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Crystal Structures of M_2FeO_4 (M = K, Rb, Cs)

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The crystal structure of K_2FeO_4, which is isomorphous with β-K_2SO_4, K_2MnO_4 and K_2CrO_4, has been determined in detail. In addition, Rb_2FeO_4 and Cs_2FeO_4 are shown to be of the same structural type. Crystals of K_2FeO_4 are orthorhombic, space group *Pnma*, $a = 7.694(5)$, $b = 5.858(7)$, $c = 10.335(7)$ with $Z = 4$. The integrated intensities of 1174 independent reflections were measured with an automated diffractometer and refined to a weighted least-squares residue of 0.046. The average tetrahedral [Fe–O] bond length, corrected for libration effects, is 1.656(6) Å which is equal within experimental error to values observed for [Cr–O] and [Mn–O] tetrahedral bonds.

Introduction

The isomorphism of K_2FeO_4 with β-K_2SO_4 and K_2CrO_4 has previously been reported (*1–4*). Some time ago, Krebs (*2*) reported the ferrate (VI) ion to be tetrahedral and of nearly the same dimensions (within 1 %) as the chromate (VI) ion, but gave no quantitative data. However, the structural parameters for chromate (VI) ions available at that time do not appear to be reliable. $(NH_4)_2CrO_4$ was first investigated by Bujor (*5*, *6*) but both Gatehouse and Leverett (*7*) and Stephens and Cruickshank (*8*) have recently demonstrated that this structure determination is erroneous and that $(NH_4)_2CrO_4$ is of the β-K_2SO_4 structural type. Also, the original lengths given by Zachariasen and Ziegler (*9*) for the [Cr–O] bonds in K_2CrO_4 (1.60 Å) are much shorter that the average value determined more recently by McGinnety (1.643 Å) (*10*) or the values of 1.68 Å reported for Tl_2CrO_4 by Carter and Margulis (*11*).

A comparison of the accurate structural geometry of FeO_4^{2-} tetrahedra with the geometry of CrO_4^{2-} and MnO_4^{2-} tetrahedra, which have also been studied in detail (*8*, *10*, *15*), allows an examination of the effects of the occupancy of the 3*d* orbitals on bonding to ions in the (VI) oxidation state. We have therefore undertaken a detailed structural investigation of K_2FeO_4.

Experimental

Single Crystal Data

Samples of K_2FeO_4, Rb_2FeO_4 and Cs_2FeO_4 were prepared as described by Audette and Quail (*4*). The ferrate (VI) salts always precipitated as fine powders except in one preparation of K_2FeO_4 when crystals up to 0.5 mm in length were obtained. A sample with dimensions $0.05 \times 0.05 \times 0.40$ mm was selected and placed in a Lindemann glass capillary and the ends of the capillary were sealed. After 24 hr it was observed that the sample had adhered to the wall of the capillary, presumably by reacting with the residual moisture in the capillary. The sample was examined by film techniques and the systematic extinctions ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) and the Laue symmetry confirmed the space group as *Pnma*. The sample was mounted on a Picker *FACS-I* automatic diffractometer and the Mo$K\alpha$ diffraction peaks of 17 reflections, with positive and negative 2θ values ranging between 24° and 40° from the zero 2θ setting, were centered in the receiving aperature. At these 2θ values, the Mo$K\alpha_1$ and Mo$K\alpha_2$ peaks were well resolved. The positions of these reflections were used with the program *PICK2* written by W. C. Hamilton to find the least-square values of the lattice constants and orientation parameters of the crystal. The lattice constants are given below with estimated errors calculated as three times the estimated standard deviations given by the least-squares procedure. All estimated errors in this work are calculated in this manner in order to account for the effects of systematic errors in the initial data.

