

## X-Ray Studies on Some Alkali and Alkaline-Earth Chromates(V)

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The crystal structure of  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$  (apatite structure) has been refined from three-dimensional X-ray data using least-squares techniques. The mean Cr—O distance for tetrahedral coordination is 1.66<sub>6</sub> Å. In an attempt to replace the OH-group with chlorine a new phase with the composition  $\text{Ca}_2\text{ClCrO}_4$  and the unit-cell dimensions  $a = 6.237$  Å,  $b = 7.122$  Å and  $c = 11.045$  Å (orthorhombic) was found. Unit-cell dimensions of  $\text{Li}_3\text{CrO}_4$ ,  $\text{Sr}_3(\text{CrO}_4)_2$ ,  $\text{Ba}_3(\text{CrO}_4)_2$ ,  $\text{Sr}_5\text{Cl}(\text{CrO}_4)_3$ ,  $\text{Ba}_5\text{Cl}(\text{CrO}_4)_3$  and  $\text{Sr}_2\text{ClCrO}_4$  are also given.

In connection with crystal structure studies on the systems Cr—O<sup>1-3</sup> and  $M\text{—Cr—O}^{4-6}$  ( $M =$  alkali and alkaline-earth metals), it was of interest to investigate some chromium(V) phases containing discrete  $\text{CrO}_4^{3-}$ -groups. The present work deals with the syntheses and crystallographic data of the compounds:  $\text{Li}_3\text{CrO}_4$ ,  $\text{Sr}_3(\text{CrO}_4)_2$ ,  $\text{Ba}_3(\text{CrO}_4)_2$ ,  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ ,  $M_5\text{Cl}(\text{CrO}_4)_3$  ( $M = \text{Sr, Ba}$ ), and  $M_2\text{ClCrO}_4$  ( $M = \text{Ca, Sr}$ ).<sup>\*</sup> In view of the importance of the apatite structure it was felt that a single-crystal study of the chromium analogue would be of value. Powder data of the substances treated in this article and three-dimensional single-crystal X-ray diffraction data of  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$  ( $F_o$  and  $F_c$ ) are included in a document,<sup>7</sup> copies of which may be obtained by request from the Secretary of the Institute of Inorganic Chemistry.

### EXPERIMENTAL

All the syntheses were carried out in platinum crucibles by firing pellets pressed from powdered and intimately mixed reagents of analytical grade at the desired temperature. After firing, each sample was reground and refired. This procedure was repeated until the appearance of the sample was microscopically homogeneous.

The densities of the phases were determined from the apparent loss of weight in benzene.

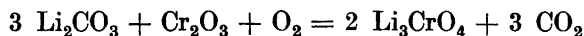
<sup>\*</sup> *Added in proof:* Banks and Jaunarajs, *Inorg. Chem.* 4 (1965) 78 have in a very recent paper shown the existence of the phases  $\text{Ca}_2\text{ClCrO}_4$ ,  $\text{Sr}_2\text{ClCrO}_4$ , and  $M_X(\text{CrO}_4)_3$  (with  $M = \text{Ca, Sr, Ba}$ , and  $X = \text{F, Cl}$ ).

Accurate powder data were obtained in a Guinier type focusing camera of 80 mm diameter (transmission position) with monochromatized  $\text{CuK}\alpha_1$  radiation. Potassium chloride (Analar, British Drug Houses,  $a = 6.2919 \text{ \AA}$  at  $20^\circ\text{C}$ , Hambling<sup>8</sup>) was added to the specimens as an internal standard. The indexing of the powder patterns of  $\text{Li}_3\text{CrO}_4$  and  $\text{Ca}_2\text{ClCrO}_4$  was facilitated by comparison with Weissenberg photographs ( $\text{CuK}$  radiation) taken from single crystals of these substances.

