

The Crystal Structure of Potassium Chromato Iodate,  $\text{KCrIO}_6$ 

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The crystal structure of potassium chromato iodate (V) has been determined using three dimensional X-ray single crystal data. The dimensions of the monoclinic cell which contains four formula units of  $\text{KCrIO}_6$  are  $a = 9.200 \pm 0.002 \text{ \AA}$ ,  $b = 4.694 \pm 0.002 \text{ \AA}$ ,  $c = 14.220 \pm 0.006 \text{ \AA}$  and  $\beta = 107.21^\circ \pm 0.32^\circ$ . The space group is  $P2_1/c$ . The structure contains isolated  $\text{CrIO}_6^-$  ions formed by a  $\text{CrO}_4$ -tetrahedron and an  $\text{IO}_3$ -pyramid sharing one corner. The interatomic distances are compared with those found in some related chromates and iodates. The conditions of the compound in a water solution are briefly discussed.

In connection with research performed at this Institute on the structural chemistry of chromium oxides and chromates an X-ray study was made of the alkali salts of heteropoly acids containing iodate(V) and chromate(VI). The results, a preliminary account of which was published some years ago,<sup>1</sup> included crystallographic evidence of the existence in solid  $\text{NH}_4\text{CrIO}_6$  of dinuclear  $\text{CrIO}_6^-$  ions. However, the analogous potassium salt was found to give X-ray diffraction data of a higher quality and this compound was therefore selected for an accurate determination of the structural details of the anion. The compounds  $\text{KCrIO}_6$  and  $\text{KCrIO}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$  were originally synthesized by Berg,<sup>2</sup> and Blomstrand.<sup>3</sup>

## EXPERIMENTAL

*Synthesis.* Ca. 7.5 g potassium dichromate (Hopkin and Williams, "Analar" standards) was dissolved in 40 ml water and 6.5 g  $\text{HIO}_3$  (Merck, zur Analyse) was added. The solution was acidified with 40 ml conc.  $\text{HNO}_3$  to obtain the anhydrous compound. Red, prismatic, water soluble crystals were obtained by allowing this solution to evaporate at room temperature.

*Analysis: Iodine.* About 50 mg of the crystals were dissolved in approximately 50 ml  $10^{-3}$  M  $\text{HCl}$ , and  $\text{SO}_2$  was bubbled through 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  $\text{AgNO}_3$ .

*Chromium.* 2 g of  $\text{KI}$  was added to the acidified solution. Titration with thiosulphate gave the sum of chromate and iodate. The amount of chromium was calculated by difference.

Table 1. Powder pattern of  $\text{KCrIO}_6$ .

$h k l$	$10^6 \sin^2 \theta_{\text{obs}}$	$10^6 \sin^2 \theta_{\text{calc}}$	$I_{\text{obs}}$
1 1 0	00767	00768	m
1 0 2	02641	02643	m
0 1 1	03006	03014	vvw
2 0 $\bar{2}$	03177	03183	vvw
1 1 0	03462	03461	m
1 1 $\bar{1}$		03488	
0 1 2	03976	03979	st
1 1 $\bar{2}$	04154	04159	m
1 0 4	04742	04736	vw
1 1 2	05330	05335	m
1 1 $\bar{3}$	05506	05472	vst
2 1 1		05499	
2 0 2		05536	
0 1 3	05580	05586	st
2 1 0	05763	05766	m
2 0 4	05874	05865	vst
2 1 $\bar{2}$		05875	
3 0 2	06443	06436	w
2 1 $\bar{3}$	06908	06895	w
3 0 0		06914	
1 1 4	07428	07429	vw
0 1 4	07827	07837	w
3 0 4	08537	08529	vw
2 1 4		08557	
3 1 0	09608	09607	w
3 0 2	09961	09965	vw
2 0 4	10550	10570	vvw
1 0 $\bar{6}$		10579	
3 1 1		10811	
2 1 $\bar{5}$	10848	10863	vvw
0 2 1	11091	11092	m
2 0 $\bar{6}$	11221	11119	
3 1 4		11222	
4 0 $\bar{2}$		11225	
1 2 0	11543	11539	m
1 2 $\bar{1}$		11567	
0 0 6		11575	
1 2 1	12141	12155	vvw
3 1 $\bar{5}$	13258	13233	m
2 1 4		13263	
1 1 $\bar{6}$		13272	
2 1 6	13819	13811	m
2 2 0		13844	
2 2 1	14765	14754	w
2 2 $\bar{3}$	14961	14973	m
4 1 0		14985	
1 2 4	15524	15507	w
3 1 6	15911	15888	m
0 2 4		15915	
4 0 2		15931	
4 1 1	16469	16483	w
2 1 5	16721	16745	vw
4 1 $\bar{5}$	17176	17140	m
1 1 $\bar{7}$		17157	
3 2 $\bar{2}$		17206	
2 1 $\bar{7}$	17408	17403	m
0 2 5	18821	18809	w
2 2 $\bar{5}$	18943	18941	vw

