Acta Cryst. (1971). **B27**, 1270

The Crystal Structure of $K_2VO_2F_3$, a Nonlinear Dioxovanadium(V) Group*

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(*Received* 17 *August* 1970)

The crystal structure of $K_2VO_2F_3$ has been determined by a three-dimensional single-crystal X-ray diffractometer study. The crystals are orthorhombic, space group *Pnma*, with $a=7\cdot379$ (4), $b=5\cdot640$ (2), $c=11\cdot413$ (7). For $Z=4$, $D_c=3\cdot05$ g.cm^{-3}, in agreement with the measured density, $D_m=3\cdot05$ g.cm^{-3}. The structure was refined by full-matrix least squares to a weighted R' (the conventional R factor was 0·0258) value of 0·0198 for 668 observed reflections. Octahedrally coordinated vanadium atoms are linked by *cis* bridging fluorine atoms into infinite chains parallel to the b axis. The coordination polyhedron of vanadium has a plane containing *cis* oxygen atoms at a V–O distance of 1·636 (2) Å and an O–V–O angle of 102·8 (2)°, and *cis* bridging fluorine atoms at a V–F_b distance of 2·187 (1) Å and an F_b–V–F_b angle of 80·30 (5)°. Fluorine atoms occupy positions above and below this plane at V–F_a distances of 1·862 (3) and 1·914 (3) Å, and are bent away from the oxygen atoms to give an F_a–V–F'_a angle of 156·3 (1)°. The structure is discussed with regard to other Group V B and VI B fluorides and oxyfluorides.

Introduction

Vibrational studies of dioxotetrahalo complexes of molybdenum(VI), tungsten(VI), and vanadium(V) have led to the suggestion that these compounds contain a nonlinear O–M–O moiety (Kharitonov & Buslaev, 1964; Griffith & Wickins, 1968). Such *cis* dioxo groups have been found in chelates of Mo(VI) (Cotton, Morehouse & Wood, 1964; Atovmyan & Sokolova, 1969) and a *cis* O–Mo–O group in $K_2MoO_2F_4.H_2O$ has also been reported (Grandjean & Weiss, 1967), but Pinsker & Kuznetsov (1968) have reported a linear O–Mo–O group in the corresponding anhydrous salt, and Markin (1968) has proposed a linear O–V–O group in $(NH_4)_3VO_2F_4$. Recent infrared investigations (Davidovich, Sergienko & Murzakhanova, 1968; Pausewang & Dehnicke, 1969) of the related compound $K_2VO_2F_3$ (Petersen, 1889) have led to the postulate that this anion also contains a *cis* dioxo group. The anion was also presumed to be polymeric in the solid, although several models were proposed. We undertook a single-crystal X-ray study of $K_2VO_2F_3$ in order to determine unambigously the geometry of the O–V–O group, and also the structure of the presumably polymeric anion.

Experimental

Air-stable crystals were obtained in the form of yellow plates by evaporation of a mixture of V_2O_5 and KF in aqueous hydrofluoric acid. Examination of precession photographs (Mo $K\alpha$ radiation) showed that the crystals are orthorhombic. From systematic absences $hk0$, $h=2n+1$ and $0kl$, $k+l=2n+1$, the possible space groups are *Pnma* and $Pn2_1a$ (nonstandard setting of $Pna2_1$).* The unit-cell dimensions and their estimated standard deviations, obtained by least-squares refinement of the positions of twelve high-order reflections (2θ from 43–54°) as determined on an automated Picker four-circle diffractometer using Mo $K\alpha_1$ radiation (take-off angle 2°) are $a=7\cdot379$ (4), $b=5\cdot640$ (2), and $c=11\cdot413$ (7) Å. Assuming four molecules per unit cell, the calculated density is 3·05 g.cm^{-3}; the density measured by flotation in *sym*-tetrabromoethane/diiodomethane mixtures is 3·05 g.cm^{-3}.

Intensities were collected on a Picker diffractometer, using Zr-filtered Mo $K\alpha$ radiation (take off angle 5°), and a θ-2θ scan over a 2° range. The count was taken in 0·05° steps, for 2 sec at each step; a background was counted for 20 sec at each end of the scan. The data crystal was bounded by the pinacoid forms {100}, {010}, and {001}, and was mounted on **c**; it had dimensions 0·198 × 0·318 × 0·087 mm along [100], [010], and [001], respectively. Intensity data were collected for all hkl and $\bar{h}\bar{k}\bar{l}$ planes with $2\theta \le 60°$. Of the 1511 intensities measured, 1305 were observed according to the criterion $I > 2\cdot5\sigma(I)$, where I is the intensity after background correction and $\sigma(I)$ is its standard deviation based on counting statistics (Evans, 1961). A standard reflection was measured after every fifteen reflections during the first half of data collection, and after every thirty reflections during the second half. A drop of about 3·6% was observed in the intensity of this reflection during data collection. Multiplicative correc-

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* This work was done under the auspices of the U.S. Atomic Energy Commission.

