

# The Disordered Structure of Cesium Fluorooxidiperoxovanadate(2-), $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$

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As shown by Stomberg and Olson the ammonium and potassium fluorooxidiperoxovanadates(2-) are not isomorphous,<sup>1,2</sup> neither are the anions isostructural. Potassium, unlike ammonium, does not seem to form a difluorooxidiperoxovanadate(3-).<sup>3</sup> In addition, judging from different stoichiometry, the ammonium and potassium tetraperoxodivanadates,  $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ <sup>4,5</sup> and  $\text{K}_4[\text{V}_2\text{O}_3(\text{O}_2)_4] \cdot 2\text{H}_2\text{O}$ ,<sup>6</sup> are not isomorphous, either. These differences may be due to cation size, ammonium being the larger, and/or the existence of hydrogen bonding in the ammonium compounds. To investigate whether the cation size is of crucial importance the even larger cesium ion was chosen as counterion, and the structure of  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$  is reported in this paper.

*Preparation.* 0.09 g  $\text{V}_2\text{O}_5$  and 1.5 g CsF were dissolved in 5 ml 15%  $\text{H}_2\text{O}_2$ . The solution was kept at 5 °C. After a couple of days rather large, light-yellow, plate-like, irregular crystals of  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$  had separated. A fragment, suitable for the X-ray work, was cut out.

*X-Ray method.* Intensity data were collected at 18 °C for  $3.5^\circ \leq 2\theta \leq 60^\circ$  using a SYNTEX P<sub>21</sub> X-ray diffractometer (graphite-monochromated  $\text{MoK}\alpha$  radiation, crystal size  $0.09 \times 0.11 \times 0.14$  mm,  $\theta$ - $2\theta$  scan method,  $2\theta$  speed 3.5–29.3°/min). Integrated intensity values were obtained with the Lehmann-Larsen profile analysis method.<sup>7</sup> Three test reflexions (330, 004 and 112) showed only minor difference in intensity during the collection of the data [ $\sigma(I)$  was 3.7, 3.2 and 3.1 %, respectively]. A total of 1116 independent reflexions were measured and 922 of these, having  $I \geq 3\sigma(I)$ , were used in the subsequent calculations. The intensities were corrected for Lorentz, polarisation and absorption effects. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

## CRYSTAL DATA

$\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$  F.W.=415.75  
Space group  $P2_12_12_1$  (No. 19)  
 $a=6.692(1)$  Å,  $b=11.853(2)$  Å,  $c=8.668(2)$  Å,  
 $V=687.5(2)$  Å<sup>3</sup>,  $Z=4$ ,  $D_x=4.017$  g cm<sup>-3</sup>,  
 $\mu(\text{MoK}\alpha)=12.1$  mm<sup>-1</sup>.

*Structure determination.*  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$  crystallizes in the same space group as  $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ , and the ratio between the corresponding unit cell axes in these compounds are 1.083, 1.072 and 1.084, respectively. This indicates possible isomorphism. The potassium com-

Table 1. Atomic fractional coordinates for  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$ . The occupancies for atoms marked with A and B are 0.6 and 0.4, respectively.  $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ .

Atom	x	y	z	$B_{\text{eq}}/\text{Å}^2$ (or $B/\text{Å}^2$ )
V	0.2661(2)	0.1682(1)	0.2272(2)	1.82(3)
Cs1	0.2454(1)	0.46491(4)	-0.01148(6)	2.37(1)
Cs2	0.7438(1)	0.34449(5)	0.31652(8)	3.28(2)
F(A)	0.270(2)	0.321(1)	0.283(1)	2.7(2)
O1(A)	0.386(3)	0.211(2)	0.037(2)	2.6(4)
O2(A)	0.288(3)	0.102(1)	0.034(2)	2.9(3)
O3(A)	0.055(3)	0.063(1)	0.257(2)	3.4(3)
O4(A)	0.035(3)	0.162(1)	0.354(2)	4.4(3)
O5(A)	0.448(3)	0.114(2)	0.326(2)	2.6(4)
F(B)	0.032(3)	0.091(2)	0.285(3)	3.7(5)
O1(B)	0.171(3)	0.281(2)	0.365(2)	3.6(4)
O2(B)	0.332(3)	0.326(2)	0.266(2)	2.0(3)
O3(B)	0.348(4)	0.201(3)	0.027(4)	3.0(6)
O4(B)	0.219(5)	0.096(3)	0.032(4)	3.9(6)
O5(B)	0.455(5)	0.100(3)	0.299(4)	3.0(7)

Table 2. Bond distances (Å) in  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$ .

