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)\textsuperscript{1−2}, arsenic(VI)\textsuperscript{1}, sulphur(VI)\textsuperscript{4}, iodine(V)\textsuperscript{5} and cationic cerium(III)\textsuperscript{8} and chromium(III)\textsuperscript{16}.

The present work has been confined to the chromate-iodate system and deals with the crystallographic and analytical data of the compounds (NH\textsubscript{4})\textsubscript{2}CrO\textsubscript{4}·2H\textsubscript{2}O, K\textsubscript{2}O·2CrO\textsubscript{4}·I\textsubscript{2}O\textsubscript{3}, Rb\textsubscript{2}O·2CrO\textsubscript{4}·I\textsubscript{2}O\textsubscript{3} and Cs\textsubscript{2}O·2CrO\textsubscript{4}·I\textsubscript{2}O\textsubscript{3}. Crystallographic evidence is given for the existence of a CrIO\textsubscript{4} 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\textsubscript{α} 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\textsubscript{α} radiation.

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

Synthesis. The compounds were prepared according to Blomstrand\textsuperscript{4} by dissolving ca. 20 g of alkali dichromate (or chromium trioxide and alkali chromate) in water and adding a stoichiometric quantity of HIO\textsubscript{4}. 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 iodide acid or adding HNO\textsubscript{3} to the solutions. These attempts were unsuccessful but two phases were observed in the potassium system, viz. KCrIO\textsubscript{4} and KCrIO\textsubscript{4}·H\textsubscript{2}O, the former crystallizing from solutions containing HNO\textsubscript{3}, the latter from HNO\textsubscript{3}-free solutions.

Chemical analysis. The results are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>% Alkali</th>
<th>% Chromium</th>
<th>% Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
</tr>
<tr>
<td>NH\textsubscript{4}CrIO\textsubscript{4}</td>
<td>6.23 ± 0.05</td>
<td>6.16</td>
<td>18.3 ± 0.3</td>
</tr>
<tr>
<td>KCrIO\textsubscript{4}·H\textsubscript{2}O</td>
<td>11.8 ± 0.1</td>
<td>12.1</td>
<td>15.7 ± 0.3</td>
</tr>
<tr>
<td>CrIO\textsubscript{4}</td>
<td>12.5 ± 0.1</td>
<td>12.5</td>
<td>16.7 ± 0.3</td>
</tr>
<tr>
<td>RbCrIO\textsubscript{4}</td>
<td>23.7 ± 0.1</td>
<td>23.7</td>
<td>15.1 ± 0.3</td>
</tr>
<tr>
<td>CsCrIO\textsubscript{4}</td>
<td>32.6 ± 0.1</td>
<td>32.6</td>
<td>13.3 ± 0.3</td>
</tr>
</tbody>
</table>

Table 2. Crystallographic data.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>(\beta)</th>
<th>Formula units in the cell</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_4)CrIO(_4)</td>
<td>6.05</td>
<td>14.32</td>
<td>13.38</td>
<td>(_)</td>
<td>8</td>
<td>3.34</td>
</tr>
<tr>
<td>KCrO(_4)</td>
<td>9.25</td>
<td>4.86</td>
<td>14.28</td>
<td>108°</td>
<td>4</td>
<td>3.56</td>
</tr>
<tr>
<td>KCrO(_4)\cdot)H(_2)O</td>
<td>14.91</td>
<td>5.48</td>
<td>15.76</td>
<td>95°</td>
<td>8</td>
<td>3.35</td>
</tr>
<tr>
<td>RbCrO(_4)</td>
<td>8.12</td>
<td>7.70</td>
<td>10.45</td>
<td>108°</td>
<td>4</td>
<td>3.85</td>
</tr>
<tr>
<td>CeCrO(_4)</td>
<td>8.26</td>
<td>8.08</td>
<td>10.75</td>
<td>110°</td>
<td>4</td>
<td>4.05</td>
</tr>
</tbody>
</table>

M\(_4\)Cr\(_2\)O\(_7\)(s) + H\(_2\)O = 2 M\(^+\) + 2 HCrO\(_4\)^\(-\)
HCrO\(_4\)^\(-\) + OH\(^-\) = CrO\(_4\)^{2-} + H\(_2\)O

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 equil. 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.