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* Note that Pausewang & Dehnicke (1969) considered only the acentric space group.

tion factors for the data were derived by fitting these measurements as a function of time with a fourth-order polynomial. The order of the polynominal was determined from significance tests based on the sum of the squares of the residuals (Hamilton, 1965). Standard corrections were made for Lorentz and polarization effects. An absorption correction was made by the Busing & Levy (1957) method using Burnham's program (1962), modified by Larson, Cromer & Roof (1964). The linear absorption coefficient for Mo $K\alpha$ radiation is 38·9 cm^{-1} and the calculated transmission factors varied from 0·382 to 0·625.

Structure factors were calculated using the scattering factors of Doyle & Turner (1968) for the neutral atoms potassium, vanadium, oxygen, and fluorine with appropriate anomalous dispersion corrections (Cromer, 1965) for potassium and vanadium.

Structure determination and refinement

Because of overlapping of heavy-atom vectors in the three-dimensional Patterson synthesis, heavy-atom positions could not be determined uniquely. Initially, four possible sets of position parameters were found for a heavy atom, and a difference-Fourier synthesis was phased on each of these. One of these difference-Fourier maps produced a chemically reasonable heavy-atom structure, which refined to a conventional R index of 0·35 in *Pnma*. A difference-Fourier synthesis phased on this model revealed the light-atom positions. Interatomic distance were calculated for the model at this point, and peaks were assigned as specific atom types on the basis of these distances by analogy with known structures. Refinement of this model in *Pnma* gave an R index of 0·075 with all atoms isotropic. However, the resulting factors were physically unreasonable for all atoms in the model, being about a factor of two smaller than those for similar atoms in known structures. Attempts to refine this model in the acentric space group led to no improvement of either the R index or the magnitude of the temperature factors.

Indications of a secondary extinction effect were found upon examining a listing of the observed and calculated structure factors for the centric model. Inclusion of this parameter in the refinement (Zachariasen, 1967; Larson, 1967) did not significantly affect the atomic position parameters for the model, but the isotropic temperature factors for all atoms were approximately doubled and the R index was 0·048. At this stage anisotropic temperature factors were introduced for all atoms and refinement was continued by full-matrix least squares (Larson, 1968) in *Pnma* using 688 independent observed reflections. The function minimized was $\sum w_i^2(|F_o|-|F_c^*|)^2$, where w_i is the weight defined as $1/\sigma_i\ (F_o)$, $\sigma(F_o)=\dfrac{\sigma(I)}{2F_o}$, and $F_c^*=kF_c/\{1+g\,\mathrm{Lp}\left[\dfrac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]F_c^2\}^{1/2}$ in which k is a scale constant, Lp is the Lorentz–polarization factor, g is the extinction coefficient, and F_c is the structure factor calculated in the usual way. The parameter shifts in the last refinement cycle were less than 0·001 σ for all parameters.

Table 1. *Observed and calculated structure factors for* $K_2VO_2F_3$

Column headings are l, F_o, and F_c^*.

