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The Crystal Structure of $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$

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The crystal structure of the isomorphous compounds $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$ formed at high pressure has been determined by single crystal X-ray diffraction techniques. The cell constants are:
$Na_2Cr_3O_8OH$: $a=8.518\pm1$ Å; $b=5.998\pm1$ Å; $c=7.536\pm1$ Å; $\beta=111.12\pm1°$; $V=359.2$ Å^3
$K_2Cr_3O_8OH$: $a=9.267\pm1$ Å; $b=6.077\pm1$ Å; $c=7.813\pm1$ Å; $\beta=114.08\pm1°$; $V=402.7$ Å^3
with two formula units per cell. The space group is $P2_1/m$ (No. 11). The final R value is 0.098 for the sodium compound and 0.080 for the potassium compound. The rubidium phase belongs also to this group of compounds with the approximate cell constants: $a=9.60$ Å, $b=6.11$ Å, $c=7.99$ Å, $\beta=114.6°$.

The formulae of the compounds have been deduced from analytical and structural evidence and from IR measurements.

The new structure type reported is formed by $Cr^{III}O_6$ octahedra, arranged in strings by sharing of edges, and $Cr^{VI}O_4$ tetrahedra, attached to the strings of octahedra by corner sharing to form a $^1_\infty|Cr_3O_8OH^{2-}|$ chain.

The bond distances are compared with those found in other related chromium compounds.

The structural chemistry of chromium oxides and chromates has been studied extensively during recent years by a research group at this Institute. The binary oxide Cr_5O_{12}[1] and a family of ternary oxides ACr_3O_8 (A = Na, K, Rb, Tl, and Cs)[2] have been shown to contain both CrO_6 octahedra and CrO_4 tetrahedra. The dimensions of the CrO_6 tetrahedra and CrO_4 octahedra have revealed the existence of an ordered arrangement of the valence states of chromium in all these compounds, corresponding to $Cr^{VI}O_4$ tetrahedra and $Cr^{III}O_6$ octahedra. The ternary oxide $LiCr_3O_8$ (with a $CrVO_4$(o–rh) type of structure), however, exhibits structural disorder.[3] This structure is built up of $Cr^{VI}O_4$ tetrahedra and $(Cr_{0.5}Li_{0.5})O_6$ octahedra with a random distribution of the metal atoms on the latter sites. In 1966, the knowledge of the structural chemistry of binary and ternary chromium oxides as well as chromates of that time was summed up by Wilhelmi.[4]

In the same year, the existence of a new ternary oxide, given the composition $Na_{0.67}CrO_3$, was demonstrated by Bither *et al.*[5] Preliminary notes, dealing

with the structure and stoichiometry of this compound as well as the corresponding potassium and rubidium compounds have been published recently.[6,7]

In Ref. 6, Wilhelmi *et al.* suggested, as a result of a preliminary structure determination, a valency distribution of +4 and +6 for the family of compounds first given the formula $A_2Cr_3O_9$ (A = Na, K, and Rb). The normal valency distribution, supported by magnetic susceptibility measurements on KCr_3O_8[8] and by further structural analogies, is, however, +3 and +6 in compounds containing both CrO_6 octahedra and CrO_4 tetrahedra with an average valency of +5 or close to +5 (*vide supra*). Therefore the result for the present type of compounds was considered unusual.

In Ref. 7 the result of an IR study of the potassium compound was reported. The absorption band at 3400 cm^{-1} was interpreted as belonging to the stretching vibration of an OH group, indicating a hydrogen bond of medium strength. In order to obtain the very plausible distribution of the chromium valences into +3 and +6, a hydrogen content of one atom per formula unit would be required, and for this reason the formula $K_2Cr_3O_8OH$ was proposed.

A chemical analysis by straight-forward techniques of this compound presents considerable difficulties, and so far it has not been possible to support the conclusions given above in such a way. A careful study of the formation conditions showed that the addition of water to the starting materials increased the yields considerably (*vide infra*). These observations give further support to the proposed formulation $A_2Cr_3O_8OH$ for all the members of the family (A = Na, K, Rb). Similar observations have been made by Wilhelmi, when investigating the systems MoO_3-MoO_2[9] and WO_3-WO_2[10] at 25 kb in the same high pressure apparatus. In both systems oxide hydroxides were formed, even from dry oxide mixtures. It was found that the formation of these compounds was due to the presence in the apparatus of pyrophyllite which gives off water and hydrogen in the temperature interval 600 – 1000°C in quantities which can explain the formation of oxide hydroxides.

To establish the valency distribution and also the stoichiometry of the chromium compounds studied, magnetic susceptibility measurements must be of interest. Such measurements are now in progress.

EXPERIMENTAL

The starting materials were chromium trioxide CrO_3 ("Bakers Analyzed"), dried over phosphorus pentoxide and the chromates(VI) of sodium, potassium, and rubidium of analytical grade. At a later stage of the investigation, chromium dioxide, CrO_2, was used as a starting material instead of CrO_3. Samples of this CrO_2 oxide were obtained from CrO_3 kept in a gold capsule by heat-treatment in autoclaves at an oxygen pressure of 2 kb as described earlier.[11]

The high-pressure experiments were performed at 25 kb using a girdle-apparatus built at this Institute.[12] The samples were kept in platinum tubes with a diameter of 3 mm and a wall thickness of 0.1 mm, with pyrophyllite as pressure medium.

At an early stage of the investigation the Na-compound was prepared according to the method given by Bither *et al.*[5] Mixtures of CrO_3 and Na_2CrO_4 in the mole ratio 1:1.25 were heated in the temperature range 500 – 800°C at 25 kb for 3 – 8 h, followed by slow cooling to 100°C over 4 – 12 h. Unreacted

Na_2CrO_4 was removed from the reaction products by hot water extraction, and ferromagnetic CrO_2 was removed by magnetic separation of the slurry, leaving the water-insoluble compound as deep red crystals. If the Na_2CrO_4 was substituted by $Na_2Cr_2O_7$ the same products were obtained.

At a later stage, pure specimens of the Na- and K-compounds were obtained by a modified procedure; the chromium trioxide as starting material was replaced by chromium dioxide and water was added to the reaction mixture. It was also found that the slow cooling process under pressure was a prerequisite condition for the formation of the compounds; rapid quenching

Table 1. Computer programs used for the crystallographic calculations. All programs are written in FORTRAN IV.

Program name and function. Computer.	Authors.
1. DATAP2. Lp- and absorption corrections. Preparative calculations for extinction correction according to Zachariasen's 1963-formula.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel. Modified by O. Olofsson and M. Elfström, Uppsala, Sweden. Inclusion of calculations for extinction correction by B. G. Brandt and S. Åsbrink, Stockholm, Sweden. Further modifications by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
2. DRF. Fourier summations and structure factor calculations.	A. Zalkin, Berkeley, USA. Modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg, and A. G. Nord and B. G. Brandt, Stockholm, Sweden.
3. LALS. Full matrix least-squares refinement of positional and thermal parameters and of scale factors.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, Berkeley, USA, and by J.-O. Lundgren, R. Liminga and C.-I. Brändén, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg, and by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
4. DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations.	A. Zalkin, Berkeley, USA. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
5. DATA. Reflexion data handling including storing on disk, correction of erroneous reflexions or inclusion of new ones in a data set stored on disk; index transformation.	B. G. Brandt, Stockholm, Sweden.
6. SFLS. Block diagonal least-squares refinement of positional and isotropic thermal parameters and of scale factors. IBM 1800.	S. Åsbrink, Stockholm, and C.-I. Brändén, Uppsala, Sweden. Modified and extended by B. G. Brandt, Stockholm, Sweden.
7. LIST. Editing of structure factor tables.	I. Carlbom, Stockholm, Sweden.
8. POWDER. Generation of $\sin^2\theta$ values. Indexing of powder lines from preliminary cell constants. Refinement of cell constants.	O. Lindqvist and F. Wengelin, Göteborg, Sweden. Modified by B. G. Brandt and A. G. Nord, Stockholm, Sweden.

from 800°C only resulted in a mixture of the starting materials. This observation might indicate a reversible reaction occurring at higher temperatures.

The sodium and chromium contents in weight% were reported by Bither *et al.*[5] to be 12.94 and 44.53 %, in good agreement with the calculated values for $Na_2Cr_3O_8OH$ (13.29 and 45.09 %, respectively).

The infrared spectrum of the K-compound was registered at 25°C using a Perkin Elmer 337 IR spectrophotometer in the region 4000 – 400 cm^{-1}. The sample for this experiment consisted of finely divided crystal powder of the compound which was mulled with KBr and pressed to a disk.

Powder photographs of the reaction products, obtained at normal pressure and room temperature, were used in order to identify the phases and to determine accurate lattice dimensions. The powder photographs were taken in a Guinier-Hägg focusing camera of 80 mm diameter with monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). In order to depress the back-ground fogging caused by the fluorescence radiation, an aluminium filter foil of 35 μ thickness was placed in contact with the film. Potassium chloride (Analar BDH, ground and recrystallized) was added to the powder specimens as an internal standard, and its lattice parameter was taken to be $a = 6.2919$ Å (20°C) according to Hambling.[13] The indexing of the powder patterns was facilitated by comparison with the intensities observed from the Weissenberg photographs and afterwards checked by calculations of I_{calc}. The results are given in Table

Table 2. Crystallographic data for $A_2Cr_3O_8OH$.

Laue symmetry: 2/*m*.
Absent reflections: 0*k*0 with *k* odd.
Space group: $P2_1/m$ (No. 11).

		$Na_2Cr_3O_8OH$	$K_2Cr_3O_8OH$
Unit-cell dimensions		$a = 8.518 \pm 1$ Å	9.267 ± 2 Å
		$b = 5.998 \pm 1$ Å	6.077 ± 1 Å
		$c = 7.536 \pm 1$ Å	7.813 ± 1 Å
		$\beta = 111.122° \pm 7$	$114.082° \pm 12$
		$V = 359.2$ Å^3	401.7 Å^3
Density	Calc.	3.21 g/cm^3	3.15 g/cm^3
	Obs.	3.19 g/cm^3	3.13 g/cm^3

3a – b. The densities of the samples were determined from the loss of weight in benzene. Rotation photographs around [010] and Weissenberg photographs (*hkl*: $k = 0 - 4$) proved the crystals to be monoclinic. No systematic extinctions of reflections were observed except for 0*k*0 with $k = 2n + 1$. As only 010 and 030 were within the observed range of the powder pattern, space groups $P2_1/m$, $P2_1$, $P2/m$, or $P2$ might all be possible.

Multiple film (3 films) Weissenberg photographs were taken with Ni-filtered Cu$K\alpha$ radiation. The intensities of the reflections were estimated visually with a standard scale, obtained by photographing a reflection with different exposure times.

Table 3a. Powder photograph of $Na_2Cr_3O_8OH$. Cu$K\alpha_1$ radiation. The intensities were calculated from the expression $(P/100)(F_c)^2$. P is the number of equivalent reflections.