Crystal Data for K_2FeO_4

$a = 7.694(5)$ Å
$b = 5.858(7)$ Å
$c = 10.335(7)$ Å
λ (Mo$K\alpha_1$) $= 0.70926$ Å
μ (Mo$K\alpha$) $= 50$ cm^{-1}

Space group *Pnma*
$V = 465.8$ Å^3
$F(000) = 380e$
$T = 19$°C
$Z = 4$

The integrated intensities of 1174 independent reflections were measured between 3.5° and 75° in 2θ using Mo$K\alpha$ radiation and a θ-2θ scan mode. A highly oriented graphite monochromator was used with a take-off angle of 2.0°; 40 sec background counts were collected at each limit of the scan. The scan base width was set at 1.5° at 0° in 2θ and compensation for spectral dispersion of the incident beam was added. The scan rate was $\frac{1}{2}$° min^{-1}. The intensities of three standard reflections were monitored after every 50 reflections and did not give any indication of crystal degradation.

Structure Analysis

The data were reduced to observed structure factors by standard procedures. The Lp factor used here is

$$(\cos^2 2\theta m + \cos^2 2\theta s)/(2 \sin 2\theta s)$$

where θm is the monochromator Bragg angle and θs is the Bragg angle of the sample. The experimental conditions used during data collection allowed a variation in the X-ray path length within the crystal from 0.05 to 0.07 mm. The data were therefore not corrected for the effects of absorption. The standard deviations, $\sigma(F)$, of the observed reflections were calculated as $0.25 + 0.0025|F| + \sigma'$, where σ' is determined from the counting statistics of the background and integrated peak counts. These coefficients were chosen such that the average contribution of σ, the constant term and the term proportional to $|F|$ to the total σ' were roughly equal. The scattering factors were calculated from the coefficients given by Cromer and Mann for K^+, Fe^{3+} and O^{2-} ions (*12*). The anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ as given by Cromer (*13*) were applied to the scattering factors of the K and Fe atoms. The structure factors of the reflections which were below the background level were set at zero and the value of σ was set at 10.0. All of the data were used with the Busing, Martin and Levy full matrix least-squares program *ORFLS* (*14*), and starting variables taken from the coordinates reported for K_2MnO_4 by Palenik (*15*). The coordinates of the atoms and individual anisotropic temperature factors were varied to obtain a final weighted residue R_ω, defined by

$$R_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}; \quad \omega = \sigma(F)^{-2}$$

of 0.046 and a traditional R factor of 0.088.* A weighting scheme based on the assumption that the average value of $||F_o| - |F_c||$ in a range of $|F_o|$ is a good approximation to $\sigma(F)$ was tried but slightly higher least-squares estimated standard deviations were obtained. A few strong reflections, two of which were of the type $0k0$, appeared to be subject to extinction and were not included in the refinement. Also the other $0k0$ reflections showed low values of $|F_o|$, although they were not sufficiently intense that the discrepancy between $|F_o|$ and $|F_c|$ could be explained on the basis of extinction. The b axis was collinear with the phi axis of rotation during data collective and these reflections may have been affected by Renninger scattering. These reflections were also deleted from the refinement. The parameters based on the calculated $\sigma(F)$ were accepted as final and are reported in Table I. The interatomic distances and bond angles are given in Table II. The lengths of the [Fe–O] bonds have been corrected

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* A table of observed and calculated structure amplitudes from this analysis has been deposited as Document No. NAPS-02104 with the National Auxiliary Publications Service c/o Microfiche Publications 305 East 46th Street New York, N. Y. 10017. A copy may be secured by citing the document number and by remitting \$5.00 for photocopies or \$1.50 for microfiche. Advance payment is required. Make cheque or money order payable to ASIS-NAPS.

TABLE I

Positional and Thermal Parameters for K_2FeO_4[a]

Atom	x/a	y/b	z/c
K(1)	0.6629(4)	1/4	0.4104(4)
K(2)	−0.0148(4)	1/4	−0.3032(3)
Fe	0.2311(3)	1/4	0.4214(2)
O(1)	0.0193(14)	1/4	0.4143(13)
O(2)	0.2980(15)	1/4	0.5720(11)
O(3)	0.3086(10)	0.0210(14)	0.3492(8)

Atom	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	20(1)[c]	26(2)	32(2)	0	−2(1)	0
K(2)	18(1)	24(2)	21(1)	0	1(1)	0
Fe	13(1)	16(1)	16(1)	0	−1(1)	0
O(1)	9(4)	58(9)	46(8)	0	−5(5)	0
O(2)	28(4)	33(6)	22(5)	0	−5(5)	0
O(3)	32(4)	23(4)	40(5)	4(4)	9(4)	−9(4)

[a] The numbers in parentheses are estimated errors (3 × e.s.d's).

