of the observable reciprocal lattice sphere. The intensity measurements for the individual lattice points were performed by 40 scanning steps for $\theta \leq 40°$ and by 45 steps for $40° \leq \theta \leq 57°$. The step length was 0.05°. Three standard reflections were automatically monitored throughout the data collection, indicating no deterioration of the crystal.

A check of the intensity data established that the systematic extinctions were the same as for the X-ray data, viz., hkl, $h + k = 2n + 1$; and $0kl$, $l = 2n + 1$. Of the remaining 565 lattice points 427 reflections with $\sigma(I_n)/I_n \leq 0.60$ were used in the refinement. The net intensity, I_n, was calculated as $I_t - I_b$, where I_b is scaled to the same measuring level as I_t. The estimated standard deviations were obtained from the expression $\sigma(I_n) = (I_t + I_b)^{1/2}$, where I_t and I_b are the total and background intensities, respectively.

The data were then corrected for Lorentz, polarization, and absorption effects. The experimentally determined linear absorption coefficient, $\mu_{\text{obs}} = 0.81$ cm^{-1}, was used in calculating a transmission factor for each reflection. The observed absorption coefficient is several times larger than the theoretical value of $\mu_{\text{calc}} = 0.21$ cm^{-1} ($\lambda = 1.08$ Å) (*9*). This discrepancy between μ_{obs} and μ_{calc} is explained by incoherent scattering by the hydrogen atoms, which is estimated to be $\sigma(\text{abs})_{\text{incoh}} = 52 \times 10^{-24}$ cm^2.

The transmission was estimated by the Gaussian integration method with $10 \times 12 \times 10$ grid points. The factor A in the formula $I = \text{Lp} \cdot I_n/A$ ranged from 0.8518 to 0.8850.

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

Refinement

From the systematic extinctions, mentioned above, the space groups $Ccmm$ (No. 63), $Cc2m$ (No. 40), and $Ccm2_1$ (No. 36) were possible.

An initial three-dimensional $F_{\text{obs},N}$ synthesis was calculated in the centric space group $Ccmm$, with signs given by the atomic positions previously reported for this compound (*2*). The R value at this stage was 0.19. Two negative areas were observed at a distance of 0.9 Å from the ligand with the longest vanadium–ligand distance (viz., 2.29 Å). The ligand was identified as a water molecule. Both of the negative areas had their minima 0.4 Å out of the mirror plane, perpendicular to the b axis, generating four minima related to each other by the two orthogonal mirror planes.

The refinement was started with the assumption that the structure was centric (space group $Ccmm$). With a full-matrix least-squares program a hydrogen position in point set 8(f) was now refined together with the atoms given by the X-ray study. The refinement was continued with anisotropic temperature factors and anisotropic extinction corrections included, giving an R_w value of 0.036, but resulting in a very high β_{22} factor (~0.12) for the hydrogen atom. Therefore it was assumed that the hydrogens were situated in positions on both sides of the mirror plane orthogonal to the b axis. These hydrogen positions with half occupancy in point set 16(h) of the space group $Ccmm$ were refined, giving positions 0.4 Å out of the mirror plane. At the same time the β_{22} factor of the hydrogen atom dropped to a quite normal magnitude.

In an attempt to refine the occupancy factors for the two hydrogen sites on each side of the mirror plane the calculations were continued in the acentric space group $Cc2m$, with the nonhydrogen atoms kept in a restrained model with centric positions. This assumption was based upon the results obtained by the X-ray data (see below). The coordinates and anisotropic temperature factors of the two hydrogen sites were restricted by the mirror plane perpendicular to b present in space group $Ccmm$. The occupancy factors were refined with the assumption that the sum should be equal to 1 for the two positions. These refinements converged very slowly to a distribution of 0.67(2) and 0.33(2) for the two sites. The R_w value was 0.0298. Refinements of models with equal distributions of hydrogens in the two positions, as well as with full occupancy in one of the two sites, resulted in R_w values of 0.0302 and 0.0324, respectively. As judged from the nonhydrogen atom model, a hydrogen-bond system with the hydrogens equally distributed in the two sites seems to be more likely than a partly ordered system. So far no explanation has been found why a partly ordered model with 67% of all the H_2O molecules orientated in the same direction should exist in the crystal. Since the R_w value for the hydrogen-bond system with equal distributions of the hydrogens is just slightly higher than the R_w value for the partly ordered model, it is assumed that the former model is the most probable one.