$h\ k\ l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
1 0 0	942	940	m	26.4
0 0 $\bar{1}$	1199	1201	m	42.8
1 0 $\bar{1}$	1374	1375	w	11.0
1 1 0	2585	2589	st	173.5
0 1 $\bar{1}$	2852	2850	w	19.2
2 0 $\bar{1}$	3428	3428	w	66.4
0 0 $\bar{2}$	4803	4804	st	252.0
2 1 $\bar{1}$	5077	5077	m	99.5
1 1 $\bar{2}$	5862	5861	m	396.8
0 2 0	6597	6596	m	210.0
2 1 $\bar{2}$	7148	7149	vvw	47.2
1 0 $\bar{2}$	7268	7275	vw	112.0
3 0 $\bar{1}$	7356	7361	w	284.0
1 2 0	7534	7536	w	79.2
0 2 $\bar{1}$	7793	7797	vw	48.8
1 2 $\bar{1}$	7962	7971	m	146.0
2 1 $\bar{1}$	8139	8140	m	400.2
3 0 $\bar{2}$	8670	8667	vw	105.0
1 1 2	8919	8924	vw	178.2
1 2 $\bar{1}$	9494	9503	st	456.0
3 1 $\bar{2}$	10313	10316	vw	155.0
0 0 $\bar{3}$	10813	10809	vw	18.7
1 2 $\bar{2}$		10809		48.8
1 1 $\bar{3}$	11106	11100	diff	21.6
0 2 $\bar{2}$	11403	11400	vw	96.4
3 0 $\bar{3}$	12367	12375	diff	21.8
2 2 $\bar{1}$	13082	13087	vw	76.8
4 0 $\bar{2}$	13711	13713	vw	182.0
3 2 $\bar{1}$	13953	13957	vw	230.0
4 0 0	15060	15034	diff	20.2
3 2 0		15053		39.6
3 2 $\bar{2}$	15253	15263	vvw	27.2
0 3 $\bar{1}$	16044	16043	vvw	15.6
1 2 $\bar{3}$		16048		50.4
2 2 $\bar{3}$	16562	16566	vw	50.0
2 0 $\bar{4}$	16842	16842	st	88.1
2 3 $\bar{1}$	18271	18270	w	75.5
4 1 $\bar{3}$		18294		188.8
3 0 $\bar{4}$	18489	18484	vw	167.0
2 1 $\bar{4}$		18498		54.4
1 3 $\bar{2}$	19061	19054	vvw	118.0
0 0 $\bar{4}$	19194	19215	vvw	138.0
4 2 $\bar{1}$	19774	19769	vvw	129.2
5 0 $\bar{2}$	20628	20638	w	37.8
1 2 3		20642		580.0
2 3 1	21337	21333	w	308.0
4 2 0	21640	21631	vvw	148.0
4 0 $\bar{4}$	21992	21999	diff	100.2
1 0 $\bar{4}$	23254	23217	vw	69.2
4 2 $\bar{3}$		23251		150.0
2 2 $\bar{4}$	23439	23445	vw	209.4
1 2 $\bar{4}$	23693	23688	vvw	98.4
3 2 $\bar{2}$	24471	24451	vw	6.1
5 1 $\bar{3}$		24464		105.5
2 2 3	25746	25757	vw	236.0
0 4 0	26389	26386	st	600.0
5 2 $\bar{1}$	27466	27460	m	390.0

Table 3a. Continued.

5 2 $\bar{3}$	29455	29411	vw	152.8
6 0 $\bar{2}$		29443		124.0
0 4 $\bar{2}$	31181	31190	diff	138.5
4 3 $\bar{3}$	31506	31497	diff	145.2
4 2 $\bar{2}$	32557	32559	vw	248.0
2 2 $\bar{5}$	32722	32722	vw	51.0
3 2 3		32752		104.8

Table 3b. Powder photograph of $K_2Cr_3O_8OH$. Cu$K\alpha_1$ radiation. The intensities were calculated from the expression $(P/100)(F_c)^2$. P is the number of equivalent reflections.

$h\ k\ l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
1 0 0	828	828	vw	21.6
0 0 $\bar{1}$	1168	1166	vw	26.4
1 0 $\bar{1}$	1195	1193	vw	27.0
1 1 0	2442	2436	w	101.6
0 1 $\bar{1}$	2784	2773	vw	51.6
1 0 $\bar{2}$	3900	3888	vw	30.1
1 1 $\bar{1}$	4415	4404	vvw	26.8
2 1 $\bar{1}$	4490	4484	w	50.0
0 0 2	4664	4665	m	184.0
1 1 $\bar{2}$	5497	5498	vst	700.0
3 0 $\bar{1}$	6217	6218	st	470.0
0 2 0	6421	6427	st	210.0
1 0 2	7106	7098	m	107.0
1 2 0	7255	7256	m	106.0
0 2 $\bar{1}$	7623	7593	m	69.2
1 2 $\bar{1}$		7619		160.8
2 1 1	7690	7693	st	668.0
1 1 $\bar{2}$	8706	8705	w	188.0
3 1 $\bar{2}$	8922	8917	m	191.0
1 0 $\bar{3}$		8917		37.6
1 2 $\bar{1}$	9221	9224	m	308.0
1 2 $\bar{2}$	10324	10316	vvw	44.8
0 0 $\bar{3}$	10510	10495	diff	52.0
1 1 $\bar{3}$		10524		9.4
0 2 $\bar{2}$	11098	11091	m	190.0
4 0 $\bar{2}$	11511	11507	m	215.0
3 1 $\bar{1}$	12640	12640	st	0.1
3 2 $\bar{1}$		12645		456.0
1 0 $\bar{3}$	13733	13731	w	123.0
3 2 $\bar{2}$		13737		60.0
1 1 $\bar{3}$	15343	15338	vvw	2.8
1 2 $\bar{3}$		15344		64.0
2 0 $\bar{4}$	15563	15555	vw	184.0
4 1 $\bar{3}$	15728	15736	w	284.0
3 2 $\bar{3}$	17171	17161	vvw	70.4
2 1 $\bar{4}$		17162		3.0
2 3 $\bar{1}$	17370	17337	diff	50.0
5 0 $\bar{2}$		17362		20.6
4 2 $\bar{1}$	17651	17645	vw	54.8
1 3 $\bar{2}$	18353	18349	w	212.0
0 0 $\bar{4}$	18664	18658	vw	159.0
4 0 $\bar{4}$	19074	19083	vw	201.0
2 3 $\bar{2}$	19243	19231	vw	12.6
4 1 1		19244		101.0
4 2 0	19689	19688	vw	132.8
1 2 3	20149	20158	st	628.0
2 3 1	20542	20546	m	420.0
4 2 $\bar{3}$		20555		47.6
2 2 $\bar{4}$	21987	21982	w	329.0
5 1 0	22330	22328	vvw	94.0

A crystal which measured $0.015(a)\times0.02(c)\times0.05(b)$ mm^3 was used for the collection of X-ray diffraction data for the potassium compound. The crystals of the sodium and rubidium compounds were of approximately the same size.

Lp and absorption corrections (for the potassium compound, $\mu=446$ cm^{-1}) were applied on the intensities. Mass absorption coefficients were taken from Ref. 14. The transmission factors were all in the range $0.45-0.50$.

The computer programs used are given in Table 3. All calculations were performed with the computer IBM 360/75.

The scattering factor curves used for all atoms were those given in Ref. 15, corrected by the real part of the anomalous dispersion coefficient. There are 744 (687) independent reflections for $K_2Cr_3O_8OH$ ($Na_2Cr_3O_8OH$) using CuK radiation, but only 564 (483) reflections were observed and measured.

DETERMINATION OF THE STRUCTURE

From the intensity distribution of the Weissenberg photographs and from the increase of the a and c axes (*cf.* Table 2) with the size of the cation, it was assumed that all three phases were isomorphous. It was also noticed that the intensities of $h0l$ and $h4l$ reflections were nearly identical for all members of the family, and therefore the metal atoms were assumed to be situated in planes normal to the y axis and $b/4$ apart. The structure determination was started with the assumption that the space group $P2_1/m$ was the correct one.

In $P2_1/m$ the following point positions exist:

2(a)	0,0,0	$0,\frac{1}{2},0$
2(b)	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},0$
2(c)	$0,0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$,
2(d)	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$
2(e)	$x,\frac{1}{4},z$	$\bar{x},\frac{3}{4},\bar{z}$
4(f)	$\pm(x,y,z)$	$\pm(x,\frac{1}{2}-y,z)$

The Harker sections $P(u,0,w)$ and $P(u,\frac{1}{2},w)$ and the section $P(u,\frac{1}{4},w)$ were then calculated. From the sections of the Rb phase, possible sets of positions of the rubidium and chromium atoms were derived and then tested and refined by the least-squares method. Good agreement between calculated and observed vectors was obtained with the following positions for the rubidium and chromium atoms in the unit cell:

Rb(1)	in 2(e)	$x=0.08$	$y=3/4$	$z=0.16$
Rb(2)	in 2(e)	$x=0.24$	$y=3/4$	$z=0.75$
Cr(1)	in 2(d)	$x=1/2$	$y=0$	$z=1/2$
Cr(2)	in 2(e)	$x=0.17$	$y=1/4$	$z=0.45$
Cr(3)	in 2(e)	$x=0.33$	$y=1/4$	$z=0.07$

The R index of the trial structure including the metal atoms was only 0.40. The positions of the eighteen oxygen atoms were then successively derived from Fourier sections and refined by the least-squares method. During this process the R-value dropped to 0.12. The temperature factors for the

Rb, Cr, and O atoms were in the ranges 2.19 – 1.70 Å², 1.43 – 1.27 Å², and 2.47 – 1.69 Å², respectively, except for one oxygen atom whose temperature factor was negative (– 1.7 Å²). Since the data were collected from a crystal showing some disorder, the investigation of the rubidium phase was discontinued, but the result was accepted as a starting point for a refinement of the sodium and potassium compounds.

The result was used to derive and refine the coordinates for the metal and oxygen atoms in $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$. The structure factors were weighted by Cruickshank's weighting function:

$$w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$$

with

$a = 9.0$, $c = 0.0215$, $d = 0$ ($Na_2Cr_3O_8OH$)
$a = 12.50$, $c = 0.0132$, $d = 0.0005$ ($K_2Cr_3O_8OH$)

At the end of the refinement, 13 strong reflections with low sin θ/λ were omitted from the data of the sodium compound as suffering from extinction.

Table 4a–b. Weight analysis obtained in the final cycle of the least-squares refinement of $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$.

a. $Na_2Cr_3O_8OH$ (The 14 reflections of zero weight omitted).

Interval F_{obs}	No. of independent reflections	$\overline{w\Delta^2}$	Interval sin θ	No. of independent reflections	$\overline{w\Delta^2}$
0.0 – 12.1	47	1.06	0.00 – 0.46	78	1.36
12.1 – 15.6	46	0.51	0.46 – 0.58	74	0.75
15.6 – 18.9	47	0.92	0.58 – 0.67	62	0.80
18.9 – 22.1	47	0.94	0.67 – 0.74	50	0.98
22.1 – 25.7	47	1.12	0.74 – 0.79	52	1.13
25.7 – 28.7	47	1.47	0.79 – 0.84	40	0.91
28.7 – 32.5	47	0.93	0.84 – 0.89	29	0.86
32.5 – 37.4	47	0.73	0.89 – 0.93	31	0.86
37.4 – 46.0	47	1.03	0.93 – 0.97	35	0.81
46.0 – 88.1	47	1.28	0.97 – 1.00	18	1.89

b. $K_2Cr_3O_8OH$ (The 9 reflections of zero weight omitted).

Interval F_{obs}	No. of independent reflections	$\overline{w\Delta^2}$	Interval sin θ	No. of independent reflections	$\overline{w\Delta^2}$
0.0 – 10.3	50	1.33	0.00 – 0.46	100	0.92
10.3 – 13.1	53	1.40	0.46 – 0.58	86	0.87
13.1 – 16.2	57	1.28	0.58 – 0.67	78	1.13
16.2 – 19.0	56	1.26	0.67 – 0.74	62	1.34
19.0 – 22.8	57	0.94	0.74 – 0.79	57	0.91
22.8 – 25.9	56	0.54	0.79 – 0.84	42	0.57
25.9 – 31.5	56	0.63	0.84 – 0.89	41	1.09
31.5 – 37.9	57	0.78	0.89 – 0.93	48	1.05
37.9 – 49.0	56	1.12	0.93 – 0.97	29	0.77
49.0 – 160.0	57	0.61	0.97 – 1.00	12	1.98

No extinction effects were observed for the potassium compound. The refinement was considered to be complete, when the shifts were well below 5 % of the standard deviations. At this point the discrepancy index

$$R = \sum||F_o(hkl)| - |F_c(hkl)||/\sum|F_o(hkl)|$$

was 0.098 for $Na_2Cr_3O_8OH$ and 0.080 for $K_2Cr_3O_8OH$. The non-observed reflections were not introduced in the refinement. The results from these computations are collected in Tables 4a – b (weight analysis), 5a – b (final coordinates, temperature factors, and standard deviations), and 6a – b(comparison between observed and calculated structure factors).