#### ALKALI AND ALKALINE-EARTH METAL CHROMATES(V)

##### $\text{Li}_3\text{CrO}_4$

Lithium chromate(V) was obtained by oxidizing  $\text{Li}_2\text{CO}_3$  and  $\text{Cr}_2\text{O}_3$  in air at  $800^\circ\text{C}$ . After 12 h, all of the sample was reground and refired in argon at the same temperature for another 12 h. The net reaction was



A different procedure was mentioned in a paper by Scholder and Schwarz.<sup>9</sup> The starting materials in their investigations were  $\text{Li}_2\text{CrO}_4 + \text{Li}_2\text{O}$  or  $\text{Li}_2\text{CrO}_4 + \text{Cr}_2\text{O}_3 + \text{Li}_2\text{O}$ . By comparing the powder pattern of  $\text{Li}_3\text{CrO}_4$  with those of  $\text{Li}_3\text{VO}_4$  and  $\text{Li}_3\text{MnO}_4$  they concluded that the compounds are isomorphous.

Table 1. Crystallographic data of  $\text{Li}_3\text{CrO}_4$ .

Laue symmetry:  $mmm$

Unit-cell dimensions:  $a = 6.31 \text{ \AA}$

$b = 10.86 \text{ \AA}$

$c = 4.94 \text{ \AA}$

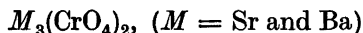
Absent reflections:  $h0l$  with  $h+l$  odd  $hk0$  with  $k$  odd

Space group: No. 62  $Pmnb$  (special orientation chosen to concord with the structure determination by Zemann<sup>10</sup>)

Density (observed):  $2.67 \text{ g cm}^{-3}$ .

Density (calculated):  $2.68 \text{ g cm}^{-3}$  (for  $\text{Li}_{12}\text{Cr}_4\text{O}_{16}$ ).

From Weissenberg photographs we concluded that the dark flaky crystals are isomorphous with  $\text{Li}_3\text{PO}_4$ , the structure of which, as determined by Zemann,<sup>10</sup> is built up of  $\text{PO}_4$  groups linked together by Li in tetrahedral coordination (Table 1).



Chromates(V) of strontium and barium were prepared by decomposing mixtures of the corresponding chromates(VI) and carbonates at  $800^\circ\text{C}$  in argon according to the equation:



The Sr-compound was also easily made by the air oxidation of a mixture of chromium sesquioxide and strontium oxide.  $\text{Sr}_3(\text{CrO}_4)_2$  and  $\text{Ba}_3(\text{CrO}_4)_2$  proved to be isomorphous with  $\text{Ba}_3(\text{PO}_4)_2$ , the structure of which was determined by Zachariasen.<sup>11</sup> The cell dimensions of  $\text{Sr}_3(\text{CrO}_4)_2$  and  $\text{Ba}_3(\text{CrO}_4)_2$  agree well with values reported by Scholder and Schwarz<sup>9</sup> (*cf.* Table 2). Recently Scholder

Table 2. Crystallographic data of  $M_3(\text{CrO}_4)_2$  ( $M = \text{Sr}, \text{Ba}$ ).Laue symmetry:  $\bar{3}m$ Absent reflections (hexagonal indices):  $hkl$  with  $-h+k+l \neq 3n$ Space group: No. 166  $R\bar{3}m$ 

Unit-cell dimensions (hexagonal axes):

	$a$	$c$
$\text{Sr}_3(\text{CrO}_4)_2$	5.576 Å	20.195 Å
$\text{Ba}_3(\text{CrO}_4)_2$	5.74 Å	21.39 Å

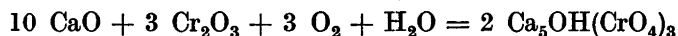
Density (observed): 4.41 g cm<sup>3</sup> ( $M = \text{Sr}$ )Density (calculated): 4.53 g cm<sup>3</sup> (for  $\text{Sr}_3(\text{CrO}_4)_2$ ).

and Suchy<sup>12</sup> reported a maximum solubility of 0.3 mole  $MO$  ( $M = \text{Sr}, \text{Ba}$ ) per  $M_3(\text{CrO}_4)_2$  with a nonperceptible or very small change in the unit-cell dimensions. Several mechanisms seem possible for the formation of this solution and studies on this matter are in progress. In this connection it is worth mentioning that Balz<sup>13</sup> has found compounds with the formula  $4MO \cdot P_2O_5$  ( $M = \text{Ca}, \text{Sr}, \text{and Ba}$ ) in the systems  $MO - P_2O_5$  with still unknown structures.