*Potassium.* Potassium was determined gravimetrically both as  $(C_6H_5)_4BK$ <sup>4</sup> and as  $KClO_4$ <sup>5</sup>.

*Water.* The air-dried sample was heated to 150°C in a Pyrex tube according to the method of Penfield.<sup>6</sup>

Analytical data

	% found	% calc.
K	12.5 ± 0.1	12.5
Cr	16.7 ± 0.3	16.6
I	40.0 ± 0.2	40.4
H <sub>2</sub> O	0.3 ± 0.1	0

X-RAY DATA

Accurate unit-cell dimensions were obtained from a powder photograph taken in a Guinier type focusing camera of 80 mm diameter using  $CuK\alpha_1$  radiation and potassium chloride ( $a = 6.2919 \text{ \AA}$ ) as an internal standard. The powder pattern is given in Table 1.

The prismatic crystals have an approximately diamond shaped cross section with the  $b$  axis of the unit cell along the prism axis. Two single crystals were used for the Weissenberg photographs. The layer lines  $h0l$  through  $h3l$  were obtained from a crystal rotated around the  $b$  axis and having the following dimensions: 0.11 mm (along the prism axis) and in the cross section  $0.07 \times 0.10 \text{ mm}^2$ . Additional data ( $0kl$  through  $5kl$ ) were collected from another crystal rotated about the  $a$  axis. This crystal measured 0.07 mm along the prism axis and the cross section was  $0.02 \times 0.03 \text{ mm}^2$ .

The photographs were taken with  $CuK$  radiation and the multiple film technique was used. The intensities were estimated visually comparing them with a calibrated scale and corrected for absorption. The mass absorption coefficients, taken from the *International Tables*,<sup>7</sup> gave the linear absorption coefficient  $\mu = 651 \text{ cm}^{-1}$ . After absorption and Lorentz polarization corrections had been applied, scale factors for the various layer lines were obtained by means of a least squares calculation based on a comparison of common  $F^2$  values from the different photographs. The data used throughout the calculations were composed of all the  $F_o$  obtained from the rotation around the  $b$  axis accompanied by the  $F_o$  obtained from the rotation around the  $a$  axis. The scattering curves for the neutral atoms were obtained from Ref. 8.

*Computer programs.* Most of the calculations were carried out by means of the digital computers BESK and FACIT EDB of the *Computer Division of the National Swedish Rationalization Agency*. The following crystallographic programs were used:

Subject	Authors	No. in World List *
Least squares refinement of unit cell parameters	Werner, P.-E.	6027
Absorption factors	»	6019
Lorentz and polarization factors	Lundberg, B.	—

Scale factors	Werner, P.-E.	(Ref. 10)
Structure amplitudes	Liminga, R. and Olovsson, I.	6014
Projections and sections	»	6015
Interatomic distances and angles	»	6016
Least-squares refinement	Åsbrink, S. and Brändén, C.-I.	6023
Standard deviations in distances	Åsbrink, S. and Norrestam, R.	6030

## DETERMINATION OF THE STRUCTURE

The dimensions of the monoclinic unit cell derived from the powder pattern are the following:

$$a = 9.200 \pm 0.005 \text{ \AA}, b = 4.694 \pm 0.002 \text{ \AA}, c = 14.220 \pm 0.006 \text{ \AA}, \\ \beta = 107.21 \pm 0.03^\circ, V = 586.6 \text{ \AA}^3.$$

Table 1 gives a comparison between the observed and calculated values of  $\sin^2\theta$ . Four formula units  $\text{KCrIO}_6$  correspond to a calculated density  $3.56 \text{ g cm}^{-3}$  in perfect agreement with the value found from the loss of weight in benzene.