Table 5a. Coordinates, isotropic temperature factors and standard deviations for $Na_2Cr_3O_8OH$. Space group $P2_1/m$ (No. 11).

2(*d*)	$\frac{1}{2},0,\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
2(*e*)	$x,\frac{1}{4},z$ $\bar{x},\frac{3}{4},\bar{z}$
4(*f*)	x,y,z $\bar{x},\bar{y},\bar{z}$ $\bar{x},\frac{1}{2}+y,\bar{z}$ $x,\frac{1}{2}-y,z$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
Na(1) in 2(e)	0.0930±12	3/4	0.1666±14	2.64±19
Na(1) in 2(e)	0.2413±11	3/4	0.7658±13	2.01±17
Cr(1) in 2(*d*)	1/2	0	1/2	0.54± 7
Cr(2) in 2(e)	0.1668± 4	1/4	0.4948± 5	0.84± 7
Cr(3) in 2(e)	0.3237± 4	1/4	0.0646± 5	0.78± 7
O(1) in 4(*f*)	0.2879±11	0.0250±13	0.5557±13	1.41±17
O(2) in 2(e)	0.4250±16	1/4	0.3175±20	1.41±26
O(3) in 2(e)	0.4047±15	3/4	0.3222±18	0.77±23
O(4) in 2(*e*)	0.0592±20	1/4	0.2663±23	2.05±30
O(5) in 2(*e*)	0.0422±18	1/4	0.6087±21	1.77±28
O(6) in 4(*f*)	0.2075±12	0.0329±14	0.9968±14	1.80±19
O(7) in 2(*e*)	0.4681±21	1/4	0.9720±27	3.04±38

Table 5b. Coordinates, isotropic temperature factors and standard deviations for $K_2Cr_3O_8OH$. Space group $P2_1/m$ (No. 11).

2(*d*)	$\frac{1}{2},0,\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
2(*e*)	$x,\frac{1}{4},z$ $\bar{x},\frac{3}{4},\bar{z}$
4(*f*)	x,y,z $\bar{x},\bar{y},\bar{z}$ $\bar{x},\frac{1}{2}+y,\bar{z}$ $x,\frac{1}{2}-y,z$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
K(1) in 2(e)	0.0867± 4	3/4	0.1778± 5	1.86± 7
K(2) in 2(e)	0.2445± 4	3/4	0.7521± 5	1.95± 8
Cr(1) in 2(*d*)	1/2	0	1/2	0.85± 6
Cr(2) in 2(e)	0.1736± 3	1/4	0.4578± 4	1.20± 6
Cr(3) in 2(e)	0.3345± 3	1/4	0.0682± 3	1.11± 6
O(1) in 4(*f*)	0.2864± 8	0.0273±16	0.5035±10	1.76±14
O(2) in 2(e)	0.4460±14	1/4	0.3183±18	2.25±24
O(3) in 2(e)	0.4311±12	3/4	0.3237±15	1.24±18
O(4) in 2(e)	0.0524±14	1/4	0.2405±18	2.37±24
O(5) in 2(e)	0.0730±14	1/4	0.5832±17	2.35±24
O(6) in 4(*f*)	0.2229± 9	0.0389±17	0.0106±11	2.25±16
O(7) in 2(e)	0.4484±15	1/4	0.9583±19	2.69±25

Table 6. Observed and calculated structure factors for (*a*) $Na_2Cr_3O_8OH$ and (*b*) $K_2Cr_3O_8OH$. Non observed reflections and reflections given zero weight are indicated by one asterisk. Reflections excluded from the refinement because of assumed secondary extinction are marked with two asterisks.