[b] The temperature factor expression is $\exp[-2\pi^2(h^2b_1{}^2U_{11} + \cdots + 2hkb_1b_2U_{12} + \cdots)]$.

[c] The U_{ij} are multiplied by 10^3.

for libration using the method of Schomaker and Trueblood (*16*). The FeO_4^{2-} tetrahedron was assumed to be a rigid body and the center of gravity of the group was assumed to have the coordinates of the iron atom. Bond lengths are also given in Table II, with libration corrections applied.

Powder Diffraction Data

Powder data were obtained using a General Electric XRD-5D/F recording diffractometer, with a flat sample holder mounted on a SPG spectrogoniometer and a No. 2 SPG counter tube and detector system. A CA-8L high intensity iron radiation X-ray tube was employed with a manganese oxide filter to remove the K_β radiation.

Samples of Rb_2FeO_4 and Cs_2FeO_4 were prepared by grinding the compounds and suspending the fine powder in a Nujol mull on a glass slide. The system was calibrated using a quartz sample. The 2θ values for the diffraction lines were recorded directly from the diffractometer tracing obtained. The relative intensities of the various diffraction lines for Rb_2FeO_4 and Cs_2FeO_4 were measured using an Otis planimeter. For K_2FeO_4 the fine powder was packed into a bakelite sample holder to give a flat sample of depth 0.20 mm. To minimize preferred orientations, the surface of the sample was corregated using a serrated packer (*17, 18*). In order to obtain background intensities for the sample, fifteen 2θ angles were chosen where no diffraction lines occurred and a graph of average background versus 2θ was plotted.

After the scaler was set at zero, the spectrogoniometer and the scaler unit were then started simultaneously and the integrated intensity of the line was accumulated. The scaler unit automatically rezeroed itself, reversed direction of the scan on the spectrogoniometer unit and recounted the peak. Each peak was counted ten times. Background counts were subtracted to obtain the average relative intensities of the diffraction lines. Where two or more diffraction lines overlapped, the total relative intensity was first obtained as above. A graph of counts per unit time versus 2θ was constructed by making counts at intervals of 0.03° in 2θ. The overlapping peaks were separated into their components assuming Gaussian line shapes (*19*). The ratio of areas was scaled to the total intensity of that group of peaks.

The *d* spacings and normalized line intensities of all three compounds were calculated using the program POWDER written by D. K. Smith (*20*),

TABLE II

Interatomic Distances and Bond Angles for K_2FeO_4

(a) Interatomic distances (Å)

	Uncorrected	Corrected for libration
Fe–O(1)	1.631(10)[a]	1.646
Fe–O(2)	1.639(11)	1.655
Fe–O(3)	1.647(8)	1.662
O(1)–O(2)	2.692(16)	
O(1)–O(3)	2.684(12)	
O(2)–O(3)	2.666(13)	
O(3)–O(3′)	2.683(12)	

[K–O] contacts shorter than 3.5 Å

	Contact distances (Å)	Number of contacts
K(1)–O(1)	2.742(10)	1
K(1)–O(2)	2.950(2)	2
K(1)–O(3)	2.957(9)	2
K(1)–O(3′)	3.103(9)	2
K(1)–O(3″)	3.202(9)	2
K(1)–O(2′)	3.267(12)	1
K(2)–O(2)	2.731(12)	1
K(2)–O(3)	2.742(9)	2
K(2)–O(2′)	2.790(12)	1
K(2)–O(3′)	2.803(9)	2
K(2)–O(1)	2.931(14)	1
K(2)–O(1′)	3.147(5)	2

(b) Bond angles (in degrees)

O(1)–Fe–O(2)	111.1[b]
O(1)–Fe–O(3)	109.8
O(2)–Fe–O(3)	108.4
O(3)–Fe–O(3′)	109.4

[a] Estimated errors are based on the errors given in Table I.

