Chemical Composition and Crystal Data of Some Chromium(VI) — Iodine(V) Compounds

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In connection with crystal structure studies on *isopolyacids* of hexavalent chromium, it was found of interest to consider the possibility of the interaction of chromate(VI) with other ions, giving rise to complex *heteropolyacids*. A literature survey showed that several articles have appeared dealing with chromate(VI) complexes containing *anionic* phosphorus(V) [1-3], arsenic(V) [1], sulphur(VI) [4], iodine(V) [5] and *cationic* cerium(III) [6] and chromium(III) [7,8].

The present work has been confined to the chromate-iodate system and deals with the crystallographic and analytical data of the compounds $(NH_4)_2O \cdot 2CrO_3 \cdot I_2O_5$, $K_2O \cdot 2CrO_3 \cdot I_2O_5$, $K_2O \cdot 2CrO_3 \cdot I_2O_5 \cdot H_2O$, $Rb_2O \cdot 2CrO_3 \cdot I_2O_5$ and $Cs_2O \cdot 2CrO_3 \cdot I_2O_5$. Crystallographic evidence is given for the existence of a $CrIO_6^-$ complex in the solid state.

Experimental. Analytical grade reagents were used throughout. Chromium trioxide was dried at 120°C and weighed out of contact with air.

pH measurements were made at 25°C with a Radiometer pH meter M 3, using Radiometer glass and calomel electrodes standardized against a commercial phosphate buffer, pH = 6.50.

The powder patterns were obtained in a Guinier type focusing camera of 80 mm diameter (transmission position) with strictly monochromatized $CuK\alpha_1$ radiation. Potassium chloride (Analar, British Drug Houses, $a = 6.2919$ Å at 20°C) was added to the specimens as internal standard.

The structural investigation was based on X-ray data. The exposures were made with a commercial Nonius Weissenberg camera with CuK radiation.

The density of the crystals was determined from the apparent loss of weight in benzene.

Synthesis. The compounds were prepared according to Blomstrand [5] by dissolving ca. 20 g of alkali dichromate (or chromium trioxide and alkali chromate) in water and adding a stoichiometric quantity of HIO_3. Single crystals were obtained by allowing this solution to evaporate slowly at room temperature. The crystals were removed from the solutions by decanting at equal time intervals and the phase purity was controlled by X-ray and chemical analyses.

Attempts to prepare other phases than the 1:1 compounds were made by varying the proportions of chromate and iodic acid or adding HNO_3 to the solutions. These attempts were unsuccessful but two phases were observed in the potassium system, *viz.* $KCrIO_6$ and $KCrIO_6 \cdot \frac{1}{2}H_2O$, the former crystallizing from solutions containing HNO_3, the latter from HNO_3-free solutions.

Chemical analysis. The results are given in Table 1.

Iodine. The crystals were dissolved in appr. 50 ml 10^{-3} M HCl, and SO_2 was then bubbled into the acid solution. The iodate was reduced over iodine to iodide. The reduction was stopped 1 min after the brown iodine colour had disappeared. The solution was then titrated potentiometrically with 0.015 M $AgNO_3$.

Chromium. The original solution was acidified with HCl and KI was added. Titration with thiosulphate gave the sum of chromate and iodate. The amount of chromium was calculated by difference.

Water. The sample was heated to 150°C in a Pyrex tube according to the method of Penfield [9].

Alkali. The alkali metals were determined gravimetrically with $(C_6H_5)_4BNa$ [10] or with the following technique utilizing cation exchange.
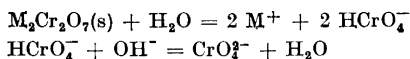
When an alkali dichromate solution is titrated potentiometrically with NaOH, the weak acid $HCrO_4^-$ is determined according to the equations:

Table 1. Analytical data.

	% Alkali		% Chromium		% Iodine		% Water	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
NH_4CrIO_6	6.23 ± 0.05	6.16	18.3 ± 0.3	17.7	43.2 ± 0.2	43.3	—	0
$KCrIO_6 \cdot \frac{1}{2}H_2O$	11.8 ± 0.1	12.1	15.7 ± 0.3	16.1	40.1 ± 0.2	39.3	2.4 ± 0.1	2.8
$KCrIO_6$	12.5 ± 0.1	12.5	16.7 ± 0.3	16.6	40.0 ± 0.2	40.4	0.3 ± 0.1	0
$RbCrIO_6$	23.7 ± 0.1	23.7	15.1 ± 0.3	14.4	35.3 ± 0.2	35.2	0	0
$CsCrIO_6$	32.6 ± 0.1	32.6	13.3 ± 0.3	12.8	31.2 ± 0.2	31.1	0	0

Table 2. Crystallographic data.

