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Abstract

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CRYSTALLOGRAPHY

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In recent years, in a number of silicates, phosphates, etc., isolated triortho groups $[Z_3O_{10}]$ have been demonstrated by X-ray methods (¹⁻³), and this has aroused interest in the radicals $[Z_4O_{13}]$, for which two chemically difficult-to-distinguish configurations are possible (Fig. 1A and 1B)*.

In the first X-ray study of K tetrachromate (⁴), for monoclinic crystals of $K_2Cr_4O_{13}$ it was established that: $a = 7.50$, $b = 8.55$, $c = 9.47$ Å; $\beta = 92^\circ$, $Z = 2^{**}$. It was pointed out that tetrachromate is thermodynamically unstable even at ordinary temperature, but that the decomposition reaction proceeds slowly, and this makes X-ray investigation possible.

Fig. 1. Island (terminal) radicals of 4 tetrahedra: **A** and **B**—with formula $[Z_4O_{13}]$, **V** and **G**—with metaformula $[Z_4O_{12}]$

For the present analysis, crystals of $K_2Cr_4O_{13}$ were grown from an aqueous solution by the method described in (⁵). Two specimens, $0.1 \times 0.2 \times 0.2$ mm³ and $0.2 \times 0.2 \times 0.4$ mm³, coated with a protective cellulose film, gave a good diffraction pattern. The unit-cell parameters were obtained from rotation and zero-layer Weissenberg photographs (RGNS goniometer, equi-inclination method): $a = 8.71$, $b = 7.55$, $c = 9.37$ Å; $\beta = 93^\circ$.

The three-dimensional experimental material for the X-ray structural analysis consisted of 550 nonzero reflections $h0l - h6l$ and $0kl - 1kl$

* But clearly differing from radicals also with 4 tetrahedra but with formula $[Z_4O_{12}]$ (Fig. 1V and 1G).

** The parameters differ from those established by us by a somewhat incomprehensible interchange of a and b .

(Mo radiation, $\max \sin \vartheta / \lambda = 0.7 \text{ \AA}^{-1}$). The intensities of the reflections were estimated on the V^2 blackening-mark scale, using multiple exposures for strong reflections. After introduction of the LP factor, no absorption correction was introduced. With Laue symmetry $2/m$, the extinctions $l = 2n - 1$ in the $h0l$ zone make possible two Fedorov groups: $C_s^2 = Pc$ and $C_{2h}^4 = P2/c$.

Most of the peaks of the three-dimensional Patterson function constructed from the experimental data were concentrated in four sections parallel to the xz plane. This indicated a pseudosymmetric arrangement of the heavy Cr and K atoms and considerably complicated the solution of the structure. Using the symmetry and a new method of representing the Patterson function in the form of a system of segments⁶, it was possible to localize the chromium and potassium atoms within the acentric group Pc . The lighter O atoms were fixed in a cycle of three-dimensional syntheses of the electron density $\rho(xyz)$. The value of the discrepancy factor achieved (for all atoms) was 20%. Least-squares refinement reduced R_{hkl} to 10.8%. The coordinates of the basis atoms (55 independent positional parameters) are given in Table 1. The temperature correction common to all atoms is $B = 1.3 \text{ \AA}^{-2}$.

Fig. 2. Structure of K tetrachromate $K_2Cr_4O_{13}$. The spheres show the parallel c axes of the crystallographically independent columns of K_1 and K_2 . Between them, two tetragroups $[Cr_4O_{13}]$, related by the glide plane c (parallel to the plane of the drawing), are shown.

Complete solution of the structure did not confirm the idea of the radical Cr_4O_{13} as a member of the series $ZO_4 - Z_2O_7 - Z_3O_{10} - Z_4O_{13} - Z_5O_{16}$ (terminating in a zunyite five-membered unit), but neither is there a strictly linear configuration.

