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Crystal structure of $\alpha\text{-Al}_2(\text{CrO}_4)_2\text{Cr}_2\text{O}_7, 4\text{H}_2\text{O}$

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In a previous publication relating to the preparation of aluminum chromates, an aluminum chromate bichromate has been described [1]. The choice of this new formula was based solely, upon results of thermolysis and IR spectrophotometric studies. It was thus necessary to determine the crystal structure.

This determination has been carried out on the basis of an isomorphism with the homologous iron compound, the structure of which has been determined by Gérault et al.[2]

CRYSTAL STRUCTURE DETERMINATION

$\alpha\text{-Al}_2(\text{CrO}_4)_2\text{Cr}_2\text{O}_7, 4\text{H}_2\text{O}$ occurs in the form of red needles. Laue photographs show it to be monoclinic. The systematic extinctions $hol, l = 2n$ are consistent with the space group P2/c or Pc. The nonconventional centrosymmetric space group P2/n has been chosen as in the iron compound study. The unit-cell dimensions obtained and refined by least-squares methods from a powder pattern are:

--in the space group P2/c

$a = 13,30 (3) \text{ \AA}; b = 10,48 (2) \text{ \AA}; c = 14,32 (3) \text{ \AA}; \beta = 158,15 (5)^\circ; Z = 2$

--in the space group P2/n

$a = 5,329 (6) \text{ \AA}; b = 10,48 (2) \text{ \AA}; c = 13,30 (3) \text{ \AA}; \beta = 90,00 (5)^\circ; Z = 2$

During the whole intensity gathering process, the single crystal was placed in a dry nitrogen stream. MoK α radiation was used to minimize absorption effects which are weak for aluminum compounds, so that no correction for absorption was made. The reciprocal planes hkl ($l = 0-6$) have been collected on a B $\ddot{u}$ erger apparatus. Integrated intensities were measured with a NONIUS microdensitometer and corrected solely, for LORENTZ and polarisation effects. 483 independent reflections were collected.

The form factors used are those of Al^{3+} , Cr^{3+} , O^{-1} . They are computed from the Vand *et al.*[3] relation and coefficients taken from the Moore tables [4]. Computations have been carried out on a CII 10070 computer, using the refinement program SFLS5 [5].

The refinement of the atomic and isotropic thermal parameters was made from the iron chromate bichromate data. Four cycles of refinements reduced the residual $R = \Sigma |KF_0 - |F_c|| / \Sigma F_0$, to 0.082.

Table 1 gives the final atomic and thermal parameters. Table 2 lists the interatomic bond distances

and angles and their errors, calculated with the Busing *et al.* Program [6]. We give, below, the key which permits identification of each atom.

(i)	x	y	z
(ii)	$-x$	$-y$	$-z$
(iii)	$1/2 + x$	$-y$	$1/2 + z$
(iv)	$1/2 - x$	y	$1/2 - z$
(v)	$-1 + x$	y	z
(vi)	$1 - x$	$-y$	$-z$
(vii)	$3/2 - x$	y	$1/2 - z$
(viii)	x	$-1 + y$	z
(ix)	$1 - x$	$1 - y$	$-z$

DISCUSSION

The results obtained confirm the original hypothesis for the compound formula. The solid phase belongs to a new family of compounds in which CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ groups coexist. It is isotypic with the iron compound. The hydration step is higher than the one deduced from chemical and thermogravimetric studies. This hygroscopic phase, as already mentioned, does not contain 3 but 4 water molecules. Observed analytical results are in close agreement with calculated-ones [1].

The average Al-O distance (1.89 Å) agrees well with that found in other compounds where the coordination polyhedron of aluminum is an octahedron. The average Cr-O distance (1.65 Å) is similar to that observed in the iron chromate bichromate [2]. The shortest Cr-O distance corresponds to an oxygen which does not belong to any other polyhedron; the longest one (1.76 Å) belongs to the bridge Cr-O-Cr. Bonds of similar length exist in alkaline bichromates.