In the final least-squares refinement there were 42 variables, including 10 positional parameters, 24 anisotropic temperature factors, 1 isotropic temperature factor, 1 scale factor, and 6 anisotropic extinction parameters. The positional parameter of the vanadium atom was taken from the X-ray determination and was kept fixed throughout the refinement, while the isotropic temperature factor was refined. The reason for doing this was the small scattering length of vanadium, resulting in an unreasonably large uncertainty in the vanadium position, compared with the X-ray work. No increase in the R_w value was detected.

The coherent neutron scattering lengths were taken from Bacon (*10*): Cs, 0.55; V, −0.05; O, 0.580; F, 0.56; and H, -0.374×10^{-12} cm. The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. Statistical weights were applied to the structure factors: $w = 1/\sigma^2(F_o)$.

In a final three-dimensional $(F_{obs,N} - F_{calc,N})$ synthesis there were only small residual maxima and minima.

The differences in positional parameters were less than 2σ between the refinement in the space group $Cc2m$ ($R_w = 0.0216$; 509 observations and 54 variables), and that in the centric space group $Ccmm$ ($R_w = 0.0220$; 36 variables), both based on X-ray data. A significance test according to Hamilton (*11*) shows that the $Ccmm$ model cannot be rejected even at a 25% significance level. Therefore the model of nonhydrogen atoms, derived from the X-ray data, could be regarded as centric.

The final positional and thermal parameters together with their estimated standard deviations, as well as the root-mean-square thermal displacements, are given in Table II. Also, the parameters from

TABLE IIa

THE CRYSTAL STRUCTURE OF $Cs_2[VOF_4(H_2O)]^a$

Atom (n)	Point set	Neutron positions	X-Ray positions
Cs(1)	4(c)	$x = 0.24983(20)$	$x = 0.25025(5)$
		$y = 0$	$y = 0$
		$z = \frac{1}{4}$	$z = \frac{1}{4}$
Cs(2)	4(c)	$x = 0.45152(22)$	$x = 0.45151(6)$
		$y = \frac{1}{2}$	$y = \frac{1}{2}$
		$z = \frac{1}{4}$	$z = \frac{1}{4}$
V	4(c)	$x = 0.13022^b$	$x = 0.13032(13)$
		$y = \frac{1}{2}{}^b$	$y = \frac{1}{2}$
		$z = \frac{1}{4}{}^b$	$z = \frac{1}{4}$
O	4(c)	$x = 0.23664(19)$	$x = 0.23537(52)$
		$y = \frac{1}{2}$	$y = \frac{1}{2}$
		$z = \frac{1}{4}$	$z = \frac{1}{4}$
F	16(h)	$x = 0.11158(21)$	$x = 0.11147(22)$
		$y = 0.29345(55)$	$y = 0.29320(54)$
		$z = 0.05786(39)$	$z = 0.05862(49)$
O_w	4(c)	$x = -0.01970(18)$	$x = -0.01837(51)$
		$y = \frac{1}{2}$	$y = \frac{1}{2}$
		$z = \frac{1}{4}$	$z = \frac{1}{4}$
H	16(h)^c	$x = -0.04955(39)$	—
		$y = 0.43968(134)$	—
		$z = 0.13819(90)$	—

[a] MW = 426.78; space group, *Ccmm* (No. 63); cell dimensions, $a = 15.251(2)$ Å, $b = 6.486(1)$ Å, $c = 7.010(1)$ Å, and $V = 693.46$ Å^3; $D_{calc} = 4.088$ g cm^{-3}, $D_{obs} = 4.09$ g cm^{-3} (*2*); cell content, 4 $Cs_2[VOF_4(H_2O)]$.