H= 0 K= 0		
0	0	419
2	51	47
4	45	42
6	105	102
8	33	33
10	66	65
12	17	19
14	32	31
16	6	7
H= 0 K= 1		
1	25	24
3	106	109
5	25	25
7	-3	2
9	47	46
11	37	37
13	11	12
15	8	8
H= 0 K= 2		
0	123	121
2	28	26
4	11	11
6	96	95
8	80	80
10	20	19
12	13	14
14	35	35
H= 0 K= 3		
1	3	4
3	79	80
5	25	25
7	10	10
9	38	38
11	38	38
13	9	9
H= 0 K= 4		
0	146	144
2	24	24
4	17	17
6	64	65
8	24	25
10	41	42
12	13	14
H= 0 K= 5		
1	15	15
3	70	71
5	13	13
7	9	9
9	29	28
11	22	21
H= 0 K= 6		
0	66	66
2	-5	2
4	7	7
6	47	47
8	36	36
10	11	12
H= 0 K= 7		
1	-5	-0
3	37	36
5	15	13
7	-6	4
H= 1 K= 0		
1	37	36
2	32	31
3	9	10
4	9	10
5	100	98
6	32	33
7	39	38
8	12	12
9	18	17
10	7	6
11	14	14
12	35	34
13	16	16
14	28	29
15	22	21
16	8	6
H= 1 K= 1		
1	47	48
2	7	7
3	19	19
4	21	22
5	18	17
6	9	8
7	35	35
8	33	33
9	38	37
10	34	34
11	6	5
12	7	7
13	16	16
14	16	15
15	28	28
H= 1 K= 2		
1	7	7
2	48	46
3	65	66
4	12	11
5	28	29
6	66	66
7	59	58
8	31	32
9	9	9
10	21	21
11	26	25
12	45	47
13	-4	3
14	22	22
15	8	8
H= 1 K= 3		
1	21	21
2	4	3
3	23	22
4	20	20
5	-3	1
6	12	12
7	28	28
8	24	24
9	38	38
10	26	26
11	7	7
12	8	8
13	17	18
14	14	14
H= 1 K= 4		
1	19	19
2	12	12
3	6	7
4	9	8
5	52	53
6	24	24
7	25	25
8	8	9
9	12	12
10	6	6
11	12	12
12	27	27
13	12	12
H= 1 K= 5		
1	24	24
2	8	8
3	6	7
4	13	12
5	12	12
6	-4	4
7	16	16
8	21	22
9	20	19
10	22	22
11	6	5
12	6	2
H= 1 K= 6		
1	-5	3
2	9	8
3	21	20
4	-5	2
5	14	15
6	26	27
7	26	26
8	12	13
9	-5	4
10	12	11
H= 1 K= 7		
1	-5	4
2	-5	-0
3	11	11
4	11	11
5	6	4
6	8	8
7	12	12
H= 2 K= 0		
0	49	48
1	46	47
2	91	92
3	32	33
4	111	109
5	50	49
6	95	95
7	4	4
8	25	24
9	44	44
10	8	7
11	19	20
12	35	36
13	6	5
14	9	10
15	18	19
H= 2 K= 1		
0	59	60
1	59	62
2	39	40
3	36	37
4	26	26
5	60	60
6	37	38
7	22	22
8	30	30
9	25	26
10	5	4
11	15	14
12	21	21
13	21	21
14	8	8
15	22	22
H= 2 K= 2		
0	40	41
1	73	73
2	105	110
3	71	72
4	33	34
5	29	30
6	44	44
7	28	28
8	17	17
9	40	41
10	-4	2
11	4	1
12	51	52
13	-4	2
14	8	8
15	10	10
H= 2 K= 3		
0	58	58
1	41	41
2	33	33
3	21	22
4	30	30
5	49	49
6	35	35
7	13	12
8	19	19
9	24	24
10	8	8
11	15	15
12	17	17
13	19	19
14	-5	4
H= 2 K= 4		
0	27	27
1	28	28
2	57	57
3	25	25
4	63	64
5	29	28
6	55	57
7	-4	1
8	18	18
9	30	30
10	6	5
11	14	14
12	28	28
13	6	3
H= 2 K= 5		
0	22	22
1	37	36
2	20	19
3	24	24
4	9	9
5	31	31
6	20	20
7	15	16
8	20	20
9	19	19
10	-5	-0
11	8	6
12	16	16
H= 2 K= 6		
0	20	19
1	27	26