[b] The estimated errors in the bond angles are *ca.* 0.7°.

and are reported in Table III. The atomic coordinates used to calculate I_{cal} in the case of K_2FeO_4 were taken from the single crystal analysis reported here. However, the values for the others were obtained by fitting I_{cal} to I_{obs}. Because of the limited data available, the accuracy of these coordinates is low (*21*) and we, therefore, do not report the molecular geometry obtained from them. The lattice constants obtained by fitting the observed and calculated *d* spacings are given in Table IV. The estimated errors are three times the e.s.d.'s given by the least-squares procedure. The values of *a* and *b* determined from the single crystal and the powder in the case of K_2FeO_4 do not differ significantly but the value of *c* determined from the powder is 0.025 Å longer than that obtained from the single crystal. This discrepancy may be spurious or it may indicate some differences between the crystal and powder samples.

Discussion

The data in Table III clearly shows that M_2FeO_4 (M = K, Rb and Cs) are isomorphous and the single crystal parameters demonstrate that their structure is the β-K_2SO_4 type. The coordination polyhedra and contact distances of the K^+ polyhedra are similar to those reported by Palenik (*15*) for K_2MnO_4. The distortions of the

TABLE III

Observed and Calculated X-Ray Diffraction Patterns of K_2FeO_4, Rb_2FeO_4 and Cs_2FeO_4