	Probable symmetry	a (Å)	b (Å)	c (Å)	β	Formula units in the cell	Density Found	(g cm^{-3}) Calcd.
NH_4CrIO_6	$Pbca$	6.05	14.32	13.38	—	8	3.34	3.36
$KCrIO_6$	$P2_1/c$	9.25	4.86	14.28	108°	4	3.56	3.42
$KCrIO_6 \cdot \frac{1}{2}H_2O$	$C2/m$	14.91	5.48	15.76	95°	8	3.35	3.34
$RbCrIO_6$	$P2_1/n$	8.12	7.70	10.45	109°	4	3.85	3.86
$CsCrIO_6$	$P2_1/n$	8.26	8.08	10.75	110°	4	4.05	4.02

$$M_2Cr_2O_7(s) + H_2O = 2\ M^+ + 2\ HCrO_4^-$$
$$HCrO_4^- + OH^- = CrO_4^{2-} + H_2O$$

An aliquot part of the dichromate solution is then introduced into a cation exchange column saturated with hydrogen ions. The effluent is titrated with NaOH and a curve is obtained with two titration points. The amount of NaOH required for the first equiv. points is equivalent to the alkali ions present.

When the chromium(VI)—iodine(V) complex is dissolved in water, the compound will be hydrolyzed and the solution will contain alkali, hydrogen-, hydrogen chromate- and iodate ions.

$$MCrIO_6(s) + H_2O = M^+ + H^+ + HCrO_4^- + IO_3^-$$
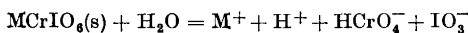
The solution is titrated with NaOH before and after running through the ion exchange column. The difference between the amount of NaOH required for the two first equiv. points is equivalent to the alkali content. It is also clear from the reaction formula that the amount of NaOH required for the first titration point (without ion exchange) is equivalent to the iodate present in the compound. Thus the amounts of alkali, hexavalent chromium and pentavalent iodine could be determined from the two titrations. The equivalent points were determined by plotting $\Delta V/\Delta pH$ versus V according to Gran [11]. The method has also been used successfully for analyzing trichromates and tetrachromates.

Crystallographic data. The unit cell parameters and probable symmetry of the various phases are summarized in Table 2. The rubidium and cesium salts present the single instance of isomorphism among these compounds. So far only the crystal structure of NH_4CrIO_6 has been investigated (*v. infra*) — studies of further phases of this group are in progress.

The crystal structure of NH_4CrIO_6. Rotation and Weissenberg photographs about all three axes were taken of a small crystal of NH_4CrIO_6 (CuK radiation). Analysis of

the photographs showed a systematic absence for $0kl$ when k odd, $h0l$ when l odd and $hk0$ when h odd, indicating the space group to be No. 61, $Pbca$.
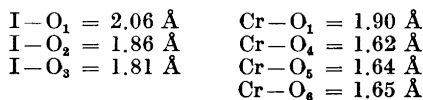
Space group No. 61 $Pbca$.

Unit cell dimensions: $a = 6.05$ Å, $b = 14.32$ Å, $c = 13.38$ Å.

Unit cell content: 8 NH_4CrIO_6.

The structure may be described as built up of $CrIO_6^-$-ions formed by a CrO_4-tetrahedron and a trigonal IO_3-pyramid sharing one corner (the O_1 atom).

The following interatomic distances are obtained:

$I - O_1 = 2.06$ Å		$Cr - O_1 = 1.90$ Å
$I - O_2 = 1.86$ Å		$Cr - O_4 = 1.62$ Å
$I - O_3 = 1.81$ Å		$Cr - O_5 = 1.64$ Å
		$Cr - O_6 = 1.65$ Å

The distances are of reasonable length throughout. The central bond distances $Cr - O_1$ and $I - O_1$ are significantly longer than the peripheral bond lengths.

The $Cr - O_1 - I$ angle is $\sim 118°$.

A three-dimensional refinement process is in progress and the result with a full description of the structure analysis and a further discussion of the structure will be published elsewhere.

1. Friedheim, C. and Mozkin, J. *Z. anorg. Chem.* **6** (1894) 273.
2. Holloway, F. J. *Am. Chem. Soc.* **74** (1952) 224.