The structure may be described as an imbrication of wavy sheets parallel with the plane (a, c). The only bond between the different sheets, are hydrogen bonds. The IR studies show relatively low frequencies for ν_1 and ν_3 of the water molecules [1], indicating the presence of hydrogen bonds. Table 2 gives the interatomic hydrogen bond distances and angles as defined by Gerault *et al.*[2].

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Table 1. Final atomic and thermal parameters and standard deviations of α -
 $\text{Al}_2(\text{CrO}_4)_2\text{Cr}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Al ₁	0	0	0	0.21 (11)
Al ₂	0.25	0.3459 (7)	0.25	0.48 (11)
Cr ₁	0.5171 (4)	0.0953 (3)	0.1299 (4)	0.29 (5)
Cr ₂	0.5797 (5)	0.6029 (3)	0.1519 (5)	0.78 (6)
O (1)	0.8044 (16)	0.1131 (9)	0.0758 (17)	0.07 (16)
O (2)	0.2916 (19)	0.0874 (11)	0.046(2)	0.52 (18)
O (3)	0.514 (2)	−0.0315 (13)	0.192 (2)	1.6 (3)
O (4)	0.468 (2)	0.2197 (12)	0.208 (2)	1.1 (2)
O (5)	0.75	0.6757 (19)	0.25	1.6 (4)
O (6)	0.367 (3)	0.7015 (16)	0.120 (3)	2.6 (3)
O (7)	0.466 (3)	0.4683 (14)	0.188 (3)	2.1 (3)
O (8)	0.763 (4)	0.5746 (18)	0.055 (4)	3.6 (4)
OW (1)†	0.013 (2)	−0.1158 (13)	0.107 (2)	1.1 (3)
OW (2)†	0.058 (2)	0.3407 (13)	0.130 (2)	1.1 (2)

†Water molecule.

