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A new chromate of tetravalent cerium: $Ce_2(CrO_4)_4 \cdot 2H_2O$

Uwe Kolitsch* and Karolina Schwendtner

Universität Wien, Institut für Mineralogie und Kristallographie, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria
Correspondence e-mail: uwe.kolitsch@univie.ac.at

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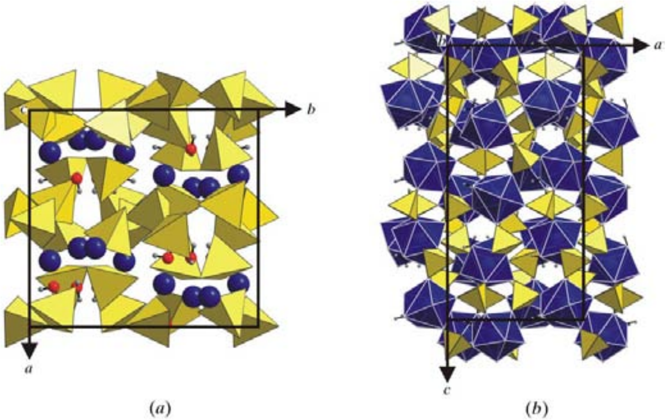
Dicerium(IV) tetrachromate(VI) dihydrate, $Ce^{IV}_2(CrO_4)_4 \cdot 2H_2O$, has been prepared from an acidic aqueous solution at room temperature. Its novel crystal structure, which was solved from single-crystal X-ray diffraction data, is built from isolated CrO_4 tetrahedra and isolated $Ce(O,H_2O)_n$ ($n = 8$ and 9) polyhedra. All atoms are in general positions. The mean Ce—O and Cr—O bond lengths are 2.358 and 1.651 Å, respectively. Comparisons are drawn with the structure of $Ce^{IV}(CrO_4)_2 \cdot 2H_2O$.

Comment

$Ce^{IV}_2(CrO_4)_4 \cdot 2H_2O$, dicerium(IV) tetrachromate(VI) dihydrate, (I), represents a new structure type among chromates (and sulfates or molybdates) of comparable M^{IV} cations (M = Ce, Th, U, Zr and Ti). The atomic arrangement has space-group symmetry *Pbca*, and the asymmetric unit contains two Ce, four Cr, 18 O and four H atoms, all of which occupy general positions. The structure is built from isolated CrO_4 tetrahedra, Ce atoms and two water molecules, which belong to the coordination environments of the Ce atoms (Figs. 1 and 2). The mean Cr—O bond lengths in the four CrO_4 tetrahedra are similar (1.658, 1.648, 1.650 and 1.646 Å for atoms Cr1, Cr2, Cr3 and Cr4, respectively). The $Cr1O_4$ tetrahedron shows the largest bond-length distortion (Table 1) and, accordingly, the largest mean Cr—O bond length, an observation in strict accordance with the distortion theorem (Brown & Shannon, 1973; Brown, 1981). The observed distortion of the $Cr1O_4$ tetrahedron (with an unusually short Cr1—O1 distance and a long Cr1—O4 bond) is due to the fact that atom O1 is bonded only to one metal atom (Cr1), whereas atoms O2, O3 and O4 are each bonded to atom Cr1 and one of the two Ce atoms; atom O4 has a very short bond to Ce1 and therefore needs a relatively long bond to Cr1 in order to satisfy its bond-valence requirements. The four mean Cr—O bond lengths are all larger than the corresponding average (1.642 Å) in the single CrO_4 tetrahedron present in the more highly hydrated cerium(IV) chromate $Ce^{IV}(CrO_4)_2 \cdot 2H_2O$ (monoclinic, $P2_1/m$; Lindgren, 1977). The geometry of the CrO_4 tetrahedra in (I) is regular; the maximum deviation from an ideal tetrahedral O—Cr—O angle is 1.81°.

The two Ce atoms are, as seen in a view along [001] (Fig. 1*a*), located in undulating layers roughly parallel to (100). Interestingly, in monoclinic $Ce^{IV}(CrO_4)_2 \cdot 2H_2O$, the Ce atoms are also located in (slightly less) undulating layers parallel to (100). In (I), atom Ce1 is coordinated to eight oxygen ligands (one of which is a water molecule, O*W*18), while atom Ce2 has a coordination sphere consisting of nine O atoms (again one of these is a water molecule, O*W*17). The two $Ce(O,H_2O)$ coordination polyhedra do not share any faces, edges or corners. The polyhedra can be described as a distorted bicapped trigonal prism, where two faces of the prism are capped (Ce1), and a distorted monocapped square antiprism, where one of the basal planes is capped (Ce2). The single Ce atom in $Ce^{IV}(CrO_4)_2 \cdot 2H_2O$ is eight-coordinate and the isolated $Ce(O,H_2O)_8$ coordination polyhedron is similar to that of atom Ce1 in the title compound. The mean Ce1—O and Ce2—O bond lengths in (I) are 2.337 and 2.379 Å, respectively. In $Ce^{IV}(CrO_4)_2 \cdot 2H_2O$, the corresponding value is very similar (2.342 Å).

The O—H vectors of the two water molecules in (I) point towards small voids in the structure. The hydrogen bonds are



(*a*) (*b*)

Figure 1
A view of (I) along (*a*) [001] (shown with CrO_4 tetrahedra, Ce atoms and water molecules) and (*b*) [010] [shown with CrO_4 tetrahedra and $Ce(O,H_2O)_n$ (n = 8 and 9) polyhedra]. Note the (100) layered arrangement of the Ce atoms in (*a*).