a. $Na_2Cr_3O_8OH$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	30.8	-36.3	7	0	-4	* 0.1	-6.0	1	1	7	26.0	22.1	6	2	1	29.1	-26.1
2	0	0	15.5	-15.9	8	0	-4	23.8	19.6	2	1	7	* 0.1	3.6	7	2	1	28.6	24.3
3	0	0	40.6	-39.5	9	0	-4	37.7	-41.0	3	1	7	* 0.1	-1.9	8	2	1	12.3	-13.2
4	0	0	31.4	31.8	10	0	-4	25.9	25.0	4	1	7	* 0.1	4.3	9	2	1	18.9	-19.0
5	0	0	32.9	-32.7	1	0	-5	32.7	29.1	0	1	8	11.0	11.3	0	2	2	44.2	43.7
6	0	0	37.4	38.9	2	0	-5	28.9	-27.7	1	1	8	* 0.1	4.0	1	2	2	24.6	-21.5
7	0	0	18.0	-16.6	3	0	-5	35.7	34.2	2	1	8	23.0	-24.7	2	2	2	35.8	38.1
8	0	0	13.9	-12.9	4	0	-5	30.3	27.8	1	1	-1	* 0.1	-6.0	3	2	2	12.5	-12.1
9	0	0	21.7	-19.4	5	0	-5	17.5	-12.5	2	1	-1	48.0	49.9	4	2	2	80.1	78.6
10	0	0	13.0	13.9	6	0	-5	40.8	-40.9	3	1	-1	21.6	23.1	5	2	2	28.7	-27.5
0	0	1	40.6	-46.2	7	0	-5	31.9	29.4	4	1	-1	15.2	-16.5	6	2	2	27.9	-25.2
1	0	1	* 0.1	-0.8	8	0	-5	* 0.1	-9.1	5	1	-1	* 0.1	-0.9	7	2	2	13.3	-12.3
2	0	1	31.6	-32.5	9	0	-5	31.2	27.3	6	1	-1	14.0	14.1	8	2	2	12.0	13.7
3	0	1	*15.4	6.4	10	0	-5	* 0.1	3.0	7	1	-1	* 0.1	-4.3	0	2	3	26.6	-17.3
4	0	1	31.7	-29.9	1	0	-6	* 0.1	-4.3	8	1	-1	24.1	21.0	1	2	3	**88.8	120.4
5	0	1	18.5	17.0	2	0	-6	14.7	11.2	9	1	-1	* 9.8	13.1	2	2	3	**58.9	-76.6
6	0	1	22.1	-19.2	3	0	-6	**77.9	-91.2	10	1	-1	29.1	-29.5	3	2	3	39.5	-51.2
7	0	1	14.3	-13.4	4	0	-6	28.6	27.5	1	1	-2	**82.9	-99.6	4	2	3	13.0	-12.1
8	0	1	16.3	-17.5	5	0	-6	* 0.1	-6.2	2	1	-2	34.4	-34.3	5	2	3	18.9	19.0
9	0	1	52.9	61.0	6	0	-6	* 0.1	4.9	3	1	-2	58.6	62.2	6	2	3	20.2	-17.5
0	0	2	**81.0	112.4	7	0	-6	* 0.1	-4.3	4	1	-2	24.4	21.3	7	2	3	22.7	18.8
1	0	2	62.7	-74.8	8	0	-6	*11.8	10.3	5	1	-2	26.1	24.2	8	2	3	15.3	-19.1
2	0	2	24.3	-20.6	9	0	-6	40.2	-39.4	6	1	-2	29.3	27.4	0	2	4	* 0.1	9.8
3	0	2	39.2	-39.9	10	0	-6	23.0	23.6	7	1	-2	25.4	-22.6	1	2	4	14.6	-14.8
4	0	2	28.5	-25.5	1	0	-7	*41.5	34.2	8	1	-2	11.4	-9.9	2	2	4	5.5	5.1
5	0	2	17.8	-17.8	2	0	-7	* 0.1	-3.9	9	1	-2	* 0.1	6.1	3	2	4	* 0.1	3.5
6	0	2	79.0	78.1	3	0	-7	32.8	29.3	10	1	-2	* 0.1	1.6	4	2	4	32.7	29.6
7	0	2	28.2	-23.7	4	0	-7	* 0.1	-7.4	1	1	-3	25.7	-23.4	5	2	4	26.5	-27.8
8	0	2	* 0.1	2.4	5	0	-7	18.6	18.0	2	1	-3	* 0.1	-4.3	6	2	4	* 0.1	8.8
9	0	2	15.8	-14.5	6	0	-7	38.9	-43.9	3	1	-3	* 0.1	7.5	7	2	4	12.4	-11.5
0	0	3	29.0	-30.6	7	0	-7	* 0.1	6.2	4	1	-3	64.9	-68.6	0	2	5	17.7	15.0
1	0	3	30.5	-27.4	8	0	-7	* 0.1	-3.4	5	1	-3	48.3	-51.4	1	2	5	36.7	36.6
2	0	3	* 0.1	4.9	9	0	-7	11.2	11.2	6	1	-3	38.7	40.8	2	2	5	48.1	-51.8
3	0	3	68.2	69.5	1	0	-8	* 0.1	6.8	7	1	-3	14.9	13.1	3	2	5	* 0.1	-3.6
4	0	3	19.7	-16.9	2	0	-8	21.7	18.3	8	1	-3	16.1	14.8	4	2	5	* 0.1	-7.9
5	0	3	45.9	49.5	3	0	-8	60.2	-57.3	9	1	-3	19.5	15.4	5	2	5	10.5	13.1
6	0	3	31.2	-26.9	4	0	-8	38.2	31.6	10	1	-3	* 0.1	-9.6	6	2	5	* 0.1	-4.2
7	0	3	* 0.1	-0.8	5	0	-8	18.4	16.1	1	1	-4	20.8	-19.0	0	2	6	18.9	14.5
8	0	3	* 0.1	-3.8	6	0	-8	20.2	18.5	2	1	-4	36.9	-36.9	1	2	6	27.9	-28.3
0	0	4	**7C.6	83.2	7	0	-8	30.2	-32.2	3	1	-4	16.4	17.2	2	2	6	* 0.1	2.0
1	0	4	63.3	-58.9	8	0	-8	15.8	15.2	4	1	-4	10.5	10.4	3	2	6	* 0.1	4.0
2	0	4	37.0	35.5	2	0	-9	* 0.1	-1.6	5	1	-4	5.1	-6.3	4	2	6	33.6	34.6
3	0	4	50.5	-47.5	3	0	-9	13.1	14.8	6	1	-4	16.3	17.5	5	2	6	24.1	-32.2
4	0	4	* 0.1	4.6	4	0	-9	* 0.1	-1.8	7	1	-4	26.8	-23.2	0	2	7	26.4	21.7
5	0	4	* 0.1	-2.1	5	0	-9	18.0	20.6	8	1	-4	36.8	-32.0	1	2	7	36.5	34.4
6	0	4	36.2	34.4	6	0	-9	31.2	-36.8	9	1	-4	31.5	23.7	2	2	7	42.1	-44.8
7	0	4	24.9	-23.4	1	1	0	55.9	-65.8	10	1	-4	24.5	19.0	3	2	7	13.7	14.6
0	0	5	41.5	-41.7	2	1	0	* 0.1	2.8	1	1	-5	43.7	43.2	0	2	8	21.3	15.8
1	0	5	35.7	34.1	3	1	0	13.6	-10.7	2	1	-5	* 0.1	-1.3	1	2	8	28.0	-31.7
2	0	5	15.0	-11.6	4	1	0	* 0.1	-3.8	3	1	-5	20.1	18.7	1	2	-1	49.0	60.4
3	0	5	21.0	23.1	5	1	0	27.0	31.3	4	1	-5	17.9	-17.3	2	2	-1	19.1	-16.4
4	0	5	* 0.1	-10.9	6	1	0	* 0.1	6.7	5	1	-5	36.1	-37.4	3	2	-1	65.2	-75.8
5	0	5	34.2	29.8	7	1	0	56.1	-59.8	6	1	-5	5.7	-3.1	4	2	-1	56.9	-56.8
6	0	5	25.8	-32.8	8	1	0	12.4	-10.8	7	1	-5	5.8	7.2	5	2	-1	88.1	98.7
0	0	6	37.7	34.3	9	1	0	* 0.1	6.5	8	1	-5	* 0.1	-5.2	6	2	-1	8.0	-10.8
1	0	6	18.0	-15.5	0	1	1	28.2	-21.9	9	1	-5	* 0.1	2.8	7	2	-1	16.9	16.1
2	0	6	44.8	37.4	1	1	1	17.6	19.5	10	1	-5	* 0.1	-5.3	8	2	-1	21.5	-18.5
3	0	6	48.8	-43.6	2	1	1	**71.0	100.0	1	1	-6	15.0	-14.8	9	2	-1	* 9.6	10.0
4	0	6	9.8	-13.0	3	1	1	* 0.1	3.3	2	1	-6	43.0	-44.0	10	2	-1	18.7	-23.5
5	0	6	17.8	14.5	4	1	1	41.6	-46.9	3	1	-6	35.2	34.5	1	2	-2	40.3	-34.9
0	0	7	39.0	-37.3	5	1	1	* 0.1	-1.8	4	1	-6	45.4	47.0	2	2	-2	18.7	15.1
1	0	7	* 0.1	6.9	6	1	1	* 0.1	4.0	5	1	-6	* 0.1	-6.0	3	2	-2	30.3	-26.1
2	0	7	* 0.1	-2.4	7	1	1	* 0.1	-1.4	6	1	-6	* 0.1	2.5	4	2	-2	28.8	22.5
3	0	7	* 0.1	7.7	8	1	1	31.7	27.9	7	1	-6	* 0.1	-3.6	5	2	-2	* 0.1	-2.8
4	0	7	* 0.1	-0.7	0	1	2	28.0	-22.4	8	1	-6	16.4	-16.3	6	2	-2	41.0	-39.2
0	0	8	15.3	13.5	1	1	2	55.4	-66.9	9	1	-6	* 0.1	0.5	7	2	-2	43.7	-47.6
1	0	8	* 0.1	6.2	2	1	2	9.3	9.8	10	1	-6	20.0	20.6	8	2	-2	50.9	49.0
2	0	8	11.8	11.3	3	1	2	19.4	-18.7	1	1	-7	29.1	23.3	9	2	-2	* 0.1	-8.3
1	0	-1	25.1	23.5	4	1	2	10.0	8.6	2	1	-7	* 0.1	0.7	10	2	-2	16.1	14.9
2	0	-1	48.8	-57.6	5	1	2	26.9	24.3	3	1	-7	* 0.1	6.5	1	2	-3	41.8	35.6
3	0	-1	**86.2	119.2	6	1	2	* 0.1	-5.3	4	1	-7	* 0.1	0.5	2	2	-3	39.9	-35.4
4	0	-1	13.8	-14.5	7	1	2	20.7	-18.2	5	1	-7	24.2	-29.5	3	2	-3	24.5	18.5
5	0	-1	* 4.3	-5.1	8	1	2	* 0.1	3.6	6	1	-7	* 0.1	8.4	4	2	-3	61.4	-61.3
6	0	-1	30.6	-27.8	0	1	3	7.4	5.0	7	1	-7	36.2	33.4	5	2	-3	59.6	61.8
7	0	-1	* 0.1	-7.2	1	1	3	23.2	24.1	8	1	-7	* 0.1	-5.4	6	2	-3	13.8	10.9
8	0	-1	26.6	-24.4	2	1	3	31.3	35.5	9	1	-7	11.3	-7.4	7	2	-3	* 0.1	2.2
9	0	-1	36.5	39.5	3	1	3	26.3	-27.7	1	1	-8	* 0.1	-2.0	8	2	-3	11.7	-10.7
10	0	-1	* 0.1	-1.2	4	1	3	* 0.1	-9.1	2	1	-8	30.9	-25.4	9	2	-3	17.8	13.9
1	0	-2	12.6	-10.3	5	1	3	5.8	-10.4	3	1	-8	* 0.1	-5.8	10	2	-3	29.2	-28.5
2	0	-2	24.4	-21.7	6	1	3	20.9	-19.1	4	1	-8	25.4	21.7	1	2	-4	47.5	-49.6
3	0	-2	63.9	-72.4	7	1	3	* 0.1	3.5	5	1	-8	* 0.1	5.1	2	2	-4	66.5	72.3
4	0	-2	**81.9	95.2	8	1	3	26.4	28.9	6	1	-8	11.8	-12.0	3	2	-4	* 0.1	-7.3
5	0	-2	41.6	-43.6	0	1	4	32.6	-33.4	7	1	-8	* 0.1	1.4	4	2	-4	24.9	23.6
6	0	-2	66.3	78.6	1	1	4	20.2	-20.6	8	1	-8	17.9	-17.4	5	2	-4	24.4	-20.2
7	0	-2	* 0.1	6.4	2	1	4	19.3	-18.5	1	1	-9	25.5	28.4	6	2	-4	* 0.1	-5.6
8	0	-2	19.5	-15.8	3	1	4	37.6	-39.5	2	1	-9	* 0.1	-0.4	7	2	-4	48.2	-43.7
9	0	-2	33.3	-29.5	4	1	4	25.8	24.7	3	1	-9	8.7	-10.4	8	2	-4	27.0	23.7
10	0	-2	23.8	22.0	5	1	4	35.9	36.4	4	1	-9	* 0.1	1.6	9	2	-4	8.7	6.8
1	0	-3	7.2	7.5	6	1	4	* 0.1	-7.8	5	1	-9	* 0.1	-6.2	10	2	-4	* 0.1	5.9
2	0	-3	29.3	-30.1	7	1	4	*11.9	-9.7	1	2	0	35.2	-44.5	1	2	-5	* 0.1	2.7
3	0	-3	31.4	33.0	0	1	5	38.2	-42.8	2	2	0	15.6	13.9	2	2	-5	36.3	-35.7
4	0	-3	8.7	-9.9	1	1	5	26.6	23.7	3	2	0	32.5	-31.5	3	2	-5	25.4	22.4
5	0	-3	19.4	16.3	2	1	5	24.6	28.0	4	2	0	54.5	60.8	4	2	-5	71.0	-74.1
6	0	-3	37.6	-42.0	3	1	5	21.8	-18.2	5	2	0	22.1	-21.6	5	2	-5	67.0	60.8
7	0	-3	14.6	14.6	4	1	5	* 0.1	0.3	6	2	0	* 0.1	5.2	6	2	-5	14.6	12.3
8	0	-3	39.8	-43.6	5	1	5	* 0.1	-7.2	7	2	0	20.7	-21.4	7	2	-5	* 0.1	-1.6
9	0	-3	35.0	37.3	6	1	5	12.0	-16.9	8	2	0	38.4	35.3	8	2	-5	41.2	-41.7
10	0	-3	* 0.1	9.7	0	1	6	* 0.1	-5.4	9	2	0	11.4	-13.6	9	2	-5	14.2	15.7
1	0	-4	30.2	28.0	1	1	6	* 0.1	5.3	0	2	1	33.5	-34.9	10	2	-5	16.5	-16.9
2	0	-4	61.4	-66.4	2	1	6	* 0.1	-4.9	1	2	1	**74.7	106.9	1	2	-6	23.7	-19.2
3	0	-4	**69.6	-91.5	3	1	6	* 0.1	-3.5	2	2	1	45.9	-43.9	2	2	-6	23.6	18.2
4	0	-4	67.8	71.3	4	1	6	32.2	31.1	3	2	1	* 0.1	-0.2	3	2	-6	15.3	13.5
5	0	-4	4.7	-3.6	5	1	6	8.8	9.7	4	2	1	21.8	-22.1	4	2	-6	34.1	31.2
6	0	-4	33.9	32.8	0	1	7	* 0.1	2.2	5	2	1	60.0	71.8	5	2	-6	* 0.1	-8.5