2	47	46
3	29	28
4	19	19
5	16	15
6	22	22
7	12	11
8	11	11
9	21	22
10	-5	1
H= 2 K= 7		
0	27	26
1	21	19
2	15	15
3	10	10
4	16	16
5	24	23
6	19	10
H= 3 K= 0		
1	67	65
2	22	21
3	54	53
4	34	33
5	20	19
6	-3	2
7	5	4
8	30	30
9	79	79
10	15	14
11	17	18
12	23	23
13	10	11
14	13	12
15	24	25
H= 3 K= 1		
1	33	33
2	9	9
3	10	10
4	9	9
5	13	13
6	50	50
7	32	33
8	13	13
9	9	8
10	-4	2
11	10	9
12	44	45
13	17	18
14	6	5
15	12	12
H= 3 K= 2		
1	32	32
2	30	29
3	52	53
4	26	27
5	30	30
6	6	7
7	32	31
8	28	29
9	31	30
10	19	18
11	-4	1
12	23	24
13	7	6
14	10	9
H= 3 K= 3		
1	22	22
2	22	22
3	9	8
4	11	10
5	7	7
6	32	32
7	27	27
8	15	16
9	9	8
10	6	6
11	9	8
12	35	35
13	16	16
14	-5	6
H= 3 K= 4		
1	27	27
2	9	9
3	29	29
4	21	21
5	14	14
6	-4	-0
7	-4	4
8	19	19
9	54	54
10	12	11
11	11	12
12	17	17
13	8	8
H= 3 K= 5		
1	16	16
2	-4	1
3	-4	4
4	-4	-0
5	-4	3
6	35	35
7	18	18
8	5	4
9	6	5
10	-5	1
11	9	7
H= 3 K= 6		
1	9	8
2	8	8
3	23	23
4	13	13
5	11	11
6	6	4
7	13	13
8	14	14
9	21	21
H= 3 K= 7		
1	8	7
2	12	12
3	-5	3
4	-5	3
5	-5	-0
6	15	14
H= 4 K= 0		
0	87	88
1	7	5
2	5	5
3	86	87
4	31	30
5	47	46
6	12	12
7	13	12
8	9	8
9	35	35
10	21	21
11	46	47
12	-5	-0
13	12	12
14	21	20
H= 4 K= 1		
0	78	79
1	24	24
2	33	34
3	23	23
4	13	13
5	9	9
6	60	61
7	17	17
8	28	29
9	-4	-0
10	4	5
11	14	15
12	17	17
13	5	4
14	25	26
H= 4 K= 2		
0	58	59
1	29	28
2	32	32
3	105	110
4	9	10
5	28	28
6	38	39
7	39	41
8	21	22
9	32	33
10	10	11
11	26	26
12	11	10
13	15	15
14	8	8
H= 4 K= 3		
0	75	75
1	16	16
2	27	27
3	23	23
4	20	20
5	7	7
6	54	55
7	11	10
8	20	20
9	-4	1
10	7	9
11	12	11
12	13	12
13	6	4
H= 4 K= 4		
0	51	53
1	-4	2
2	6	5
3	61	61
4	17	17
5	29	29
6	9	10
7	10	10
8	5	6
9	26	26
10	14	14
11	34	34
12	-5	1
H= 4 K= 5		
0	42	42
1	13	14
2	17	17
3	14	14
4	-5	3
5	-5	4
6	35	35
7	11	9
8	23	22
9	-5	-0
10	6	2
H= 4 K= 6		
0	26	25
1	13	12
2	13	13
3	54	53
4	-5	1
5	16	16
6	18	17
7	18	18
8	11	11
H= 4 K= 7		
0	42	40
1	7	6
2	13	12
3	15	13
4	13	13
H= 5 K= 0		
1	16	16
2	-4	1
3	23	22
4	32	32
5	57	57
6	35	36
7	32	31
8	10	10
9	20	20
10	5	5
11	21	22
12	9	9
13	27	27
14	5	4
H= 5 K= 1		
1	14	13
2	7	6
3	-4	1
4	39	38
5	19	19
6	12	11
7	-4	2
8	22	22
9	10	10
10	37	37
11	19	19
12	18	19
13	6	4
H= 5 K= 2		
1	17	13
2	24	24
3	18	19
4	19	19
5	9	8
6	17	17
7	40	41
8	20	20
9	16	15
10	11	10
11	30	30
12	-5	2
13	9	8
H= 5 K= 3		
1	15	16
2	11	11
3	-4	-0
4	33	33
5	21	21
6	6	5
7	5	3
