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Dipotassium tetrachromate(VI), $K_2Cr_4O_{13}$

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The structure of dipotassium tetrachromium(VI) tridecaoxide, $K_2Cr_4O_{13}$, has been determined from single-crystal X-ray data collected at 173 (2) K on a racemically twinned crystal with monoclinic *Pc* space-group symmetry. The structure is composed of discrete $[Cr_4O_{13}]^{2-}$ zigzag chains held together by the charge-balancing potassium ions. The conformations adopted by the tetrachromate anion in alkali metal salts and Cr_8O_{21} are different and can be divided into three categories.

Comment

CrO_3 derivatives are a field of current interest for surface finishing, which proceeds in systems containing CrO_3 dissolved in water. The structure of the predominant species in chromium electroplating baths has been investigated extensively (Radnai & Dorgai, 1992; Šarmaitis *et al.*, 1996; Çengeloglu *et al.*, 2003). These compounds are also continuing to attract interest (Carlsen *et al.*, 1995; Islam *et al.*, 2005; Karunakaran & Suresh, 2004) as they represent the most widely used group of oxidizing agents in organic chemistry, able to oxidize almost every organic functional group (Cainelli & Cardillo, 1984). Chromic acid is a common reagent but the active species in the oxidizing solutions may vary depending on the reaction conditions. The polymerization of the $[CrO_4]^{2-}$ units into corner-sharing dimers, trimers or longer chains is pH and concentration dependent (Šarmaitis *et al.*, 1996). The deformation of the CrO_4 tetrahedra increases with the length of the chains (Gili & Lorenzo-Louis, 1999). Pressprich *et al.* (1988) studied and compared the Cr—O bond lengths within anions of the formula $[Cr_nO_{3n+1}]^{2-}$. They found that, with increasing polymerization, the average bridging bond length increases, while the average non-bridging bond length decreases. The structure of CrO_3 (Hanic & Štempelová, 1960; Stephens & Cruickshank, 1970) consists of infinite chains of corner-sharing CrO_4 tetrahedra, with the bridging Cr—O distances 0.15 Å longer than the mean terminal distance, resulting in deformed CrO_4 units. The structures of trichromate compounds consist of $[Cr_3O_{10}]^{2-}$ anions, together with inorganic cations (Mattes & Meschede, 1973; Kolitsch, 2003; Blum *et al.*, 1979; Blum & Guitel, 1980; Löfgren, 1974) or organic cations (Ding *et al.*, 2004; Stępień & Grabowski, 1977; Garrison *et al.*, 2001; Luis *et al.*, 1995; Fossé *et al.*, 2001). In these structures, the $[Cr_3O_{10}]^{2-}$ units adopt different conformations as a result of the diversity in packing (Casari & Langer, 2006).

Four compounds containing the tetrachromate unit have been structurally characterized before now, including three alkali metal salts and one mixed-valence binary oxide. The chemical analogues $K_2Cr_4O_{13}$ (Golovachev *et al.*, 1970; Kuz'min *et al.*, 1972), $Rb_2Cr_4O_{13}$ (Löfgren, 1971, 1973) and $Cs_2Cr_4O_{13}$ (Kolitsch, 2004) all belong to the monoclinic system, and have space groups *Pc*, *P*2$_1$/*c* and *P*2$_1$/*n*, respectively. Blum & Tran Qui (1979) reported indexed powder diffraction data on $(NH_4)_2Cr_4O_{13}$ and assigned the space group to be *P*2$_1$/*c*, as determined for $Rb_2Cr_4O_{13}$ (Löfgren, 1973) and unpublished work on $K_2Cr_4O_{13}$ by Löfgren. Doubts about both the space-group assignment and the unit-cell parameters of the $K_2Cr_4O_{13}$ structure were expressed by Kolitsch (2004). Furthermore, neither s.u. values nor anisotropic displacement parameters are given in the papers (Golovachev *et al.*, 1970; Kuz'min *et al.*, 1972), and an *R* value of 0.108 was reported, based on film data. We present here a redetermination of the structure of $K_2Cr_4O_{13}$.