In the single crystal data the reflections,  $h0l$ ,  $l \neq 2n$  and  $0k0$ ,  $k \neq 2n$  are the only ones systematically missing: this is characteristic of the space group  $P2_1/c$  (No. 14). The point positions in this space group are:

$$\begin{aligned} 2(a): & 0,0,0; 0, \frac{1}{2}, \frac{1}{2} \\ 2(b): & \frac{1}{2}, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\ 2(c): & 0, 0, \frac{1}{2}; 0, \frac{1}{2}, 0 \\ 2(d): & \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0 \\ 4(e): & \pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z) \end{aligned}$$

In order to determine the  $x$ - and  $z$ -coordinates of the iodine atoms, the Harker section  $P(u, \frac{1}{2}, w)$ , Fig. 1a, was calculated. From this section, the special positions could be excluded as there are no maxima in  $u = 0$ ,  $w = 0$ ;  $u = \frac{1}{2}$ ,  $w = 0$  or  $u = \frac{1}{2}$ ,  $w = \frac{1}{2}$ ; thus the general position, 4(e), remained. It was assumed that the largest maximum at  $u = 0.84$ ,  $w = 0.18$  was the symmetrical I—I vector,  $2x, 0, \frac{1}{2} + 2z$ . To get the  $y$ -parameter, the Harker section  $P(0, v, \frac{1}{2})$ , Fig 1b, was also calculated. In this section the largest maximum was at  $v = 0.18$  corresponding to the I—I vector  $0, \frac{1}{2} + 2y, \frac{1}{2}$ . Thus, the approximate parameters for the iodine atom were assumed to be:

$$4 \text{ I in } 4(e): x \approx 0.42, y \approx 0.16, z \approx 0.34$$

The electron density projection  $\rho(xyz)$  was calculated using only those  $F$  values whose signs could be derived with certainty from the iodine contribu-

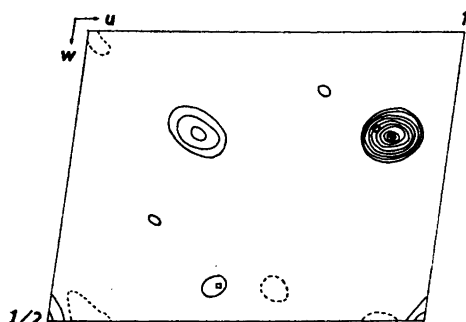


Fig. 1a. Harker section  $P(u_{\frac{1}{2}} w)$ . Negative contours are dotted. The symmetrical vectors I—I (+), Cr—Cr ( $\square$ ) and K—K ( $\circ$ ) for the final structure are indicated.

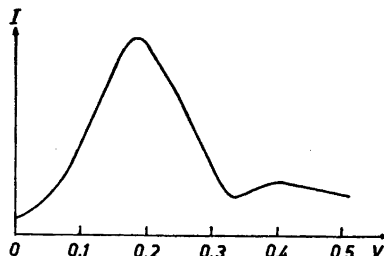


Fig. 1b. Harker line  $P(0v_{\frac{1}{2}})$ .

tions. In addition to the iodine maximum there were two pronounced maxima  $M(1)$  and  $M(2)$ . They were interpreted as corresponding to the positions of the chromium and potassium atoms which, however, could not be distinguished at this stage. With a mean value of the scattering factors for potassium and chromium the  $y$  parameters of  $M(1)$  and  $M(2)$  were determined from electron density sections parallel to the  $xz$  plane.

$$4 M(1) \text{ in } 4(e): x \approx 0.22, y \approx 0.47, z \approx 0.46$$

$$4 M(2) \text{ in } 4(e): x \approx 0.10, y \approx 0.58, z \approx 0.16$$

The parameters for the three heaviest atoms were refined by means of  $(F_o - F_c)$  synthesis. Including these atoms in the structure factor calculation improved the agreement between observed and calculated  $F$  values. Using the new parameters a new electron density projection  $\rho(xpz)$  was calculated which clearly indicated two oxygen positions. The  $y$  parameters of these oxygen atoms and parameters for the four remaining oxygen atoms were found by means of successive bounded electron density projections and sections at different height perpendicular to the  $b$  axis.