	A	B
V-F	1.87(1)	1.88(2)
V-O1	1.90(2)	1.91(2)
V-O2	1.85(2)	1.96(2)
V-O3	1.90(2)	1.86(3)
V-O4	1.90(2)	1.92(3)
V-O5	1.62(2)	1.62(3)
O1-O2	1.44(3)	1.48(3)
O3-O4	1.46(2)	1.52(4)

pound is, however, disordered. The structure was solved by Patterson and electron density calculations and refined by the least-squares method. With an ordered anion, isotropic thermal parameters and application of an empirical method for correcting diffractometer data for absorption effects due to Walker and Stuart,<sup>8</sup> the  $R$ -value became 0.045 (0.086 before absorption correction) ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ). One extra peak with approximately half the height of an oxygen peak at 1.9 Å from vanadium, observed in the electron density maps, one unacceptably short peroxy oxygen-oxygen bond distance (1.27 Å), an unacceptably high thermal parameter for one ligand atom ( $B = 7.2 \text{ Å}^2$ ) and rather high  $B$ -values for the other ligand atoms, indicated a disordered anion. Since the same kind of observations were made for  $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ , that model was used in the subsequent structure analysis.<sup>2</sup> This means an anion with mainly two orientations. Refinement of occupancy, positional parameters, anisotropic thermal parameters for Cs and V, and isotropic thermal parameters for F and O led to a final

$R$ -value of 0.030. The scattering factors for Cs, V, F and O were taken from Ref. 9. Weights were used according to  $w = (60 + |F_o| + 0.004|F_o|^2 + 0.0002|F_o|^3)^{-1}$ .<sup>10</sup> The final electron density difference map showed a maximum peak height of 1.2  $e/\text{Å}^3$  (0.95 Å from Cs2). Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Ref. 11. Lists of structure factors and anisotropic thermal parameters are available from R.S. on request.

**Results.** Positional parameters and  $B_{\text{eq}}$  are given in Table 1 and bond distances in Table 2. Fig. 1a shows the vanadium coordination.

The structure analysis has shown that  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$  is isomorphous with  $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ .<sup>2</sup> Even though they both contain disordered anions, the disorder is of the same kind and magnitude (occupancy), despite the considerable difference in cation size between cesium and potassium. The crystals of  $\text{Cs}_2[\text{VFO}(\text{O}_2)_2]$ , therefore, consist of cesium ions and pentagonal-pyramidal  $[\text{VFO}(\text{O}_2)_2]^{2-}$  ions, the latter being disordered with two main orientations A and B (Fig. 1b) with undistinguishable centra. The basal pentagonal planes form an angle of 8.2° (5.6°) (Values for  $\text{K}_2[\text{VFO}(\text{O}_2)_2]$  are given in parentheses throughout for comparison) with one another, and the pentagons are mutually twisted 125° (126°) (Fig. 1b). This type of disorder was observed for the anion in  $(\text{C}_{12}\text{H}_{10}\text{N}_2)[\text{NbF}_5(\text{O}_2)]$ ,<sup>12</sup> but differs from the one met with in a couple of other fluoroperoxometallates (see Refs. 47, 49–51 in Ref. 2).

