

Structure of Dipotassium Ferrate(VI)

BY MARTIN L. HOPPE, E. O. SCHLEMPER* AND R. K. MURMANN*

Department of Chemistry, University of Missouri, Columbia, Missouri 65201, USA

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Abstract. K_2FeO_4 , orthorhombic, space group $Pnam$, $a = 7.690$ (1), $b = 10.328$ (1), $c = 5.855$ (1) Å, $V = 465.0$ (2) Å³, $Z = 4$, $D_x = 2.829$ (2) Mg m⁻³. $R = 0.029$ for the 1527 reflections above 2σ in intensity. The title compound is isomorphous with K_2SO_4 , K_2CrO_4 and K_2MnO_4 . The tetrahedral FeO_4^{2-} has three independent Fe–O bond lengths 1.645 (2), 1.653 (1) and 1.656 (2) Å. The thermally corrected bond lengths, using the rigid-body model, are 1.660 (2), 1.667 (1) and 1.671 (2) Å respectively. These are slightly longer than those in the isomorphous K_2CrO_4 and K_2MnO_4 .

Introduction. Although the ferrate(VI) ion has been known for over 100 years, little quantitative information is available probably due to its instability in the presence of liquid or gaseous water. In recent years there has been an increasing interest in the ion as an industrial oxidant in water purification (Murmman, 1974). Ferrate ion has several advantages over other oxidizing agents in that the products are relatively harmless, it is highly bactericidal and is composed of relatively cheap and abundant elements.

K_2FeO_4 is isomorphous with K_2SO_4 (Scholder, 1955) and thus with K_2MnO_4 (Palenik, 1967) and K_2CrO_4 (Mellor, 1932). Accurate values for the atomic parameters of K_2MnO_4 (Palenik, 1967) and K_2CrO_4 (McGinnety, 1972) have been reported. For predictive purposes in dealing with the effects of increasing numbers of $3d$ electrons on the M –O bond distances in the first transition series M^{VI} tetrahedral oxyanions, the M –O bond distance in K_2FeO_4 was needed.

Impure dipotassium ferrate(VI) was prepared in water as described by Thompson, Schreyer & Ockerman (1951). Crystallization was accomplished by adding a saturated KOH solution to a 1 M KOH solution saturated with K_2FeO_4 and $Na_3H_2IO_6$ at 253 K. After 12 h the crystals were collected, rapidly rinsed with absolute ethanol, followed by anhydrous diethyl ether and dried under vacuum. They are stable in dry air for extended periods of time.

A crystal $0.07 \times 0.07 \times 0.27$ mm mounted roughly along the c axis (needle axis) was selected for the X-ray study which employed an Enraf–Nonius

CAD-4 diffractometer. Accurate values of the unit-cell parameters were determined by a least-squares fit of the angle settings of 25 automatically centered reflections between $2\theta = 20.5$ and 51.7° using Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å).

A set of three-dimensional intensity data was collected using Mo $K\alpha$ radiation from a graphite monochromator. The θ – 2θ step-scan technique was used ($\theta = 1.5$ – 50.0°). The 4136 intensities measured included eight equivalent forms from $\theta = 1.5$ – 10.0° , two from 10.0 – 30.0° , and one from 30.0 – 50.0° . Variable scan speeds were employed to maintain counting statistics of $\pm 2.0\%$ up to a maximum scan time of 120 s. Three standard reflections measured every 6000 s of X-ray exposure showed no significant decrease in intensity. Crystal orientation was maintained by checking the centering of three reflections after every 200 reflections and reorienting when necessary. Empirical absorption correction factors from ψ scans were applied and ranged from 0.98 to 1.00 ($\mu = 49.5$ mm⁻¹). Background and L_p corrections were made in the usual manner giving 2384 reflection intensities greater than 2σ . Averaging equivalent and duplicate measurements gave 1527 independent reflections. Friedel pairs were equal within experimental error as required in $Pnam$.

