

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Compounds of the Alkali Metals and Chromium of the Type  $M\text{Cr}_3\text{O}_8$ <sup>1,2,3</sup>BY LAWRENCE SUCHOW, I. FANKUCHEN AND ROLAND WARD<sup>4</sup>

A procedure is described for the preparation of all the alkali metal compounds of composition  $M\text{Cr}_3\text{O}_8$ . The lithium compound is orthorhombic while the sodium, potassium and rubidium compounds are monoclinic, the  $\beta$ -angle showing a progressive increase with increasing size of the alkali metal ion. For all of these, the unit cell formula is  $M_2\text{Cr}_6\text{O}_{16}$ . The cesium compound has a different structure which was not determined. While the average oxidation number of the chromium in these compounds is +5, the X-ray data indicate that two of the chromium atoms occupy positions in the unit cell which are not equivalent to the positions occupied by the other four. This suggests the possibility that two of the chromium atoms are trivalent and four are hexavalent.

The stable oxidation states for chromium in its ternary compounds are 3 and 6. The major exceptions appear to be oxy-halogeno complexes such as  $M_3\text{CrOCl}_5$  where  $M = \text{K}^+, \text{Rb}^+, \text{Cs}^+$  or  $\text{NH}_4^+$ ,  $M\text{CrOCl}_4$  where  $M$  is the pyridonium or quinolonium ion and an oxy-fluoro compound of potassium fluoride with  $\text{CrO}_2\text{F}$  reported by Olsson.<sup>7</sup> There are also the peroxy compounds  $M_3\text{CrO}_8$  which probably contain pentavalent chromium.<sup>8</sup> Jatkari, Athavale, Datar and others have investigated the thermal decomposition of alkaline earth chromates and their reactions with alkaline earth oxides and carbonates.<sup>9</sup> A large number of intermediate compounds of the type  $x\text{MO} \cdot y\text{CrO}_3 \cdot z\text{Cr}_2\text{O}_3$  are postulated to explain certain arrests in the reactions in various temperature ranges. None of these compounds appears to have been isolated in a pure form but the magnetic susceptibilities are said to be in agreement with the formulas assigned assuming that the compounds contain chromium only in hexavalent and trivalent states.

As part of a general study of unusual oxidation states of the transition metals in their ternary compounds, this paper reports the results of our efforts to prepare and characterize compounds of chromium in an oxidation state between 3 and 6.

## Experimental

The reduction of potassium chromate or dichromate with hydrogen at temperatures from 300 to 700° gives a black product which upon extraction with water yields a solution of potassium hydroxide and a black residue the nature of which could not be determined from X-ray analysis. It was noticed, however, that some of the residues contained an appreciable amount of potassium and that the chromium content varied from 54 to 60% depending on the temperature used in the reduction. On no occasion did the analysis correspond to  $\text{Cr}_2\text{O}_3$ .

These results appeared to indicate that a chromium-rich ternary compound was formed in the reaction. The synthesis of such a compound was accomplished in the following

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- (2) Abstracted from a dissertation submitted to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements of the degree of Doctor of Philosophy, 1951.
- (3) For tables of the X-ray powder diagrams order Document 3428 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$4.95 for photocopies (6 X 8 inches) readable without optical aid.
- (4) University of Connecticut, Storrs, Connecticut.
- (5) R. F. Weinland and W. Fridrich, *Ber.*, **38**, 3784 (1905); R. F. Weinland and M. Fiederer, *ibid.*, **39**, 4042 (1906); **40**, 2090 (1907).
- (6) R. J. Meyer and H. Best, *Z. anorg. Chem.*, **22**, 192 (1899).
- (7) F. Olsson, *Arkiv Kemi, Mineral., Geol.*, **9**, No. 10, 10 (1924).
- (8) W. Klemm and H. Werth, *Z. anorg. Chem.*, **216**, 127 (1933).
- (9) A series of 17 papers appear in the *J. Indian Inst. Sci.* from 1937 to 1941. The final paper is D. S. Datar, *Quart. J. Indian Inst. Sci.*, **5**, 43 (1942).