The $K_2Cr_4O_{13}$ structure belongs to the non-centrosymmetric space group *Pc*, while the other three chemical analogues belong to space group *P*2$_1$/*c*, with unit cells doubled in the *a* direction (Löfgren, 1973; Kolitsch, 2004; Blum & Tran Qui, 1979). The reciprocal space was searched carefully for weak extra reflections, especially for $h = (2n - 1)/2$, but without success. The crystal under investigation was twinned by an inversion operation and the twin volume ratio was refined to 0.64 (3)/0.36 (3).

There are one discrete chromate tetramer and two non-equivalent potassium ions in the asymmetric unit of $K_2Cr_4O_{13}$ (Fig. 1). The tetrachromate ion, $[Cr_4O_{13}]^{2-}$, is composed of a chain of four CrO_4 tetrahedra, joined by shared corners. The Cr—O bridging distances, can be divided into two groups (Table 1). The two terminal CrO_4 units have longer Cr—O bridging distances [mean 1.834 (4) Å] than the two inner units [mean 1.74 (4) Å]. The non-bridging Cr—O bonding distances

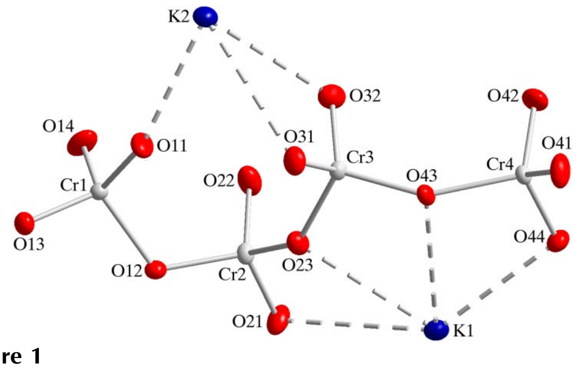

Figure 1
The asymmetric unit of $K_2Cr_4O_{13}$, with atomic displacement ellipsoids drawn at the 50% probability level.

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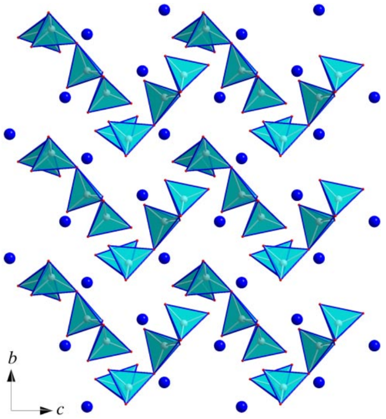

Figure 2
The packing in $K_2Cr_4O_{13}$.

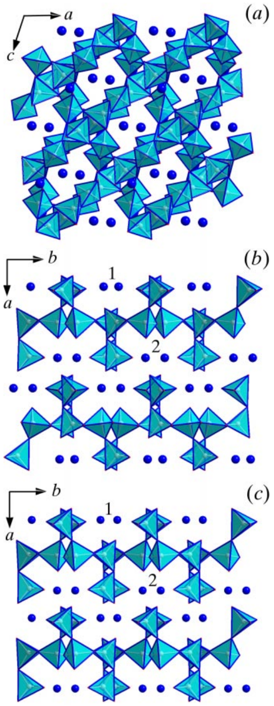

Figure 3
A comparison of the packing in (*a*) $Cs_2Cr_4O_{13}$ (Kolitsch, 2004), (*b*) $Rb_2Cr_4O_{13}$ (Löfgren, 1973) and (*c*) $K_2Cr_4O_{13}$ (this work). The numbers 1 and 2 denote *M*1–*M*1 and *M*2–*M*2 cation pairs in (*b*) and (*c*).

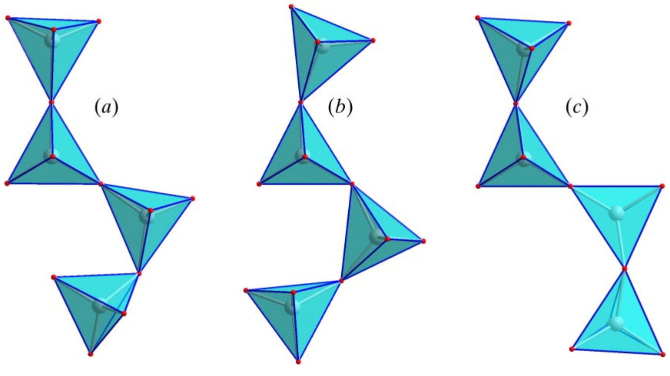

Figure 4
The configuration of $[Cr_4O_{13}]^{2-}$ chains in (*a*) $K_2Cr_4O_{13}$ (this paper), (*b*) $Cs_2Cr_4O_{13}$ (Kolitsch, 2004) and (*c*) Cr_8O_{21} (Norby *et al.*, 1991).