K_2FeO_4					Rb_2FeO_4					Cs_2FeO_4				
h k l	d_{obs}	d_{cal}	I_{obs}	$I_{cal}{}^a$	h k l	d_{obs}	d_{cal}	I_{obs}	$I_{cal}{}^b$	h k l	d_{obs}	d_{cal}	I_{obs}	$I_{cal}{}^c$
1 0 1	—	6.183	—	0.8	1 0 1	—	6.421	—	2	1 0 1	—	6.721	—	0
0 0 2	5.169	5.180	11.3	9.3	0 0 2	—	5.333	—	1	0 0 2	—	5.564	—	1
0 1 1	5.095	5.103	4.9	6.5	0 1 1	—	5.264	—	0	0 1 1	—	5.475	—	2
1 0 2	4.309	4.299	30.2^d	28.0	1 0 2	—	4.444	—	1	1 0 2	—	4.644	—	2
1 1 1	4.271	4.254	47.6^d	42.3	1 1 1	—	4.404	—	0	1 1 1	—	4.592	—	3
2 0 0	3.8597	3.8525	20.4	24.1	2 0 0	4.029	4.020	7	6	2 0 0	—	4.217	—	0
2 0 1	3.6247	3.6109	5.0	5.1	2 0 1	3.7671	3.7617	19	12	2 0 1	3.9502	3.9433	24	21
1 1 2	3.4688	3.4668	13.5	7.3	1 1 2	3.5897	3.5820	46	44	1 1 2	3.7426	3.7359	64	62
2 1 0	3.2266	3.2196	11.2	9.9	2 1 0	3.3503	3.3486	20	21	2 1 0	3.5089	3.5025	20	22
1 0 3	3.1558	3.1513	6.0	3.9	1 0 3	3.2556	3.2514	19	14	1 0 3	3.3986	3.3952	18	11
2 0 2	3.1006	3.0913	28.6^d	31.0	2 0 2	3.2123	3.2100	48	34	2 0 2	3.3641	3.3609	36	34
2 1 1	3.0834	3.0746	54.8^d	45.4	2 1 1	3.2000	3.1948	84	86	2 1 1	3.3475	3.3409	95	92
0 1 3	2.9791	2.9756	100.0	100.0	0 1 3	3.0696	3.0653	100	100	0 1 3	3.1965	3.1948	100	100
0 2 0	2.9381	2.9315	58.7	64.0	0 2 0	3.0267	3.0260	55	77	0 2 0	3.1498	3.1445	70	72
1 1 3	2.7815	2.7758	1.3	1.1	1 1 3	2.8666	2.8642	7	3	1 1 3	2.9920	2.9876	2	6
2 1 2	2.7417	2.7345	7.1	5.4	2 1 2	2.8383	2.8358	12	11	2 1 2	2.9671	2.9640	10	11
1 2 1	2.6549	2.6488	2.9	2.2	1 2 1	2.7404	2.7372	4	2	1 2 1	—	2.8482	—	0
0 0 4	2.5914	2.5900	17.5^d	13.0	0 0 4	2.6667	2.6660	34	11	2 0 3	2.7841	2.7850	34	17
2 0 3	2.5758	2.5915	17.5^d	11.5	2 0 3		2.6630		19	0 0 4		2.7815		8
0 2 2	2.5550	2.5513	8.7	8.7	0 2 2	2.6319	2.6318	3	3	0 2 2	2.7391	2.7375	5	0
3 0 1	2.4965	2.4929	21.2	19.8	3 0 1	2.6005	2.5992	30	29	3 0 1	2.7278	2.7257	37	26
1 0 4	2.4539	2.4550	1.0	0.2	1 0 4	2.5323	2.5307	6	5	1 0 4	2.6400	2.6418	14	4
1 2 2	2.4196	2.4220	4.6	1.6	1 2 2	2.5006	2.5012	11	11	1 2 2	2.6038	2.6038	13	14
2 1 3	2.3584	2.3549	5.3	3.5	2 1 3	—	2.4375	—	3	2 1 3	—	2.5465	—	0
2 2 0	—	2.3329	—	0.5	2 2 0	—	2.4176	—	1	2 2 0	—	2.5208	—	2
3 0 2	2.3050	2.3010	7.1	5.4	3 0 2	2.3966	2.3946	3	2	3 0 2	—	2.5092	—	1
3 1 1	2.2981	2.2941	15.1	16.2	3 1 1	2.3886	2.3883	7	9	3 1 1	2.5028	2.5009	6	8
2 2 1	2.2750	2.2759	17.4	12.8	2 2 1	2.3566	2.3578	13	18	2 2 1	2.4588	2.4585	16	20
1 1 4	2.2650	2.2645	20.5	9.5	1 1 4	2.3349	2.3348	13	18	1 1 4	2.4356	2.4356	17	16
2 0 4	2.1521	2.1494	9.5^d	7.3	3 1 2	—	2.2266	—	0	3 1 2	—	2.3305	—	1
1 2 3	2.1477	2.1464	9.5^d	6.1	2 0 4	2.2221	2.2220	9	6	2 0 4	2.3238	2.3221	8	8
3 1 2	—	2.1420	—	0.0	1 2 3	2.2169	2.2151	8	16	1 2 3	2.3081	2.3070	16	11
2 2 2	2.1286	2.1271	27.9	20.9	2 2 2	2.2017	2.2019	23	35	2 2 2	2.2972	2.2961	27	31
3 0 3	2.0616	2.0609	7.9	7.6	3 0 3	2.1396	2.1400	9	12	3 0 3	2.2398	2.2405	14	13
2 1 4	2.0187	2.0181	3.1	2.0	2 1 4	2.0856	2.0858	4	6	2 1 4	2.1762	2.1783	5	12
1 0 5	2.0000	2.0009	5.2	3.3	1 0 5	2.0619	2.0617	15	10	1 0 5	2.1502	2.1518	26	16
0 1 5	1.9491	1.9536	3.7	3.2	3 1 3	—	2.0176	—	0	3 1 3	—	2.1105	—	1
3 1 3	—	1.9443	—	0.0	0 1 5	2.0100	2.0117	8	6	4 0 0	—	2.1085	—	4
0 2 4	1.9396	1.9410	0.9	1.2	4 0 0		2.0100		7	0 1 5	—	2.0979	—	1
2 2 3	1.9325	1.9331	14.3	9.0	0 2 4	1.9991	2.0005	11	2	2 2 3	2.0846	2.0849	15	16
4 0 0	1.9254	1.9263	5.9	6.5	2 2 3		1.9991		18	0 2 4		2.0835		2
0 3 1	—	1.9205	—	0.0	0 3 1	—	1.9822	—	0	4 0 1	—	2.0716	—	0
3 2 1	1.8979	1.8991	4.8^d	2.4	4 0 1	—	1.9752	—	0	0 3 1	2.0599	2.0601	13	0
4 0 1	1.8940	1.8938	—	0.0	3 2 1	1.9708	1.9717	10	14	3 2 1		2.0596		15
1 1 5		1.8937	1.4^d	2.0	1 1 5	—	1.9516	—	0	1 1 5	—	2.0359	—	2
1 2 4	1.8832	1.8822	2.6	1.9	1 2 4	—	1.9413	—	0	1 2 4	—	2.0227	—	0
1 3 1	1.8636	1.8635	1.7	2.1	1 3 1	1.9240	1.9246	3	1	1 3 1	—	2.0013	—	1
4 1 0	1.8290	1.8300	4.0^d	3.3	4 1 0	1.9063	1.9076	7	8	4 1 0	1.9987	1.9991	10	8
2 0 5	1.8239	1.8248	3.7^d	2.5	3 0 4	—	1.8902	—	1	3 0 4	—	1.9774	—	1
3 0 4		1.8237	2.2^d	2.5	2 0 5	1.8852	1.8842	3	3	4 0 2	—	1.9717	—	3