[b] From the X-ray data.

[c] Half occupancy.

the new X-ray refinements are included for comparison.

All the structural figures are pictorial representations of the thermal vibrations of the atoms. The thermal ellipsoids are drawn at 50% probability. The O_w–H distances have been corrected for thermal motions, based on the riding-motion model. The most important distances and angles from both neutron and X-ray determination are included in Table III.

The V–X distances (X = O, F, or O_w) determined from the neutron data have very low accuracy because of the small scattering length of -0.05×10^{-12} cm for the V atoms. Therefore the X-ray values are used for these distances in the following discussion.

Description of the Structure

The structure is visualized in Fig. 3. The unit cell contains 8 cesium atoms, 4 vanadiums, 16 fluorines, 4 oxygens, and 4 water molecules. The crystal data are collected in Table II.

The vanadium octahedral coordination is pictured in Fig. 4. The vanadium is bonded to one oxygen by a double bond, the distance being 1.602(8) Å, forming a vanadyl ion, VO^{2+}, to four fluorines by σ bonds (4 ×

TABLE IIb

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 (*n*)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1 (Å)	R_2 (Å)	R_3 (Å)	R (Å)
Neutron data										
Cs(1)	202(12)	1079(93)	1189(67)	0	0	0	0.152	0.154	0.172	0.276
Cs(2)	254(13)	3378(159)	751(63)	0	0	0	0.137	0.173	0.268	0.347
O	144(10)	1436(104)	1288(69)	0	0	0	0.130	0.175	0.179	0.282
F	259(12)	2102(94)	1691(63)	−56(34)	−11(27)	−1197(65)	0.124	0.176	0.267	0.343
O_w	137(10)	1410(98)	901(70)	0	0	0	0.127	0.150	0.173	0.262
H	275(25)	2399(356)	1014(123)	−35(58)	−43(46)	−70(130)	0.156	0.182	0.227	0.330
V	0.92(38)$Å^2$									
X-ray data										
Cs(1)	192(3)	1107(19)	1069(19)	0	0	0	0.150	0.154	0.163	0.270
Cs(2)	277(5)	2859(34)	650(17)	0	0	0	0.127	0.181	0.247	0.331
V	165(9)	889(50)	457(37)	0	0	0	0.107	0.138	0.139	0.223
O	214(42)	666(191)	1104(203)	0	0	0	0.119	0.159	0.166	0.259
F	344(17)	1859(115)	1702(87)	−25(37)	−35(34)	−1261(86)	0.108	0.202	0.265	0.350
O_w	224(40)	913(205)	687(176)	0	0	0	0.131	0.140	0.163	0.251

[a] β_{ij} values are given in $Å^2 \times 10^5$. Estimated standard deviations are given within parentheses. The rms components (R_i) of thermal displacements along the ellipsoid axes and the rms radial (R) thermal displacements are included.

1.919(4)(Å) and to one water molecule with a distance of 2.268(8) Å. The vanadium atom is situated 0.29 Å out of the plane formed by the four fluorines, toward the oxygen atom.

The observed V–O distance is realistic for a V–O double bond. The corresponding two V–O double bonds observed in the vanadate (IV) $CsVOF_3 \cdot \frac{1}{2}H_2O$ (*12*) are 1.583 and 1.595 Å. The V^{5+}–O distances found in $CsVOF_4$ (*13*) and VOF_3 (*14*) are 1.529 and 1.57 Å, respectively, and in $K_2VO_2F_3$ (*15*) the two V–O bonds within the same octahedron are both 1.636 Å.

The observed V–F distances are terminal, and they are in fair agreement with the average terminal V–F distances found in $K_2VO_2F_3$, K_2VOF_4 (*16*), and $CsVOF_4 \cdot \frac{1}{2}H_2O$ of 1.89, 1.90 and 1.89 Å, respectively, but longer than those in $CsVOF_4$ and VOF_3 (1.79 and 1.70 Å).

