CRYSTAL STRUCTURE OF POTASSIUM BICHROMATE K$_{2}$Cr$_{2}$O$_{7}$ (LOPEZITE)

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Abstract

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E. A. KUZ' MIN, V. V. ILYUKHIN, Academician N. V. BELOV

CRYSTAL STRUCTURE OF POTASSIUM BICHROMATE $K_2Cr_2O_7$ (LOPEZITE)

Single crystals of chrompik—the triclinic modification of $K_2Cr_2O_7$—were isolated from solution and kindly placed at our disposal by E. N. Slavnova. The unit-cell parameters ($a = 7.52$; $b = 13.40$; $c = 7.40$ Å; $\alpha = 98°$, $\beta = 90°50'$, $\gamma = 96°10'$; $Z = 4$) are in agreement with those previously reported for natural lopezite ([1]). The good solubility of potassium bichromate in water made it possible without difficulty to obtain specimens of almost spherical shape. The experimental material for the X-ray structural analysis consisted of 2600 nonzero reflections $hk0$—$hk8$ and $0kl$—$3kl$ (MoK$_\alpha$ radiation, $\max \sin\vartheta/\lambda = 0.85$ Å^{-1}).

A detailed analysis of the three-dimensional Patterson synthesis (together with the well-established absence of a piezoelectric effect) made it possible to carry out the analysis under the assumption of a centrosymmetric variant of the structure. In interpreting the three-dimensional Patterson function, the most effective proved to be the "method of combining points of a vector system into n identical n-gons" ([2,8]), which made it possible to localize the Cr and K atoms. Further refinement of the structure proceeded at the stage of electron-density syntheses $\rho(xyz)$. At this stage (an isotropic thermal correction, averaged over groups of atoms, was introduced: $B_{\mathrm{Cr}} \approx 1.1$ Å^2, $B_{\mathrm{K}} \approx 1.4$ Å^2, $B_{\mathrm{O}} \approx 1.7$ Å^2) the discrepancy factor R_{hkl} over the entire volume of the sphere of reflections is equal to 16.1%*. The coordinates of the basis atoms at the achieved value of the R-factor are given in Table 1. The centrosymmetric structure (space group $P\bar{1}$) is characterized by 66 parameters.

Table 1

Coordinates of the basis atoms in the structure of $K_2Cr_2O_7$

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Cr_1	0.192	0.086	0.207	O_4	0.299	0.160	0.358
Cr_2	0.768	0.108	0.592	O_5	0.387	0.849	0.291
Cr_3	0.846	0.583	0.188	O_6	0.095	0.804	0.450
Cr_4	0.574	0.387	0.182	O_7	0.327	0.954	0.583
K_1	0.668	0.139	0.104	O_8	0.697	0.476	0.067
K_2	0.232	0.152	0.751	O_9	0.483	0.301	0.047

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
K_3	0.344	0.636	0.302	O_{10}	0.705	0.332	0.301
K_4	0.084	0.341	0.340	O_{11}	0.416	0.434	0.306
O_1	0.325	0.057	0.030	O_{12}	0.005	0.543	0.313
O_2	0.025	0.135	0.136	O_{13}	0.721	0.650	0.324
O_3	0.107	0.978	0.290	O_{14}	0.933	0.645	0.037

Each of the four crystallographically independent chromium atoms is surrounded by four oxygen atoms in a tetrahedron. The Cr tetrahedra are joined in pairs into diortho groups Cr_2O_7. Among the Cr–O distances in each diortho group, two elongated ones stand out (Cr_1–O_3 and Cr_2–O_3, Cr_3–O_8 and Cr_4–O_8, respectively) to the common atom O in the diortho group at

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* The noncentrosymmetric variant of the structure, differing from the selected one only by a small displacement of the light atoms, did not give a substantial improvement of the *R*-factor (15.8%), but led to a sharp worsening of the interatomic distances.

against the background of the other six:

$$\text{Dichromate group I } (\mathrm{Cr_1 - Cr_2}): \quad \mathrm{Cr_1 - O_3} = 1.72_5 \text{ Å}$$
$$\mathrm{Cr_2 - O_3} = 1.85_6 \text{ Å}$$
$$\text{with the remaining } \mathrm{Cr_1},\ \mathrm{Cr_2 - O} = 1.53\text{–}1.68 \text{ Å},$$
$$\text{Dichromate group II } (\mathrm{Cr_3 - Cr_4}): \quad \mathrm{Cr_3 - O_8} = 1.84_2 \text{ Å}$$
$$\mathrm{Cr_4 - O_8} = 1.74_5 \text{ Å}$$
$$\text{with the remaining } \mathrm{Cr_3},\ \mathrm{Cr_4 - O} = 1.51\text{–}1.63 \text{ Å},$$
$$\text{Angles: (I) } \mathrm{Cr_1 - O_3 - Cr_2} = 127^\circ$$
$$\text{(II) } \mathrm{Cr_3 - O_8 - Cr_4} = 122^\circ.$$