TABLE III—*continued*

K_2FeO_4					Rb_2FeO_4					Cs_2FeO_4				
h k l	d_{obs}	d_{cal}	I_{obs}	I_{cal}[a]	*h k l*	d_{obs}	d_{cal}	I_{obs}	I_{cal}[b]	*h k l*	d_{obs}	d_{cal}	I_{obs}	I_{cal}[c]
3 2 2	—	1.8100	—	0.8	4 0 2	1.8810	1.8808	2	2	2 0 5	1.9678	1.9682	14	1
4 0 2	—	1.8055	—	0.0	3 2 2	1.8722	1.8778	5	0	4 1 1		1.9676		14
4 1 1	—	1.8021	—	0.5	4 1 1		1.8778		7	3 2 2	—	1.9613	—	0
1 3 2	—	1.7791	—	0.6	1 3 2	—	1.8369	—	7	1 3 2	—	1.9107	—	9
2 3 0	1.7426	1.7429	3.0[d]	2.0	3 1 4	1.8036	1.8042	12	20	3 1 4	1.8857	1.8863	21	20
2 1 5		1.7424	0.3[d]	0.8	2 3 0		1.8030		4	4 1 2	—	1.8814	—	0
3 1 4		1.7414	5.6[d]	3.0	2 1 5	—	1.7990	—	0	2 1 5	—	1.8783	—	0
2 2 4	—	1.7334	—	0.9	4 1 2	—	1.7961	—	0	2 3 0	—	1.8772	—	4
0 0 6	1.7260	1.7267	4.0[d]	3.5	2 2 4	—	1.7910	—	1	2 2 4	—	1.8680	—	3
4 1 2	1.7251	1.7255	0.8[d]	0.1	2 3 1	1.7775	1.7778	13	15	0 0 6	1.8555	1.8545	2	2
2 1 3	1.7193	1.7188	7.1[d]	4.7	0 0 6		1.7775		2	2 3 1	1.8510	1.8510	8	15
0 3 3	1.7003	1.7009	13.9	12.6	0 3 3	1.7548	1.7545	6	18	4 0 3	1.8331	1.8330	4	6
										0 3 3	1.8249	1.8250	16	18

[a] Values were calculated assuming the atom positions found from the single crystal analysis.

[b] Values are calculated assuming the following atom positions: Rb(1): 0.667, $\frac{1}{4}$, 0.411; Rb(2): −0.011, $\frac{1}{4}$, −0.309; Fe: 0.226, $\frac{1}{4}$, 0.421; O(1): 0.027, $\frac{1}{4}$, 0.421; O(2): 0.292, $\frac{1}{4}$, 0.562; O(3): 0.292, 0.034, 0.346.

[c] Values are calculated assuming the following atom positions; Cs(1): 0.660, $\frac{1}{4}$, 0.402; Cs(2): −0.015, $\frac{1}{4}$, −0.301; Fe: 0.226, $\frac{1}{4}$, 0.421; O(1): 0.037, $\frac{1}{4}$, 0.421; O(2): 0.289, $\frac{1}{4}$, 0.557; O(3): 0.289, 0.042, 0.349.