	$x$	$y$	$z$
4 O(1) in 4(e)	0.38	0.25	0.46
4 O(2) in 4(e)	0.23	0.08	0.26
4 O(3) in 4(e)	0.44	0.53	0.30
4 O(4) in 4(e)	0.28	0.72	0.56
4 O(5) in 4(e)	0.12	0.25	0.02
4 O(6) in 4(e)	0.12	0.57	0.37

To identify which of the  $M(1)$  and  $M(2)$  atoms was chromium and which was potassium their distances to the oxygen atoms were calculated. The distances  $M(1)$ —O were found to be 1.6, 1.6, 1.7, and 1.9 Å while the  $M(2)$ —O distances were considerably longer. Thus  $M(1)$  could be identified as chromium and  $M(2)$  as potassium.

Using the 986 observed reflections the positional parameters were then refined by means of the method of least squares. The applied weighting function was determined according to Cruickshank's formula

$$w = (a + |F_o| + c|F_o|^2)^{-1}$$

where the final values were:  $a = +6$ ,  $c = 0.01$ . The final  $R$ -value was 8.9 % at which point no shift in the coordinates exceeded 2 % of their standard deviations. The weight analysis from the last cycle is given in Table 2. In Table 3 the parameters, isotropic temperature factors, and standard deviations are given. Introducing 212 non-observed reflections in the refinement,

Table 2. Weight analysis used in the last cycle of the refinement of  $\text{KCrIO}_6$ .  $w$  = weighting factor.  $\Delta = ||F_o| - |F_c||$ .

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	1.37	122	0—15	0.78	71
0.46—0.58	1.19	115	15—30	0.81	219
0.58—0.67	0.96	114	30—45	0.93	223
0.67—0.74	0.99	115	45—60	1.15	183
0.74—0.79	1.04	105	60—75	0.97	120
0.79—0.84	0.81	92	75—90	1.17	72
0.84—0.89	0.76	103	90—105	1.35	36
0.89—0.93	0.64	91	105—120	1.74	24
0.93—0.97	0.86	90	120—135	0.95	14
0.97—1.00	1.56	39	135—150	1.34	24

Table 3. The crystal structure of  $\text{KCrIO}_6$ .

Space group:  $P2_1/c$  (No. 14).

Unit-cell dimensions:  $a = 9.200 \text{ \AA}$ ,  $b = 4.694 \text{ \AA}$ ,  $c = 14.220 \text{ \AA}$ ,  $\beta = 107.21^\circ$

Cell content: 4  $\text{KCrIO}_6$

4 K, 4 Cr, 4 I, 4 O(1) — 4 O(6) in 4(e):  $\pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$

Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement.

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B) \text{ \AA}^2$
I	0.4212 $\pm$ 0.0001	0.1572 $\pm$ 0.0002	0.3388 $\pm$ 0.0001	1.35 $\pm$ 0.02
Cr	0.2177 $\pm$ 0.0003	0.4624 $\pm$ 0.0007	0.4723 $\pm$ 0.0002	1.66 $\pm$ 0.05
K	0.8982 $\pm$ 0.0005	0.0853 $\pm$ 0.0011	0.3305 $\pm$ 0.0003	2.39 $\pm$ 0.07
O(1)	0.3833 $\pm$ 0.0016	0.2597 $\pm$ 0.0032	0.4586 $\pm$ 0.0010	2.32 $\pm$ 0.23
O(2)	0.2371 $\pm$ 0.0017	0.0754 $\pm$ 0.0035	0.2672 $\pm$ 0.0011	2.92 $\pm$ 0.26
O(3)	0.4458 $\pm$ 0.0019	0.5035 $\pm$ 0.0037	0.2935 $\pm$ 0.0012	3.34 $\pm$ 0.29
O(4)	0.2847 $\pm$ 0.0018	0.7179 $\pm$ 0.0034	0.5543 $\pm$ 0.0011	2.73 $\pm$ 0.25
O(5)	0.1159 $\pm$ 0.0017	0.2478 $\pm$ 0.0034	0.5127 $\pm$ 0.0011	2.74 $\pm$ 0.25
O(6)	0.1162 $\pm$ 0.0020	0.5860 $\pm$ 0.0040	0.3673 $\pm$ 0.0013	3.49 $\pm$ 0.30

