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## Zirconium dihydroxide chromate

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The crystal structure of the title compound,  $\text{Zr}(\text{OH})_2\text{CrO}_4$ , has been reinvestigated [Mark (1972). *Acta Chem. Scand.* **26**, 3744–3756]. It is composed of ordered layers whose stacking in the  $c$  direction is disordered. The symmetry of the superposition structure is tetragonal, space group  $I4_1/amd$  with  $a = 6.8709$  (1) and  $c = 29.0432$  (2) Å. The true 0D structure has ordered layers of the dimensions  $a_L = b_L = 2a$  and  $c_0 = c/4$ , where  $c_0$  is the spacing between adjacent layers. The Zr atoms are joined by double hydroxide bridges and the structure consists of infinite nets with the composition  $[\text{Zr}_3(\text{OH})_6\text{CrO}_4]_n^{4n+}$ , joined together in  $c$  direction by chromate groups. The zirconium polyhedra are not influenced by the 0D phenomenon.

### Comment

Investigations of the  $x\text{ZrO}_2-y\text{CrO}_3-z\text{H}_2\text{O}$  system were carried out by Lundgren (1958) and Mark (1972, 1973). They showed that three different phases can be obtained by hydrothermal hydrolysis and indicated that two phases have similar structures, while the third structure,  $\text{Zr}(\text{OH})_2\text{CrO}_4$ , is essentially different. In the title compound, the zirconium is more highly polymerized than in the other phases. This phase is obtained at lower chromium trioxide concentration and higher temperature than the others. The  $\text{Zr}(\text{OH})_2\text{CrO}_4$  crystallizes as small red square plates with a tetragonal shape.

The structure of zirconium dihydroxide chromate has been redetermined. In accordance with the earlier investigation (Mark, 1972) of this compound, this structure is an 0D structure (Dornberger-Shiff, 1956, 1982) consisting of ordered layers whose stacking in  $c$  direction is disordered. The space group of the superposition structure is tetragonal  $I4_1/amd$  with  $a = 6.8709$  (1) Å and  $c = 29.0432$  (2) Å and  $Z = 12$ . There are four equivalent layers  $L_0, L_1, L_2$  and  $L_4$  in the true structure. The space group of the superposition structure implies consecutive layers  $L$  to be linked by the operation:

$$\begin{pmatrix} x_{L_{i+1}} \\ y_{L_{i+1}} \\ z_{L_{i+1}} \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{L_i} \\ y_{L_i} \\ z_{L_i} \end{pmatrix} + \begin{pmatrix} \frac{1}{4} \\ \frac{1}{4} \\ \frac{1}{4} \end{pmatrix}$$

The superposition structure,  $\rho_S(x,y,z)$  is related to the true structure,  $\rho(x,y,z)$  by the relation:  $\rho_S(x,y,z) = \frac{1}{4}[\rho(x,y,z) + \rho(x + \frac{1}{2}, y, z) + \rho(x, y + \frac{1}{2}, z) + \rho(x + \frac{1}{2}, y + \frac{1}{2}, z)]$  (Mark, 1972)

There are two structurally non-equivalent Zr atoms in the structure; one with eightfold coordination forming a dodecahedron,  $\text{ZrO}_8$ , and one with sevenfold coordination forming a pentagonal bipyramid,  $\text{ZrO}_7$ . There also are two structurally non-equivalent chromate groups. The zirconium polyhedra are well described by the space group symmetry of the superposition structure. The disorder in the structure is, in accordance with the earlier structure determination (Mark, 1972), due to the chromate groups. One particular chromate tetrahedron (Cr1) may be situated either above or below the edge sharing  $\text{ZrO}_8$  dodecadron, thus affecting the available positions for the (Cr2) chromate tetrahedron. The only atoms affected by the disorder are the Cr1, O6, Cr2, O5 and the O2 bonded H atoms. The 0D-groupoids associated to the disordered atoms was formulated by Mark (1972) as follows:

Starting from layer  $L_0$  or  $L_2$ :

$$P m m (n)_{1,1/2} \quad 1 \quad 1$$

$$\left\{ 1 \quad 1 \quad \begin{pmatrix} \bar{4} \\ 4_4 \end{pmatrix} \quad \frac{2_{1/2}}{n_{1/4,2}} \quad \frac{2}{n_{1/4,2}} \right\}$$

Starting from layer  $L_1$  or  $L_3$ :

$$P m m (n)_{1,2,1} \quad 1 \quad 1$$

$$\left\{ 1 \quad 1 \quad \begin{pmatrix} \bar{4} \\ 4_4 \end{pmatrix} \quad \frac{2}{n_{1/4,2}} \quad \frac{2_{1/2}}{n_{1/4,2}} \right\}$$

The main structural feature in zirconium and related hydroxide salts (Lundgren, 1958; Mark, 1972, 1973; Hansson, 1973*b*; El Brahimi *et al.*, 1988), is the forming of infinite parallel chains with the formula  $[\text{Zr}(\text{OH})_2]_n^{2n+}$ , all running in the same direction. The coordination numbers of the metal atoms seem to be of importance for the type of chains adopted by the compounds. In structures containing parallel linear chains (Hansson, 1969; Hansson & Lundgren, 1968; Hansson & Mark, 1973; Mark, 1973) the metal atoms are seven-coordinated to O atoms, while in the structures containing parallel zigzag chains (Lundgren, 1950; Hansson, 1973*a,b*; El Brahimi *et al.*, 1988), with the metal atoms situated at alternate sides of the rows of hydroxide ions, the metal atoms are eight-coordinated.

In every layer of the title compound, the Zr atoms form parallel linear and intersecting chains. There are two kinds of layers, containing chains of zirconium polyhedra either along the *a* axis or along the *b* axis. The layers alternate, creating nets with the composition  $[\text{Zr}_3(\text{OH})_6\text{CrO}_4]_n^{4n+}$ , joined together in *c* direction by chromate groups. The most important interatomic distances and angles in the structure are given in Table 1. One third of the Zr atoms (Zr1, Wyckoff position 4*a*) exhibit eightfold oxygen coordination while the remaining two thirds (Zr2, Wyckoff position 8*e*) are coordinated to seven O atoms. Each Zr1 atom is joined by double hydroxide bridges to four Zr2 atoms. Each  $\text{ZrO}_7$  pentagonal bipyramid shares two edges with  $\text{ZrO}_8$  dodecahedra. One third of the Cr atoms (Cr1, Wyckoff position 8*e*, site occupancy 0.125) are included in the infinite nets while the others (Cr2, Wyckoff position 16*h*, site occupancy 0.25) are net-connecting. The net-included chromate group shares one of its tetrahedral edges with an edge of a  $\text{ZrO}_8$  dodecahedron, in this case, the two bridging hydroxide ions have been displaced by two chromate O atoms. The net-connecting chromate group shares three vertices with three different  $\text{ZrO}_7$  polyhedra, two belonging to the same net and one belonging to a net above or below. The extent of distortion of the chromate groups from ideal tetrahedral symmetry is in accordance with that expected from bond valence sum calculations (Brown & Kung Wu, 1976; Brown & Altermatt, 1985). The H-atom positions were not located.

## Experimental

Zirconium compounds of the system  $x\text{ZrO}_2\text{-}y\text{CrO}_3\text{-}z\text{H}_2\text{O}$  were prepared by hydrothermal hydrolysis, according to Briggs (1929). The synthesis was performed in two steps. First, an amorphous product was prepared (Lundgren, 1958), which was then converted to crystals by hydrothermal hydrolysis as described earlier by Mark (1972).