are significantly shorter [mean 1.605 (6) Å] (Fig. 1 and Table 1). Despite the variation of bond lengths, the mean Cr—O distance within the individual tetrahedra remains constant [1.66 (5) Å]. The $[Cr_4O_{13}]^{2-}$ anions form isolated zigzag chains in the *c* direction, whose charge is counterbalanced by the intercalating potassium ions (Fig. 2).

The two cations, K1 and K2, are irregularly coordinated (within 3.28 Å) by 11 and 10 O atoms, respectively (Table 1), but have similar mean K—O bond lengths [2.96 (3) Å]. The O atoms neighbouring each potassium ion belong to six different tetrachromate chains. The relatively high potassium coordination, compared with the ninefold coordination in $K_2Cr_3O_{10}$ (Blum *et al.*, 1979), may be attributed to the high oxygen/potassium ratio (Löfgren, 1973) or to the packing features, as in the case of the 11-coordinate ammonium ions in α-$(NH_4)_2Cr_3O_{10}$ (Casari & Langer, 2006).

Comparing the structural arrangement in the tetrachromate analogues, it is evident that $Cs_2Cr_4O_{13}$ (Fig. 3*a*) differs from $Rb_2Cr_4O_{13}$ and $K_2Cr_4O_{13}$ (Figs. 3*b* and 3*c*). The latter are quite similar but contain different cation–cation distances for the Rb1–Rb1, Rb2–Rb2, K1–K1 and K2–K2 pairs (Figs. 3*b* and 3*c*). These distances vary by 0.111 (3) Å in $Rb_2Cr_4O_{13}$ and 0.038 (4) Å in $K_2Cr_4O_{13}$. Furthermore, every other tetrachromate group is rotated in $Rb_2Cr_4O_{13}$ compared with $K_2Cr_4O_{13}$, but the shapes of the tetrachromate chains are almost the same (Fig. 4*a*). In $Cs_2Cr_4O_{13}$, the packing of the $[Cr_4O_{13}]^{2-}$ anions and cations is different, as is the shape of the chromate chain (Fig. 4*b*). Structural data have so far been determined for only one other compound containing the $[Cr_4O_{13}]^{2-}$ unit, *i.e.* the mixed-valence Cr_8O_{21} oxide, which is better described as $Cr_2^{III}(Cr^{VI}O_4)_2(Cr_4^{VI}O_{13})$ (Norby *et al.*, 1991). In this compound, the tetrachromate chain adopts a third conformation (Fig. 4*c*), resembling a section of the one-dimensional chains in CrO_3 (Hanic & Štempelová, 1960), except for the Cr—O—Cr angle of 180.0 (7)°.

Values of the Cr1—Cr2—Cr3—Cr4 torsion angles, and the Cr1—Cr2—Cr3 and Cr2—Cr3—Cr4 angles in tetrachromate structures, are presented in Table 2. In the nearly planar tetrachromate units, the Cr1—Cr2—Cr3 and Cr2—Cr3—Cr4 angles seem to occur in pairs of a small and a large angle. A combination of two extreme values [86.48 (2) and 127.29 (2)°] is encountered in the $Cs_2Cr_4O_{13}$ structure (Kolitsch, 2004). The Cr1—Cr2—Cr3 angles have also been examined in trichromates (Casari & Langer, 2006), which interestingly showed a range of angles between 86.85 (2) and 127.73 (4)°.

In summary, the structure of $K_2Cr_4O_{13}$ has been redetermined from a racemic twinned crystal and it has been shown that, even if the structure shows similarities with $Rb_2Cr_4O_{13}$ (Löfgren, 1973), the compounds are different enough to lead to a different unit cell and space group.