where  $F_o$  values being taken as half the threshold values, did not appreciably change the structural parameters. The  $R$  value increased to 9.9 % and the standard deviations diminished somewhat. The parameter values in Table 3 are based only on the observed reflections.

From the results of the least-squares refinement three-dimensional ( $F_o - F_c$ ) synthesis was computed. The maxima and minima of this function are less than 15 % of the height of an oxygen atom in the  $F_o$  synthesis except for a negative region in the neighbourhood of iodine with a magnitude of 25 % of the oxygen.

A complete list of the observed and calculated structure factors is given in a separate document<sup>11</sup> together with  $F_c$  for the non-observed reflections. The ( $F_o - F_c$ ) syntheses in sections around the atoms at  $y$  values corresponding to the atomic sites are also included.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

In Table 4 the interatomic distances and bond angles are given together with the standard deviations. A complete list of the interatomic distances  $\leq 4 \text{ \AA}$  is included in Ref. 11.

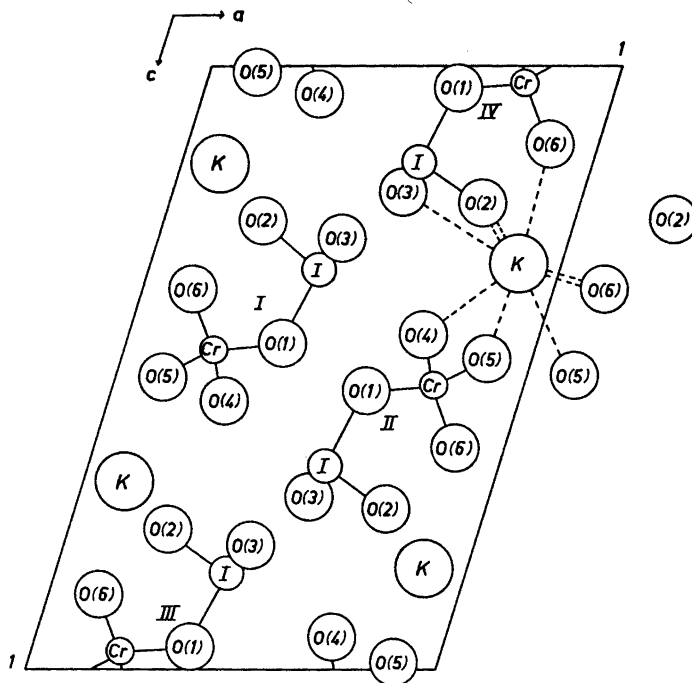


Fig. 2. Projection of the structure of  $\text{KCrIO}_6$  along  $[010]$ . Bonds between the atoms of the  $\text{CrIO}_6^-$  ions are indicated with full drawn lines while  $\text{K}-\text{O}$  bonds are broken.

The structure contains isolated  $\text{CrIO}_6^-$  ions and potassium ions (Fig. 2). The  $\text{CrIO}_6^-$  complex is formed by a  $\text{CrO}_4$  tetrahedron and a trigonal  $\text{IO}_3$  pyramid sharing one corner (Fig. 3). In the  $\text{CrO}_4$ -tetrahedron there are three short Cr—O distances 1.593–1.659 Å, mean value 1.62 Å, and a longer one in the bridge, 1.855 Å. In the  $\text{IO}_3$  pyramid there are two short I—O distances 1.742 and 1.787 Å, mean value 1.76 Å, while it is 1.899 Å in the bridge. The height of the  $\text{IO}_3$  pyramid, *i.e.* the distance from I to the plane O(1)—O(2)—O(3) is 0.84 Å. The two bonds in the Cr—O—I bridge form an angle of 126.8°. The distance Cr—I is 3.357 Å.