The anion has the unusual pentagonal-pyramidal six-coordination, first met with for

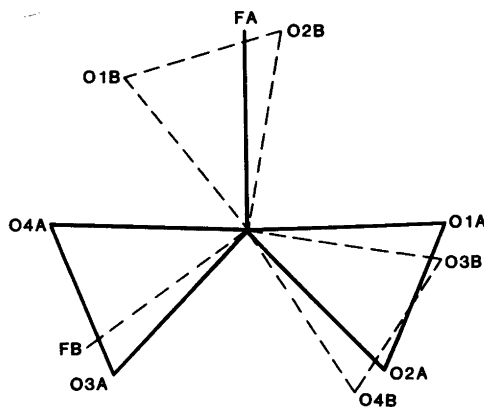
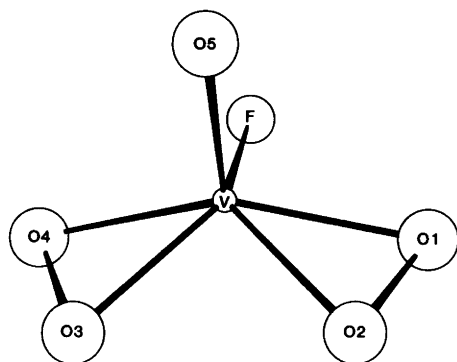


Fig. 1. a. The anion  $[\text{VFO}(\text{O}_2)_2]^{2-}$  and b. the relative orientation of the equatorial planes in the anions A and B. These planes are inclined at 8° to each other.

$[\text{CrO}(\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})]$ ,<sup>13</sup> most peroxometallates being seven-coordinated pentagonal bipyramids (see, e.g., Refs. 25, 30, 32–34, 37, 38, 44–48 in Ref. 2). The r.m.s. deviation from the respective basal plane is 0.04 Å (0.027 Å) in anion A and 0.06 Å (0.034 Å) in anion B. The plane defined by F, O5 and the midpoint between O2 and O3 form an angle of 88° (90.6°) with the basal plane in A and of 87° (87.4°) in B. The vanadium atom is displaced 0.47 Å (0.457 Å) and 0.53 Å (0.471 Å) from the respective basal planes towards the apical oxygen atom O5. Such large displacements are typical for six-coordinated peroxometallates, the displacement being 0.51 Å in  $[\text{CrO}(\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})]$ ,<sup>13</sup> and 0.47 Å in  $\text{NH}_4[\text{VO}(\text{O}_2)_2(\text{NH}_3)]$ ,<sup>14</sup> while seven-coordinated peroxometallates show minor displacements (see Table V in Ref. 15).

All bond lengths are normal (see Refs. 25, 32, 47 in Ref. 2), but due to the disorder they are not very accurately determined. It has not been possible to observe any asymmetry in the bonding of the peroxo groups as has been found in a number of peroxovanadates.

The cesium ions are surrounded by seven to ten nearest fluorine and oxygen atoms at distances ranging from 2.80 Å (2.549 Å) to 3.40 Å (3.150 Å).

1. Stomberg, R. and Olson, S. *Acta Chem. Scand. A* 38 (1984) 801.
2. Stomberg, R. *Acta Chem. Scand. A* 38 (1984) 223.
3. Stomberg, R. *Acta Chem. Scand. A* 38 (1984) 541.
4. Svensson, I.-B. and Stomberg, R. *Acta Chem. Scand.* 25 (1971) 898.
5. Stomberg, R., Olson, S. and Svensson, I.-B. *Acta Chem. Scand. A* 38 (1984) 653.
6. Schwendt, P. and Úškert, D. *Chem. Zvesti* 35 (1981) 229.
7. Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr. A* 30 (1974) 580.
8. Walker, N. and Stuart, D. *Acta Crystallogr. A* 39 (1983) 158.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
10. Cruickshank, D. W. J. *Crystallographic Computing*, Munksgaard, Copenhagen 1970, p. 195.
11. Lindgren, O. *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*, Diss., Chalmers University of Technology and University of Göteborg, Göteborg 1977.

12. Stomberg, R. *Acta Chem. Scand. A* 36 (1982) 101.
13. Stomberg, R. *Arkiv Kemi* 22 (1964) 29.
14. Drew, R. E. and Einstein, F. W. B. *Inorg. Chem.* 11 (1972) 1079.
15. Szentivanyi, H. *Structural Studies on Some Heteroligand Oxoperoxovanadium(V) Compounds*, Diss., University of Göteborg and Chalmers University of Technology, Göteborg 1983.

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