way. Mixtures of potassium dichromate and chromium trioxide were heated at 350° in air at ordinary pressure and in oxygen pressures up to 500 p.s.i. Under these conditions mixtures of compositions  $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{CrO}_3$  showed a constant weight loss and gave rise to black lustrous crystals which were insoluble in water and were not attacked by aqua regia. The X-ray diffraction pattern was distinct from that of any of the known decomposition products of either reactant. The same product is obtained by using an excess of potassium dichromate which is readily leached out with water. With higher proportions of chromium trioxide, however, the product was contaminated with  $\text{Cr}_2\text{O}_3$  as revealed by X-ray analysis. The most satisfactory procedure for preparing the new compound is to heat a mixture of composition  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{CrO}_3$  at 350° in air for two hours and to extract the excess potassium dichromate with water.

The reaction proceeds slowly at 200°. After two hours at 250 to 280° a black liquid is obtained which, on cooling, sets to a glassy solid which shows conchoidal fracture. After 24 hours at this temperature, however, complete conversion to the crystalline product is obtained. The intermediate glassy substance is amorphous to X-rays and dissolves in water to give dichromate ion and some chromic ion. The crystalline product obtained by prolonged heating at 250° contained some rod shaped crystals approximately  $0.08 \times 0.01 \times 0.01$  mm. in size. These were used for single crystal X-ray analysis.

Analogous compounds of  $\text{Li}^+, \text{Na}^+, \text{Rb}^+$  and  $\text{Cs}^+$  were prepared by the same procedure. The analyses of these compounds are given in Table I. The chromium was determined by dissolving a sample in hot 60% perchloric acid and digesting on a hot-plate for 15 minutes. The solution was diluted with distilled water, excess potassium iodide added and the iodine determined by titration with standard thiosulfate solution. The sodium was determined as sodium zinc uranyl acetate and the potassium as potassium perchlorate. From these data and from the weight loss from stoichiometric mixtures the over-all reaction appears to be

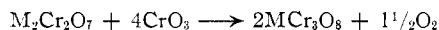


TABLE I  
CHEMICAL ANALYSIS OF REACTION PRODUCTS  
Based on the formula  $\text{MCr}_3\text{O}_8$

Alkali metal in compound	Chromium, %		Alkali ion, %	
	Found	Calcd.	Found	Calcd.
Li	52.6	53.62	...	2.39
Na	50.8	50.81	7.00	7.49
K	48.0	48.29	11.6	12.10
Rb	41.8	42.22	...	23.13
Cs	36.5	37.42	...	31.88

**X-Ray Study of the Products.**—From the X-ray powder diagrams it could readily be seen that the structures of the sodium, potassium and rubidium compounds were similar. The lithium compound also appeared to have a related structure but the cesium compound gave a quite different pattern. From the single crystal data, obtained only with the potassium compound, it was possible to determine the lattice constants and space groups for all except the cesium compound.

The crystal was first studied by means of a single crystal microcamera of radius 2.37 cm. using a slit width 0.15 mm. and was found to have at least one orthogonal axis which was parallel to the long axis of the crystal. The crystal aligned on this axis was transferred to a Weissenberg camera (5.73

cm. diameter with slit width 1 mm.). A 25-hour exposure gave a diagram containing eight spots from which the crystal was seen to be monoclinic and from which the lattice constants could be determined. These data are given in Table II. This information permitted the indexing of the powder diagram of the potassium compound. The diagrams of the lithium, sodium and rubidium compounds were then indexed by comparison. The lattice constants and space groups for the lithium to rubidium compounds are given in Table III and the interplanar spacings for the cesium compound are listed in Table IV.

TABLE II

INDEXING OF  $h0l$  WEISSENBERG PHOTOGRAPHY OF  $\text{KCr}_2\text{O}_8$  188° OSCILLATION ABOUT AXIS (LENGTH 5.47) Å. LB-95°

Plane	Corresponding $d$ -spacing	Intensity
001	7.62	280
003	2.54	40
201	3.87	160
402	1.935	25
200	4.27	240
400	2.14	5
201	3.59	400
402	1.795	10

TABLE III

LATTICE CONSTANTS AND SPACE GROUPS OF THE COMPOUNDS  $M\text{Cr}_2\text{O}_8$  ( $M = \text{Li, Na, K; Rb}$ )