The O—O distances within the  $\text{CrIO}_6^-$  ion are given in Table 4. As can be seen, the shortest O—O distance of the structure is between O(5) and O(6) in the  $\text{CrO}_4$  tetrahedron, *viz.* 2.607 Å.

The  $\text{CrIO}_6^-$  ion is rather symmetrically built up around a plane through the iodine and chromium atoms and O(1), the bridge atom (*cf.* Fig. 3). The distances from the peripheral oxygen atoms O(2)—O(6) to this plane are:

Table 4. Distances (Å) and angles (°) with estimated standard deviations in the structure of  $\text{KCrIO}_6$ . The numbering of the atoms refers to Figs. 2 and 3. The notation  $+a$  and  $-b$  denotes an atom translated  $+a$  and  $-b$ , respectively.

*Distances I—O within the iodate pyramid*

I—O(1) 1.899 ± 0.014      I—O(2) 1.742 ± 0.015      I—O(3) 1.787 ± 0.017

*Distances I—O of adjacent ions < 3.5 Å*

I—O(3)<sub>I(-b)</sub> 3.157 ± 0.017      I—O(3)<sub>IV</sub> 2.630 ± 0.016      I—O(4)<sub>II</sub> 2.746 ± 0.015

*Distances Cr—O within the chromate tetrahedron*

Cr—O(1) 1.855 ± 0.014      Cr—O(5) 1.593 ± 0.016  
Cr—O(4) 1.659 ± 0.016      Cr—O(6) 1.617 ± 0.017

*Distances O—O within the  $\text{CrIO}_6^-$  ion < 3.5 Å*

O(1)—O(2) 2.793 ± 0.021      O(2)—O(3) 2.727 ± 0.023  
O(1)—O(3) 2.820 ± 0.021      O(2)—O(6) 3.154 ± 0.024  
O(1)—O(4) 2.834 ± 0.021      O(4)—O(5) 2.662 ± 0.022  
O(1)—O(5) 2.786 ± 0.021      O(4)—O(6) 2.724 ± 0.023  
O(1)—O(6) 2.860 ± 0.023      O(5)—O(6) 2.607 ± 0.023

*Bond angles within the  $\text{CrIO}_6^-$  ion*

O(1)—I—O(2) 100.1      O(1)—Cr—O(4) 107.4  
O(1)—I—O(3) 99.8      O(1)—Cr—O(5) 107.6  
O(2)—I—O(3) 101.2      O(1)—Cr—O(6) 110.7  
      O(4)—Cr—O(5) 109.9  
Cr—O(1)—I 126.8      O(4)—Cr—O(6) 112.5  
      O(5)—Cr—O(6) 108.6

Estimated standard deviations in the angles are ±1.3°

*Interatomic distances K—O < 3.5 Å*

K—O(2)<sub>I(+a)</sub> 3.492 ± 0.016      K—O(5)<sub>I(+a)</sub> 2.870 ± 0.016  
K—O(2)<sub>IV</sub> 2.783 ± 0.017      K—O(5)<sub>II(-b)</sub> 2.758 ± 0.016  
K—O(2)<sub>IV(-b)</sub> 2.861 ± 0.017      K—O(6)<sub>I(+a)</sub> 3.033 ± 0.019  
K—O(3)<sub>IV</sub> 3.157 ± 0.017      K—O(6)<sub>I(+a-b)</sub> 3.028 ± 0.019  
K—O(4)<sub>II</sub> 2.828 ± 0.016      K—O(6)<sub>IV</sub> 2.777 ± 0.018



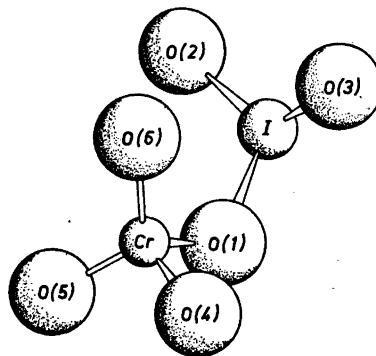


Fig. 3. Perspective view of the structure of  $\text{CrIO}_6^-$  ions. Bond distances and angles are given in Table 4.

