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α-$Cs_2Cr_3O_{10}$

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The title compound, dicaesium trichromium(VI) oxide, is the orthorhombic (space group *Pbca*) modification of $Cs_2Cr_3O_{10}$. The compound is isotypic with its NH_4 and Rb trichromate analogues. The structure contains discrete $[Cr_3O_{10}]^{2-}$ anions [Cr—O—Cr = 136.58 (11) and 140.30 (12)°] linked *via* two non-equivalent irregularly 11-coordinated Cs^+ cations [d_{av}(Cs—O) = 3.224 and 3.272 Å]. All atoms are in general positions.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Cr–O) = 0.002 Å
R factor = 0.019
wR factor = 0.052
Data-to-parameter ratio = 29.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

During recent attempts to prepare kröhnkite-type chromate oxysalts (Fleck *et al.*, 2002; Fleck & Kolitsch, 2003), two alkali chromates containing polymerized CrO_4 tetrahedra were obtained from acidic aqueous solutions at room temperature. The first compound, α-$Cs_2Cr_3O_{10}$, is reported here. The second compound, a new, fourth modification of $Rb_2Cr_2O_7$, will be reported elsewhere (Kolitsch, 2003).

The asymmetric unit of α-$Cs_2Cr_3O_{10}$ contains two non-equivalent Cs atoms, three Cr atoms and ten O atoms. All atoms are in general positions. The main building unit in the crystal structure is a discrete $[Cr_3O_{10}]^{2-}$ anion in which three CrO_4 tetrahedra are joined *via* common corners into a finite non-linear chain (Figs. 1 and 2). The charge balance is provided by the two Cs^+ cations, both of which are irregularly 11-coordinated by O atoms, with similar mean Cs—O bond lengths [d_{av}(Cs1—O) = 3.224 Å and d_{av}(Cs2—O) = 3.272 Å]. Bond-valence sums for all atoms were calculated using the metal–O parameters of Brese & O'Keeffe (1991). For the metal atoms, these sums are 5.94 (Cr1), 5.97 (Cr2), 5.90 (Cr3), 0.97 (Cs1) and 1.02 (Cs2) valence units (v.u.), if an arbitrary 'cut-off limit' at a Cs—O distance of 3.30 Å is chosen. If all 11 O-atom neighbours of the two Cs atoms are taken into

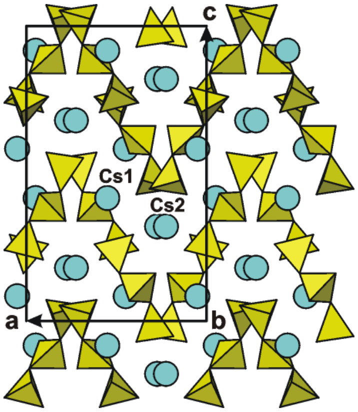

Figure 1
View of α-$Cs_2Cr_3O_{10}$ along [010]. Isolated non-linear $[Cr_3O_{10}]^{2-}$ anions (yellow) are linked *via* two irregularly 11-coordinated Cs^+ cations (blue). The unit cell is outlined.

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account, the bond-valence sums would amount to relatively high values, 1.30 and 1.29 v.u.; still, and also in view of the often insufficiently flexible bond-valence parameters for very large cations, it is preferred to consider the Cs atoms as 11-coordinated. The O atoms have bond-valence sums of 1.94 (O1), 1.93 (O2), 1.97 (O3), 2.29 (O4), 1.98 (O5), 1.95 (O6), 2.26 (O7), 1.94 (O8), 2.08 (O9) and 1.96 v.u. (O10), if all weak contributions from the Cs atoms are included. Values further from the ideal valency of 2.00 are obtained for several O atoms if these weak contributions are neglected. The anomalously high values for the two bridging O atoms in the Cr_3O_{10} group, O4 and O7, are noteworthy.

α-$Cs_2Cr_3O_{10}$ (space group *Pbca*) is isotypic with its NH_4 (Seiter, 1957) and Rb (Löfgren, 1974) analogues. $K_2Cr_3O_{10}$, on the other hand, is monoclinic (space group $P2_1/n$; Soldatov *et al.*, 1978; Blum *et al.*, 1979). Among these trichromates, a second, hexagonal modification (space group $P6_3/m$) is also known to exist for the NH_4 (Blum & Guitel, 1980) and Rb members (Blum, 1979), whereas a rhombohedral modification (space group *R*3*c*) was determined only for $Cs_2Cr_3O_{10}$ (β-$Cs_2Cr_3O_{10}$; Mattes & Meschede, 1973). The latter authors also reported the existence of orthorhombic α-$Cs_2Cr_3O_{10}$ and that it is probably isotypic with $(NH_4)_2Cr_3O_{10}$ (Seiter, 1957); this assumption is confirmed by the present study.