#### CHROMATE-APATITES. REFINEMENT OF THE $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ STRUCTURE

The existence of chromate-apatites,  $M_5\text{OH}(\text{CrO}_4)_3$ , was reported by Balz,<sup>13</sup> Johnson<sup>14</sup> and recently by Scholder and Schwarz.<sup>9</sup> A further examination of the chromate-apatite system has been made by the present authors and some new results have been obtained. These studies have included a refinement of the crystal structure of  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ .

The study was made with crystals obtained by partial oxidation of a mixture of calcium oxide and chromium sesquioxide in humid air at 900°C according to the equation:



A small number of well developed dark crystals (hexagonal prisms) suitable for single crystal studies were obtained in an apatite matrix. They proved to be single crystals of  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$  and were used for the structure determination. The cell parameters reported in Table 3 are in excellent agreement with those reported by Johnson<sup>14</sup> ( $a = 9.67 \text{ Å}$ ,  $c = 7.01 \text{ Å}$ ).

Zerth to fourth level integrated Weissenberg photographs were taken with filtered  $\text{CuK}$  radiation around  $c$ , the axis of elongation of the prisms, using

Table 3. Crystallographic data of some chromium apatites.

Laue symmetry:  $6/m$ Absent reflections:  $00l$  with  $l$  oddSpace group: No. 176  $P6_3/m$ 

Unit-cell dimensions:

	$a$	$c$
$\text{Ca}_5\text{OH}(\text{CrO}_4)_3$	9.683 Å	7.01 Å
$\text{Sr}_5\text{Cl}(\text{CrO}_4)_3$	10.149 Å	7.333 Å
$\text{Ba}_5\text{Cl}(\text{CrO}_4)_3$	10.511 Å	7.764 Å

the multiple-film technique. The intensities were estimated visually with a standard scale. The scattering curves for  $\text{Ca}^{2+}$  and  $\text{Cr}^{5+}$  were derived from Thomas and Umeda's table,<sup>15</sup> that of  $\text{O}^{2-}$  from a paper by Suzuki.<sup>14</sup>

No corrections for absorption or extinction were made. Using  $\text{CuK}$  radiation there are about 470 possible independent reflections for  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ . About 300 of these were within the range of the data recorded and 271 reflections were actually observed. The scaling was carried out by calculating structure factors, based on the parameters given by Posner *et al.*<sup>17</sup> for  $\text{Ca}_5\text{OH}(\text{PO}_4)_3$  and matching the sums of the observed and calculated structure factors for each level. This set of  $F_o$  was used in a least-squares refinement<sup>18</sup> of the 24 variable parameters (twelve atomic position parameters, seven isotropic temperature factors and five separate scale factors, one for each layer). The parameters obtained are listed in Table 4. Observed and calculated

Table 4. Final set of atomic coordinates, isotropic temperature factors and their standard deviations for  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ .

	$x$	$\sigma(x)$ Å	$y$	$\sigma(y)$ Å	$z$	$\sigma(z)$ Å	$B$ Å <sup>2</sup>	$\sigma(B)$ Å <sup>2</sup>
Ca(1) in 4( <i>f</i> )	1/3	—	2/3	—	0.9995	0.006	1.38	0.06
Ca(2) in 6( <i>h</i> )	0.2650	0.006	0.0143	0.006	1/4	—	2.20	0.09
Cr in 6( <i>h</i> )	0.4052	0.004	0.3754	0.004	1/4	—	1.50	0.06
O(1) in 6( <i>h</i> )	0.3392	0.022	0.5021	0.022	1/4	—	2.55	0.35
O(2) in 6( <i>h</i> )	0.6019	0.018	0.4589	0.018	1/4	—	1.65	0.27
O(3) in 12( <i>i</i> )	0.3489	0.012	0.2550	0.012	0.6565	0.017	1.95	0.20
OH in 2( <i>a</i> )	0	—	0	—	1/4	—	2.28	0.29

$F$  values and a three-dimensional difference synthesis, calculated over the unique part of the unit cell, are given in Ref.<sup>7</sup> The largest maxima in the  $(F_o - F_c)$ -function have a magnitude of less than 20 % of the mean height of the oxygen maxima in the electron density function.

After twelve cycles of refinement the  $R$ -value was 0.102 for the observed reflections and the shifts in all parameters were less than one tenth of the standard deviations.