O(2) 1.07 Å, O(3) 1.60 Å, O(4) 1.19 Å, O(5) 1.42 Å and O(6) 0.22 Å. It can be observed that O(6) is situated rather close to this plane.

It is of interest to compare the Cr—O distances in the  $\text{CrIO}_6^-$  ion with those present in the  $\text{Cr}_2\text{O}_7^{2-}$  ion. The latter consists of two  $\text{CrO}_4$  tetrahedra sharing one corner as found in the structure of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .<sup>12</sup> Better accuracy in the interatomic distances and angles has recently been obtained in structural studies on  $\text{Rb}_2\text{Cr}_2\text{O}_7$  ( $C2/c$ )<sup>13</sup> and  $\text{SrCr}_2\text{O}_7$ .<sup>14</sup> The  $\text{CrO}_4$  tetrahedra of these compounds show three short Cr—O distances of 1.58–1.63 Å with a mean value of 1.60 Å while the Cr—O distance to the bridging atom is 1.82 and 1.75, respectively. In the  $\text{IO}_3$  pyramid the two shortest I—O distances may be compared with those found in  $\text{Zr}(\text{IO}_3)_4$  (average 1.83 Å).<sup>15</sup> In  $\text{KCrIO}_6$  the distance between I and O(1) in the bridge is significantly longer, *viz.* 1.899 Å, than between the iodine atom and unshared oxygen atoms. This also holds for the Cr—O distance in the bridge. Even in the isopolyions, such as  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{S}_2\text{O}_7^{2-}$ ,<sup>16</sup> we have a significant difference between distances from the central atoms to shared or unshared oxygen atoms.

In addition to the three oxygen atoms in the  $\text{IO}_3$  group, there are three more at 2.746–3.157 Å (the next is 3.508 Å) forming a very distorted octahedron around the iodine atom (*cf.* Table 4). A similar octahedron is found in  $\text{Ce}(\text{IO}_3)_4 \cdot \text{H}_2\text{O}$ <sup>17</sup> while in  $\text{Zr}(\text{IO}_3)_4$  there are five oxygen atoms in addition to those in the  $\text{IO}_3$  group at 2.55–3.11 Å forming a rather crude antiprism.

The interionic contacts are between the potassium and oxygen atoms. The potassium atoms are irregularly surrounded by 9 oxygen atoms belonging to 6 different  $\text{CrIO}_6^-$  ions at the distances 2.758–3.157 Å, mean value 2.90 Å, *cf.* Table 4 and Fig. 2 (broken lines). Similar contacts are found in  $\text{K}_2\text{S}_2\text{O}_7$ <sup>16</sup> with nine K—O distances between 2.71 and 3.22 Å, mean value 2.89 Å.

#### SOME REMARKS ON THE CONDITIONS OF $\text{KCrIO}_6$ IN A WATER SOLUTION

Equilibrium measurements in aqueous solutions have revealed the existence of several weak complexes containing hexavalent chromium, *e.g.*  $[\text{HCrPO}_4^{2-}]$ ,<sup>18</sup>  $[\text{CeCrO}_4^{2+}]$ ,<sup>19</sup>  $[\text{Cr}(\text{III})\text{Cr}(\text{VI})\text{O}_4^+]$ ,<sup>20,21</sup> and  $[\text{FeCrO}_4^+]$ ,<sup>22</sup> but no equilibrium

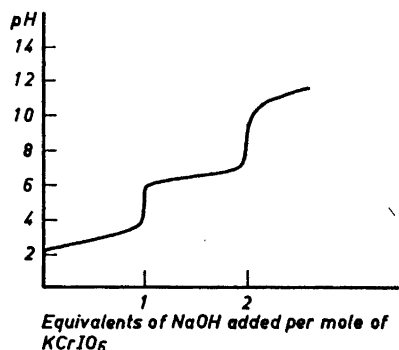


Fig. 4a. Titration curve of a solution of  $\text{KCrIO}_6$ .