Table 6a. Continued.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	2	-6	23.7	19.8	1	3	5	29.3	-28.7	4	3	-6	36.0	-30.1	2	4	6	26.8	28.8
7	2	-6	47.5	-47.0	2	3	5	29.3	-29.9	5	3	-6 *	0.1	0.8	3	4	6	28.5	-33.3
8	2	-6	31.6	28.7	3	3	5	19.9	21.5	6	3	-6 *	0.1	-9.3	0	4	7	28.8	-33.0
9	2	-6	14.4	14.0	4	3	5 *	0.1	4.8	7	3	-6 *	0.1	5.7	1	4	7 *	0.1	5.3
1	2	-7 *	0.1	-5.3	5	3	5 *	0.1	3.4	8	3	-6	17.4	18.6	2	4	7 *	0.1	-0.1
2	2	-7	49.2	-48.8	6	3	5 *	0.1	7.8	9	3	-6 *	0.1	-1.6	1	4	-1	15.6	13.7
3	2	-7	18.7	15.5	0	3	6 *	C.1	2.1	1	3	-7	29.6	-27.2	2	4	-1	30.0	-33.9
4	2	-7	28.7	-22.8	1	3	6 *	C.1	-6.2	2	3	-7 *	0.1	1.5	3	4	-1*	*63.9	78.5
5	2	-7	21.5	16.5	2	3	6 *	0.1	5.2	3	3	-7 *	0.1	-0.6	4	4	-1	12.8	-10.7
6	2	-7	13.5	13.0	3	3	6 *	0.1	3.1	4	3	-7 *	0.1	-0.7	5	4	-1 *	0.1	-7.8
7	2	-7	27.8	23.4	4	3	6	22.4	-24.6	5	3	-7	30.4	25.5	6	4	-1	25.9	-21.1
8	2	-7	35.3	-38.5	5	3	6 *	0.1	-6.8	6	3	-7 *	0.1	-7.9	7	4	-1 *	0.1	0.6
9	2	-7	16.6	19.8	0	3	7 *	0.1	1.8	7	3	-7	31.9	-31.9	8	4	-1	18.5	-18.2
1	2	-8	28.4	-29.8	1	3	7	26.1	-25.8	8	3	-7 *	C.1	6.C	9	4	-1	*30.2	30.8
2	2	-8 *	0.1	12.8	2	3	7 *	0.1	-5.8	1	3	-8 *	0.1	0.9	1	4	-2	8.1	-7.7
3	2	-8 *	0.1	6.6	3	3	7 *	C.1	6.1	2	3	-8	20.9	18.6	2	4	-2	7.8	-5.3
4	2	-8 *	0.1	5.4	0	3	8	8.8	-9.8	3	3	-8 *	0.1	6.2	3	4	-2	37.9	-39.1
5	2	-8	28.3	-26.5	1	3	8 *	0.1	-3.5	4	3	-8	15.0	-14.2	4	4	-2	46.0	50.1
6	2	-8 *	0.1	9.4	0	3	9 *	0.1	-0.3	5	3	-8 *	0.1	-5.3	5	4	-2	35.4	-32.1
7	2	-8	13.9	-15.2	1	3	-1 *	0.1	2.3	6	3	-8 *	0.1	5.0	6	4	-2	54.8	54.5
8	2	-8	15.2	15.2	2	3	-1	38.2	-43.5	7	3	-8 *	0.1	-0.5	7	4	-2 *	0.1	4.8
2	2	-9	34.7	-40.7	3	3	-1	21.3	-17.9	1	4	0	25.3	-21.8	8	4	-2	12.8	-10.4
3	2	-9	14.8	15.1	4	3	-1	29.7	29.1	2	4	0	4.8	-3.8	9	4	-2	24.5	-23.1
4	2	-9	14.9	-15.5	5	3	-1 *	0.1	4.0	3	4	0	24.4	-23.3	1	4	-3	17.1	12.7
5	2	-9 *	0.1	6.6	6	3	-1	25.8	-22.8	4	4	0	19.9	15.4	2	4	-3	22.4	-21.1
6	2	-9 *	0.1	5.9	7	3	-1 *	C.1	0.8	5	4	0	27.2	-23.6	3	4	-3	29.3	29.4
1	3	C	17.5	22.8	8	3	-1	10.3	-10.8	6	4	0	36.5	32.1	4	4	-3 *	0.1	-5.7
2	3	C *	0.1	-4.1	9	3	-1 *	9.9	-10.2	7	4	0	10.2	-11.2	5	4	-3 *	0.1	6.5
3	3	0	22.2	20.0	1	3	-2	54.3	54.3	8	4	0	7.9	-7.8	6	4	-3	32.7	-33.2
4	3	0 *	0.1	5.1	2	3	-2	22.6	18.7	0	4	1	29.9	-29.5	7	4	-3	14.5	16.2
5	3	C	36.7	-31.2	3	3	-2	35.3	-29.3	1	4	1 *	0.1	-1.1	8	4	-3	26.3	-30.6
6	3	0 *	0.1	-6.8	4	3	-2	10.5	-8.6	2	4	1	18.8	-18.9	9	4	-3	25.7	27.6
7	3	0	51.8	47.8	5	3	-2	28.9	-27.2	3	4	1	21.1	21.5	1	4	-4	17.8	14.3
8	3	0 *	0.1	8.9	6	3	-2	24.9	-24.5	4	4	1	19.7	-21.8	2	4	-4	35.7	-33.9
0	3	1	19.5	19.8	7	3	-2	22.8	21.2	5	4	1	5.4	7.7	3	4	-4	49.2	-55.0
1	3	1	17.7	-18.2	8	3	-2 *	0.1	9.9	6	4	1	18.5	-14.6	4	4	-4	50.2	42.6
2	3	1*	*67.6	-87.6	9	3	-2 *	0.1	-4.1	7	4	1 *	0.1	-5.9	5	4	-4 *	0.1	-8.2
3	3	1 *	0.1	0.8	1	3	-3	13.2	11.1	8	4	1	12.8	-14.7	6	4	-4	29.0	25.5
4	3	1	42.8	52.4	2	3	-3 *	C.1	C.4	0	4	2	60.4	58.9	7	4	-4 *	0.1	-2.5
5	3	1 *	0.1	-0.4	3	3	-3 *	C.1	-8.9	1	4	2	45.1	-42.1	8	4	-4	16.4	13.2
6	3	1	11.4	-12.5	4	3	-3 *	56.5	60.2	2	4	2	4.6	-2.6	9	4	-4	27.5	-33.9
7	3	1 *	0.1	1.0	5	3	-3	43.7	44.3	3	4	2	27.9	-25.1	1	4	-5	30.1	24.0
8	3	1	23.1	-19.4	6	3	-3	37.2	-41.2	4	4	2	17.5	-16.7	2	4	-5	20.6	-17.7
0	3	2	16.3	11.5	7	3	-3	19.7	-15.5	5	4	2	16.2	-14.2	3	4	-5	30.1	25.4
1	3	2 *	29.8	33.1	8	3	-3 *	0.1	-5.3	6	4	2	53.3	56.4	4	4	-5	21.4	16.5
2	3	2	7.0	-4.8	9	3	-3 *	0.1	-9.6	7	4	2	18.4	-19.0	5	4	-5 *	0.1	-8.0
3	3	2	21.1	21.4	1	3	-4 *	C.1	5.5	0	4	3	26.3	-27.5	6	4	-5	30.4	-33.5
4	3	2 *	0.1	-6.5	2	3	-4	23.5	20.5	1	4	3	21.9	-19.6	7	4	-5	25.5	24.4
5	3	2	24.6	-21.6	3	3	-4 *	0.1	-3.2	2	4	3 *	0.1	3.7	8	4	-5 *	0.1	-7.1
6	3	2 *	0.1	6.6	4	3	-4 *	0.1	-0.2	3	4	3	48.9	51.9	1	4	-6 *	0.1	-4.3
7	3	2	9.5	12.6	5	3	-4 *	C.1	-3.1	4	4	3	19.0	-17.0	2	4	-6 *	0.1	10.0
8	3	2 *	0.1	-1.7	6	3	-4	22.7	-20.7	5	4	3	34.2	32.2	3	4	-6	57.7	-61.5
0	3	3	9.7	7.6	7	3	-4	27.6	22.4	6	4	3	21.7	-21.2	4	4	-6	23.3	20.0
1	3	3	24.6	-26.2	8	3	-4	31.0	29.9	7	4	3 *	0.1	C.1	5	4	-6 *	0.1	-6.3
2	3	3	38.2	-40.2	9	3	-4	22.4	-20.4	0	4	4	49.5	49.7	6	4	-6 *	0.1	6.2
3	3	3	25.0	27.4	10	3	-4	12.1	-15.7	1	4	4	39.8	-37.6	7	4	-6 *	0.1	-1.0
4	3	3	16.1	18.3	1	3	-5	37.3	-40.0	2	4	4	33.1	27.3	8	4	-6 *	0.1	8.3
5	3	3	6.4	4.5	2	3	-5 *	0.1	3.8	3	4	4	36.9	-34.6	1	4	-7	24.5	26.3
6	3	3	5.7	10.3	3	3	-5	10.9	-12.6	4	4	4 *	0.1	2.1	2	4	-7 *	0.1	-2.5
7	3	3 *	0.1	-1.7	4	3	-5	16.2	15.8	5	4	4 *	0.1	-3.1	3	4	-7	21.1	22.2
0	3	4	21.5	20.3	5	3	-5	34.0	33.5	6	4	4	21.0	27.6	4	4	-7 *	0.1	-7.0
1	3	4 *	0.1	8.7	6	3	-5 *	0.1	-2.7	0	4	5	38.7	-35.6	5	4	-7	14.0	13.9
2	3	4	15.7	16.0	7	3	-5	12.6	-12.6	1	4	5	19.0	19.3	6	4	-7	27.5	-35.6
3	3	4	34.2	33.2	8	3	-5 *	C.1	8.7	2	4	5 *	0.1	-5.7	7	4	-7 *	0.1	7.8
4	3	4	26.3	-19.3	9	3	-5 *	0.1	2.2	3	4	5	19.1	21.0	2	4	-8	13.5	15.3
5	3	4	27.1	-29.0	1	3	-6 *	0.1	8.5	4	4	5	11.1	-11.2	3	4	-8	38.8	-43.8
6	3	4 *	0.1	5.2	2	3	-6	33.6	30.1	0	4	6	26.5	23.8	4	4	-8	19.5	23.1
0	3	5	38.0	40.4	3	3	-6	28.7	-22.5	1	4	6	13.8	-12.4					

At this stage of the investigation it was evident that there are screw axes along the *b* direction, and that the space groups $P2/m$ and $P2$ are incompatible with the structure. An attempt was now made to refine the structure of $K_2Cr_3O_8OH$ in the space group $P2_1$ (No. 4). The coordinates thus obtained did not differ significantly more than two standard deviations from those found for $P2_1/m$. Hence, there is sufficient evidence that the structure is centrosymmetric.

A three-dimensional difference-synthesis was computed for the K compound in sections 0.3 Å apart along the *b* axis. The charts showed maxima and minima, the largest of which had magnitudes of less than 15 % of the mean peak height of the oxygen atoms in the electron density function.