The weights,  $w$ , were calculated according to an equation suggested by Cruickshank *et al.*,<sup>19</sup> as follows:

$$w = 1/(a + |F_o| + c|F_o|^2) \text{ with } a = 4 \text{ and } c = 0.013$$

The least-squares program computes a weight analysis for each cycle of refinement, where the mean value of  $w(|F_o| - |F_c|)^2$  is calculated both as a function of  $\sin \theta$  and  $F_o$ . The weight analysis for the last cycle of refinement is given in Table 5.

In Table 6 a survey of the interatomic distances and angles in the structure is given. As is seen, the Cr—O distances within the  $\text{CrO}_4$  tetrahedra are all of the same magnitude, the range being 1.64<sub>0</sub>—1.68<sub>6</sub> Å with a mean of 1.66<sub>6</sub> Å.

Table 5. Weight analysis used in the last cycle of the refinement of  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ .  
 $w = \text{weighting factor}$ .  $\Delta = \|\overline{F}_o\| - |F_c|$ .

Interval $\sin \Theta$	$\overline{w \Delta^2}$	Number of independent reflections	Interval $ F_o $	$\overline{w \Delta^2}$	Number of independent reflections
0.00–0.46	0.95	43	0–6	8.93	2
0.46–0.58	0.92	36	6–12	1.61	34
0.58–0.67	1.17	32	12–18	1.09	37
0.67–0.74	1.08	28	18–24	1.17	34
0.74–0.79	1.09	19	24–30	0.77	27
0.79–0.84	0.97	19	30–36	0.82	27
0.84–0.89	0.69	20	36–42	1.01	23
0.89–0.93	0.78	16	42–48	0.50	13
0.93–0.96	1.46	17	48–54	0.59	13
0.96–1.00	0.94	18	54–60	0.40	37

Table 6. Interatomic distances (in Å) and angles (°) in the structure of  $\text{Ca}_5\text{OH}(\text{CrO}_4)_3$ .

Distances Cr–O, O–O and angles O–Cr–O in the tetrahedra around chromium.

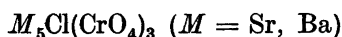
Cr–O(1)	1.640	O(1)–Cr–O(2)	115.0
Cr–O(2)	1.653	2(O(1)–Cr–O(3))	113.6
2(Cr–O(3))	1.686	2(O(2)–Cr–O(3))	103.6
		O(3)–Cr–O(3)	106.4
O(1)–O(2)	2.78		
2(O(1)–O(3))	2.78		
2(O(2)–O(3))	2.62		
O(3)–O(3)	2.70		

Distances in the coordination figure around Ca(1) and Ca(2).

3(Ca(1)–O(1))	2.39	Ca(2)–O(1)	3.04 and 3.46
3(Ca(1)–O(2))	2.39	Ca(2)–O(2)	2.31
3(Ca(1)–O(3))	2.81	2(Ca(2)–O(3))	2.38
		2(Ca(2)–O(3))	2.45
		Ca(2)–OH	2.50

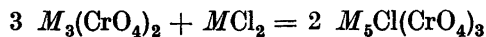
Distances in the coordination figure around OH.

3(OH–Ca(2))	2.50
6(OH–O(3))	3.31



In an attempt to replace the OH-group with chlorine, halide-apatites with  $M = \text{Sr}$  and  $\text{Ba}$  were obtained. The corresponding calcium compound was not obtained under the experimental conditions used.

Well developed dark rod-like prisms of the  $M_5\text{Cl}(\text{CrO}_4)_3$  compounds were obtained from melts of  $M_3(\text{CrO}_4)_2$  in an excess of  $M\text{Cl}_2$  at 1000–1200°C in argon.



The excess chlorides were extracted with water.

The crystallographic data of the halide-apatites are given in Table 3.

HALIDE-CHROMATES  $M_2\text{ClCrO}_4$  ( $M = \text{Ca}, \text{Sr}$ )

By heating calcium chromate(V) at 700°C in argon with an excess of calcium chloride, extremely well developed crystals of a new compound  $\text{Ca}_2\text{ClCrO}_4$  were obtained.



The excess of chloride was extracted with methanol. The black crystals were stable in air but were decomposed in dilute acids. The chromium(VI) content was determined iodometrically, as was also the total chromium after oxidation by perchloric acid. The chlorine was determined gravimetrically in nitric acid solution as silver chloride. (Check experiments showed no interfering influence from the formation of chromium(III) complexes.)