In α-$Cs_2Cr_3O_{10}$, the three CrO_4 tetrahedra in the Cr_3O_{10} group exhibit similar average Cr—O bond lengths [d_{av}(Cr1—O) = 1.652 Å, d_{av}(Cr2—O) = 1.659 Å and d_{av}(Cr3—O) = 1.661 Å]. The longest Cr—O bonds are those between the bridging O atoms (O4 and O7) and the terminal Cr1 and Cr3 atoms (Table 1 and Fig. 2), a situation equivalent to that in β-$Cs_2Cr_3O_{10}$ (Mattes & Meschede, 1973). This observation is explained by the need to avoid oversaturation of the bridging O atoms. The O—Cr—O angles in all three CrO_4 tetrahedra do not deviate much from ideal tetrahedral angles. The Cr—O_{bridge}—Cr bond angles are 136.58 (11) and 140.30 (12)°, very similar to the equivalent values in isotypic $Rb_2Cr_3O_{10}$, [136.0 (4) and 140.0 (4)°; Löfgren, 1974]. In the rhombohedral modification of $Cs_2Cr_3O_{10}$, the corresponding angles are smaller and also show a stronger variation [123 and 133°, no s.u. values given in original publication (Mattes & Meschede, 1973); note that the second value given in the original paper, 139°, is a misprint]. In monoclinic $K_2Cr_3O_{10}$ (Soldatov *et al.*, 1978; Blum *et al.*, 1979), the Cr—O_{bridge}—Cr bond angles [123.0 (3) and 133.8 (3)°; Blum *et al.*, 1979] are similar to those in rhombohedral $Cs_2Cr_3O_{10}$.

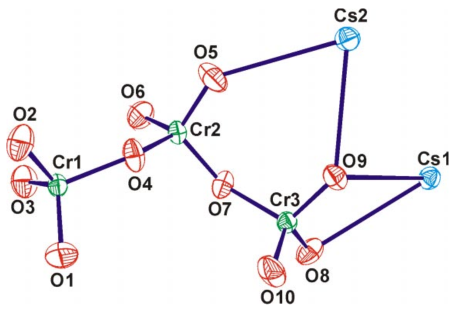

Figure 2
View of the atoms in the asymmetric unit of α-$Cs_2Cr_3O_{10}$, shown with displacement ellipsoids at the 50% probability level. The two similar Cr—O_{bridge}—Cr bond angles are 136.58 (11) (Cr2—O7—Cr3) and 140.30 (12)° (Cr1—O4—Cr2).

Experimental

The title compound crystallized at room temperature from an acidic solution (pH 2–3) containing dissolved Cs_2CO_3, $Ni(NO_3)_2{\cdot}6H_2O$ and CrO_3. α-$Cs_2Cr_3O_{10}$ formed large orange rhomb-shaped plates and clusters of small plates.

Crystal data

$Cs_2Cr_3O_{10}$
M_r = 581.82
Orthorhombic, *Pbca*
a = 11.887 (2) Å
b = 9.671 (2) Å
c = 19.493 (4) Å
V = 2240.9 (8) $Å^3$
Z = 8
D_x = 3.449 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 4564 reflections
θ = 2.0–32.6°
μ = 9.29 mm^{-1}
T = 293 (2) K
Tablet, orange
0.10 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.457, T_{max} = 0.654
7678 measured reflections

4071 independent reflections
3587 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 32.6°
h = −17 → 17
k = −14 → 14
l = −29 → 29

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.053
S = 1.05
4071 reflections
137 parameters

$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 1.72P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.59 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.87 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00197 (7)

Table 1
Selected geometric parameters (Å, °).

Cr1—O1	1.597 (2)	Cr2—O4	1.7168 (18)
Cr1—O3	1.605 (2)	Cr2—O7	1.7190 (18)
Cr1—O2	1.6111 (19)	Cr3—O10	1.6021 (18)
Cr1—O4	1.8209 (18)	Cr3—O8	1.6063 (19)
Cr2—O5	1.584 (2)	Cr3—O9	1.6128 (17)
Cr2—O6	1.588 (2)	Cr3—O7	1.8243 (18)
Cr2—O4—Cr1	140.30 (12)	Cr2—O7—Cr3	136.58 (11)

The atomic coordinates of $Rb_2Cr_3O_{10}$ (Löfgren, 1974) were taken as starting values for the refinement.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997) software used to prepare material for publication: *SHELXL*97.

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