Table 1

$K_2Cr_4O_{13}$. Coordinates of the basis atoms

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cr ₁	0.441	0.439	0.335	O ₅	0.959	0.562	0.332
Cr ₂	0.434	0.105	0.102	O ₆	0.263	0.568	0.323
Cr ₃	0.759	0.930	0.829	O ₇	0.070	0.244	0.268
Cr ₄	0.095	0.429	0.383	O ₈	0.119	0.633	0.050
K ₁	0.796	0.405	0.104	O ₉	0.447	0.349	0.166
K ₂	0.079	0.892	0.246	O ₁₀	0.448	0.311	0.466
O ₁	0.906	0.064	0.802	O ₁₁	0.425	0.970	0.238
O ₂	0.588	0.069	0.001	O ₁₂	0.750	0.128	0.309
O ₃	0.282	0.103	0.997	O ₁₃	0.767	0.779	0.093
O ₄	0.578	0.563	0.345				

The 4 independent Cr atoms form, in the direction of the a axis, a radical of two corners with 4 Cr tetrahedra. The tetragroup $[Cr_4O_{13}]^{2-}$ may be represented

Fig. 3

Figure 2: Fig. 3

as a trioorthogroup Cr_3O_{10} elongated by 1 tetrahedron (more precisely, by one umbrella molecule CrO_3). The idea of con-

condensation of two diortho groups Cr_2O_7 , as is seen from Fig. 2 and is indirectly confirmed by the easier preparation of $[\text{Cr}_4\text{O}_{13}]^{2-}$, rather than $[\text{Cr}_3\text{O}_{10}]^{2-}$, from the corresponding bichromates.

Among the Cr–O distances, 6 bridging ones are distinguished:

$$\text{Cr}_4 - \text{O}_6 = 1.91, \quad \text{Cr}_1 - \text{O}_6 = 1.83, \quad \text{Cr}_1 - \text{O}_9 = 1.75,$$

$$\text{Cr}_2 - \text{O}_9 = 1.96, \quad \text{Cr}_2 - \text{O}_2 = 1.70, \quad \text{Cr}_3 - \text{O}_2 = 1.84 \text{ \AA}.$$

They are substantially longer than the remaining Cr–O distances, which are equal: in the first tetrahedron, 1.56 and 1.51 Å; in the second, 1.61 and 1.63 Å; in the third, 1.63, 1.54, and 1.69 Å; in the fourth, 1.61, 1.77, and 1.64 Å. The angles $\text{Cr}_1 - \text{O}_9 - \text{Cr}_2$ are 128° , $\text{Cr}_2 - \text{O}_2 - \text{Cr}_3$ 144° , and $\text{Cr}_4 - \text{O}_6 - \text{Cr}_1$ 110° . The two independent K cations are characterized by a large coordination number –11—but by very compact and almost identical polyhedra. The mean distances $\text{K}_1 - \text{O} = 3.00 \text{ \AA}$ and $\text{K}_2 - \text{O} = 3.03 \text{ \AA}$ are exceptionally close; moreover, the next K–O distances, which are not included in the first coordination sphere, 3.88 and 4.52 Å, respectively, are clearly not bonded to K.

Fig. 3. $\text{K}_2\text{Cr}_4\text{O}_{13}$, xy projection. Two tetragroups $[\text{Cr}_4\text{O}_{13}]$ are shown; they are connected by a plane perpendicular to the plane of the drawing—the glide plane c .

The potassium 11-vertex polyhedra are very large, but do not form a three-dimensional framework. Each type of K-polyhedron is built up into its own infinite chain (Fig. 2), which is “stretched” along its own glide plane c , perpendicular to the y axis, at the level ~ 0 for the K_2 -polyhedra and $\sim b/2$ for the K_1 -polyhedra. The two kinds of K chains are combined into infinite layers of large 11-vertex polyhedra. The layers are parallel to the plane (100) and are connected to one another by the Cr_4O_{13} tetragroups. The two tetragroups per cell, at the levels $\sim b/4$ and $\sim 3b/4$, are linked to one another by the same c planes (Fig. 3).

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