b. $K_2Cr_3O_8OH$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	40.3	-32.8	4	0	-4	106.3	99.4	6	1	4 *	5.2	5.8	7	1	-8	24.3	20.2
2	0	0	21.7	-20.6	5	0	-4	17.3	-12.3	7	1	4	10.7	6.2	8	1	-8 *	4.8	7.6
3	0	0	46.7	-45.2	6	0	-4	11.7	9.9	0	1	5	62.5	-67.6	9	1	-8	21.8	19.3
4	0	0	46.7	42.9	7	0	-4	10.4	-11.7	1	1	5 *	5.5	3.8	10	1	-8 *	2.9	10.9
5	0	0	39.2	-40.0	8	0	-4	10.8	7.9	2	1	5	26.1	29.3	1	1	-9	15.0	13.7
6	0	0	16.3	13.8	9	0	-4	14.5	-13.6	3	1	5	6.1	4.2	2	1	-9	26.3	-28.1
7	0	0	35.1	-36.6	10	0	-4	37.4	39.4	4	1	5	18.2	15.3	3	1	-9	20.6	-20.0
8	0	0	10.2	-10.4	11	0	-4	18.3	-21.5	5	1	5 *	5.1	-9.7	4	1	-9	16.4	14.5
9	0	0 *	4.5	-6.1	1	0	-5	66.2	75.3	6	1	5	13.4	-10.0	5	1	-9 *	4.5	9.2
10	0	0 *	3.6	0.5	2	0	-5	10.4	-9.7	0	1	6	14.9	14.5	6	1	-9	20.3	-19.2
0	0	1	42.8	-42.7	3	0	-5 *	4.0	-0.3	1	1	6	17.7	20.0	7	1	-9 *	4.0	-0.8
1	0	1 *	2.1	-2.4	4	0	-5	19.7	-22.5	2	1	6 *	6.0	-0.3	8	1	-9 *	3.4	-4.7
2	0	1	37.9	-39.5	5	0	-5	39.1	-33.9	3	1	6 *	5.6	1.7	9	1	-9 *	2.0	-5.4
3	0	1	10.0	7.3	6	0	-5	36.7	-34.4	4	1	6	20.7	16.5	1	2	0	55.7	-51.6
4	0	1	43.6	-45.9	7	0	-5	44.4	39.5	5	1	6 *	8.6	-3.5	2	2	0	13.5	13.8
5	0	1	24.9	26.1	8	0	-5 *	5.2	-0.1	0	1	7	12.2	7.9	3	2	0	19.1	-20.1
6	0	1	23.3	-23.1	9	0	-5	14.7	13.4	1	1	7 *	5.6	9.0	4	2	0	60.7	61.7
7	0	1	28.8	-30.7	10	0	-5	12.9	-9.4	2	1	7 *	5.1	-9.3	5	2	0	20.9	-20.8
8	0	1 *	4.7	-0.6	11	0	-5 *	3.4	8.7	3	1	7 *	4.2	9.2	6	2	0	16.9	17.4
9	0	1	64.3	64.3	1	0	-6	20.1	-23.0	0	1	8	23.6	21.9	7	2	0 *	4.8	-2.1
10	0	1	12.8	-14.4	2	0	-6	20.8	20.5	1	1	8	24.4	25.3	8	2	0	36.5	41.3
0	0	2	90.0	90.6	3	0	-6	46.0	-44.7	2	1	8	12.3	-13.4	9	2	0	21.4	-23.4
1	0	2	83.6	-73.0	4	0	-6	72.7	66.2	1	1	-1	9.6	-9.1	10	2	0	27.8	30.5
2	0	2	26.8	-21.5	5	0	-6	20.2	-21.7	2	1	-1	33.2	35.4	0	2	1	43.7	-41.5
3	0	2	42.5	-44.0	6	0	-6 *	5.0	2.2	3	1	-1	14.1	15.6	1	2	1	81.2	87.6
4	0	2	41.9	-44.1	7	0	-6	17.0	-18.5	4	1	-1	14.7	7.7	2	2	1	33.7	-33.8
5	0	2	9.9	-9.6	8	0	-6	13.2	-12.7	5	1	-1	19.2	21.6	3	2	1	19.2	16.4
6	0	2	59.1	59.8	9	0	-6	21.3	-19.9	6	1	-1	24.0	23.9	4	2	1	10.5	-8.1
7	0	2 *	4.9	-6.9	10	0	-6	56.2	51.2	7	1	-1 *	5.6	-2.5	5	2	1	54.5	56.8
8	0	2	17.0	18.6	11	0	-6 *	3.1	4.4	8	1	-1	29.4	30.2	6	2	1	25.3	-25.5
9	0	2	9.9	-14.0	1	0	-7	69.0	70.4	9	1	-1 *	5.4	-10.4	7	2	1	34.2	38.8
0	0	3	49.0	-51.0	2	0	-7 *	5.0	9.9	10	1	-1	44.3	-46.9	8	2	1	25.7	-24.4
1	0	3	81.7	-78.5	3	0	-7	16.5	-11.6	11	1	-1 *	3.2	-6.0	9	2	1	19.5	-18.5
2	0	3 *	3.8	-3.3	4	0	-7	25.6	-28.0	1	1	-2	120.5	-137.2	0	2	2	74.3	69.0
3	0	3	68.9	72.3	5	0	-7	47.8	44.2	2	1	-2	28.0	-27.2	1	2	2	16.1	-12.1
4	0	3 *	4.8	-4.4	6	0	-7	26.0	-28.2	3	1	-2	61.1	69.9	2	2	2	19.0	18.1
5	0	3	60.5	61.8	7	0	-7 *	5.0	10.2	4	1	-2	10.9	10.1	3	2	2	10.3	-6.6
6	0	3	25.6	-26.3	8	0	-7	19.6	-19.7	5	1	-2 *	4.7	-1.2	4	2	2	119.5	116.4
7	0	3 *	4.5	4.8	9	0	-7 *	4.3	-2.6	6	1	-2	13.2	12.0	5	2	2	37.3	-39.4
8	0	3 *	9.2	-3.1	10	0	-7	19.2	-16.2	7	1	-2	14.2	-12.9	6	2	2	28.4	-28.6
0	0	4	87.2	89.1	1	0	-8	23.5	-22.3	8	1	-2	19.1	16.1	7	2	2	24.0	-22.4
1	0	4	23.8	-24.7	2	0	-8 *	4.7	-0.8	9	1	-2	20.4	18.9	8	2	2	13.2	10.3
2	0	4	37.2	37.7	3	0	-8	26.6	-23.1	10	1	-2 *	4.9	-4.9	9	2	2	11.8	-11.6
3	0	4	25.1	-27.3	4	0	-8	60.7	61.2	11	1	-2 *	3.7	4.8	0	2	3	17.8	-17.8
4	0	4	25.2	27.7	5	0	-8 *	4.8	5.0	1	1	-3	15.8	-15.2	1	2	3	127.5	132.2
5	0	4 *	5.0	-6.6	6	0	-8 *	4.7	-6.4	2	1	-3	20.1	-16.9	2	2	3	48.4	-49.9
6	0	4	12.6	12.6	7	0	-8	33.0	-29.9	3	1	-3	20.2	-19.3	3	2	3	36.9	-37.7
7	0	4	16.3	-15.4	8	0	-8	37.0	31.1	4	1	-3	77.8	-83.7	4	2	3	30.1	-33.3
0	0	5	30.2	-32.3	9	0	-8	19.4	-21.6	5	1	-3	22.8	-21.4	5	2	3 *	5.0	2.9
1	0	5	39.3	38.8	1	0	-9 *	5.2	7.6	6	1	-3	66.1	69.8	6	2	3	14.2	-13.8
2	0	5	14.8	-9.9	2	0	-9 *	3.6	0.6	7	1	-3	16.8	13.9	7	2	3 *	4.1	7.7
3	0	5	15.5	12.7	3	0	-9	7.0	-8.5	8	1	-3 *	5.8	9.7	8	2	3	16.5	-17.0
4	0	5	16.7	-13.9	4	0	-9	18.7	-19.9	9	1	-3 *	5.7	6.5	0	2	4	25.0	23.7
5	0	5	46.5	49.2	5	0	-9	30.6	29.9	10	1	-3 *	5.1	-0.0	1	2	4	31.8	-36.6
6	0	5	32.8	-37.9	6	0	-9 *	5.8	-3.3	11	1	-3 *	4.0	5.9	2	2	4	26.6	-24.5
0	0	6	16.4	19.0	7	0	-9	28.3	28.8	1	1	-4 *	4.1	2.4	3	2	4	10.5	-7.8
1	0	6	11.1	-11.7	8	0	-9 *	3.1	2.2	2	1	-4 *	4.1	-8.6	4	2	4	29.2	30.5
2	0	6	45.3	41.2	1	1	0	49.0	-50.0	3	1	-4	25.9	29.0	5	2	4	31.6	-31.8
3	0	6	35.5	-31.0	2	1	0	18.1	19.4	4	1	-4	12.3	-7.7	6	2	4	9.2	9.7
4	0	6	14.1	-12.0	3	1	0	17.6	-14.9	5	1	-4	37.7	-37.6	7	2	4 *	3.2	-8.0
5	0	6	15.0	-16.6	4	1	0	11.6	9.4	6	1	-4	17.8	-11.3	0	2	5	18.0	-18.1
0	0	7	30.3	-29.7	5	1	0	40.3	48.4	7	1	-4	53.2	-55.4	1	2	5	12.4	10.8
1	0	7 *	4.9	-2.7	6	1	0 *	5.3	-6.4	8	1	-4	8.9	-9.9	2	2	5	31.0	-30.2
2	0	7	21.2	-23.8	7	1	0	56.0	-63.2	9	1	-4	48.6	42.2	3	2	5	15.2	11.7
3	0	7	7.9	-6.6	8	1	0 *	5.7	-4.8	10	1	-4	14.9	11.6	4	2	5	17.3	-15.4
0	0	8 *	4.3	-0.3	9	1	0 *	5.1	2.9	11	1	-4	13.4	-10.0	5	2	5 *	4.1	-4.9
1	0	8 *	3.8	-2.6	10	1	0 *	4.1	1.9	1	1	-5	33.9	37.7	6	2	5 *	3.0	6.1
2	0	8 *	6.0	3.1	0	1	1	34.1	-35.9	2	1	-5	37.0	-38.8	0	2	6	42.4	47.6
1	0	-1	40.1	36.6	1	1	1	26.6	25.9	3	1	-5 *	4.8	4.6	1	2	6	32.7	-32.3
2	0	-1	32.7	-31.0	2	1	1	114.5	129.1	4	1	-5	7.4	6.1	2	2	6	29.6	-26.2
3	0	-1	160.6	153.4	3	1	1 *	5.9	-1.0	5	1	-5 *	5.3	-12.3	3	2	6 *	4.5	5.9
4	0	-1	23.3	-23.6	4	1	1	47.4	-50.3	6	1	-5 *	5.6	7.8	4	2	6	42.3	49.3
5	0	-1	9.1	5.4	5	1	1	13.2	-12.8	7	1	-5	12.4	-9.0	5	2	6	13.0	-13.2
6	0	-1	33.3	-36.5	6	1	1	10.1	-11.0	8	1	-5	27.1	-22.6	0	2	7 *	4.8	-6.7
7	0	-1	7.0	11.0	7	1	1 *	5.7	-1.7	9	1	-5 *	5.7	-4.3	1	2	7	31.6	33.5
8	0	-1	17.8	-17.2	8	1	1 *	5.5	11.4	10	1	-5	15.7	-14.7	2	2	7 *	4.0	-5.3
9	0	-1	35.6	36.2	9	1	1 *	4.6	-11.9	11	1	-5 *	3.9	-3.4	3	2	7	23.7	25.2
10	0	-1	23.9	-23.8	10	1	1 *	3.2	-9.0	1	1	-6 *	5.6	-5.4	0	2	8	39.3	42.2
11	0	-1	6.0	-6.9	0	1	2 *	2.8	5.2	2	1	-6 *	5.5	-0.9	1	2	8	25.7	-28.2
1	0	-2	35.1	-38.9	1	1	2	63.3	-68.4	3	1	-6	72.5	76.6	1	2	-1	62.7	63.5
2	0	-2	23.2	-19.5	2	1	2 *	4.1	-0.9	4	1	-6	34.2	39.1	2	2	-1	43.6	-44.4
3	0	-2	28.8	-29.6	3	1	2	25.8	-29.6	5	1	-6	29.1	-30.4	3	2	-1	99.6	-105.9
4	0	-2	108.3	103.6	4	1	2 *	5.1	8.2	6	1	-6 *	5.9	-1.8	4	2	-1	33.2	-37.0
5	0	-2	31.4	-32.1	5	1	2	10.1	9.8	7	1	-6 *	6.0	10.0	5	2	-1	98.9	92.8
6	0	-2	106.4	96.3	6	1	2	12.2	-12.1	8	1	-6 *	5.9	-4.0	6	2	-1	18.9	-18.3
7	0	-2	23.6	-25.5	7	1	2 *	5.6	-1.6	9	1	-6 *	11.5	-3.1	7	2	-1 *	4.8	-0.6
8	0	-2	36.5	-33.3	8	1	2 *	5.0	8.2	10	1	-6 *	4.6	-4.2	8	2	-1	12.5	-14.3
9	0	-2	30.9	-28.2	9	1	2 *	3.8	-8.5	11	1	-6	25.8	-26.1	9	2	-1	16.2	16.0
10	0	-2	26.3	25.2	0	1	3	10.6	-10.6	1	1	-7	10.6	6.5	10	2	-1	5.4	-8.4
11	0	-2	9.8	-12.9	1	1	3	10.2	8.4	2	1	-7	27.4	-29.7	1	2	-2	30.4	-33.4
1	0	-3	42.1	43.4	2	1	3	23.1	22.9	3	1	-7	17.2	-11.9	2	2	-2	16.0	15.7
2	0	-3	33.9	-35.8	3	1	3	24.0	-25.1	4	1	-7 *	5.8	8.5	3	2	-2	36.5	-38.7
3	0	-3	34.6	-28.9	4	1	3 *	5.8	8.0	5	1	-7 *	5.9	2.2	4	2	-2	15.3	12.9
4	0	-3	26.1	-25.7	5	1	3	12.1	-11.8	6	1	-7	45.3	38.4	5	2	-2	31.5	-28.9
5	0	-3	21.7	20.5	6	1	3	36.3	-34.3	7	1	-7	21.9	20.1	6	2	-2	51.6	-51.0
6	0	-3	18.5	-19.9	7	1	3	10.8	12.2	8	1	-7	28.5	-25.2	7	2	-2	16.0	-16.5
7	0	-3	29.1	33.2						9	1	-7	14.8	-10.9	8	2	-2	59.6	64.7
8	0	-3	21.0	-22.9	8	1	3	33.2	-34.5	10	1	-7	15.8	14.3	9	2	-2 *	4.6	-6.2
9	0	-3	58.3	61.0	0	1	4	21.5	-21.2	1	1	-8	13.4	11.4	10	2	-2	14.3	11.8
10	0	-3	21.8	-20.6	1	1	4 *	7.1	0.2	2	1	-8 *	5.4	-9.2	11	2	-2	15.8	-12.7
11	0	-3	25.0	-23.5	2	1	4	22.0	-19.7	3	1	-8 *	5.5	-9.4	1	2	-3	38.9	39.9
1	0	-4	15.5	-18.6	3	1	4	48.7	-56.0	4	1	-8 *	5.5	2.7	2	2	-3	28.3	-27.2
2	0	-4	110.3	-96.0	4	1	4	17.8	18.7	5	1	-8 *	5.5	-12.8	3	2	-3	39.6	42.0
3	0	-4	49.3	-54.8	5	1	4	38.1	37.7	6	1	-8 *	5.4	-6.2	4	2	-3	34.1	-36.5

Table 6b. Continued.