The O–O distances in the tetrahedra are: 2.58-2.79 Å (Cr_1 tetrahedron), 2.48-2.87 Å (Cr_2 tetrahedron), 2.45-2.84 Å (Cr_3 tetrahedron), 2.67-2.90 Å (Cr_4 tetrahedron).

The large K cations also occupy 4 independent crystallographic positions and, as usual, have an ill-defined environment: K_1 and K_2 in seven-vertex polyhedra, which occur more frequently for moderately large

Fig. 1. K bichromate $K_2Cr_2O_7$. Arrangement of K cations in the *yz* projection. A quadrupole of 4 seven-vertex polyhedra around K is highlighted. Common edges are marked by triple lines

(r_i = 0.97-0.99 Å) Na and Ca cations: this is a combination of a trigonal prism and a semioctahedron "attached" to one of the rectangular faces of the prism.

Fig. 1. K-bichromate $K_2Cr_2O_7$. Arrangement of K cations in the yz projection. A quadrupole of 4 seven-vertex polyhedra around K is highlighted. Common edges are marked by triple lines

Figure 1: Fig. 1. K-bichromate $K_2Cr_2O_7$. Arrangement of K cations in the yz projection. A quadrupole of 4 seven-vertex polyhedra around K is highlighted. Common edges are marked by triple lines

Fig. 2. K-bichromate K2Cr2O7. Second quadrupole of K-polyhedra: two octahedra and two octads in the same yz projection. Common edges are marked by triple lines

Figure 2: Fig. 2. K-bichromate K2Cr2O7. Second quadrupole of K-polyhedra: two octahedra and two octads in the same yz projection. Common edges are marked by triple lines

If the K_1 polyhedron is sufficiently compact: 6 distances K_1–O are 2.67-2.78 Å (with an average of 2.73 Å) and one anion is removed to 2.97 Å, then the K_2 polyhedron may be characterized as very loose: 6 neighbors are removed to distances of 2.78-3.00 Å (average 2.91 Å), and only one distance is much shorter and almost equal to the sum of the ionic radii: 2.69 Å.

The coordination of K_3 is sixfold, which for such a large cation is a rather rare case. The coordination polyhedron is a flattened octahedron, noted earlier for the still larger Rb ([4],[5]). The distances K_3–O = 2.73-2.93 Å, with an average of 2.84 Å (anions more than 3.10 Å away were not included in the coordination sphere). Finally, K_4 is located in the eight-vertex polyhedron already described by us ([6]), encountered in compounds of the type M_nBX_4, where $M = K, Rb, Cs, NH_4, Ba$; $B = S, Be, Cr, P$ and $X = F, O$. Seven distances K_4–O vary within the narrow interval 2.82-2.95 Å around an average of 2.88 Å, and again one (the eighth) is substantially shorter: 2.69 Å.

In the structural motif of $K_2Cr_2O_7$ (lopezite) one can distinguish two quadrupoles of K-polyhedra. The first quadrupole is composed of two pairs of hemivertex polyhedra: K_1 and K_2^{**}, K_2 and K_1^{***}, situated (each pair) at approximately the same height (along the a axis):

$$K_1^{**} = 0.20, \qquad K_2 = 0.14, \qquad K_2^{**} = 0.46, \qquad K_1 = 0.40 \qquad \text{(Fig. 1)}.$$

The hemivertex polyhedra are joined along a common edge into pairs, which condense into foursomes also along edges. At the midpoint of the edge common to K_1 and

Fig. 2. K-bichromate $K_2Cr_2O_7$. The second quadrupole of K-polyhedra: two octads and two octahedra in the same yz projection. Common edges are marked by triple lines.

