β-K$_2$Cr$_2$O$_7$

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The monoclinic modification of dipotassium dichromate, β-K$_2$Cr$_2$O$_7$, has been synthesized in the K$_2$Cr$_2$O$_7$–H$_2$O system. The structure consists of K$^+$ cations and Cr$_2$O$_7^{2-}$ dimers. In contrast with triclinic α-K$_2$Cr$_2$O$_7$ [Kuz'min, Ilyukhin, Kharitonov & Belov (1969). *Krist. Tech.* **4**, 441–461], the Cr$_2$O$_7^{2-}$ groups in β-K$_2$Cr$_2$O$_7$ have twofold crystallographic symmetry and are parallel to each other.

Comment

The monoclinic modification of K$_2$Cr$_2$O$_7$, *i.e.* β-K$_2$Cr$_2$O$_7$, was first described by Klement & Schwab (1960). Powder electron diffraction studies were performed by Zhukova & Pinsker (1964), who suggested space group $P2_1/c$. However, the structure resisted solution due to the absence of appropriate crystals. We present here the synthesis and single-crystal structure of β-K$_2$Cr$_2$O$_7$.

The crystal structure of β-K$_2$Cr$_2$O$_7$ is shown in Figs. 1(a) and 1(b). It consists of K$^+$ cations and Cr$_2$O$_7^{2-}$ dimers, which have twofold crystallographic symmetry and are composed of two CrO$_4$ tetrahedra sharing a common corner (atom O3; Fig. 2). The K atom is coordinated by eight O atoms forming a KO$_8$ square antiprism. The structure may be described as built from layers of composition [K$_2$Cr$_2$O$_7$] parallel to the (100) plane
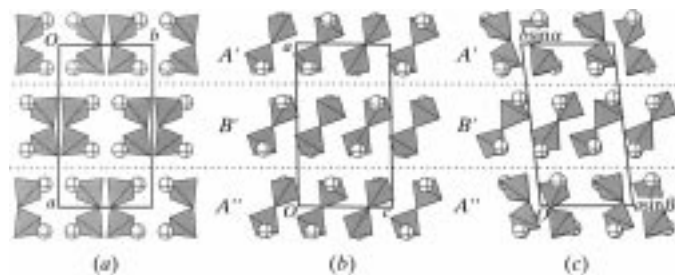

Figure 1
The crystal structures of (a) β-K$_2$Cr$_2$O$_7$ projected along the c axis, (b) β-K$_2$Cr$_2$O$_7$ projected along the b axis and (c) lopezite, α-K$_2$Cr$_2$O$_7$, projected along the c axis. Dashed lines indicate the layers (A', B' and A'') composed of Cr$_2$O$_7^{2-}$ anions (shown as polyhedra) and K$^+$ cations (shown as spheres).

(Figs. 1a and 1b). All the Cr$_2$O$_7^{2-}$ anions in β-K$_2$Cr$_2$O$_7$ are approximately parallel to each other.

Fig. 1 compares the crystal structure of β-K$_2$Cr$_2$O$_7$ with that of triclinic α-K$_2$Cr$_2$O$_7$ (lopezite; Kuz'min *et al.*, 1969). In contrast with β-K$_2$Cr$_2$O$_7$, the Cr$_2$O$_7^{2-}$ groups in α-K$_2$Cr$_2$O$_7$ have two preferential positions at angles of 25–35° (Fig. 1c). The structure of α-K$_2$Cr$_2$O$_7$ may also be described as built from [K$_2$Cr$_2$O$_7$] layers [parallel with (010)]. The structure of the triclinic modification may be obtained from that of the monoclinic modification by rotation of one of the two adjacent layers by 90°. Thus, layers A' and B' shown in Fig. 1(c) have the same structure but are rotated relative to each other by 90° in comparison with the mutual position of adjacent layers (A', B' and A'') in β-K$_2$Cr$_2$O$_7$.
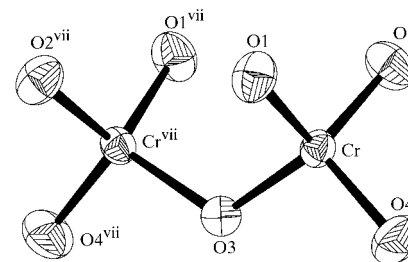

Figure 2
An *ORTEP* (Johnson, 1965) plot of the Cr$_2$O$_7^{2-}$ anions in the title compound. Displacement ellipsoids are drawn at the 50% probability level. The symmetry code is as in Table 2.