The hydrogens in the H_2O molecule are symmetry related by a mirror plane orthogonal to *c*. The O_w–H distance is 0.987(7) Å, or 1.005 Å if corrected for thermal vibrations. The H–H distance is 1.568(12) Å, or 1.621 Å if corrected for thermal motions based on an independent-motion model. The H–O_w–H angle is 105.1(9)°.

The hydrogen bonds (O_w–H · · · F) result in an orientation of the two hydrogens in a water molecule toward the fluorines on one of the sides of the mirror plane perpendicular to *b*. The hydrogens may be supposed to be equally distributed on both sides of the mirror plane.

The water molecules as ligands to the vanadium makes it possible to describe the structure as formed by chains of octahedra running infinitely in the *c* direction. The $[VOF_4(H_2O)]^{2-}$ ions are connected to each other by two hydrogen bonds. The acceptor atoms are the flurorines (see Fig. 3). The hydrogen-bond distance (O_w · · · F) is 2.901(3) Å, the donor distance (O_w-H) 0.987(7) Å, and the acceptor distance (H · · · F) 1.919(7) Å. The O_w–H · · · F angle is 172.6(7)°. These values are in fair

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES IN $Cs_2[VOF_4(H_2O)]$[a]

(*a*) $[VOF_4(H_2O)]^{2-}$ ion

Metal–ligand distances

	Neutron	X-ray
V–O	1.62	1.602(8)
-F 4(×)	1.92	1.919(4)
-O_w	2.29	2.268(8)

	Angles (°)		Distances between ligands	
	Neutron	X-ray	Neutron	X-ray
O–V–F (4×)	99	98.6(1)	2.692(4)	2.678(7)
-O_w	180	180.0	3.910(4)	3.870(11)
F–V–F (2×)	89	88.7(2)	2.694(5)	2.683(7)
-F (2×)	88	88.7(2)	2.679(5)	2.683(7)
-F (2×)	163	162.8(2)	3.800(4)	3.794(7)
-O_w (4×)	81	81.4(1)	2.760(4)	2.742(7)

(*b*) H_2O molecule

	Neutron	Corrected
O_w–H (2×)	0.987(7)	1.005
H–H	1.568(12)	1.621
H–O_w–H angle	105.1(9)°	(107.5°)

(*c*) Cs(1) polyhedron

	Neutron	X-Ray
Cs(1)–F (4×)	3.144(4)	3.146(3)
-H (2×)	3.183(7)	—
-O (2×)	3.249(1)	3.251(1)
-F (4×)	3.304(4)	3.306(3)
-O (2×)	3.511(1)	3.512(1)
-O_w	3.515(4)	3.529(8)

(*d*) Cs(2) polyhedron

	Neutron	X-ray
Cs(2)–H (2×)	2.958(9)	—
-F (4×)	3.034(3)	3.036(3)
-O_w (2×)	3.273(1)	3.276(1)
-O	3.277(4)	3.296(1)
-F (4×)	3.376(4)	3.372(3)
-H (2×)	3.718(9)	—

(*e*) Remaining important distances and angles

	Neutron	X-ray
F–H	1.919(7)	—
-H	2.404(8)	—
-O_w (2×)	2.901(3)	2.915(5)
F–H–O_w angle	172.6(7)°	

---

[a] Estimated standard deviations in last decimal place are given within parentheses. For the neutron data the errors in the vanadium–ligand distances are estimated to be ±0.05 Å.

