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$Cs_2Cr_4O_{13}$: a new structure type among alkali tetrachromates

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Dicaesium tetrachromium(VI) tridecaoxide, $Cs_2Cr_4O_{13}$, contains finite $[Cr_4O_{13}]^{2-}$ anions composed of four corner-linked CrO_4 tetrahedra. These anions are linked by Cs^+ cations whose Cs—O bond lengths range between 3.015 (2) and ~3.7 Å. Although $Cs_2Cr_4O_{13}$ is not isotypic with its NH_4, K or Rb analogs, the $[Cr_4O_{13}]^{2-}$ anions in all these compounds exhibit a similar zigzag-like geometry.

Comment

Three alkali chromates containing polymerized CrO_4 tetrahedra were recently obtained during attempts to prepare kröhnkite $[Na_2Cu^{II}(S^{VI}O_4)_2{\cdot}2H_2O]$-type chromate oxysalts (Fleck *et al.*, 2002; Fleck & Kolitsch, 2003). The crystal structures of two of these compounds, α-$Cs_2Cr_3O_{10}$ and $Rb_2Cr_2O_7$ (a new, fourth, modification), were characterized by Kolitsch (2003, 2004). The present article reports the structure of the third polychromate, $Cs_2Cr_4O_{13}$, which has a structure type previously unknown among alkali chromates.

The title compound contains two non-equivalent Cs atoms, four Cr atoms and 13 O atoms, all of which are in general positions. The main building unit in the crystal structure is a discrete $[Cr_4O_{13}]^{2-}$ anion, in which four CrO_4 tetrahedra are joined *via* common corners into a finite zigzag-like chain (Figs. 1 and 2). This anion, to be discussed further below, is counterbalanced by the two Cs^+ cations, which are both irregularly coordinated to ten O atoms within 3.53 Å. For each of the Cs^+ cations there exist two additional, fairly remote, O-atom neighbors [at distances of between 3.672 (3) and 3.797 (3) Å], which are not considered as ligands. The Cs^+ cations are characterized by slightly different mean Cs—O bond lengths (mean Cs1—O = 3.202 Å and mean Cs2—O = 3.304 Å). Bond-valence sums for all atoms were calculated using the metal–oxygen parameters of Brese & O'Keeffe (1991). For the metal atoms, the bond-valence sums are 5.93 (Cr1), 5.99 (Cr2), 6.00 (Cr3), 6.08 (Cr4), 1.27 (Cs1) and 0.97 (Cs2) valence units (v.u.), if an arbitrary 'cut-off limit' at a Cs—O distance of 3.53 Å is chosen. The bond-valence sums of the O atoms are 2.11 (O1), 1.93 (O2), 1.99 (O3), 2.23 (O4), 1.88 (O5), 1.90 (O6), 2.18 (O7), 1.90 (O8), 2.01 (O9), 2.19 (O10), 2.07 (O11), 2.03 (O12) and 1.84 v.u. (O13). The 'unusually' high value obtained for atom Cs1 reflects the insufficient flexibility of the bond-valence parameters for very large cations, whereas the 'unusually' high values calculated for the bridging O atoms O4, O7 and O10 (*cf.* Fig. 2) are caused by the inflexibility of these parameters in the case of strongly distorted polyhedra (compare also the difficulties reported during the calculation of bond-valence sums for the atoms in α-$Cs_2Cr_3O_{10}$; Kolitsch, 2003).

$Cs_2Cr_4O_{13}$ exhibits a structure type that is new among alkali tetrachromates. However, the three structurally characterized chemical analogs $Rb_2Cr_4O_{13}$ (Löfgren, 1971, 1973), $K_2Cr_4O_{13}$ [Löfgren (unpublished) cited by Blum & Tran Qui (1979)] and $(NH_4)_2Cr_4O_{13}$ (Blum & Tran Qui, 1979), which are all isotypic (monoclinic, space group $P2_1/c$, with a $\simeq$ 17.8 Å, $b \simeq$ 7.7 Å, $c \simeq$ 9.4 Å and $\beta \simeq 92°$), contain $[Cr_4O_{13}]^{2-}$ anions with similar zigzag-like structures. Only the mutual arrangement between these anions and the alkali cations is different (Fig. 3). The zigzag character of the tetrachromate anion may be explained by the need to achieve a configuration with minimum electrostatic repulsion between adjacent CrO_4 tetrahedra. The crystal structure of CrO_3 (Byström & Wilhelmi, 1950) consists of infinite zigzag-like chains of corner-linked CrO_4 tetrahedra, which, as shown in Fig. 4, are topologically similar to the finite chains in $Cs_2Cr_4O_{13}$ (the similarity is less pronounced in the

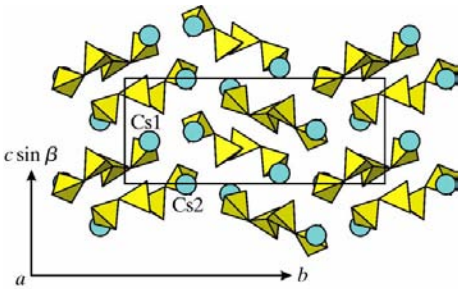

Figure 1
A view of $Cs_2Cr_4O_{13}$ along [100]. Isolated zigzag $[Cr_4O_{13}]^{2-}$ anions are linked *via* two Cs^+ cations. The unit cell is outlined.