The values for the coordinates of the atoms in the K_2CrO_4 unit cell (McGinnety, 1972) were used as the initial values for the least-squares refinement of K_2FeO_4 . The neutral-atom scattering factors were those from *International Tables for X-ray Crystallography* (1974) and included anomalous-scattering factors. Full-matrix least-squares refinement was performed with 1527 reflections having F_o^2 greater than $2\sigma(F_o^2)$ where $\sigma(F_o^2) = [\sigma_{count}^2 + (0.05F_o^2)^2]^{1/2}$. Least-squares refinement, in which the scale factor, the isotropic extinction parameter ($g = 6.654 \times 10^{-7}$, Zachariasen, 1969), the positional coordinates and the anisotropic temperature factors were varied, converged with $R = 0.029 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.040$. The least-squares program minimized the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$. The largest shift-to-error ratio was 0.2 in

* Persons to whom inquiries should be addressed.

Table 1. Atomic coordinates with *e.s.d.*'s in parentheses and equivalent isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} * (Å ²)
Fe	0.23110 (4)	0.42132 (3)	0.2500	1.03
K(1)	0.66297 (7)	0.41054 (6)	0.2500	1.88
K(2)	-0.01456 (6)	0.69667 (5)	0.2500	1.53
O(1)	0.0173 (2)	0.4148 (2)	0.2500	2.60
O(2)	0.2997 (3)	0.5733 (2)	0.2500	2.06
O(3)	0.3084 (2)	0.3488 (1)	0.0197 (2)	2.33

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

the last cycle of refinement. The standard deviation of an observation of unit weight was 0.980. Libration corrections for the Cr—O (McGinnety, 1972), Mn—O (Palenik, 1967) and Fe—O bond distances were calculated using the rigid-body model proposed by Schomaker & Trueblood (1968). The final atomic positional parameters with their standard deviations calculated from the last least-squares refinement and thermal parameters are given in Table 1.*

Discussion. The ferrate ion has a tetrahedral structure as shown in Fig. 1. The bond angles are close to the 109.5° required for a perfect tetrahedron.

The environments of the two K atoms were calculated to a distance of 3.5 Å. The coordination number for one is ten with contacts to O between 2.725 (2) and 3.260 (2) Å. The coordination for the other is nine with contacts 2.732–3.145 (2) Å (see Fig. 2*a* and *b**). The Fe—O bond distances, thermally corrected, are 1.660 (2), 1.667 (1) and 1.671 (2) Å. The Fe—O bond distances are slightly longer than the Cr—O distances [1.652 (3), 1.659 (3) and 1.668 (2) Å] which are nearly equal to the Mn—O distances

* Lists of structure factors, anisotropic thermal parameters, and Fig. 2*a* and *b* have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36806 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

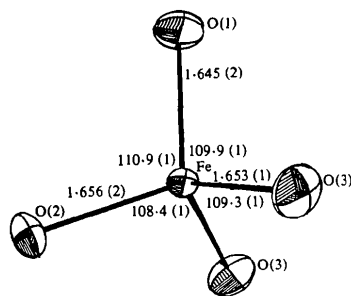


Fig. 1. The FeO_4^{2-} anion; Fe—O bond distances (Å) and angles (°).

[1.645 (8), 1.661 (8) and 1.674 (8) Å]. This is not what would have been expected if a prediction was based simply on the decreasing size of the M^{VI} ions. Comparison of the *average* corrected distance [1.659 (4), 1.660 (8) and 1.666 (2) Å for chromate, manganate and ferrate respectively] with the suggested ionic size (0.40, 0.395 and 0.39 Å for Cr^{VI} , Mn^{VI} and Fe^{VI} , Shannon & Prewitt, 1970) suggests that the effect of ionic size is overcome by the lengthening effect of increasing the number of *d* electrons. This conclusion, however, is based on results which are just outside the estimated experimental error.

Using empirical parameters for calculating cation—oxygen bond valences (Brown & Wu, 1976), the O(1), O(2) and O(3) valences are 1.92, 2.05 and 2.02 respectively. O(1) has four K atoms within the 3.5 Å distance, only one of which is less than 2.9 Å distant while O(2) and O(3) both have five K atoms within 3.5 Å with each having two less than 2.9 Å away. This is consistent with the shorter Fe—O(1) distance and the nearly equal Fe—O(2) and Fe—O(3) distances.