H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	2	-3	71.2	76.8	9	3	1 *	3.2	8.7	2	3	-5	24.1	23.4	2	4	5 *	4.7	-5.5
6	2	-3	30.3	-30.3	0	3	2	6.0	-5.6	3	3	-5 *	4.7	-3.6	3	4	5	12.1	10.8
7	2	-3	23.2	-22.0	1	3	2	25.5	26.0	4	3	-5	10.1	5.6	4	4	5	11.7	-11.6
8	2	-3	14.8	-12.9	2	3	2 *	3.9	3.0	5	3	-5	10.5	10.2	5	4	5	34.0	36.2
9	2	-3 *	4.7	-3.1	3	3	2	16.1	37.6	6	3	-5	16.3	-18.0	0	4	6	10.7	9.7
10	2	-3	14.8	-12.2	4	3	2	8.9	-6.8	7	3	-5 *	5.7	7.1	1	4	6	6.5	-6.9
11	2	-3	32.9	36.2	5	3	2	17.0	-15.7	8	3	-5	28.4	28.1	2	4	6	33.6	35.3
1	2	-4	30.1	-30.9	6	3	2	10.5	10.9	9	3	-5 *	4.4	3.3	3	4	6	22.9	-24.8
2	2	-4	96.9	90.7	7	3	2 *	4.5	3.7	10	3	-5 *	3.5	7.7	0	4	7	25.8	-23.5
3	2	-4	9.6	-8.3	8	3	2 *	3.6	-6.7	1	3	-6 *	5.1	-4.7	1	4	7 *	3.2	-1.3
4	2	-4 *	11.9	-4.1	0	3	3	13.3	10.6	2	3	-6 *	5.0	-1.5	2	4	7	16.2	-17.9
5	2	-4	35.4	-38.2	1	3	3	11.9	-9.3	3	3	-6	47.9	-54.1	1	4	-1	21.5	18.7
6	2	-4	25.4	24.8	2	3	3	24.0	-22.0	4	3	-6	29.1	-29.7	2	4	-1	18.5	-15.6
7	2	-4	27.1	-27.8	3	3	3	25.6	22.9	5	3	-6	22.8	21.5	3	4	-1	97.0	94.7
8	2	-4	23.8	25.5	4	3	3 *	5.2	1.5	6	3	-6 *	5.1	0.9	4	4	-1	21.7	-18.0
9	2	-4	22.3	-20.3	5	3	3	7.6	6.6	7	3	-6	7.5	-8.4	5	4	-1 *	4.5	-5.5
10	2	-4 *	4.1	-0.1	6	3	3	20.6	22.6	8	3	-6	4.7	4.4	6	4	-1	31.0	-26.0
11	2	-4 *	3.0	-5.0	7	3	3 *	3.8	-8.7	9	3	-6 *	12.0	4.4	7	4	-1	12.8	12.5
1	2	-5	12.2	-8.4	0	3	4	14.5	13.4	10	3	-6 *	3.1	3.1	8	4	-1	13.8	-14.3
2	2	-5	33.2	-33.7	1	3	4	15.6	-15.7	1	3	-7	7.1	-5.6	9	4	-1	24.5	24.5
3	2	-5	20.1	20.4	2	3	4	18.3	18.5	2	3	-7	20.0	20.5	1	4	-2	21.6	-23.0
4	2	-5	28.5	-30.2	3	3	4	52.0	55.7	3	3	-7	10.4	9.2	2	4	-2 *	3.1	-2.7
5	2	-5	106.6	107.2	4	3	4	18.7	-17.2	4	3	-7 *	4.9	-0.3	3	4	-2	17.0	-16.0
6	2	-5	7.3	-7.6	5	3	4	35.2	-37.2	5	3	-7 *	4.9	-1.4	4	4	-2	51.7	53.3
7	2	-5	28.3	-27.4	6	3	4 *	3.8	-4.2	6	3	-7	40.6	-40.6	5	4	-2	24.0	-21.7
8	2	-5	35.0	-33.4	0	3	5	48.8	53.7	7	3	-7	18.6	-18.0	6	4	-2	57.8	65.5
9	2	-5	39.1	37.5	1	3	5	9.1	-5.6	8	3	-7	28.0	28.7	7	4	-2	17.1	-16.7
10	2	-5	20.3	-20.5	2	3	5	27.6	-27.0	9	3	-7	11.2	10.0	8	4	-2	23.1	-23.5
1	2	-6	14.5	-13.0	3	3	5 *	5.1	-2.0	1	3	-8	13.8	-15.5	9	4	-2	25.5	-22.3
2	2	-6	10.1	-5.3	4	3	5	9.5	-9.2	2	3	-8 *	4.1	5.6	1	4	-3	31.0	29.7
3	2	-6 *	4.7	-4.3	5	3	5 *	3.6	6.4	3	3	-8	13.3	12.9	2	4	-3	24.3	-22.1
4	2	-6 *	4.8	0.4	0	3	6	15.2	-14.6	4	3	-8 *	4.3	-1.3	3	4	-3 *	3.9	-1.5
5	2	-6	23.1	-20.0	1	3	6	25.0	-26.0	5	3	-8 *	4.2	9.0	4	4	-3	19.1	-17.5
6	2	-6	27.9	28.8	2	3	6 *	4.8	3.1	6	3	-8 *	4.0	4.6	5	4	-3 *	4.6	7.4
7	2	-6	15.9	-15.9	3	3	6 *	4.2	4.7	7	3	-8	20.0	-17.7	6	4	-3	18.0	-12.5
8	2	-6	41.9	40.4	4	3	6	13.6	-15.6	8	3	-8 *	3.1	-6.3	7	4	-3	30.6	29.7
9	2	-6	15.3	-11.9	0	3	7	6.9	-7.8	9	3	-9	11.7	16.7	8	4	-3	19.0	-17.0
10	2	-6	17.8	-13.1	1	3	7	10.1	-8.5	4	3	-9	8.5	-8.4	9	4	-3	40.3	41.3
1	2	-7	24.1	-23.9	2	3	7 *	3.5	6.9	5	3	-9 *	2.7	-1.8	10	4	-3	16.9	-15.9
2	2	-7	44.8	-39.0	3	3	7 *	2.2	-7.0	1	4	0	21.8	-18.6	1	4	-4	17.9	-15.1
3	2	-7	33.9	29.1	0	3	8	19.4	-21.0	2	4	0 *	3.2	-3.1	2	4	-4	48.8	-50.9
4	2	-7	14.6	-14.5	1	3	-1 *	2.0	3.1	3	4	0	25.4	-26.0	3	4	-4	36.6	-35.0
5	2	-7	18.0	15.7	2	3	-1	32.8	-35.3	4	4	0	22.2	18.7	4	4	-4	55.5	59.0
6	2	-7 *	10.3	-3.7	3	3	-1	8.8	-7.6	5	4	0	28.8	-27.2	5	4	-4 *	4.7	-11.6
7	2	-7 *	4.8	0.6	4	3	-1	13.6	13.0	6	4	0	19.8	15.4	6	4	-4	10.3	9.6
8	2	-7	11.5	-12.1	5	3	-1	20.2	-19.4	7	4	0	24.7	-25.8	7	4	-4 *	4.8	-7.4
9	2	-7	44.3	44.8	6	3	-1	31.3	-31.7	8	4	0 *	3.8	-6.1	8	4	-4 *	4.3	6.7
10	2	-7	11.0	-10.1	7	3	-1 *	5.0	3.8	9	4	0 *	2.8	-6.1	9	4	-4	11.5	-11.3
1	2	-8 *	4.2	-2.6	8	3	-1	19.7	-16.9	0	4	1	27.1	-26.6	10	4	-4	26.1	30.0
2	2	-8	17.2	14.4	9	3	-1	8.9	7.4	1	4	1 *	2.8	-1.2	1	4	-5	46.0	48.2
3	2	-8	11.6	-11.1	10	3	-1	33.3	35.6	2	4	1	23.7	-21.4	2	4	-5 *	10.3	-7.7
4	2	-8	20.2	-15.5	1	3	-2	77.9	72.8	3	4	1	20.6	16.9	3	4	-5	8.4	6.0
5	2	-8	32.7	-32.7	2	3	-2	18.5	17.8	4	4	1	33.9	-33.5	4	4	-5	18.4	-17.6
6	2	-8	31.9	31.2	3	3	-2	33.7	-33.6	5	4	1	10.0	13.2	5	4	-5	33.3	-26.6
7	2	-8 *	4.1	1.4	4	3	-2 *	4.0	-5.3	6	4	1	16.8	-15.5	6	4	-5	29.8	-25.7
8	2	-8	7.9	-5.5	5	3	-2	11.8	-8.5	7	4	1	19.5	-17.5	7	4	-5	37.0	35.0
9	2	-8 *	3.0	-6.4	6	3	-2 *	7.3	-10.6	8	4	1 *	3.3	-1.8	8	4	-5 *	4.2	-1.1
1	2	-9	23.6	21.2	7	3	-2	15.1	12.3	0	4	2	40.6	42.7	9	4	-5	7.1	7.5
2	2	-9	20.8	-21.5	8	3	-2	14.8	-12.2	1	4	2	38.3	-41.6	1	4	-6	16.8	-16.5
3	2	-9	21.1	23.7	9	3	-2	16.2	-14.7	2	4	2 *	4.0	2.5	2	4	-6	18.9	18.8
4	2	-9	12.6	-11.3	10	3	-2 *	3.5	3.5	3	4	2	28.2	-29.0	3	4	-6	29.4	-29.0
5	2	-9	11.5	11.4	1	3	-3	8.9	7.6	4	4	2	30.2	-31.6	4	4	-6	39.8	42.9
6	2	-9	18.9	-18.6	2	3	-3 *	3.5	1.5	5	4	2 *	4.7	-7.7	5	4	-6	16.9	-16.6
7	2	-9	17.0	-16.3	3	3	-3	15.7	14.8	6	4	2	45.2	46.4	6	4	-6 *	4.5	1.9
1	3	0	11.0	8.3	4	3	-3	72.1	79.4	7	4	2 *	3.6	-5.7	7	4	-6	12.8	-13.6
2	3	0	14.7	-14.3	5	3	-3	18.1	15.3	0	4	3	33.8	-36.6	8	4	-6	9.7	-8.6
3	3	0	23.6	26.5	6	3	-3	67.0	-68.1	1	4	3	39.5	-46.5	9	4	-6	17.2	-16.9
4	3	0	8.8	-7.1	7	3	-3	10.9	-10.3	2	4	3 *	4.5	-2.9	1	4	-7	48.8	50.5
5	3	0	42.7	-49.2	8	3	-3 *	5.0	2.3	3	4	3	43.2	50.8	2	4	-7 *	4.2	7.0
6	3	0	5.0	4.9	9	3	-3 *	4.6	-6.4	4	4	3 *	4.8	-6.6	3	4	-7 *	4.2	-4.9
7	3	0	50.5	54.2	10	3	-3	7.8	-5.0	5	4	3	37.9	40.0	4	4	-7	21.9	-20.3
8	3	0 *	4.6	5.0	1	3	-4	15.1	-16.8	6	4	3	20.1	-18.4	5	4	-7	30.7	29.2
9	3	0 *	3.8	-1.2	2	3	-4 *	4.1	4.2	7	4	3 *	2.6	5.7	6	4	-7	23.3	-21.5
0	3	1	23.8	24.0	3	3	-4	12.5	-10.9	0	4	4	46.1	48.1	7	4	-7	14.3	12.6
1	3	1	25.3	-22.5	4	3	-4 *	4.4	7.9	1	4	4	19.6	-15.5	8	4	-7	15.2	-14.7
2	3	1	107.6	-102.5	5	3	-4	25.7	22.4	2	4	4	31.8	32.7	1	4	-8	16.1	-18.9
3	3	1	6.0	4.7	6	3	-4	7.6	7.4	3	4	4	20.3	-20.1	2	4	-8 *	2.9	2.9
4	3	1	45.6	51.7	7	3	-4	43.3	44.2	4	4	4	19.7	16.4	3	4	-8	18.9	-16.7
5	3	1 *	4.9	6.3	8	3	-4	13.1	9.2	5	4	4	5.6	-5.1	4	4	-8	39.2	44.8
6	3	1 *	5.1	-0.5	9	3	-4	36.4	-34.1	6	4	4	10.3	11.8	5	4	-8 *	3.1	1.5
7	3	1 *	4.9	3.6	10	3	-4	11.7	-10.8	0	4	5	24.4	-24.4	6	4	-8 *	2.9	-4.3
8	3	1 *	4.2	-2.9	1	3	-5	29.3	-30.5	1	4	5	25.6	25.3	7	4	-8	16.4	-22.2

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The interatomic distances and bond angles are given in Table 7. The arrangement of the atoms is shown in Fig. 1. The structure of this family of compounds can be visualized by regarding it as composed of polyhedra, connected by sharing of corners and edges, arranged in a composite

chain with the formula $^{1}_{\infty}|Cr_3O_8OH^{2-}|$. The structure contains three crystallographically independent chromium atoms Cr(1) – Cr(3). The following discussion concerns, for the sake of simplicity, only the potassium compound, the structure of which was determined with a somewhat higher precision.