8	16	17
9	-5	4
10	29	29
11	17	18
12	14	14
H= 5 K= 4		
1	12	12
2	-4	3
3	13	12
4	18	19
5	35	35
6	22	22
7	24	23
8	8	9
9	14	14
10	5	4
11	17	17
H= 5 K= 5		
1	-5	2
2	-5	2
3	6	4
4	22	21
5	10	9
6	10	10
7	-5	2
8	16	16
9	11	10
H= 5 K= 6		
1	7	7
2	11	10
3	7	6
4	9	8
5	6	6
6	10	10
7	24	23
H= 6 K= 0		
0	68	68
1	55	56
2	8	8
3	35	34
4	4	1
5	42	41
6	20	20
7	7	6
8	-4	3
9	46	46
10	20	20
11	11	10
12	5	4
13	10	9
H= 6 K= 1		
0	36	36
1	-4	3
2	38	37
3	49	48
4	24	24
5	-4	3
6	27	26
7	11	11
8	28	27
9	19	19
10	-5	3
11	12	12
12	20	21
H= 6 K= 2		
0	15	15
1	58	58
2	17	18
3	40	41
4	6	6
5	33	33
6	23	22
7	13	14
8	23	23
9	38	40
10	-5	4
11	-5	3
12	-5	1
H= 6 K= 3		
0	32	33
1	-4	3
2	32	33
3	34	34
4	22	22
5	-5	5
6	23	23
7	5	4
8	23	21
9	17	16
10	-5	2
11	12	14
H= 6 K= 4		
0	45	45
1	39	38
2	5	4
3	26	25
4	5	2
5	30	30
6	15	16
7	6	5
8	-5	1
9	34	34
10	15	14
H= 6 K= 5		
0	21	20
1	-5	4
2	25	24
3	33	33
4	15	15
5	-5	1
6	20	19
7	11	11
8	20	19
H= 6 K= 6		
0	13	14
1	31	30
2	7	7
3	24	23
4	-6	1
5	20	19
H= 7 K= 0		
1	-4	3
2	29	29
3	10	9
4	9	8
5	14	14
6	24	23
7	12	11
8	18	19
9	34	34
10	6	6
11	6	6
H= 7 K= 1		
1	4	2
2	20	20
3	13	12
4	14	14
5	-5	2
6	25	25
7	7	7
8	13	13
9	29	28
10	9	8
11	-5	-0
H= 7 K= 2		
1	13	13
2	-5	3
3	23	22
4	15	15
5	-5	1
6	38	38
7	6	3
8	7	6
9	24	23
10	-5	3
11	-5	-0
H= 7 K= 3		
1	6	6
2	16	15
3	15	14
4	12	10
5	-5	3
6	21	22
7	6	6
8	11	10
9	28	28
10	7	8
H= 7 K= 4		
1	-5	1
2	18	18
3	8	8
4	8	6
5	9	10
6	18	18
7	9	8
8	12	13
H= 7 K= 5		
1	-5	2
2	13	13
3	6	6
4	10	9
5	-6	6
6	17	16
H= 8 K= 0		
0	33	32
1	8	8
2	21	21
3	44	43
4	33	33
5	7	6
6	33	34
7	10	10
8	18	19
9	7	5
10	-5	4
H= 8 K= 1		
0	26	25
1	31	30
2	6	3
3	32	32
4	8	8
5	25	24
6	16	15
7	15	14
8	8	7
9	25	25
10	-5	1
H= 8 K= 2		
0	26	25
1	13	13
2	30	29
3	33	32
4	6	4
5	7	6
6	16	15
7	-5	3
8	19	19
9	-5	3
H= 8 K= 3		
0	20	19
1	24	23
2	6	4
3	26	24
4	10	9
5	23	23
6	12	12
7	10	9
8	8	8
H= 8 K= 4		
0	25	24
1	-6	6
2	18	17
3	33	31
4	24	24
5	7	4
6	27	26
H= 8 K= 5		
0	22	21
1	23	22
H= 9 K= 0		
1	15	15
2	-5	2
3	6	5
4	28	28
5	-5	1
6	-5	6
7	6	4
8	16	14
H= 9 K= 1		
1	10	10
2	10	10
3	-5	2
4	17	17
5	11	11
6	-5	3
7	22	23
H= 9 K= 2		
1	6	5
2	7	7
3	-5	-0
4	25	24
5	-5	1
6	-5	1
H= 9 K= 3		
1	8	7
2	-6	5
3	-6	2
4	15	13
5	10	10
H= 10 K= 0		
0	34	33
1	19	18
2	20	19
3	10	9
4	6	5
H= 10 K= 1		
0	21	20
1	9	9
2	6	6
3	32	30
H= 10 K= 2		
0	23	21
1	10	9

