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Two new aluminum hydroxychromates $\text{Al}_{13}(\text{OH})_{11}(\text{CrO}_4)_{14} \cdot x\text{H}_2\text{O}$ ($x = 41$ and 51)

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The study of the ternary system: Al_2O_3 , CrO_3 , H_2O at 70°C and 20°C reveals two new hydroxychromates; the formulae of which are: $\text{Al}_{13}(\text{OH})_{11}(\text{CrO}_4)_{14} \cdot x\text{H}_2\text{O}$, x being equal to 41 ± 1 and 51 ± 1 . $\text{Al}_2(\text{CrO}_4)_3 \cdot 5\text{H}_2\text{O}$, the compound announced by Raychoudhury [1] is not observed. Experimental techniques are the same as those used for the ternary system at 110°C and 150°C , and described in a precedent publication, where a detailed analysis of previous work on aluminum chromates is given [2].

RESULTS AND DISCUSSION

H_1 , the least hydrated chromate, is obtained from the following system, composed of: 13.5% Al_2O_3 , 50.6% CrO_3 , 35.9% H_2O , placed at 70°C for one year. The highest hydrate H_2 , is produced from a system having the following composition: 13.5% Al_2O_3 , 46% CrO_3 , 40.5% H_2O , placed for 6 months at 20°C . These results were checked by testing several systems prepared from different starting materials, Some of them, were carried out under the same conditions as those of Raychoudhury.

H_1 and H_2 present a hygroscopic or efflorescent character depending on the hygrometric conditions. Separation of reacted mother liquor was achieved in glacial acetic acid, the solids being dried out in air of known fixed moisture content. The chemical analysis results are:

	% Cr_{exp}	% Cr_{calc}	% Al_{exp}	% Al_{calc}	$r_{\text{exp}} = \frac{\text{Cr}}{\text{Al}}$	$r_{\text{calc}} = \frac{\text{Cr}}{\text{Al}}$
H_1	25.22	25.10	12.08	12.10	1.084	1.077
H_2	23.49	23.64	11.45	11.40	1.065	1.077

The initial assumption of a more simple formula of the type $\text{Al}(\text{OH})\text{CrO}_4 \cdot x\text{H}_2\text{O}$ was abandoned, since all chemical analyses of products obtained from different preparations, give a Cr/Al ratio always greater than 1 and varying from 1.04 to 1.09. Crystallographic studies, carried out on single crystals to determine unit-cell, space-group, and calculated density, lead to the formula $\text{Al}_{13}(\text{OH})_{11}(\text{CrO}_4)_{14} \cdot x\text{H}_2\text{O}$. The hydrate H_1 is monoclinic. The systematic presence of reflections hol , $l = 2n$; $0k0$, $k = 2n$, are consistent with the space group $\text{P}2_1/c$. The hydrate H_2 is triclinic. The unit-cell dimensions obtained and refined by least-squares methods from a powder pattern* are:

	a(Å)	b(Å)	c(Å)	α°	β°	γ°	Z	ρ_{exp}	ρ_{calc}
H_1	15.91(2)	18.66(3)	27.83(4)		148.39(6)		2	2.17	2.22
H_2	15.39(3)	11.811(16)	32.56(5)	107.37(12)	109.93(11)	107.17(14)	2	(2.07-2.11)	2.15

Important information regarding the choice of the H₁ formula can be obtained from crystallographic data of the corresponding phase. In the spatial group P2₁/c, all particular atomic positions are placed on symmetry centers. These positions are not consistent with the tetrahedral coordination of chromium. Thus it is certain that all chromium atoms occupy general positions, having four equivalents and consequently their number, in the unit-cell, is a multiple of 4. In this case, only the formula Al₁₃(OH)₁₁(CrO₄)₁₄ · xH₂O (x = 41) with z = 2 is in close agreement both with chemical analyses and with crystallographic results, as shown in Table 1.

For H₂, the comparison of the experimental density (2.07-2.11) with those calculated from possible formulae consistent with the chemical analysis results, leads to a choice between two formula types: the first one with a Cr/Al ratio equal to 27/26 (z=1), the second with a ratio equal to 14/13 (z = 2), as can be seen from Table 2. For H₂, we have chosen, the simplest formula that is the one having the same ratio Cr/Al = 14/13 as the H₁ phase.

The hydration step is estimated to be 4l for H₁ and 5l for H₂. These values, agreeing well with the chemical analysis results, have been confirmed by thermogravimetric analysis. Water losses are respectively 25.21 % and 29.74 % for H₁ and H₂, observed experimentally at a constant temperature of 225°C for 12 hr. This temperature was chosen from differential thermal analysis results. These experimental losses are in close agreement with those calculated for 4l H₂O and 5l H₂O, namely 25.45 % and 29.80 %. The anhydrous compound obtained Al₁₃(OH)₁₁(CrO₄)₁₄ is amorphous. Thermolysis continues with OH degradation and, then, with hexavalent chromium reduction. The end-product at 700°C is a well-crystallized solid solution, of corundum type, of Al₂O₃ and Cr₂O₃. The total experimental losses are respectively: 40.60 and 43.60 %, in excellent agreement with the calculated values of 40.45 and 43.93 %.

These complex phases show, as already mentioned, a hygroscopic or efflorescent character, with cell-parameter variations. When H₁ is obtained from poor water systems, practically at the limit of experimental possibilities, cell parameter values are different:

$$a (\text{Å}) = 15.53(2), \quad b (\text{Å}) = 18.52(3), \quad c (\text{Å}) = 27.38(9), \quad \beta^\circ = 148.33(12)$$

This variation is accompanied by a volume reduction of the unit-cell corresponding to the loss of about 4 or 5 water molecules per formula. The H₂ phase dehydrates itself at 20°C when relative humidity is less than 47 %. Loss is about 15 water molecules per formula, and gives a new well-crystallized solid phase H₃*. Its powder pattern is original. If relative humidity once more exceeds 47%, the reverse reaction gives the H₂ phase again, in well-crystallized form. The new H₃ phase also presents a cell parameter variation depending on the relative humidity of the surrounding air. The loss of water may be between 8 and 10 molecules per formula.

There are good reasons for supposing that these experimentally observed facts probably depend on the different kinds of water molecules in the structure, zeolitic or weakly bound water. Identical facts were observed for alunogen: Al₂(SO₄)₃ · 17H₂O, whose determined structure shows, in particular, the presence of zeolitic water [3]. The original behaviour of these phases makes their study particularly fastidious. It will not be possible to definitely explain these results until the structure of these complex phases has been determined. We are ready to supply single crystals to laboratories interested in determining these structures.

* They can be supplied on request.

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Table 1. Comparison between calculated densities (H_1)

Cr/Al	24/23 = 1.043	28/27 = 1.037	32/31 = 1.032
Z = 1 $\rho_{\text{calc}}(\text{g/cm}^3)$	1.93	2.26	2.59
Cr/Al	12/11 = 1.091	14/13 = 1.077	16/15 = 1.067
Z = 2 $\rho_{\text{calc}}(\text{g/cm}^3)$	1.88	2.22	2.53

Table 2. Comparison between calculated densities (H_2)

Cr/Al	26/25 = 1.040	27/26 = 1.038	28/27 = 1.037
Z = 1 $\rho_{\text{calc}}(\text{g/cm}^3)$	2.03	2.11	2.19
Cr/Al	13/12 = 1.083	14/13 = 1.077	15/14 = 1.071
Z = 2 $\rho_{\text{calc}}(\text{g/cm}^3)$	1.98	2.15	2.31