M\(_4\)Cr\(_2\)O\(_7\)(s) + H\(_2\)O = 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 equil. 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 also has 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\(_4\)CrIO\(_4\) has been investigated (\textit{v. intra}) — studies of further phases of this group are in progress.

The crystal structure of NH\(_4\)CrIO\(_4\). Rotation and Weissenberg photographs of all three axes were taken of a small crystal of NH\(_4\)CrIO\(_4\) (CuK radiation). Analysis of the photographs showed a systematic absence for \(0k0\) when \(k\) odd, \(h0l\) when \(l\) odd and \(hh0\) when \(h\) odd, indicating the space group to be No. 61, \textit{Pbca}.

Space group No. 61 \textit{Pbca}.

Unit cell dimensions: \(a = 6.05\) Å, \(b = 14.32\) Å, \(c = 13.38\) Å.

Unit cell content: 8 NH\(_4\)CrIO\(_4\).

The structure may be described as built up of CrIO\(_4\)-ions formed by a CrO\(_4\)-tetrahedron and a trigonal IO\(_3\)-pyramid sharing one corner (the O\(_3\) atom).

The following interatomic distances are obtained:

\[\begin{align*}
I-O_1 &= 2.06\ Å \\
I-O_2 &= 1.86\ Å \\
I-O_3 &= 1.81\ Å \\
Cr-O_1 &= 1.90\ Å \\
Cr-O_2 &= 1.62\ Å \\
Cr-O_3 &= 1.84\ Å
\end{align*}\]

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 \(\sim 118^\circ\).

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.

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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 CrF₄ and CrBr₂ have been reported but no crystallographic data are available for these substances. In 1950 the fluoro complexes M₆CrF₁₆ (M = K, Rb, and Cs) were prepared and Bode and Voss found that these complexes have the octahedral arrangement with discrete CrF⁶⁺ ions. The coordination number 6 is also found in CrO₃ which phase is of a rutile type.

Scholder and Spërka have reported the syntheses of Ba₄CrO₄, Ba₂CrO₄ and Sr₂CrO₄, containing chromium with an average oxidation number of +4. According to these authors, there exist structural relationships between the compounds M₂TiO₄ and M₂CrO₄ (M = Ba and Sr).

The crystal structure of Ba₄TiO₄ has been determined by Bland. The space group is P2₁/n and the cell dimensions are:

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

The structure is of the \( \beta-K_2SO_4 \) type and is closely related to \( \beta-Ca_3SiO_5 \). The environment of the titanium atom is unusual; it is approximately tetrahedral and the structure is considered as an arrangement of discrete TiO₄ groups and barium atoms. Sr₂TiO₄ belongs according to Balz and Plieth to an interesting group of oxide compounds with the same crystal structure as K₄NiF₄ and K₄MgF₄. The space group is \( \text{I}4/m \text{mm} \) and the cell dimensions are:

\[ a = 3.88 \, \text{Å} \quad \quad c = 12.58 \, \text{Å} \]

The structure is formed by somewhat distorted TiO₄-octahedra arranged in layers with the composition TiO₂ by sharing corners. In the direction of the tetragonal c axis an alternation of two SrO-layers with one TiO₂ layer can be distinguished.

By a partial substitution of Sr⁴⁺ ions (about 5 mole %) in Ba₂TiO₄ specimens with the orthorhombic \( \beta-K_2SO_4 \) structure were obtained by Kwestroo and Paping. The solid solution area ends at a composition with a Ba⁶⁺/Sr⁴⁺ ratio of about 1:3. The structure of Sr₂CrO₄ has been investigated by the present authors and preliminary results are given in this paper.

Crystals of Sr₂CrO₄, 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.

\[ \text{Cr}_2\text{O}_3 + \text{SrCrO}_4 + 5 \text{Sr(OH)}_2 = 3 \text{Sr}_2\text{CrO}_4 + 5 \text{H}_2\text{O} \]

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 Sr₂CrO₄.

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