

The Crystal Structure of Cerium(IV) Dichromate Dihydrate, $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$

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The crystal structure of $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$ has been determined by Fourier and least-squares analysis from film data taken with $\text{CuK}\alpha$ radiation. The compound crystallizes in the monoclinic space group $P2_1/m$ with $a = 6.5865(12)$ Å, $b = 10.6716(7)$ Å, $c = 5.6699(6)$ Å, $\beta = 92.59(1)^\circ$ and $Z = 2$.

A distorted bicapped trigonal prism is formed by the eight oxygens coordinated to the cerium atom which lies in a mirror plane. Two of the oxygens are water oxygens also situated in the mirror plane, while the other six belong to different chromate groups. The Ce—O bond distances vary between 2.232 and 2.575 Å, the average being 2.342 Å.

The structure was refined to a final R value of 8.4 %.

Investigations on the crystal structures of basic salts of some tetravalent elements (Ce^{IV} , Th^{IV} , U^{IV} , Ti^{IV} , Zr^{IV}) were started by Lundgren,¹ who made a general survey in the field. In connection with this, and also in order to study cerium-oxygen coordinations, investigations of crystal-line phases of the system CeO_2 — CrO_3 — H_2O were started. Crystals have been prepared by a number of methods, including hydrothermal hydrolysis and room temperature crystallisation from solutions of varying acidities. In this way it was possible to obtain several solid compounds, some of which were suitable for single crystal X-ray studies. The results from the crystal structure determination of one of these compounds, $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$, are reported below.

EXPERIMENTAL

Crystals of $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$ were prepared by dissolving freshly precipitated ceric hy-

drous oxide in concentrated chromic acid. Slow evaporation of this solution at room temperature, yielded crystals suitable for X-ray investigations. They were red, of trigonal prismatic shape and elongated along the c axis. The dimensions of the crystal chosen for data collection were $0.023 \times 0.070 \times 0.16$ cm.

$\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$ forms monoclinic crystals. Guinier photographs calibrated with $\text{Pb}(\text{NO}_3)_2$ ² were taken, using $\text{CuK}\alpha_1$ radiation, and 44 lines were indexed. These were refined by means of the programme POWDER.³ The refined cell parameters with standard deviations (at 21 °C) are:

$$a = 6.5865(12) \text{ \AA}$$

$$b = 10.6716(7) \text{ \AA}$$

$$c = 5.6699(6) \text{ \AA}$$

$$\beta = 92.59(1)^\circ$$

$$V = 398.12 \text{ \AA}^3$$

A listing of the observed and calculated $\sin^2\theta$ values is available on request. The measured density, 3.37 g cm^{-3} , agrees with the calculated value, 3.40 g cm^{-3} , assuming a unit cell content of two formula units. The reflexions systematically absent were $0k0$ for $k = 2n + 1$, which indicates that the crystals belong to the space group $P2_1$ or $P2_1/m$.

Integrated multiple-film equi-inclination Weissenberg photographs $hk0$ — $hk4$ were recorded using Ni-filtered $\text{CuK}\alpha$ radiation. A total of 584 independent reflexions, which is about 32 % of those within the Cu-sphere, were obtained. The intensities were estimated visually using a scale prepared with a logarithmic wheel. The intra-level film ratios were calculated using the programme SCALE.⁴ Lorentz and polarisation corrections, as well as approximate inter-level scale factors based on exposure times, were then applied. The intensities were corrected for absorption in the later stages of the calculations, $\mu = 672 \text{ cm}^{-1}$.

Table 1. Atomic coordinates and temperature factors for $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$. Estimated standard deviations are given in parentheses. The thermal parameters have been multiplied by 10^4 for Ce and Cr and by 10^3 for O. The temperature factor is of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + klb^*c^*U_{23})]$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	0.04385(21)	0.25	0.22064	154(7)	141(7)	146(13)	0	-89(11)	0
Cr	0.25701(40)	0.04332(26)	0.74536(59)	128(13)	127(14)	138(26)	-13(17)	-51(24)	4(21)
O1	0.8401(23)	0.9014(14)	0.0092(33)	32(7)	27(7)	41(13)	-1(11)	6(13)	13(13)
O2	0.7749(18)	0.3866(12)	0.2649(28)	15(6)	17(6)	41(12)	0(9)	-11(11)	-9(11)
O3	0.5081(21)	0.9255(16)	0.2545(30)	19(6)	48(9)	26(11)	-16(11)	-10(11)	5(13)
O4	0.8570(20)	0.8891(12)	0.4833(31)	22(6)	16(6)	52(13)	-11(10)	-24(13)	23(13)
O5	0.4124(30)	0.25	0.2672(51)	16(8)	30(11)	76(22)	0	-16(18)	0
O6	0.1761(32)	0.75	0.1665(41)	31(9)	44(12)	8(15)	0	-14(16)	0

STRUCTURE DETERMINATION

The structure was determined using standard Patterson and Fourier techniques. A final refinement was carried out by the method of least squares. Scattering factors according to Cromer and Waber⁵ and Cruickshank's⁶ weighting scheme, $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$ with $a=15$, $c=0.013$ and $d=0$ were used. A total of 66 parameters were refined from 584 reflexions. After three cycles all shifts were less than 1 % of the estimated standard deviations, and the *R* value was 8.4 %. The positional and thermal parameters are listed in Table 1. A list of observed and calculated structure factors can be obtained on request from the author.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The chromate groups in $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$ are approximately layered since the *y*-coordinates of the chromium atoms differ only slightly from 0 and $\frac{1}{2}$. The cerium atoms and water molecules lie in the mirror planes between these layers. The main interatomic distances and angles, with their standard deviations, are quoted in Table 2. Fig. 1. shows a stereo drawing of the structure.