### Crystal data

$\text{Zr}(\text{OH})_2\text{CrO}_4$	Mo $K\alpha$ radiation
$M_r = 241.23$	Cell parameters from 5231 reflections
Tetragonal, $I4_1/amd$ [origin at centre (2/m)]	$\theta = 2\text{--}33^\circ$
$a = 6.8709$ (1) Å	$\mu = 4.590$ mm <sup>-1</sup>
$c = 29.0432$ (2) Å	$T = 293$ (2) K
$V = 1371.11$ (3) Å <sup>3</sup>	Square plate, red
$Z = 12$	$0.10 \times 0.10 \times 0.04$ mm
$D_x = 3.506$ Mg m <sup>-3</sup>	

### Data collection

Siemens SMART CCD diffractometer	731 independent reflections
$\omega$ scans	638 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Sheldrick, 1996)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.657$ , $T_{\text{max}} = 0.838$	$\theta_{\text{max}} = 33.03^\circ$
4914 measured reflections	$h = -7 \rightarrow 10$
	$k = -10 \rightarrow 9$
	$l = -43 \rightarrow 35$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 5.9927P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.040$	$\Delta\rho_{\text{max}} = 0.801$ e Å <sup>-3</sup>
731 reflections	$\Delta\rho_{\text{min}} = -1.021$ e Å <sup>-3</sup>
52 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.00063 (15)

**Table 1**

Selected geometric parameters (Å, °).

Zr1—O4 <sup>i</sup>	2.152 (2)	Cr1—O6	1.584 (6)
Zr1—O2	2.248 (2)	Cr1—O2	1.750 (2)
Zr2—O1	2.080 (2)	Cr2—O3 <sup>ii</sup>	1.575 (4)
Zr2—O4	2.124 (2)	Cr2—O5	1.592 (5)
Zr2—O2	2.186 (2)	Cr2—O1	1.679 (2)
Zr2—O3	2.236 (4)		
O4 <sup>i</sup> —Zr1—O2	65.40 (9)	O2—Zr2—O3	74.34 (6)
O2 <sup>iii</sup> —Zr1—O2	72.61 (12)	O6 <sup>iii</sup> —Cr1—O6	107.8 (4)
O1—Zr2—O1 <sup>i</sup>	167.24 (14)	O6—Cr1—O2	112.50 (13)
O1—Zr2—O4	94.98 (5)	O2—Cr1—O2 <sup>iii</sup>	99.01 (16)
O4—Zr2—O4 <sup>i</sup>	77.38 (12)	O3 <sup>ii</sup> —Cr2—O5	100.4 (2)
O1—Zr2—O2	88.28 (2)	O3 <sup>iii</sup> —Cr2—O1 <sup>iv</sup>	113.37 (9)
O4 <sup>i</sup> —Zr2—O2	66.98 (9)	O5—Cr2—O1 <sup>iv</sup>	110.11 (10)
O1—Zr2—O3	83.62 (7)	O1—Cr2—O1 <sup>iv</sup>	109.21 (16)

Symmetry codes: (i)  $1 - x, \frac{3}{2} - y, z$ ; (ii)  $1 - x, 1 - y, -z$ ; (iii)  $-x, \frac{3}{2} - y, z$ ; (iv)  $1 - x, \frac{1}{2} - y, z$ .

The well diffracting crystal produced a regular pattern of sharp and intense reflections. A visual exploration of the frames was performed and several frames showed continuous streaks between rows of sharp reflections. The continuous lines were parallel to the *c*\* direction and situated midway between neighbouring reflections in both *a*\* and *b*\* directions. This indicated, in accordance with the earlier structure determination (Mark, 1972) that the true structure is periodic in the *a* and *b* directions but lacks periodicity in the *c* direction.

The determination of the structure is more precise than the original one (Mark, 1972) making the structure features well defined, s.u.'s being smaller by a factor of about 5.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* (Siemens, 1995) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL* (Bruker, 1997); molecular graphics: *SHELXTL* (Bruker, 1997).

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