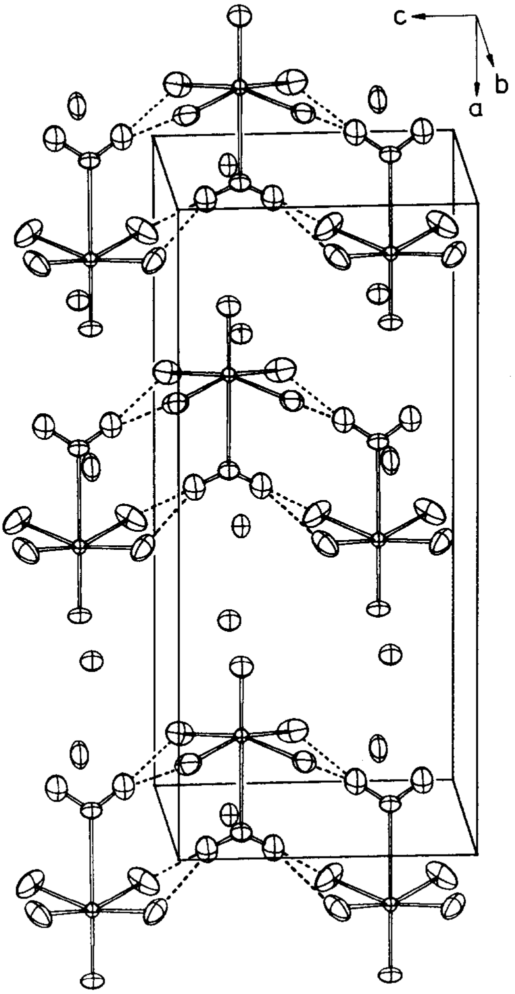

FIG. 3. The structure of $Cs_2[VOF_4(H_2O)]$. The $[VOF_4(H_2O)]^{2-}$ ions are connected by hydrogen bonds, and form chains of octahedra running infinitely in the *c* direction.

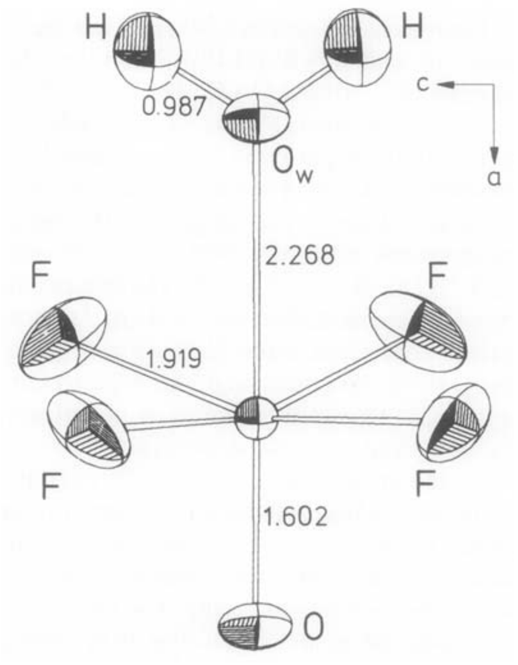

FIG. 4. The $[VOF_4(H_2O)]^{2-}$ ion. The vanadium–ligand distances (Å) are determined from the X-ray data.

agreement with corresponding data for O–H · · · F hydrogen bonds recently reviewed by Simonov and Bukvetsky (*17*). These authors list $O_w \cdots F$ hydrogen-bond lengths varying in the range 2.56–2.86 Å and H · · · F distances between 1.61 and 2.39 Å (average 1.83 Å) for a total of 46 hydrogen bonds. The O_w–H · · · F angles are in the region of 123–180°, with 80% of the reported angles with 165–180°. The two $O_w \cdots F$ hydrogen bonds found in $CsVOF_3 \cdot \frac{1}{2}H_2O$ are 2.560 and 2.814 Å (*12*).

The coordinations of the two crystallographic cesium atoms differ from each other. Within the coordination sphere of Cs(1) there are eight fluorines, four oxygens, and one water molecule; for Cs(2) there are eight fluorines, one oxygen, and two water molecules. The H_2O molecule within the coordination polyhedron of Cs(1) is orientated with the hydrogens toward the cesium atom, while the two H_2O molecules of Cs(2) have an orientation nearly perpendicular to the O_w–Cs(2) vector.

Atovmyan and Aliev (*18*) reported the crystal structure of $Cs_2[VOCl_4(H_2O)]$ based on three-dimensional X-ray diffraction data (conventional *R* value 0.08). The structure is orthorhombic; $a = 10.96$, $b = 9.27$, and $c = 10.09$ Å; $Z = 4$; space group *Cmcm* (No. 63). The general features of the deformed octahedral complex $[VOCl(H_2O)]^{2-}$ are in good agreement with my results; e.g., the V–O bond length is 1.63(4) Å, the distance to the oppositely situated OH_2 ligand, 2.31(6) Å.