The oxygen coordination of cerium is eight-fold, cf. Fig. 2. Six of the oxygen atoms belong to six different chromate groups and the other two belong to water molecules. Four of the

Table 2. Interatomic distances (Å) and angles (°).

Ce - polyhedron				
Ce - O1	(2 ×)	2.232(16)	O1 - Ce - O1'	92.7(8)
- O2	(2 ×)	2.321(13)	O5 - Ce - O6	127.8(8)
- O4	(2 ×)	2.313(16)	O2 - Ce - O4	121.1(5)
- O5		2.430(20)	O2 - O2' - O4	90.5(4)
- O6		2.575(23)	O2 - O4 - O4'	89.5(4)
Average:		2.342	O5 - O1 - O6	106.6(6)
			O1 - O5 - O1'	71.8(9)
			O1 - O6 - O1'	69.0(8)
Chromate group				
Cr - O1		1.665(18)	O1 - Cr - O2	109.3(8)
- O2		1.685(13)	O1 - Cr - O3	109.7(8)
- O3		1.583(14)	O1 - Cr - O4	109.0(8)
- O4		1.636(16)	O2 - Cr - O3	109.0(8)
Average:		1.642	O2 - Cr - O4	111.1(7)
			O3 - Cr - O4	108.8(8)
Other distances in $\text{Ce}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$				
O5 - O2		2.793(21)		
O6 - O3		2.905(22)		

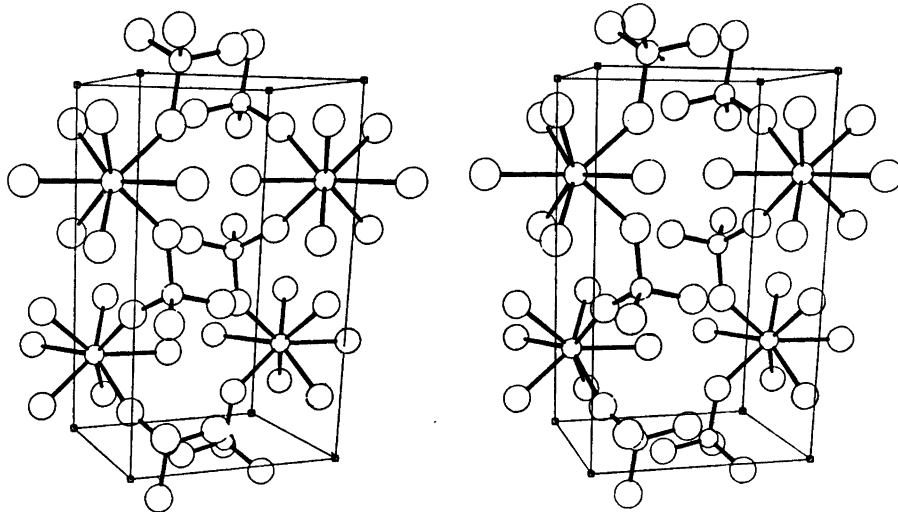


Fig. 1. A stereo drawing of the structure viewed approximately in the c -direction. The longest axis is the b axis.

chromate oxygens (O2, O2', O4, O4') are, for symmetry reasons, coplanar. They have Ce–O distances of 2.313 and 2.321 Å. The remaining two chromate oxygen atoms (O1, O1') and the two water molecules (O5, O6) form another but less regular cerium oxygen pyramid. The atoms O1 and O1' are at a distance of 2.232 Å from the cerium atom. The water molecules, on the other hand, are not equidistant from the cerium atom (2.430 and 2.575 Å) and the four oxygens O1, O1', O5 and O6 are not coplanar; the angle between the planes O1–O1'–O5 and O1–O1'–O6 is 158°. The configuration may be described as a distorted square antiprism or as

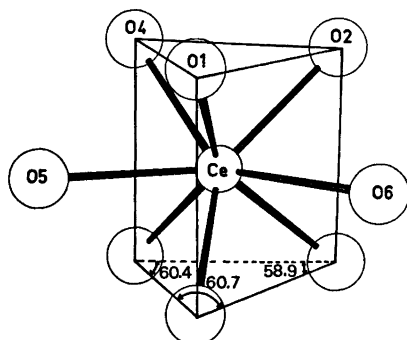


Fig. 2. A view of the coordination polyhedron.

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a trigonal prism with water molecules on two faces, *cf.* Fig. 2. The average Ce–O distance is 2.342 Å.

The chromate group is bonded to three different Ce atoms with the fourth chromate oxygen O3 probably involved in hydrogen bonding to a water molecule, the O3–O6 and O3'–O6 distances being 2.905 Å. This is also reflected in the bond lengths within the chromate group, since the distances from the chromium atom to the three cerium-bonded oxygen atoms (mean 1.662 Å) are significantly longer than the fourth Cr–O distance (1.583 Å).

The other water molecule, O5, has six nearest neighbour oxygen atoms (two O1, two O2 and two O4) at distances less than 2.80 Å, the remaining O5–O distances being > 3.30 Å. O1 and O4 are bonded to the same Ce atom as O5 while the two O2 atoms are linked to another cerium atom. The protons of O5 are probably directed towards the O2 atoms, creating the possibility for hydrogen bonding.

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