

The Crystal Structure of "Green" $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ and Its Relationship to "Blue" $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$

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Crystals of a second, "green" modification of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ were obtained from aqueous solution. Their crystal structure was studied on the basis of three-dimensional X-ray data. The structure is orthorhombic, $a = 8.231(3)$, $b = 10.323(3)$, $c = 8.497(3)$ Å, $V = 722.0$ Å³, $Z = 4$, space group *Ccmm*. The final R and R_w were 0.035 and 0.048, respectively, for 421 independent reflections. As the already known "blue" modification, the present structure contains isolated, highly deformed octahedral $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ ions with the oxygen atoms in *trans* positions. The cesium sublattice and the orientation of the anions to each other are completely different in both modifications. uv/VIS reflection, and ir and Raman spectra of both modifications are discussed.

Introduction

In the system $\text{CsF}-\text{VO}_2-\text{HF}(\text{aq})$ the following fluoro-oxo-vanadates(IV) have been isolated and structurally characterized: $\text{Cs}_3[\text{V}_2\text{O}_2\text{F}_7]$ (1, 2), $\text{Cs}[\text{VOF}_3] \cdot 0.5\text{H}_2\text{O}$ (3), and $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$ (4). A blue color has been reported for all three compounds. During the preparation of $\text{Cs}_3[\text{V}_2\text{O}_2\text{F}_7]$ we observed the precipitation of green crystals from acid V(IV) solutions with a Cs : V ratio of approximately 2 : 1. The single-crystal X-ray structure determination reported in this paper has proved the crystals to be a second, green modification of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$.

Preparation and Characterization

All preparations were performed under an atmosphere of dry nitrogen. Cesium carbonate was added to a solution of VO_2 in 40% HF until the ratio Cs : V was slightly

greater than 2. After boiling the solution had a turquoise green color; in the cold the crystallization of a green substance besides a few distinctly blue crystals was observed. The green octahedral crystals were mechanically separated and washed with water and methanol. From the mother liquid later on blue crystals of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$, already described by Waltersson (4), separated. They were identified by a Guinier powder diagram. Analysis of the green crystals yielded Cs = 63.0%, V = 11.7%, and Cs : V = 2.06. Calculated for $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$: Cs = 62.3%, V = 11.9%.

A DTA study showed an endothermic peak at 140°C, connected with a weight loss of 4.8%. It corresponds to the loss of the coordinated H_2O molecule (the theoretical weight loss for one molecule of H_2O is 4.2%). The observed magnetic moment of the green compound is 1.70 μ_B and is independent from temperature. This confirms the oxidation +IV for vanadium.

TABLE I

FINAL POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS (STANDARD DEVIATIONS IN PARENTHESES)

Atom	Site	10 ⁴ · x	10 ⁴ · y	10 ⁴ · z	B ₁₁	B ₂₂ ^a	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cs	8e	0	2194(6)	0	1.94(3)	2.40(4)	2.08(3)	0	-0.06(2)	0
V	4c	2638	0	2500	2.4(1)	1.5(1)	1.5(1)	0	0	0
F1	8g	2824(7)	1848(5)	2500	2.1(2)	2.1(2)	2.8(2)	-0.4(2)	0	0
F2	8f	2970(8)	0	4720(7)	2.8(3)	3.0(2)	1.8(2)	0	-0.5(2)	0
O	4c	614(11)	0	2500	1.1(3)	1.9(3)	2.4(4)	0	0	0
O _w	4c	5442(13)	0	1500	1.5(4)	5.4(6)	2.8(5)	0	0	0

^a B_{ij} defined as exp[-¼(B₁₁a*²h² + . . . 2B₁₂ · a*^bhk + . . .)].

Crystal Data, Solution of the Structure

A crystal with the dimensions 0.3 × 0.3 × 0.2 mm was used for data collection on a Syntex-P2₁-Diffractometer. The unit cell constants are: $a = 8.231(3)$, $b = 10.323(3)$, $c = 8.497(3)$ Å, $V = 722.0$ Å³, $Z = 4$, $\rho_{\text{calc}} = 3.93$ g · cm⁻³; possible space groups: $Ccmm = D_{2h}^{17}$, $Ccm2_1 = C_{2v}^{12}$, and $Cc2m = C_{2v}^{16}$. The intensities of 541 reflections were measured ($\vartheta - 2\vartheta$ scan, variable scan speeds 3–30° min⁻¹, $2\vartheta_{\text{max}} = 54^\circ$, MoK α radiation, graphite monochromator). Of these, 453 were symmetrically unique and 421 (93%) were judged significant ($I > 1.96 \sigma(I)$). An empirical absorption correction (ψ scan) was applied to the data. According to the statistics of the E values the structure was