Fig. 3. $K_2Cr_2O_7$. yz projection with separated diortho groups $[Cr_2O_7]$

Figure 3: Fig. 3. $K_2Cr_2O_7$. yz projection with separated diortho groups $[Cr_2O_7]$

K_1^{**} there is a center of symmetry; K_1 has common edges with K_2 and K_2^{**}; analogously K_1^{**} has common edges with K_2 and K_2^{**}, but K_2 and K_2^{**} are not directly connected to one another. The planar quadrupole (the plane of the quadrupole $\sim (\bar{1}12)$) of K_1—K_2 hemivertex polyhedra is connected with translationally identical ones not directly, but through Cr-tetrahedra: (the Cr_1 tetrahedron in the direction $a[100]$ and Cr_2 in the direction $c[001]$).

In the quadrupole of $(2K_3+2K_4)$-polyhedra the four K cations: K_3, K_3^{**}, K_4 and K_4^{**} are situated almost in the plane $(1\bar{1}1)$. The polyhedra are combined into a quadrupole as follows: K_4 has common edges with K_3 and K_3^{**}, and likewise K_4^{**} with K_3 and K_3^{**}; however, if K_3 and K_3^{**} have no common elements, then K_4 and K_4^{**} have an additional bond—a common edge passing through the center of symmetry (Fig. 2). As in the case of the first quadrupole, the second quartet of K-polyhedra is not connected with translationally identical ones directly. Here too the Cr-tetrahedra (Cr_3 and Cr_4 tetrahedra) act as the linking elements.

When the quadrupoles of both kinds are joined into a three-dimensional framework, the K_3 octahedron from the second quartet has only one common edge with the K_2 hemivertex polyhedron of the first quadrupole, whereas the K_4 octad is connected (also by one edge) with the K_1 hemivertex polyhedron, but already of a quadrupole translationally identical to the first.

In the space filled with bulky polyhedra, the remaining voids are occupied by Cr_2O_7 diortho groups (encountered in chromates for the first time). It may be noted that in the structure of lopezite (K-bichromate) the relationship between K and Cr (CrO_4) repeats that which is characteristic of Ca(Na) and Si(SiO_4)

* Here and below, K_n^{**} denotes an atom related to the basic K_n by reflection in a center of symmetry.

in silicates: the relative sizes of the K- and Cr-polyhedra are such that not a single Cr-tetrahedron, but the diortho group Cr_2O_7 (Fig. 3), is stretched over the edge of a large seven-vertex polyhedron around K, and K bichromate may be regarded as the first deciphered analogue of the diorthosilicates of Chapter II of crystal chemistry, not only of silicates,* but also of chromates, and in general of compounds with the complex anion BX_4.

Fig. 3. $K_2Cr_2O_7$. yz projection with separated diortho groups $[Cr_2O_7]$

In a number of works the "morphological" absence of a center of symmetry in $K_2Cr_2O_7$ is emphasized, in contradiction to the purely dry result of the X-ray investigation. Apparently, K bichromate is yet another example of the manifestation in a macrocrystal of lower symmetry in comparison with the microsymmetry established by X-ray structural analysis (hypomorphy, hyposymmetry according to Kleber ([9,10])).

Institute of Crystallography
Academy of Sciences of the USSR

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REFERENCES

[1] H. Strunz, *Mineralogische Tabellen*, 1962.
[2] M. J. Buerger, *Acta Crystallogr.*, **3**, 87, 243 (1950).
[3] M. Buerger, *Crystal Structure Analysis in Vector Space*, IL, 1961.
[4] V. V. Ilyukhin, N. V. Belov, *Crystallography*, **6**, 6 (1961).
[5] N. Mustafaev, V. V. Ilyukhin, N. V. Belov, *Dokl. Akad. Nauk SSSR*, **159**, No. 6 (1964).
[6] N. Mustafaev, V. V. Ilyukhin, N. V. Belov, *Dokl. Akad. Nauk SSSR*, **162**, No. 5 (1965); *Crystallography*, **10**, 6 (1965).
[7] N. V. Belov, *Essays on Structural Mineralogy*, XII, *Mineralogical Collection of the Lvov Geological Society*, No. 15, 1961.
[8] Kh. S. Mamedov, N. V. Belov, *Geochemistry*, **11**, 1087 (1964).
[9] N. V. Belov, *Essays on Structural Mineralogy*, VIII, *Mineralogical Collection of the Lvov Geological Society*, No. 11 (1957).
[10] W. Kleber, *Wissenschaftliche Zs. d. Humboldt Universität zu Berlin*, **5**, No. 1 (1956).

* Cf. also the crystal-chemical similarity and analogy with silicates of Chapter II of phosphates ([7]), borates ([8]), fluoroberyllates ([3,6]).

Note: Figure translations are in progress. See original paper for figures.