The final weighted R' factor, where $R'=\Sigma w_i||F_o|-|F_c^*||/\Sigma w_i|F_o|$, with temperature factors for all atoms isotropic was 0·0310 (excluding unobserved reflections). The R' with only potassium and vanadium temperature factors anisotropic was 0·0253; R' with temperature factors of all atoms anisotropic was 0·0198 while the conventional unweighted R factor, $R=\Sigma||F_o|-|F_c^*||/\Sigma|F_o|$ was 0·0258. Hamilton's (1965) significance tests on the sum of the squares of the residuals reject the hypotheses that all atoms have isotropic temperature factors or that only the potassium and vanadium atoms have isotropic temperature factors at better than the 0·005 significance level. A final difference-Fourier map showed residuals centered around the vanadium and potassium positions ranging in value from − 0·34 to +0·43 e.Å^{-3}; the largest residuals elsewhere were *ca.* 0·3 e.Å^{-3} with $\sigma(\varrho)=0·2$ e.Å^{-3}. The observed and calculated structure factors are given in Table 1. The

Table 2. *Final fractional coordinates and anisotropic temperature factors, with associated least-squares errors*

Anisotropic temperature factors are defined as $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$; β_{ij} values are given $\times 10^4$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0·1908 (2)	$\frac{1}{4}$	0·40712 (9)	92 (2)	110 (4)	28·5 (9)	0	−21 (3)	0
K(2)	0·4775 (1)	$\frac{1}{4}$	0·71706 (9)	71 (2)	124 (4)	26·1 (8)	0	19 (2)	0
V	0·1995 (1)	$\frac{1}{4}$	0·6940 (7)	51 (2)	90 (3)	15·4 (6)	0	−9 (2)	0
O	0·3222 (3)	0·0233 (4)	0·1106 (2)	74 (5)	98 (8)	30 (2)	37 (12)	−28 (5)	1 (6)
F(1)	0	0	0	66 (6)	139 (10)	28 (2)	−32 (13)	−7 (6)	−8 (8)
F(2)	0·0371 (4)	$\frac{1}{4}$	0·1943 (2)	96 (7)	150 (11)	20 (2)	0	20 (6)	0
F(3)	0·2726 (4)	$\frac{1}{4}$	0·9085 (2)	69 (6)	147 (10)	16 (2)	0	19 (6)	0

* Extinction coefficient, $g=1·16\pm0·02\times10^{-5}$.

Table 3. *Pertinent interatomic distances and angles* (*with least-squares standard deviations*)*

(*a*) In the vanadium coordination sphere

V–F(1)	2·187 (1) Å	O—V—O′	102·8 (2)°
V–F(2)	1·862 (3)	F(1)–V—F(1′)	80·30 (5)
V–F(3)	1·914 (3)	F(1)–V—F(2)	81·03 (8)
V–O	1·636 (2)	F(1)–V—F(3)	80·92 (8)
F(1)···F(1′)	2·820 (1)	F(2)–V—F(3)	156·3 (1)
F(1)···F(2)	2·642 (2)	F(1)–V—O	88·44 (9)
F(1)···F(3)	2·669 (2)	F(2)–V—O	97·8 (1)
F(1)···O	2·695 (3)	F(3)–V—O	96·9 (1)
F(2)···O	2·641 (4)	F(1)–V—O′	168·72 (9)
F(3)···O	2·662 (3)	V(1)–F(1)–V(1′)	180
O···O	2·557 (5)		

(*b*) In the potassium coordination sphere

K(1)···O_{III}	2·789 (3) Å	K(2)···O_{III}	2·957 (3) Å
K(1)···$F(1)_{IV}$	2·884 (2)	K(2)···O_{II}	2·903 (3)
K(1)···$F(2)_{I}$	2·681 (3)	K(2)···$F(1)_{IV}$	2·855 (2)
K(1)···$F(2)_{IV}$	2·805 (4)	K(2)···$F(2)_{III}$	2·834 (1)
K(1)···$F(3)_{III}$	2·833 (1)	K(2)···$F(3)_{I}'''$	2·657 (2)
K(1)···$O_{IV}''\,''$	3·012 (3)	K(2)···$F(3)_{IV}$	2·606 (3)

* The Roman numerals refer to atoms in the coordination sphere of the vanadium at I$=x,y,z$, II$=\bar{x},\frac{3}{4},\bar{z}$, III$=\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z$, IV$=\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z$, the symbol ″ to atoms in the 0, −1,0 unit cell, ‴ to atoms in the 0,0,1 unit cell, ″ ″ to −1,0,0.

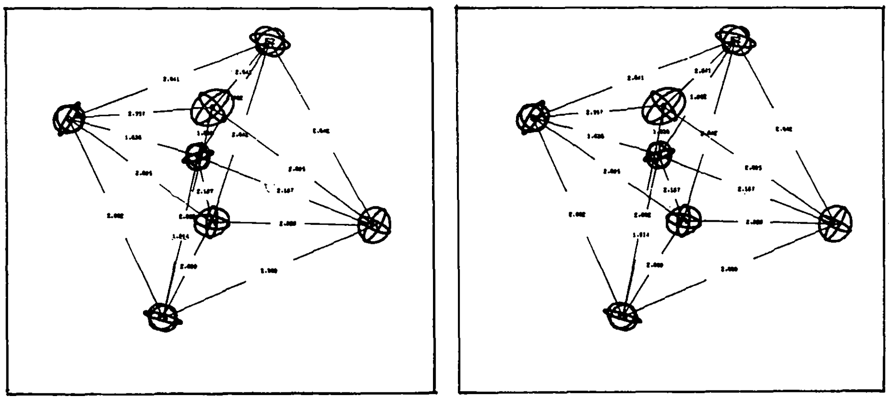

Fig. 1. A view of the coordination polyhedron of vanadium.

atomic positional and thermal parameters, with their estimated standard deviations, are given in Table 2.