Oxygen-exchange-rate comparisons between the three oxyanions and solvent water does not seem to follow any readily explainable pattern. On studies of chromate(VI)-oxygen exchange (Holyer & Baldwin, 1967) the transfer was explained in terms of dimerization equilibria such as $\text{HCrO}_4^- + \text{CrO}_4^{2-} = \text{Cr}_2\text{O}_7^{2-} + \text{OH}^-$. The slow pH-independent exchange, pH greater than 10, is consistent with the process: $\text{CrO}_4^{2-} + \text{H}_2\text{O} = \text{CrO}_4^* + \text{H}_2\text{O}^*$ with $k_1 \approx 7 \times 10^{-7} \text{ s}^{-1}$ at 298 K.

Manganate-oxygen exchange with water (McDonald, 1960) was negligible in 50 d in the alkaline region. Induced exchange was observed when the manganate ion was precipitated as BaMnO_4 . The ferrate ion exchanges much more rapidly than chromate (Goff & Murmann, 1971). In basic media the rate of ^{18}O exchange between FeO_4^{2-} and water follows the law $R = k[\text{FeO}_4^{2-}]$ where $k = 1.62 \times 10^{-2} \text{ s}^{-1}$ at 298 K. Thus there is no direct correlation between the oxygen exchange rates and the small differences in the observed *M*—O distances.

Infrared spectra of K_2CrO_4 , BaMnO_4 and K_2FeO_4 suggest that the apparent lengthening of the *M*—O bond is real. The moderately strong absorption peak at 875 cm^{-1} , an *M*—O stretch in the chromate ion (Nyquist & Kagel, 1971, and this work), is shifted regularly to lower energy in the manganate ion (Nyquist & Kagel, 1971) and ferrate ion (this work) (830 and 800 cm^{-1} , respectively).

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Structure of Potassium Azidopentacyanocobaltate(III) Dihydrate

BY E. E. CASTELLANO

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13.560, São Carlos, SP, Brazil

O. E. PIRO*† AND G. PUNTE†

Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 49 esquina 115, CC 67, 1900 La Plata, Argentina

AND J. I. AMALVY,‡ E. L. VARETTI† AND P. J. AYMÓNINO†

Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esquina 115, 1900 La Plata, Argentina

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Abstract. $K_3[Co(CN)_5N_3] \cdot 2H_2O$, $M_r = 384.38$, triclinic, $P\bar{1}$, $a = 8.514(2)$, $b = 8.943(1)$, $c = 9.397(2)$ Å, $\alpha = 81.47(2)$, $\beta = 76.32(2)$, $\gamma = 75.95(1)^\circ$, $V = 671.3(3)$ Å³, $Z = 2$, $D_c = 1.902$, $D_m = 1.88(1)$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu(Mo K\alpha) = 2.13$ mm⁻¹, $F(000) = 380$. The structure was solved by Patterson methods and refined by full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms to final R factors of $R = 0.035$ and $R_w = 0.036$ for 1184 reflections. The structure shows a local plane of symmetry perpendicular to \mathbf{a} . The coordination around the Co^{III} ion is approximately octahedral with mean Co–C and Co–N distances of 1.89(2) and 2.005(5) Å respectively. The azide group is linear and asymmetric with the N–N bond nearer to the metal of length 1.204(7) Å and the other of length 1.156(7) Å.

Introduction. As part of a study of the hydrates of hexacoordinated pentacyanometallates (previous paper in this series: Della Vedova *et al.*, 1981, and references therein), the structure of potassium azidopentacyanocobaltate(III) dihydrate has been determined. The fact that this compound contains as a sixth ligand the azide ion adds further interest to the subject because only a few azido complexes have been thoroughly studied from the structural point of view.

The title compound was obtained as a polycrystalline powder by the reaction in aqueous solution of $[Co(NH_3)_5N_3] \cdot Cl_2$ (prepared as described in Linhard & Flygare, 1950) with KCN in the presence of added $CoCl_2 \cdot 6H_2O$ as a catalyst (Barca, Ellis, Tsao & Wilmarth, 1967). Ethanol was added to the resultant solution and the yellow powder obtained was separated by filtration. The product was recrystallized from water. Single crystals, in the form of small plates parallel to the (001) plane, were obtained by slow evaporation of an aqueous solution in the ice-box.

A prismatic crystal of approximate dimensions 0.1 × 0.1 × 0.2 mm was mounted on an Enraf–Nonius

* To whom correspondence should be addressed.
 † Member of the Carrera del Investigador Científico, CONICET, Argentina.
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