The reproducibility of the analyses was found to be good and the results were in good agreement with the values calculated for  $\text{Ca}_2\text{ClCrO}_4$ .

Chromium (VI), %	Chromium total, %	Chlorine %
Found 15.0	22.4	15.2
Calc. 14.96	22.45	15.31

From the conditions limiting possible reflections and the cell dimensions it was found that  $\text{Ca}_2\text{ClCrO}_4$  is likely to be isomorphous with the mineral *spodiosite* (or chlorospodiosite),  $\text{Ca}_2\text{ClPO}_4$ , described by Mackay.<sup>20</sup>

Preliminary experiments have shown the existence of an Sr-phase, belonging to the spodiosite group. The crystallographic data of the chromium-spodiosite phases are given in Table 7.

A crystal structure determination of  $\text{Ca}_2\text{ClCrO}_4$  has been completed and will be published elsewhere.<sup>21</sup>

## DISCUSSION

Recently Schwartz<sup>22</sup> reported the existence of  $\text{LaCrO}_4$  (huttonite structure),  $\text{NdCrO}_4$  and  $\text{YCrO}_4$  (both of zircon structure) and  $\text{PrCrO}_4$  (dimorphic: huttonite and zircon type).

Table 7. Crystallographic data of  $M_2\text{ClCrO}_4$ . ( $M = \text{Ca}, \text{Sr}$ ).

Laue symmetry: *mmm*

Absent reflections: *Ok*l with *k* odd

*h*0l with *l* odd

Space group: No. 57 *Pbcm* or No. 29 *Pbc2*<sub>1</sub>

Unit-cell dimensions:

	<i>a</i>	<i>b</i>	<i>c</i>
$\text{Ca}_2\text{ClCrO}_4$	6.237 Å	7.122 Å	11.045 Å
$\text{Sr}_2\text{ClCrO}_4$	6.51 Å	7.48 Å	11.43 Å

Density observed: 3.14 g cm<sup>-3</sup> ( $M = \text{Ca}$ ).

Density calculated: 3.13 g cm<sup>-3</sup> (for  $\text{Ca}_2\text{Cl}_4(\text{CrO}_4)_4$ ).

With regard to this and the previously discussed chromate(V) compounds, it can be concluded that there exists a large group of pentavalent chromium compounds, stable in the solid state, showing strong analogies with the corresponding phosphates, and also with the arsenates, vanadates and silicates. The chromates(V), all forming black crystals, are relatively stable and often exist in a wide temperature range. However, they are readily decomposed by dilute acids, forming a solution containing Cr(III) and Cr(VI). According to Bailey and Symons<sup>23</sup> in the absence of oxygen the  $\text{CrO}_4^{3-}$ -ion is stable in aqueous solutions containing large concentration of potassium hydroxide.

The environments of the chromium atoms are tetrahedral and all the known structures can be considered as containing discrete  $\text{CrO}_4$  groups and metal atoms. The ratio of the total cation charge to the number of chromium atoms present is in every case high ( $> 3$ ), which favours the formation of discrete  $\text{CrO}_4$  groups and stabilizes the oxidation number of  $+5$  for the chromium atoms.

During recent years one of the present authors (W) has investigated the conditions for the formation of chromium compounds with two- and three-dimensional framework structures. The average oxidation number of the chromium atoms in the compounds  $M\text{Cr}_3\text{O}_8^5$  ( $M = \text{Li, Na, K, Rb}$ ) with a low cation charge-chromium ratio is  $+5$ . It was, however, shown that the structure is formed by  $\text{CrO}_6$  octahedra and  $\text{CrO}_4$  tetrahedra arranged in layers by sharing corners, the octahedra containing trivalent Cr atoms and the tetrahedra hexavalent atoms. Later this was confirmed by magnetic measurements made by Klemm.<sup>24</sup>

Recently<sup>2</sup> the compound  $\text{Cr}_5\text{O}_{12}$  has been prepared in a pure state by decomposing  $\text{CrO}_3$  at high pressures (1–3 kbar). The structure is also built up from  $\text{CrO}_6$  octahedra and  $\text{CrO}_4$  tetrahedra joined together by sharing corners and edges in a three-dimensional framework.<sup>3</sup>

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