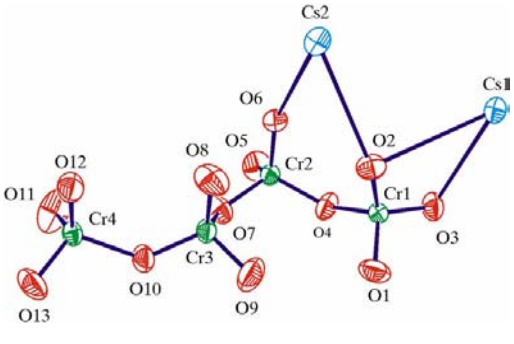

Figure 2
A view of the atoms in the asymmetric unit of $Cs_2Cr_4O_{13}$, shown with displacement ellipsoids at the 50% probability level.

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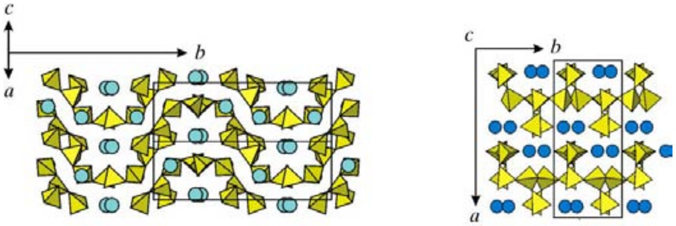


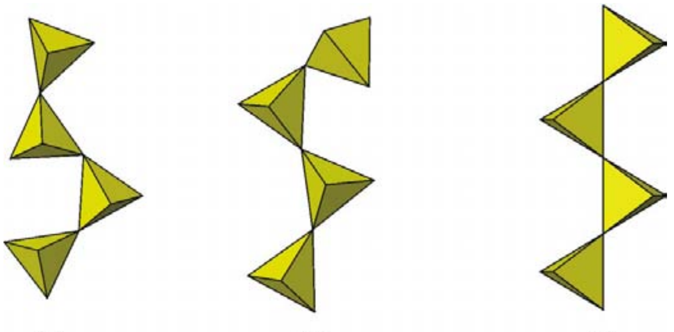
(a) (b)

Figure 3
A comparison of the packing in the structures of (*a*) $Cs_2Cr_4O_{13}$ (this work) and (*b*) $Rb_2Cr_4O_{13}$ (Löfgren, 1973). Note the different mutual arrangement of the $[Cr_4O_{13}]^{2-}$ anions and the alkali cations.

case of $Rb_2Cr_4O_{13}$). [Note that the structure model reported for $K_2Cr_4O_{13}$ by Golovachev *et al.* (1970) and Kuz'Min *et al.* (1972) appears topologically identical to that of the Rb analog, although these authors give a different, possibly erroneous, space group (*Pc*) and possibly erroneous unit-cell parameters (*a* is halved with respect to the otherwise similar cell data given for the Rb analog).]

The four CrO_4 tetrahedra in the $[Cr_4O_{13}]^{2-}$ anion exhibit similar mean Cr—O bond lengths [mean Cr1—O = 1.66 (10) Å, Cr2—O = 1.65 (8) Å, Cr3—O = 1.65 (8) Å and Cr4—O = 1.65 (11) Å]. The longest Cr—O bonds [Cr1—O4 = 1.832 (2) Å and Cr4—O10 = 1.846 (2) Å] are those between the bridging O atoms (O4 and O7) and the terminal atoms Cr1 and Cr4 (Table 1 and Fig. 2), a situation similar to that encountered in alkali trichromates $M_2Cr_3O_{10}$ (M = alkali metal; *e.g.* Kolitsch, 2003, and references therein). The observation of Löfgren (1973) that the deformation of CrO_4 tetrahedra in a given (poly)chromate increases with the number of tetrahedra forming the anionic chain is confirmed by the structure of the title compound.

The O—Cr—O angles in all four CrO_4 tetrahedra do not deviate significantly from ideal tetrahedral angles (Table 1). The Cr—O_{bridge}—Cr bond angles lie within a narrow range of between ~132 and ~136° (Table 1). The angular range is much larger in $Rb_2Cr_4O_{13}$ (120.5–147.2°; Löfgren, 1973). The angular values are slightly smaller than those in the orthorhombic caesium trichromate polymorph (α-$Cs_2Cr_3O_{10}$; Kolitsch, 2003) but larger than those in the trigonal polymorph (β-$Cs_2Cr_3O_{10}$; Mattes & Meschede, 1973). Thus, these Cr—O_{bridge}—Cr bond angles seem to be strongly dependent on the mutual arrangement between the chromate anions and the alkali cations in a given polychromate structure.



(a) (b) (c)

Figure 4
A comparison of the configuration of the $[Cr_4O_{13}]^{2-}$ anion in (*a*) $Cs_2Cr_4O_{13}$ and (*b*) $Rb_2Cr_4O_{13}$ (Löfgren, 1973) with (*c*) a fragment of the infinite tetrahedral chains in CrO_3 (Byström & Wilhelmi, 1950).