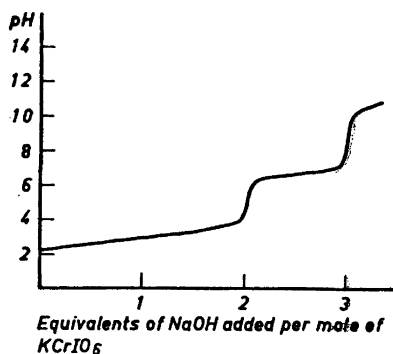
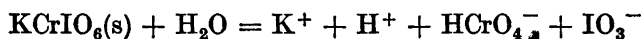


Fig. 4b. Titration curve of a solution of  $\text{KCrIO}_6$  drawn through a cation exchange column saturated with hydrogen ions.

studies have been published on chromato iodates. It is to be assumed that the  $\text{CrIO}_6$  complex also exists in concentrated water solutions. On dilution the compound is decomposed according to the equation



as proven by the following experiments. In the first experiment about 0.2 g of  $\text{KCrIO}_6$  was dissolved in water and the solution was titrated with  $\text{NaOH}$ , see Fig. 4a. In the second, the solution is drawn through a cation exchange column saturated with hydrogen ions before the titration, Fig. 4b. One can see from the titration curves that the amount of  $\text{NaOH}$  required to the first equivalence point in this second experiment is twice as much as required by the equation:



The curves give an approximate  $\text{p}K_a$  value of 6.5 for  $\text{HCrO}_4^-$ , which is in good agreement with earlier studies.<sup>23</sup> The amounts of alkali, chromium, and iodine that can be determined from the two titrations are also in good agreement with the analytical data mentioned earlier.

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## REFERENCES

1. Wilhelmi, K.-A. and Löfgren, P. *Acta Chem. Scand.* **15** (1961) 1413.
2. Berg, A. *Compt. Rend.* **104** (1887) 1514.
3. Blomstrand, C. W. *J. prakt. Chem.* [2] **40** (1889) 305.
4. Raff, P. and Brotz, W. *Z. anal. Chem.* **133** (1951) 241.
5. Charlot, G. and Bezier, D. *Quantitative Inorg. Anal.* London 1957, p. 546.
6. Penfield, S. L. *Am. J. Sci.* [3] **48** (1894) 30.
7. *International Tables for X-Ray Crystallography*, Vol. III, p. 162.
8. Hanson, H. P., Herman, F., Lea, J. D., and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
9. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed. (1966).
10. Werner, P. E. *Univ. Stockholm, Inorg. Chem.* DIS No. 3 (1964).
11. Löfgren, P. *Univ. Stockholm, Inorg. Chem.* DIS No. 22 (1966).
12. Byström, A. and Wilhelmi, K.-A. *Acta Chem. Scand.* **5** (1951) 1003.
13. Wilhelmi, K.-A. *To be published.*
14. Wilhelmi, K.-A. *Arkiv Kemi* **26** (1966) 149.
15. Larson, A. C. and Cromer, D. T. *Acta Cryst.* **14** (1961) 128.
16. Lynton, H. and Truter, M. R. *J. Chem. Soc.* **1960** 5112.
17. Ibers, J. A. *Acta Cryst.* **9** (1956) 225.
18. Holloway, F. J. *Am. Chem. Soc.* **74** (1952) 224.
19. Tong, J. Y. and King, E. L. *J. Am. Chem. Soc.* **76** (1954) 2132.
20. King, E. L. and Neptune, J. A. *J. Am. Chem. Soc.* **77** (1955) 3186.
21. Krauss, H.-L. and Gnatz, G. *Chem. Ber.* **92** (1959) 2110.
22. Espenson, J. H. and King, E. L. *J. Am. Chem. Soc.* **85** (1963) 3328.
23. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants, Part II, Inorganic Ligands*, London 1958, p. 29.

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