Discussion

Pertinent interatomic distances and angles are given in Table 3. Fig. 1 illustrates the distorted octahedral coordination around vanadium. Fig. 2 shows a section of an infinite chain formed by linking vanadium atoms through *cis*-bridging fluorine atoms. Fig. 3 is a stereo view down the vector (0·0, 0·9848, 0·1737) showing the packing of these chains in the unit cell.

This anionic chain structure differs from the models proposed by Davidovich, Sergienko & Murzakhanova (1968) and Pausewang & Dehnicke (1969) in that the vanadium polyhedra are linked by *cis* rather than *trans* bridging fluorine atoms. *Cis* fluorine bridging also occurs in Group V B and VI B pentafluorides and oxytetrafluorides (Edwards, Peacock & Small, 1962; Edwards, 1964; Edwards & Steventon, 1968; Edwards, Jones & Sills, 1968; Edwards & Jones, 1969; Edwards, 1969). The only reported exception is WOF_4, which is supposedly bridged by *cis* oxygen atoms (Edwards & Jones, 1968), but it has been pointed out that a fluorine-bridged structure is more consistent with the vibrational spectra of the compound (Beattie, Livingston, Reynolds & Ozin, 1970).

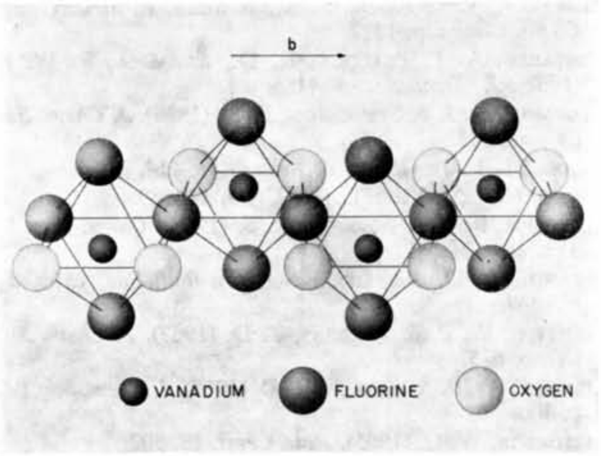

Fig. 2. A section of an infinite chain parallel to the *b* axis.

The average terminal F–V bond distance in $K_2VO_2F_3$ is 1·89 Å, approximately the sum of the effective ionic radii of 6-coordinate V(V), 0·54 Å, and F^-, 1·33 Å (Shannon & Prewitt, 1969). The bridging F–V bond in $K_2VO_2F_3$ is lengthened to 2·187 (1) Å, the difference of 0·30 Å in comparison with the average terminal F–V bond being similar to the corresponding difference of 0·28 Å in, for example, VF_5 (Edwards & Jones, 1969).

The V–O bond distance of 1·636 (2) Å found here is comparable to previously determined values: 1·56 (4) Å in gaseous $VOCl_3$ (Palmer, 1938), 1·66 (10) Å for the unshared oxygen atoms in potassium and ammonium metavanadate (Evans, 1960), and 1·62 (10) Å for the unshared oxygen atoms in KV_3O_8 (Block, 1960).

The O–V–O angle of 102·8 (2)° in $K_2VO_2F_3$ is significantly larger than the O–Mo–O angle of 95 (1)° in $K_2MoO_2F_4.H_2O$ (Grandjean & Weiss, 1967). However, the V–F bonds opposite the terminal oxygen atoms in $K_2VO_2F_3$ are about 0·25 Å longer than the corresponding Mo–F bonds in $MoO_2F_4^{2-}$, which allows greater expansion of the O–V–O angle compared with the O–Mo–O angle. The smaller axial F–M–F angle of 156·3 (1)° in $K_2VO_2F_3$ compared with the corresponding angle of 166·8 (8)° in $K_2MoO_2F_4.H_2O$ can also be explained in this way. This type of angular distortion is only possible in a compound with a *cis* dioxo configuration; a *trans* dioxo configuration would require bond stretching to relieve nonbonded repulsions, a much less favorable process energetically. Steric considerations (Gillespie & Nyholm, 1957) may thus be a factor in determining the configuration of the O–M–O group in these compounds, in addition maximazition of *d–p* π bonding (Shusterovich, 1963; Griffith & Wickins, 1968).