Experimental

β-K$_2$Cr$_2$O$_7$ was synthesized in K$_2$CrO$_4$–K$_2$Cr$_2$O$_7$–H$_2$O polycomponent eutonic solutions (K$_2$O 19.17, CrO$_3$ 20.67, H$_2$O 60.16 wt%; saturation temperature 300.8 K, supercooling of 283–288 K).

Crystal data

K$_2$Cr$_2$O$_7$	D_x = 2.724 Mg m^{-3}
M_r = 294.20	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 523
a = 13.0339 (17) Å	reflections
b = 7.3750 (10) Å	θ = 3–23°
c = 7.4672 (10) Å	μ = 4.175 mm^{-1}
β = 91.923 (2)°	T = 293 (2) K
V = 717.38 (17) Å^3	Plate, orange
Z = 4	0.46 × 0.24 × 0.09 mm

Data collection

Bruker PLATFORM diffractometer with a SMART CCD area detector	1779 measured reflections
	798 independent reflections
	718 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.045
Absorption correction: empirical *via* ψ scan (*SAINT-NT*; Bruker, 1998)	θ_{max} = 28.26°
	h = −16 → 17
	k = −9 → 9
T_{min} = 0.317, T_{max} = 0.686	l = −6 → 9

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$wR(F^2)$ = 0.084	$\Delta\rho_{min}$ = −0.52 e Å^{-3}
S = 1.107	Extinction correction: *SHELXTL*
798 reflections	(Bruker, 1997)
52 parameters	Extinction coefficient: 0.0074 (11)
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2$ $+ 0.5383P]$ where $P = (F_o^2 + 2F_c^2)/3$	

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Table 1
Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$).

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cr	0.39714 (3)	0.17429 (5)	0.13497 (5)	0.0213 (2)
K	0.14473 (5)	0.15065 (9)	0.35562 (8)	0.0328 (2)
O1	0.44153 (18)	0.3071 (3)	−0.0176 (3)	0.0337 (5)
O2	0.33753 (18)	0.2974 (3)	0.2780 (3)	0.0341 (5)
O3	1/2	0.0595 (4)	1/4	0.0283 (6)
O4	0.32025 (19)	0.0254 (3)	0.0494 (3)	0.0408 (6)

Table 2
Selected geometric parameters ($\mathring{A}$, °).

Cr—O1	1.624 (2)	K—O1^{iii}	3.039 (2)
Cr—O2	1.620 (2)	K—O2^{iv}	2.764 (2)
Cr—O3	1.7819 (13)	K—O2^{iii}	2.802 (2)
Cr—O4	1.605 (2)	K—O2	2.814 (3)
K—O1^{i}	2.746 (2)	K—O4^{v}	2.886 (2)
K—O1^{ii}	2.859 (2)	K—O4^{vi}	2.965 (2)
O4—Cr—O2	109.82 (13)	O2—Cr—O3	108.56 (9)
O4—Cr—O1	111.46 (12)	O1—Cr—O3	110.17 (9)
O2—Cr—O1	108.33 (12)	Cr^{vii}—O3—Cr	123.25 (15)
O4—Cr—O3	108.45 (11)		

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, -y, \frac{1}{2}+z$; (vii) $1-x, y, \frac{1}{2}-z$.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1998); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *CRYSTAL-MAKER* (Palmer, 1999); software used to prepare material for publication: *SHELXTL*.

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