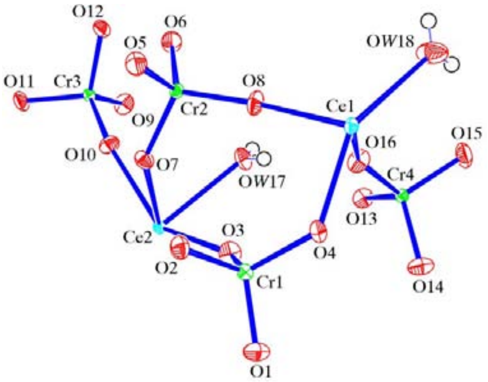


Figure 2
A view of the atoms in the asymmetric unit of (I), with displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

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all more or less weak (Table 2), and the bonds donated by atoms H1 and H3 appear to be bifurcated (note that atom H4 has no acceptor). The H atoms in $Ce^{IV}(CrO_4)_2\cdot 2H_2O$ could not be located by Lindgren (1977), but the distances between the two non-equivalent O*W* atoms and probable O acceptor atoms suggest that the hydrogen bonds are also weak in $Ce^{IV}(CrO_4)_2\cdot 2H_2O$ ($O\cdots O > 2.75$ Å).

Bond-valence sums for the metal atoms in (I) were calculated using the bond-valence parameters from Brese & O'Keeffe (1991) for Cr—O bonds and the parameters from Roulhac & Palenik (2003) for Ce^{IV}—O bonds. These sums are 4.00 (Ce1), 3.94 (Ce2), 5.84 (Cr1), 5.95 (Cr2), 5.91 (Cr3) and 5.98 (Cr4) valence units (v.u.), and are thus all reasonably close to ideal valences. It is noted that the use of bond-valence parameters from Brese & O'Keeffe (1991) for Ce^{IV}—O bonds would result in considerably underestimated sums for the Ce atoms (3.59 v.u. for Ce1 and 3.54 v.u. for Ce2). Even the improved parameters of Brown (1996; updated values, R_0 = 2.09 and b = 0.37; http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown) would give unsatisfactory (overestimated) values, *viz*. 4.24 v.u. for Ce1 and 4.18 v.u. for Ce2.

Experimental

Clusters of small dark-red bipyramidal crystals of the title compound formed at room temperature on slow evaporation of an acidic aqueous solution of $Ce^{III}Cl_3\cdot 7H_2O$ and $Cr^{VI}O_3$ (pH = 1–2). The reaction must have involved the oxidation of Ce^{III} to Ce^{IV}. The compound is stable in air.

Crystal data

$Ce_2(CrO_4)_4\cdot 2H_2O$
$M_r = 780.27$
Orthorhombic, *Pbca*
$a = 10.938$ (2) Å
$b = 11.464$ (2) Å
$c = 22.038$ (4) Å
$V = 2763.4$ (9) Å^3
$Z = 8$
$D_x = 3.751$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5599 reflections
$\theta = 2.0$–32.6°
$\mu = 9.59$ mm^{-1}
$T = 293$ (2) K
Fragment, dark red
0.15 × 0.07 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
ψ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.327$, $T_{max} = 0.554$
9513 measured reflections

5028 independent reflections
4611 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
$\theta_{max} = 32.6°$
$h = -16 \rightarrow 16$
$k = -17 \rightarrow 17$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.044$
$S = 1.15$
5028 reflections
234 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 4.3P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00037 (3)

H atoms were freely refined; the O—H distances are listed in Table 2.

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: *DIAMOND* (Brandenburg & Berndt, 1999); *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected interatomic distances (Å).

Ce2—O2^{vi}	2.4314 (18)	Cr1—O1	1.5947 (19)
Ce2—O3	2.3608 (19)	Cr1—O2	1.6420 (18)
Ce1—O4	2.1723 (19)	Cr1—O3	1.6611 (19)
Ce2—O5^{vii}	2.5024 (18)	Cr1—O4	1.7326 (18)
Ce2—O6^{v}	2.3108 (18)	Cr2—O5	1.6251 (19)
Ce2—O7	2.3645 (17)	Cr2—O6	1.6346 (18)
Ce1—O8	2.2557 (18)	Cr2—O7	1.6621 (18)
Ce1—O9^{iv}	2.3847 (18)	Cr2—O8	1.6696 (18)
Ce2—O10	2.3373 (18)	Cr3—O9	1.6316 (18)
Ce1—O11^{ii}	2.3762 (18)	Cr3—O10	1.6505 (18)
Ce2—O12^{v}	2.2793 (18)	Cr3—O11	1.6541 (18)
Ce2—O13^{iv}	2.4210 (18)	Cr3—O12	1.6624 (18)
Ce1—O14^{iii}	2.382 (2)	Cr4—O13	1.6301 (18)
Ce1—O15^{i}	2.2625 (19)	Cr4—O14	1.6458 (19)
Ce1—O16	2.3670 (18)	Cr4—O15	1.6514 (19)
Ce2—O*W*17	2.4048 (19)	Cr4—O16	1.6548 (18)
Ce1—O*W*18	2.493 (2)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O*W*17—H1$\cdots$O16	0.72 (5)	2.26 (5)	2.931 (3)	155 (5)
O*W*17—H1$\cdots$O8	0.72 (5)	2.42 (5)	2.943 (3)	130 (5)
O*W*17—H2$\cdots$O7^{vi}	0.66 (4)	2.10 (4)	2.752 (3)	168 (5)
O*W*18—H3$\cdots$O4^{iii}	0.67 (8)	2.49 (8)	3.095 (3)	151 (8)
O*W*18—H3$\cdots$O11^{viii}	0.67 (8)	2.62 (7)	3.185 (3)	143 (8)

Symmetry codes: (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (vi) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (viii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1054). Services for accessing these data are described at the back of the journal.

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