expected to be centrosymmetric. The structure could be solved in the space group $Ccmm$; the starting model was based on a Patterson synthesis. After several cycles of least-squares refinement with the weighting scheme $1/w^2 = \sigma(F_0) + (0.005 \cdot F_0)^2$ and anisotropic thermal parameters for all nonhydrogen atoms the final R value of 0.035 ($R_w = 0.048$) was reached. Hydrogen atoms were not included in the refinement. A final difference synthesis showed no significant peaks. All calculations were performed with the Syntex EXTL program system. The final positional and thermal parameters are given in Table I.

Description of the Structure and Discussion

Figure 1 shows part of the structure pro-

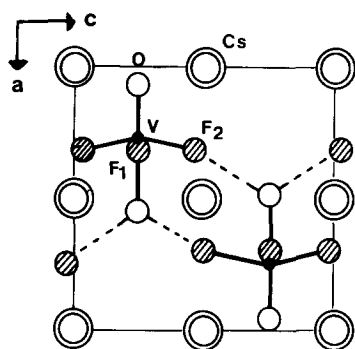


FIG. 1. Part of the structure of "Green" Cs₂[VOF₄(H₂O)] projected along b . The anions are connected by hydrogen bonds (dashed lines) and form infinite chains along c .

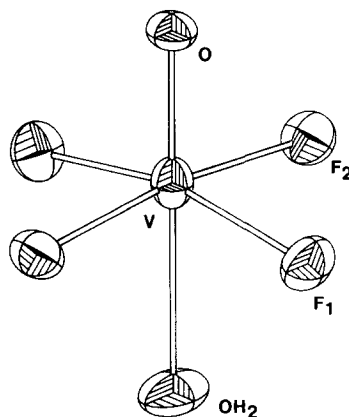


FIG. 2. The [VOF₄(H₂O)]²⁻ ion.

jected along b , and Fig. 2 is an ORTEP plot of the vanadium coordination. Table II gives a comparison of bond distances and angles in both modifications of $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$. As in the "blue" modification, which crystallizes in the same space group and is isostructural to $(\text{NH}_4)_2[\text{MoOF}_5]$ (5),¹ vanadium is octahedrally coordinated by a terminal oxygen atom and a water molecule in mutual *trans* positions; the bond distances are 1.665(9) and 2.308(11) Å, respectively. Four fluorine atoms, situated on the mirror planes, complete the coordination. In the "blue" salt these ligands are placed between the mirror planes. The bond distances to the fluorine ligands are very similar in both modifications, with mean values of 1.919(4) ("blue") and 1.910(5) Å ("green"), but the bond distances to the oxygen atoms differ markedly: The differences, 0.063 Å in the VO bond and 0.040 in the V–OH₂ bond, are greater than 4σ and therefore are highly significant. Due to the *trans* effect one would expect the shorter VO distance to be connected with the longer V–OH₂ distance. It is difficult to find a reason for the lengthening of the VO bonds in the "green" modification. In similar compounds, like $\text{Cs}[\text{VOF}_3] \cdot 0.5\text{H}_2\text{O}$ (3), $(\text{NH}_4)_2[\text{VOF}_4]$ (6), $\text{Na}_3[\text{VO}(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ (7), and $[\text{NMe}_4]_2[\text{V}_2\text{O}_2\text{F}_6(\text{OH})_2]$ (8), the VO distance does not exceed 1.612 Å. One reason might be seen in the very different environment of the terminal oxygen atom: In the "green" modification the terminal oxygen atom has four Cs atoms in a distance of 3.146(2) Å as second nearest neighbors, whereas in the "blue" form only three Cs atoms are present at distances of 3.251(1) and 3.296(1) Å.

¹ The correct space group of $(\text{NH}_4)_2[\text{MoOF}_5]$, which is isostructural to the blue $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$, is $Cmcm$ and not $Cmc2_1$ as previously reported (5). The structure could be refined in space group $Cmcm$ to R equal 0.047 ($R_w = 0.064$). Changes in bond distances and bond angles compared to the published values were less than 1σ .