Experimental

The title compound crystallized from an acidic solution (pH 2–3) containing dissolved CrO_3, Cs_2CO_3 and $CdCO_3$. On slow evaporation at room temperature, block-like dark-orange crystals of β-$Cs_2Cr_3O_{10}$ (Mattes & Meschede, 1973) precipitated from this solution. Over the course of several weeks, these crystals reacted with the mother liquid, forming lath-like-to-acicular crystals of $Cs_2Cr_4O_{13}$, up to several millimeters in length, which protruded from the surface of the β-$Cs_2Cr_3O_{10}$ crystals.

Crystal data

$Cs_2Cr_4O_{13}$
M_r = 681.82
Monoclinic, $P2_1/n$
a = 8.021 (2) Å
b = 20.457 (4) Å
c = 8.739 (2) Å
β = 107.41 (3)°
V = 1368.3 (6) Å^3
Z = 4
D_x = 3.310 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5065 reflections
θ = 2.0–32.6°
μ = 8.39 mm^{-1}
T = 293 (2) K
Thick tabular, orange–red
0.08 × 0.04 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
ψ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.553, T_{max} = 0.730
9739 measured reflections
4934 independent reflections
4108 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 32.5°
$h = -12 \rightarrow 12$
$k = -30 \rightarrow 30$
$l = -13 \rightarrow 13$

Table 1
Selected geometric parameters (Å, °).

Cr1—O1	1.594 (2)	Cr3—O8	1.572 (2)
Cr1—O2	1.604 (2)	Cr3—O9	1.576 (3)
Cr1—O3	1.611 (2)	Cr3—O10	1.692 (2)
Cr1—O4	1.832 (2)	Cr3—O7	1.774 (2)
Cr2—O5	1.577 (2)	Cr4—O11	1.579 (3)
Cr2—O6	1.578 (2)	Cr4—O12	1.595 (2)
Cr2—O4	1.704 (2)	Cr4—O13	1.595 (3)
Cr2—O7	1.752 (2)	Cr4—O10	1.846 (2)
O1—Cr1—O2	110.04 (14)	O9—Cr3—O10	110.43 (15)
O1—Cr1—O3	110.68 (14)	O8—Cr3—O7	108.96 (14)
O2—Cr1—O3	111.20 (13)	O9—Cr3—O7	108.42 (15)
O1—Cr1—O4	109.50 (12)	O10—Cr3—O7	108.82 (11)
O2—Cr1—O4	108.77 (11)	O11—Cr4—O12	112.45 (18)
O3—Cr1—O4	106.58 (12)	O11—Cr4—O13	109.2 (2)
O5—Cr2—O6	108.98 (15)	O12—Cr4—O13	108.73 (14)
O5—Cr2—O4	110.09 (13)	O11—Cr4—O10	107.98 (14)
O6—Cr2—O4	109.09 (12)	O12—Cr4—O10	109.29 (11)
O5—Cr2—O7	108.56 (13)	O13—Cr4—O10	109.16 (13)
O6—Cr2—O7	109.11 (12)	Cr2—O4—Cr1	133.03 (12)
O4—Cr2—O7	110.98 (13)	Cr2—O7—Cr3	131.55 (14)
O8—Cr3—O9	108.27 (17)	Cr3—O10—Cr4	135.66 (14)
O8—Cr3—O10	111.87 (13)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.04$
4934 reflections
173 parameters
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 1.5P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00175 (11)

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1038). Services for accessing these data are described at the back of the journal.

References

Blum D, & Tran Qui, D. (1979). *J. Appl. Cryst.* **12**, 608–609. (In French.)
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Byström, A. & Wilhelmi, K. A. (1950). *Acta Chem. Scand.* **4**, 1131–1141.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fleck, M. & Kolitsch, U. (2003). *Z. Kristallogr.* **218**, 553–567.
Fleck, M., Kolitsch, U. & Hertweck, B. (2002). *Z. Kristallogr.* **217**, 435–443.
Golovachev, V. P., Kuz'Min, E. A., Kharitonov, Yu. A. & Belov, N. V. (1970). *Dokl. Akad. Nauk SSSR*, **192**, 1272–1274. (In Russian.)
Kolitsch, U. (2003). *Acta Cryst.* E**59**, i164–i166.
Kolitsch, U. (2004). *Z. Kristallogr. New Cryst. Struct.* In the press.
Kuz'Min, E. A., Golovachev, V. P., Kharitonov, Yu. A. & Belov, N. V. (1972). *Kristallografiya*, **17**, 929–933. (In Russian.)
Löfgren, P. (1971). *Acta Chem. Scand.* **25**, 3893–3895.
Löfgren, P. (1973). *Acta Cryst.* B**29**, 2141–2147.
Mattes, R. & Meschede, W. (1973). *Z. Anorg. Allg. Chem.* **395**, 216–222. (In German.)
Nonius (2003). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Shape Software (1999). *ATOMS*. Version 5.0.4 for Windows and Macintosh. Shape Software, Kingsport, TN 37663, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.