Experimental

Crystals of $K_2Cr_4O_{13}$ were formed during an attempt to prepare $Ce(CrO_4)_2{\cdot}H_2O$ and/or $Ce(CrO_4)_2{\cdot}2H_2O$. $Ce(SO_4)_2{\cdot}4H_2O$ (1.50 g, 3.75 mmol) was dissolved in water (10 ml) and $Ce(OH)_4$ was precipitated with 15 *M* ammonia. $Ce(OH)_4$ (0.12 g 0.76 mmol) was added to a saturated solution of K_2CrO_4 (1.5 ml), and then concentrated sulfuric acid was added until the cerium hydroxide was completely dissolved. This particular sample was left covered and unguarded and dark-orange–red crystals of $K_2Cr_4O_{13}$, suitable for single-crystal X-ray analysis, were obtained after nine months.

Crystal data

$K_2Cr_4O_{13}$
$M_r = 494.20$
Monoclinic, Pc
$a = 8.6165$ (2) Å
$b = 7.4725$ (1) Å
$c = 9.2811$ (3) Å
$\beta = 92.746$ (2)°
$V = 596.89$ (3) Å^3
$Z = 2$
$D_x = 2.750$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3954 reflections
$\theta = 2.4$–33.0°
$\mu = 4.30$ mm^{-1}
$T = 173$ (2) K
Rhomb, orange–red
$0.06 \times 0.06 \times 0.04$ mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.782$, $T_{\max} = 0.847$
7800 measured reflections
4076 independent reflections
3268 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 33.0°$
$h = -13 \rightarrow 13$
$k = -11 \rightarrow 10$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.105$
$S = 1.01$
4076 reflections
173 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.0614P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}
Absolute structure: Flack (1983), 1935 Friedel pairs
Flack parameter: 0.64 (3)

Table 1
Selected interatomic distances (Å).

Cr1—O11	1.596 (4)	K1—O14^{ii}	3.189 (5)
Cr1—O12	1.835 (4)	K1—O21^{iii}	2.884 (5)
Cr1—O13	1.605 (4)	K1—O21	3.273 (5)
Cr1—O14	1.604 (5)	K1—O23	3.094 (4)
Cr2—O12	1.719 (4)	K1—O41^{iv}	2.768 (5)
Cr2—O21	1.594 (4)	K1—O42^{v}	2.777 (5)
Cr2—O22	1.590 (5)	K1—O43	3.188 (4)
Cr2—O23	1.753 (4)	K1—O44	2.921 (4)
Cr3—O23	1.783 (4)	K2—O11	2.751 (5)
Cr3—O31	1.582 (4)	K2—O12^{vi}	3.116 (4)
Cr3—O32	1.572 (4)	K2—O13^{vi}	2.892 (4)
Cr3—O43	1.694 (4)	K2—O14^{vii}	2.740 (5)
Cr4—O41	1.607 (5)	K2—O31^{iv}	2.896 (4)
Cr4—O42	1.604 (4)	K2—O31	3.246 (5)
Cr4—O43	1.833 (4)	K2—O32	2.988 (4)
Cr4—O44	1.615 (4)	K2—O42^{viii}	3.003 (5)
K1—O11^{i}	3.106 (5)	K2—O44^{ix}	2.825 (4)
K1—O13^{ii}	2.790 (5)	K2—O44^{viii}	2.937 (5)
K1—O13^{i}	2.831 (5)		

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

Table 2
A comparison of intrapolyhedral angles (°) for the different conformations of the $[Cr_4O_{13}]^{2-}$ units.

Angle	$K_2Cr_4O_{13}$^{a}	$Rb_2Cr_4O_{13}$^{b}	$Cs_2Cr_4O_{13}$^{c}	Cr_8O_{21}^{d}
Cr1—Cr2—Cr3—Cr4	172.99 (3)	172.30 (5)	177.58 (2)	180.0 (9)
Cr1—Cr2—Cr3	94.06 (3)	96.05 (5)	86.48 (2)	117.5 (5)
Cr2—Cr3—Cr4	121.45 (3)	122.33 (5)	127.29 (2)	117.5 (5)
Cr2—O—Cr3	138.0 (3)	139.3 (4)	131.6 (2)	180.0 (7)

Notes: (*a*) this work; (*b*) Löfgren (1973); (*c*) Kolitsch (2004); (*d*) Norby *et al.* (1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1081). Services for accessing these data are described at the back of the journal.

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