3. Zsakó, I. *Studii cercetari chim. Filiala Cluj* **7** (1956) 53.
4. Yatsimirskii, K. B. and Vasil'eva, V. N. *Zhur. Neorg. Khim.* **1** (1956) 1983.
5. Blomstrand, C. W. *J. prakt. Chem.* [2] **40** (1889) 328.
6. Tong, J. Y. and King, E. L. *J. Am. Chem. Soc.* **76** (1954) 2132.
7. King, E. L. and Neptune, J. A. *J. Am. Chem. Soc.* **77** (1955) 3186.
8. Krauss, H.-L. and Gnatz, G. *Chem. Ber.* **92** (1959) 2110.
9. Penfield, S. L. *Am. J. Sci.* [3] **48** (1894) 30.
10. Raff, P. and Brotz, W. *Z. anal. Chem.* **133** (1951) 241.
11. Gran, G. *Acta Chem. Scand.* **4** (1950) 559.

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Crystallographic Data of Sr2CrO4

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Rather few compounds containing tetravalent chromium are reported in literature and the information about their crystallographic properties is incomplete. The syntheses of CrF_4 and $CrBr_4$ have been reported [1,2] but no crystallographic data are available for these substances. In 1950 the fluoro complexes M_2CrF_6 (M = K, Rb, and Cs) were prepared [3] and Bode and Voss [4] found that these complexes have the octahedral arrangement with discrete CrF_6^{2-} ions. The coordination number 6 is also found in CrO_2 which phase is of a rutile type [5,6].

Scholder and Sperka [7,8] have reported the syntheses of Ba_2CrO_4, Ba_3CrO_5 and Sr_2CrO_4, containing chromium with an average oxidation number of + 4. According to these authors, there exist structural relationships between the compounds M_2TiO_4 and M_2CrO_4 (M = Ba and Sr).

The crystal structure of Ba_2TiO_4 has been determined by Bland [9]. The space group is $P2_1/n$ and the cell dimensions are:

$$a = 6.12 \text{ Å}, \ b = 7.70 \text{ Å}, \ c = 10.50 \text{ Å}, \ \beta = 93°8'$$

The structure is of the β-K_2SO_4 type and is closely related to β-Ca_2SiO_4. The environment of the titanium atom is unusual; it is approximately tetrahedral and the structure is considered as an arrangement of discrete TiO_4-groups and barium atoms.

Sr_2TiO_4 belongs according to Balz and Plieth [10] to an interesting group of oxide compounds with the same crystal structure as K_2NiF_4 and K_2MgF_4[11]. The space group is $I4/mmm$ and the cell dimensions are:

$$a = 3.88 \text{ Å} \qquad c = 12.58 \text{ Å}$$

The structure is formed by somewhat distorted TiO_6-octahedra arranged in layers with the composition TiO_2 by sharing corners. In the direction of the tetragonal c axis an alternation of two SrO-layers with one TiO_2 layer can be distinguished.

By a partial substitution of Sr^{2+} ions (about 5 mole %) in Ba_2TiO_4, specimens with the orthorhombic β-K_2SO_4 structure were obtained by Kwestroo and Paping [12]. The solid solution area ends at a composition with a Ba^{2+}/Sr^{2+} ratio of about 1:3. The structure of Sr_2CrO_4 has been investigated by the present authors and preliminary results are given in this paper.

Crystals of Sr_2CrO_4, suitable for single-crystal X-ray studies, were prepared from chromium(III)oxide, strontium chromate(VI) and carbonate-free strontium hydroxide in a platinum crucible at 900°C with argon as a protecting gas.

$$Cr_2O_3 + SrCrO_4 + 5 \ Sr(OH)_2 = 3 \ Sr_2CrO_4 + 5 \ H_2O$$
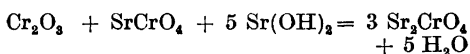
The excess of strontium hydroxide was extracted with water-free methanol. The crystals obtained were small blue-black prisms stable in air and insoluble in hot acetic acid.

The hexavalent chromium was determined iodometrically, the total chromium after oxidation by hydrogen peroxide in alkaline solution. The strontium was determined gravimetrically as strontium sulphate in chromium-free solutions. The reproducibility of the analyses was found to be good and the results in fair agreement with the values calculated for Sr_2CrO_4.

	Chromium (VI), %	Chromium total, %	Strontium %
Found	5.88 ± 0.05	17.62 ± 0.05	60.2 ± 0.1
Calc.	5.95	17.85	60.17