Vibrational spectra

Infrared measurements were made in the region 250–4000 cm^{-1} with a Perkin–Elmer Model 521 spectrophotometer on mineral oil mulls of $K_2VO_2F_3$ placed between KBr flats separated by a 0·004″ tantalum spa-

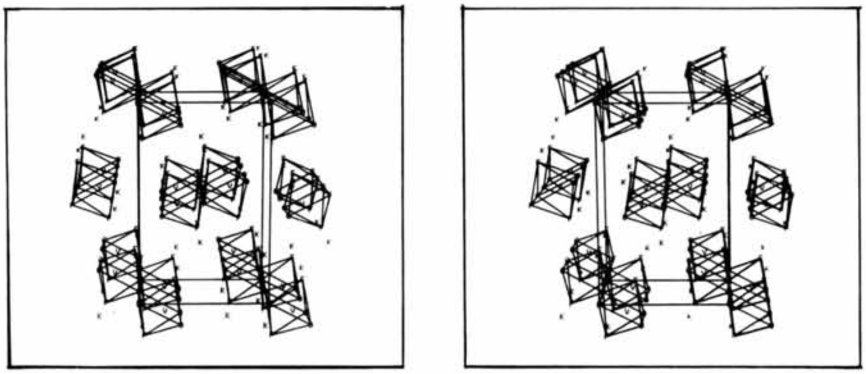

Fig. 3. Stereo view of the packing of the chains looking down the vector (0·0, 0·9848, 0·1737).

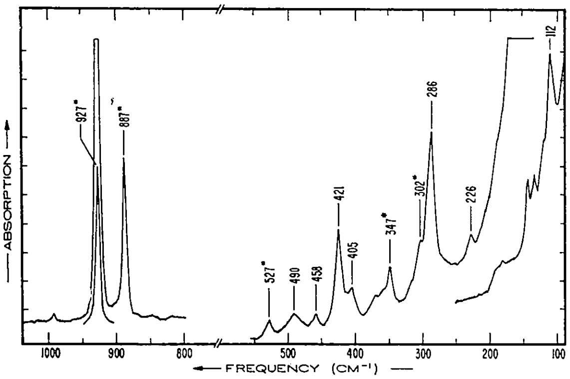

Fig. 4. Raman spectrum of powdered $K_2VO_2F_3$. The asterisks indicate peaks also observed in the infrared.

cer. Raman spectra were recorded from 100 to 1400 cm^{-1} on an Applied Physics Model 81 spectrometer, with incident radiation supplied by a Spectra-Physics Model 125 He–Ne laser operating at 6328 Å.

The Raman spectrum of powdered $K_2VO_2F_3$ is reproduced in Fig. 4. Table 4 gives the observed absorption maxima in both the Raman and the infrared spectra of the compound. In the region examined, our infrared spectrum agrees essentially with that reported by Pausewang & Dehnicke (1969). The coincidence of the Raman and infrared bands at *ca.* 925 and 887 cm^{-1}, and the high intensity of the former band in the Raman, support the assignment of these bands as symmetric and asymmetric V=O stretching frequencies. Assignment of the *cis* configuration to the O–M–O groups in a variety of compounds on the basis of similar spectroscopic evidence (Kharitonov & Buslaev, 1964; Griffith & Wickins, 1967, 1968; Dehnicke, Pausewang & Rüdorff, 1969) is thus supported by the present structural study.

Table 4. *Vibrational spectra of* $K_2VO_2F_3$*

IR(cm^{-1})	Raman (cm^{-1})
—	112*m*
—	136*m*
—	145*m*
—	287*s*
300*m*	302*m*
346*m*	347*m*
—	405*m*
430*w*	421*s*
—	458*m*
—	490*m*
523*s*	527*m*
550*m*	—
569*m*	—
887*s*	887*s*
923*s*	927*vs*
—	994*vw*

* Abbreviations: *w* = weak, *m* = medium, *s* = strong, *v* = very.

The authors wish to thank Dr D. T. Cromer for helpful discussion and Dr A. C. Larson for the use of his unpublished computer programs.

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