Compound	$\text{RbCr}_2\text{O}_8$	$\text{KCr}_2\text{O}_8$	$\text{NaCr}_2\text{O}_8$	$\text{LiCr}_2\text{O}_8$
Density $g./\text{ml.}$	3.140	3.148	3.235	3.126
$a$ (Å.)	8.62	8.57	8.52	8.32
$b$ (Å.)	5.48	5.47	5.50	5.48
$c$ (Å.)	7.96	7.65	6.86	6.16
$\beta$	95° 31'	95°	91° 33'	90°
$C \sin \beta$	7.92	7.62	6.86	6.16
Diameter of $M$	2.96	2.66	1.90	1.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$ or $P2_1/m$	$P2_1$ or $P2_1/m$	$P2_1$ or $P2_1/m$	$C m m 2$ , $C m 2 m$ , $C 2 2 2$ , or $C m m m$ .

TABLE IV

INTERPLANAR SPACINGS FOR THE  $\text{CsCr}_2\text{O}_8$

$d$  (Å.): 4.42 (W), 4.19 (W), 4.01 (W), 3.68 (M), 3.48 (S), 3.23 (W), 3.07 (M), 3.00 (W), 2.76 (W), 2.45 (W), 2.36 (W), 2.30 (W), 2.21 (W), 2.09 (W), 1.920 (W), 1.882 (W), 1.725 (W), 1.710 (W), 1.670 (W)

### Discussion

The densities of the compounds given in Table III correspond to a unit cell formula  $\text{K}_2\text{Cr}_2\text{O}_{16}$ . The measured densities agreed with the calculated values within  $\pm 4\%$ , with the exception of that of the lithium compound which was about 9% lower than

the calculated value. The reason for this discrepancy is not known.

Reference to the data in Table III shows that the distortion of the crystal from the orthorhombic form is progressively greater with increasing size of the alkali metal cations. The differences in value of  $C \sin \beta$  from one compound to another are equal to the differences in diameter of the alkali metal cations. This appears to indicate that these cations lie in a single plane parallel to the  $C$  face.

The principal lines of the diffraction patterns of the potassium compound correspond to the  $C2$  space group and only prolonged exposure yields several weak lines which indicate that the space group is  $P2_1$ , or  $P2_1/m$ . We may assume that the heavier atoms are probably located fairly closely by filling the following special positions of the  $C2$  group.

Twofold positions (a)  $0Y0$  and  $\frac{1}{2}, y + \frac{1}{2}, 0$ .

(b)  $0Y\frac{1}{2}$  and  $\frac{1}{2}, y + \frac{1}{2}, \frac{1}{2}$ .

Fourfold positions (c)  $xyz$ :  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ;  $\bar{x} y \bar{z}$ ;  $x - \frac{1}{2}, y + \frac{1}{2}, z$

The two potassium ions therefore may be assumed to have the twofold positions (a) with  $y = 0$  and are at or near  $000$  and  $\frac{1}{2}, \frac{1}{2}, 0$ . Of the six chromium atoms to be placed in the unit cell, two may be accommodated in twofold positions and four in fourfold positions. The available data were insufficient to arrive at the complete structure of the compound so that the environment of the chromium atoms could not be established. It is possible that the two chromium atoms in the twofold positions are trivalent and those in the fourfold positions are hexavalent but this would be more plausible if it could be shown that the chromium atoms in the fourfold positions have fourfold coordination with oxygen and those in the twofold positions sixfold coordination. Attempts to construct a scale model on this basis, however, were not successful.

On the other hand, the black metallic appearance and inert character of these crystals suggest that we are not dealing with a simple potassium chromium III ortho chromate  $\text{KCr}_2(\text{CrO}_4)_4$  or with a potassium chromyl dichromate  $\text{K}(\text{CrO})_2(\text{Cr}_2\text{O}_7)_2$  but that there is some interaction between the chromium atoms so that the effective oxidation number of all the chromium atoms is  $+5$ .

The complete elucidation of the structure appears to be necessary to fix unequivocally the oxidation state of the chromium in these compounds and for this larger single crystals would be necessary. Attempts to prepare suitable crystals have not yet been successful.

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