[d] Overlapping reflections. Relative Intensity of each reflection was determined from a Gaussian analysis of the overlapping reflections.

FeO_4^{2-} tetrahedron from regularity are only marginally significant but appear to be related to the [K–O] contacts. As is shown in Fig. 1, the atoms Fe, O(1) and K(1) are colinear and the distances [Fe–O(1)] and [K(1)–O(1)] are the shortest [Fe–O] and second shortest [K–O] distance, respectively. The smallest and largest O–Fe–O angles indicate that the atom O(2) is located at a position slightly further from the atom K(2) than would be the case for an ideal tetrahedron. The distance [K(2)–O(2)] is the shortest [K–O] distance in the structure.

The libration corrections increase the average [Fe–O] bond length by 0.015 Å. This compares with similar values of 0.013 Å for both $(NH_4)_2CrO_4$ (*8*) and K_2MnO_4 (*15*). The average [Cr–O] bond length in $(NH_4)_2CrO_4$, corrected for libration effects, is 1.658(7) Å (*8*) and in K_2CrO_4, using riding motion corrections the average

TABLE IV

POWDER DIFFRACTION CRYSTAL DATA

K_2FeO_4	Rb_2FeO_4	Cs_2FeO_4
$a = 7.705(6)$ Å	8.040(6) Å	8.434(6) Å
$b = 5.863(6)$ Å	6.052(3) Å	6.289(3) Å
$c = 10.360(9)$ Å	10.665(6) Å	11.127(6) Å
$V = 468.01$ Å	518.94 Å	590.10 Å
ρ exp = 2.68 g cm^{-3}	3.57 g cm^{-3}	4.14 g cm^{-3}
ρ calc = 2.81 g cm^{-3}	3.72 g cm^{-3}	4.36 g cm^{-3}
F.W. = 198.05	290.79	385.65
$\lambda(FeK\alpha) = 1.9373$ Å	1.9373 Å	1.9373 Å
$T = 20°C$	20°C	20°C

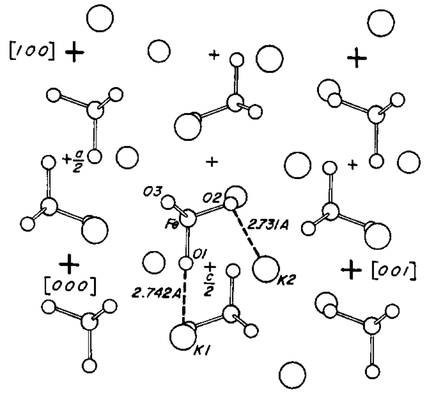

FIG. 1. The structure of K_2FeO_4 projected along the [010] axis, showing the shortest [K–O] contacts. The large circles are K^+ ions at $y = \frac{1}{4}$. The smaller circles are K^+ ions at $y = \frac{1}{4}$.

[Cr–O] bond length is 1.660(4) Å (*10*). For K_2MnO_4 (*15*), the average [Mn–O] bond length is 1.659(8) Å. The average value for [Fe–O] found here is 1.656(6) Å.

In a molecular orbital scheme for $(MO_4)^{n-}$ species, only 3*d* and 4*s* orbitals on the metal ion are involved (*22*). All *d* orbitals on M accept electrons from the ligands and, therefore, any *d* electrons on M must go into orbitals with antibonding character (presumably *e**), decreasing the net bond order in going from chromium to iron. The weakening of the covalent bonding is consistent with the observed stretching force constants (*23*). ($f_d(CrO_4^{2-}) = 5.48$ mdyn/Å, $f_d(MnO_4^{2-}) = 4.88$ mdyn/Å, $f_d(FeO_4^{2-}) = 4.73$ mdyn/Å) Ionic factors alone would predict a decrease in bond length in going from Cr to Fe but covalent factors apparently balance the ionic effects resulting in almost identical dimensions for the chromate, manganate and ferrate ions.

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