The $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ ions are connected by pairs of $\text{O}-\text{H} \cdots \text{F}$ hydrogen bonds of length 2.700(8) Å. Through these bonds the anions form infinite chains in the mirror planes orthogonal to the b axis. In the "blue" modification the length of the $\text{O}-\text{H} \cdots \text{F}$ bonds, 2.901(3) Å, is markedly longer.

Cesium is 12-fold coordinated and the closest Cs–Cs distance is 4.164 Å, compared to 3.846 Å in the "blue" form. The Cs atoms form a primitive cubic lattice, which is slightly distorted in the b direction. As in the antifluorite structure, the complex anions occupy one-half of the Cs cubes. Therefore, the main difference between the lattice of the "green" and "blue" modification consists in the Cs sublattice and in the orientation of the $[\text{VOF}_4(\text{H}_2\text{O})]^{2-}$ octahedra with respect to each other.

The ir spectra of both compounds are

TABLE II
INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)
IN THE "GREEN" AND "BLUE" MODIFICATION OF
 $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$

	"Green" (this work)	"Blue" (4) $\text{Cs}_2[\text{VOF}_4(\text{H}_2\text{O})]$
V–O	1.665(9)	1.602(8)
V–F(1)	1.914(5)	1.919(4)
V–F(2)	1.906(6)	
V–O _w	2.308(11)	2.268(8)
O–V–F(1)	94.6(2)	98.6(1)
O–V–F(2)	98.3(2)	
F(1)–V–F(2)	89.3(2)	88.7(2)
Cs–F(1)	2.949(4) 3.169(4)	3.146(3); 3.036(3) ^a 3.306(3); 3.372(3) ^a
Cs–F(2)	3.341(3) 3.352(3)	
Cs–O	3.146(2)	3.251(1); 3.296(1) ^a
Cs–O _w	3.610(1)	3.529(8); 3.276(1) ^a
F(2)···O _w	2.700(8)	2.915(5)
V–O···F(2)	119.0(3)	
Cs–Cs	4.164 ^b	Cs(2)–Cs(2)' 3.846 ^b

^a For Cs(1) and Cs(2), respectively.

^b Minimum distance.

completely identical: the bands at 973 (vs) and 954 (m) cm⁻¹ arise from the V=O (terminal) stretching vibration; the splitting is due to factor group effects. The very broad and asymmetric strong band centered at 520 cm⁻¹ is assigned to fluorine stretching modes; further peaks at 420 (w) and 330 (m) are assigned to ν V-OH₂ and δ V=O. We do not observe any band at 730 cm⁻¹ as mentioned by Waltersson (4). The Raman spectra of both forms differ considerably: besides differences in the wavenumbers and in the intensities of the lines in the region below 300 cm⁻¹, "green" Cs₂[VOF₄(H₂O)] shows two ν V-F bands of medium intensity at 487 and 515 cm⁻¹, and "blue" Cs₂[VOF₄(H₂O)] only one at 507 cm⁻¹. This reflects the difference in the symmetry of the VF₄ group between the two modifications. The V=O vibrations are observed at 973 (vs) and 935 (w) cm⁻¹ in the "green" compound and at 953 (vs) and 932 (w) cm⁻¹ in the "blue" one; their wavenumbers are lower in the latter compound, despite the fact that the VO bond distance is shorter. The shorter Cs-O distances (*vide supra*) in the "green" salt might explain this unexpected result.

We also recorded the uv/VIS reflection spectra of powdered samples of both modifications between 12,500 and 50,000 cm⁻¹. The following absorption maxima were observed: "green" salt: 15,600, 23,500 (shoulder), 27,600, and 38,400 cm⁻¹; "blue" salt: 15,800, 27,800, and 38,600 cm⁻¹.

The spectra of oxovanadium(IV) compounds have been discussed by Ballhausen

and Gray (9) and by Selbin (10). According to these authors three *d-d* bands are expected: in the range 11,000–16,000 cm⁻¹ (I), 14,500–19,000 cm⁻¹ (II), and 21,000–30,000 cm⁻¹ (III); in addition, an intense charge transfer band is usually observed at higher energy. Our observations agree well with these results (the low-energy band is just outside the registered range).

The splitting of the third band, i.e., the appearance of a shoulder at 23,500 cm⁻¹, is the only significant difference in the spectra of both modifications; it is probably responsible for their different color and may be caused by the slight difference in the symmetry of the anions.

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