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

Octahedron Al(1)	
(2×) Al(1 ⁱ)–O(1 ^v): 1.873 (14)	(2×) O(1 ^v)–Al(1 ⁱ)–OW(1 ⁱ): 91.1 (0.7)
(2×) Al(1 ⁱ)–O(2 ⁱ): 1.903 (13)	(2×) O(2 ⁱ)–Al(1 ⁱ)–OW(1 ⁱ): 92.2 (0.7)
(2×) Al(1 ⁱ)–OW(1 ⁱ): 1.88 (2)	(2×) O(1 ^v)–Al(1 ⁱ)–O(2 ⁱ) : 88.7 (0.6)
Octahedron Al(2)	
(2×) Al(2 ⁱ)–O(4 ⁱ): 1.847 (15)	(2×) O(4 ⁱ)–Al(2 ⁱ)–OW(2 ⁱ) : 93.8 (0.8)
(2×) Al(2 ⁱ)–O(7 ⁱ): 1.91 (2)	(2×) O(4 ⁱ)–Al(2 ⁱ)–OW(2 ^{iv}) : 83.8 (0.8)
(2×) Al(2 ⁱ)–OW(2 ⁱ): 1.89 (3)	(2×) O(4 ⁱ)–Al(2 ⁱ)–O(7 ⁱ) : 88.3 (0.9)
	(2×) O(7 ⁱ)–Al(2 ⁱ)–OW(2 ⁱ) : 88.9 (0.9)
	(2×) O(7 ⁱ)–Al(2 ⁱ)–OW(2 ^{iv}) : 93.4 (0.9)
	(1×) O(4 ⁱ)–Al(2 ⁱ)–O(4 ^{iv}) : 88.6 (0.8)
	(1×) O(7 ⁱ)–Al(2 ⁱ)–O(7 ^{iv}) : 95.7 (0.9)
	(2×) O(4 ⁱ)–Al(2 ⁱ)–O(7 ^{iv}) : 171.8 (0.9)
	(1×) OW(2 ⁱ)–Al(2 ⁱ)–OW(2 ^{iv}): 176.7 (0.8)
Tetrahedron Cr(1)	
(1×) Cr(1 ⁱ)–O(1 ⁱ): 1.702 (12)	(1×) O(1 ⁱ)–Cr(1 ⁱ)–O(2 ⁱ): 112.0 (0.7)
(1×) Cr(1 ⁱ)–O(2 ⁱ): 1.645 (19)	(1×) O(1 ⁱ)–Cr(1 ⁱ)–O(3 ⁱ): 109.1 (0.9)
(1×) Cr(1 ⁱ)–O(3 ⁱ): 1.57 (2)	(1×) O(1 ⁱ)–Cr(1 ⁱ)–O(4 ⁱ): 108.3 (0.8)
(1×) Cr(1 ⁱ)–O(4 ⁱ): 1.69 (2)	(1×) O(2 ⁱ)–Cr(1 ⁱ)–O(3 ⁱ): 108.0 (0.9)
	(1×) O(2 ⁱ)–Cr(1 ⁱ)–O(4 ⁱ): 110.3 (0.8)
	(1×) O(3 ⁱ)–Cr(1 ⁱ)–O(4 ⁱ): 109.0 (0.9)
Double tetrahedron Cr(2)	
(2×) Cr(2 ⁱ)–O (5 ⁱ) : 1.763 (10)	(2×) O (5 ⁱ)–Cr(2 ⁱ)–O (6 ⁱ) : 106.5 (0.8)
(2×) Cr(2 ⁱ)–O (6 ⁱ) : 1.593 (19)	(2×) O (5 ⁱ)–Cr(2 ⁱ)–O (7 ⁱ) : 110.7 (0.8)
(2×) Cr(2 ⁱ)–O (7 ⁱ) : 1.608 (18)	(2×) O (5 ⁱ)–Cr(2 ⁱ)–O (8 ⁱ) : 110.6 (1.0)
(2×) Cr(2 ⁱ)–O (8 ⁱ) : 1.64 (4)	(2×) O (6 ⁱ)–Cr(2 ⁱ)–O (7 ⁱ) : 112.3 (1.2)
(1×) Cr(2 ⁱ)–Cr(2 ^{iv}): 3.179 (8)	(2×) O (6 ⁱ)–Cr(2 ⁱ)–O (8 ⁱ) : 109.4 (1.4)
	(2×) O (7 ⁱ)–Cr(2 ⁱ)–O (8 ⁱ) : 107.4 (1.3)
	(1×) Cr(2 ⁱ)–O (5 ⁱ)–Cr(2 ^{iv}): 128.7 (0.4)
Hydrogen bonds OW(1)	
OW(1 ⁱ)–O(3 ^{iv}) : 2.81 (4)	(Intra sheet bond)
OW(1 ⁱ)–O(6 ^{viii}): 2.69 (2)	(Inter sheet bond)
O (3 ^{iv})–OW(1 ⁱ)–O(6 ^{viii}): 101.5 (0.9)	
Al(1 ⁱ)–OW(1 ⁱ)–O(3 ^{iv}) : 121.1 (1.0)	
Al(1 ⁱ)–OW(1 ⁱ)–O(6 ^{viii}) : 122.2 (1.1)	
Hydrogen bonds OW(2)	
OW(2 ⁱ)–O(1 ^v) : 2.836 (18)	(Intra sheet bond)
OW(2 ⁱ)–O(8 ^{ix}): 2.79 (5)	(Inter sheet bond)
O (1 ^v)–OW(2 ⁱ)–O(8 ^{ix}): 101.8 (0.9)	
Al(2 ⁱ)–OW(2 ⁱ)–O(1 ^v) : 119.7 (0.9)	
Al(2 ⁱ)–OW(2 ⁱ)–O(8 ^{ix}): 123.4 (1.2)	