Piovesana and Selbin (*19*) reported the ir data of the $[VOF_4(H_2O)]^{2-}$ ion in the compound $(NH_4)_2[VOF_4(H_2O)]$. They found the following absorption bands (in cm^{-1}): 980 (very strong), 955 (medium), 735 (medium), 512 (very strong, broad), and 325 (medium, sharp), and suggested the band assignments ν_1(V=O), 980, 955; ν(V—F), 735, 512; and ν(V—O), 325. The two strong bands found in the 900- to 1000-cm^{-1} region might arise from *trans* H_2O—V=O grouping, since two bands might be expected for ν(V=O) whenever there is a chemically bound group *trans* the oxo-oxygen.

In the ir spectrum of $Cs_2[VOF_4(H_2O)]$, visualized in Fig. 1, there are two absorption bands in the 900- to 1000-cm^{-1} region: 980 and 950 cm^{-1}, probably arising from the *trans* H_2O—V=O grouping. The two bands are assigned to ν(V=O). The very strong and broad band at 540 cm^{-1} is assigned to ν(V—F) vibration.

Further ir data, collected on a single-beam instrument, show all these bands, including those originating from the H_2O group, but also a weak, sharp absorption band at 730 cm^{-1} assigned to ν(V–F) vibration. The ir data of $Cs_2[VOF_4(H_2O)]$ are therefore in excellent agreement with those reported for $(NH_4)_2[VOF_4(H_2O)]$.

Acknowledgments

I am thankful to Dr. Karl-Axel Wilhelmi for helpful discussions and to Professor Arne Magnéli for his kind interest. I wish also to thank Dr. Roland Tellgren and Mr. Stig Lundholm for valuable assistance and discussions, and Dr. Sven Westman for revising the English text. This investigation has been supported by the Swedish Natural Science Research Council.

References

1. A. Carpy and K. Waltersson, *C.R. Acad. Sci. Paris* **274**, 405 (1972).
2. K. Waltersson, K. A. Wilhelmi, A. Carpy, and J. Galy, *Bull. Soc. Fr. Mineral. Cristallogr.* **97**, 13 (1974).
3. G. Pausevang, *Z. Anorg. Allg. Chem.* **381**, 189 (1971).
4. A. Carpy, Dissertation, Bordeaux (1973).
5. H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Anal. Ed.* **5**, 7 (1933).
6. P. G. Hambling, *Acta Crystallogr.* **6**, 98 (1953).
7. R. Tellgren, P. S. Ramanujam, and R. Liminga, *Ferroelectrics* **6**, 191 (1974).
8. "International Tables for X-Ray Crystallography," Vol. III, p. 197, Kynoch Press, Birmingham (1962).
9. G. E. Bacon, *Acta Crystallogr. Sect. A* **28**, 357 (1972).
10. W. C. Hamilton, *Acta Crystallogr.* **18**, 502 (1965).
11. K. Waltersson, *J. Solid State Chem*, in press.
12. G. W. Bushnell and K. C. Moss, *Canad. J. Chem.* **50**, 3700 (1972).
13. A. J. Edwards and P. Taylor, *Chem. Commun.*, 1474 (1970).
14. R. R. Ryan, S. H. Mastin, and M. J. Reisfeld, *Acta Crystallogr. Sect. B.* **27**, 1270 (1971).
15. K. Waltersson and B. Karlsson, *Cryst. Struct. Commun.* **7**, 459 (1978).
16. V. I. Simonov and B. V. Bukvetsky, *Acta Crystallogr. Sect. B* **34**, 355 (1978).
17. L. O. Atovmyan and Z. G. Aliev, *Zh. Strukt. Khim.* **11**, 782 (1970).
18. O. Piovesana and J. Selbin, *J. Inorg. Nucl. Chem.* **31**, 433 (1969).
19. K. Waltersson, *Cryst. Struct. Commun.* **7**, 507 (1978).