Table 7. Interatomic distances in Å in the structures $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$.

	$Na_2Cr_3O_8OH$		$K_2Cr_3O_8OH$	
Cr – O distances in the chromate octahedra	Cr(1) – 2 O(2)	1.978 ± 9	Cr(1) – 2 O(3)	1.974 ± 7
	Cr(1) – 2 O(3)	1.979 ± 8	Cr(1) – 2 O(1)	1.998 ± 7
	Cr(1) – 2 O(1)	2.002 ± 9	Cr(1) – 2 O(2)	1.999 ± 8
Cr – O distances in the chromate tetrahedra	Cr(2) – O(5)	1.587 ± 15	Cr(2) – O(5)	1.604 ± 13
	Cr(2) – O(4)	1.634 ± 16	Cr(2) – O(4)	1.609 ± 13
	Cr(2) – 2 O(1)	1.660 ± 12	Cr(2) – 2 O(1)	1.658 ± 9
	Cr(3) – 2 O(6)	1.604 ± 12	Cr(3) – 2 O(6)	1.593 ± 10
	Cr(3) – O(7)	1 617 ± 17	Cr(3) – O(7)	1 609 ± 13
	Cr(3) – O(2)	1.787 ± 14	Cr(3) – O(2)	1.799 ± 13
Cr – Cr distances < 4 Å	Cr(1) – Cr(1)	2.999 ± 0	Cr(1) – Cr(1)	3.038 ± 1
	Cr(1) – Cr(2)	3.198 ± 3	Cr(1) – Cr(2)	3.279 ± 2
	Cr(1) – Cr(3)	3.423 ± 3	Cr(1) – Cr(3)	3.438 ± 2
	Cr(2) – Cr(3)	3.928 ± 4	Cr(2) – Cr(3)	3.898 ± 4
Na – O distances < 4 Å	Na(1) – O(5)	2.367 ± 18	K(1) – 2 O(6)	2.780 ± 10
	Na(1) – O(3)	2.487 ± 15	K(1) – O(5)	2.816 ± 13
	Na(1) – 2 O(6)	2.524 ± 14	K(1) – O(3)	2.919 ± 11
	Na(1) – 2 O(6)	2.738 ± 14	K(1) – 2 O(6)	2.932 ± 9
	Na(1) – O(4)	3.045 ± 19	K(1) – 2 O(1)	2.983 ± 9
	Na(1) – 2 O(4)	3.130 ± 5	K(1) – O(4)	2.984 ± 14
	Na(1) – 2 O(1)	3.250 ± 13	K(1) – 2 O(4)	3.114 ± 3
	Na(1) – 2 O(2)	3.996 ± 11		
	Na(2) – 2 O(1)	2.416 ± 13	K(2) – 2 O(1)	2.716 ± 9
	Na(2) – O(4)	2.484 ± 18	K(2) – 2 O(6)	2.744 ± 10
	Na(2) – 2 O(6)	2.521 ± 13	K(2) – O(4)	2.776 ± 13
	Na(2) – O(7)	2.551 ± 19	K(2) – O(7)	2.822 ± 12
	Na(2) – O(5)	2.981 ± 17	K(2) – O(5)	3.038 ± 13
	Na(2) – O(2)	3.124 ± 16	K(2) – O(2)	3.133 ± 13
	Na(2) – 2 O(5)	3.439 ± 8	K(2) – 2 O(5)	3.433 ± 6
	Na(2) – 2 O(7)	3.602 ± 11	K(2) – 2 O(7)	3.598 ± 6
	Na(2) – O(3)	3.914 ± 15		
O – O distances < 3 Å	O(1) – O(1)	2.699 ± 25	O(1) – O(1)	2.707 ± 20
	O(2) – O(3)	2.576 ± 19	O(2) – O(3)	2.554 ± 17
	O(2) – O(7)	2.757 ± 21	O(2) – 2 O(6)	2.764 ± 14
	O(2) – 2 O(6)	2.783 ± 16	O(2) – 2 O(1)	2.804 ± 13
	O(2) – 2 O(1)	2.814 ± 16	O(2) – O(7)	2.821 ± 18
	O(2) – 2 O(1)	2.816 ± 15	O(2) – 2 O(1)	2.847 ± 13
	O(2) – O(4)	2.999 ± 21	O(3) – 2 O(1)	2.761 ± 12
	O(3) – 2 O(1)	2.790 ± 14	O(3) – O(7)	2.847 ± 17
	O(3) – O(7)	2.797 ± 21	O(3) – 2 O(1)	2.855 ± 12
	O(3) – 2 O(1)	2.840 ± 14	O(3) – 2 O(6)	2.989 ± 12
	O(3) – 2 O(6)	2.957 ± 15	O(4) – O(5)	2.606 ± 18
	O(4) – O(5)	2.636 ± 22	O(4) – 2 O(1)	2.668 ± 13
	O(4) – 2 O(1)	2.704 ± 17	O(5) – 2 O(1)	2.671 ± 13
	O(4) – 2 O(6)	2.954 ± 17	O(6) – O(6)	2.565 ± 21
	O(5) – 2 O(1)	2.639 ± 16	O(7) – 2 O(6)	2.622 ± 14
	O(6) – O(6)	2.604 ± 26		
	O(7) – 2 O(6)	2.637 ± 18		

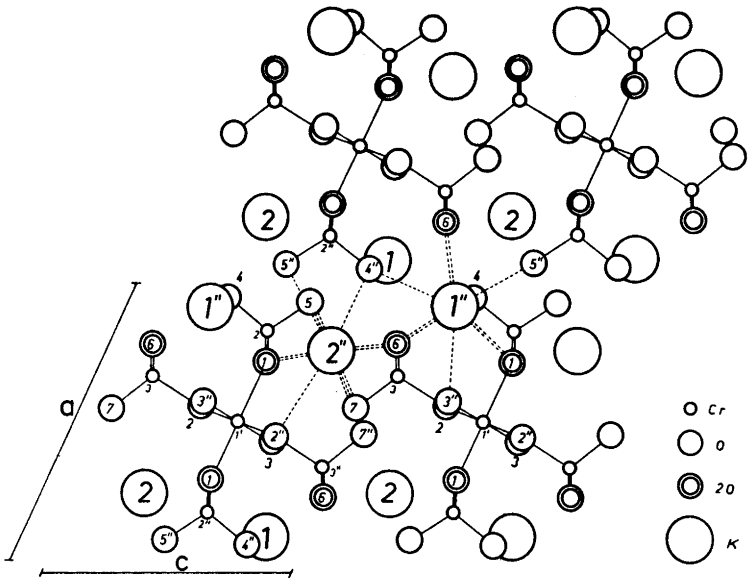

Fig. 1. The crystal structure of $K_2Cr_3O_8OH$ projected on (010). Atoms at $b=1/4$ are unmarked, atoms at $b=1/2$, and $b=3/4$ are marked with one dash or two dashes, respectively. Two concentric circles indicate 2 oxygen atoms at $b \sim 0$ and $b \sim 1/2$.

Each Cr(1) atom, situated at 1/2, 1/2, 1/2 and 1/2, 0, 1/2, is surrounded by a somewhat distorted octahedron of six oxygen atoms: (2 O(1) + 2 O(2) + 2 O(3)), the distance range being 1.97 – 1.99 Å (average 1.98 Å). By sharing edges the octahedra form a somewhat staggered string running in the *b*-direction. The length of the shared edge, O(3) – O(2), is 2.55 Å. To this rutile-like string, the two four-coordinated Cr atoms are attached. Each Cr(2) atom is surrounded by a fairly regular tetrahedron of oxygen atoms (2 O(1) + O(4) + O(5)), the distance range being 1.61 – 1.66 Å (average 1.63 Å). The Cr(2) tetrahedron is connected to the apices (2 O(1)) of two octahedra. Each Cr(3) atom is surrounded by a somewhat more distorted tetrahedron of oxygen atoms (O(2) + 2 O(6) + O(7)), the distance range being 1.59 – 1.80 Å (average 1.65 Å). The Cr(3) tetrahedron is connected to the string by one corner (O(2)) only. Thus the O(2) atom forms a common corner of two octahedra and one tetrahedron, the O(3) atom is common for two octahedra, while the O(1) atom is shared by one octahedron and one tetrahedron. Each O(4), O(5), O(6), and O(7) atom belongs to one tetrahedron only, the distances being in the range 1.59 – 1.61 Å, which is to be compared with the significantly longer distances: Cr(2) – O(1) and Cr(3) – O(2), being 1.66 and 1.80 Å, respectively (*cf.* Table 7).

There is a significant difference between the chromium-oxygen distances found in the CrO_4 tetrahedra and in the CrO_6 octahedron. The average of the former, not including oxygen atoms common to two and three chromium atoms, $Cr-O(a)_{tetr}$ is 1.60 Å. (The symbols (a), (b) and (c) indicate whether

the oxygen atom belongs to the coordination polyhedron of one, two, or three chromium atoms.) This value is in fair agreement with other Cr – O(a) values found in comparable compounds. In Cr_5O_{12} the corresponding distance has the value 1.54 Å, in KCr_3O_8 1.55 Å, and in $CsCr_3O_8$ 1.57 – 1.58 Å. The distance $Cr-O(b)_{tetr}$ observed in $K_2Cr_3O_8OH$ is 1.66 Å, which is to be compared with 1.64 (2 ×), 1.67 (2 ×) and 1.68 (2 ×) Å in Cr_5O_{12}, 1.65 and 1.64 (2 ×) in KCr_3O_8, and 1.68 (average) Å in $CsCr_3O_8$. Finally the distance $Cr-O(c)_{tetr}$ of 1.80 Å is in good agreement with the value of 1.80 Å found in Cr_5O_{12}. Thus the coordination number as well as the interatomic distances agree well with the assumption that 2/3 of the chromium atoms in the $K_2Cr_3O_8OH$ structure are in a hexavalent state. The Cr – O distances in the octahedron are in the range 1.97 – 2.00 Å (average 1.99 Å), in excellent agreement with the values found in KCr_3O_8 (average 1.97 Å) and Cr_5O_{12} (average 1.97 Å).

The chains in $K_2Cr_3O_8OH$ are held together by two crystallographically independent potassium atoms K(1) and K(2). The coordination around the potassium atoms is rather irregular, *cf.* Table 7, the K(1) – O distances are in the range 2.78 – 3.11 Å (C.N. = 11), and for the K(2) – O distances in the range 2.72 – 3.14 (C.N. = 8). In Ref. 14 the distance range given for 10-fold coordination is 2.71 – 3.03 Å, and for 8-fold coordination 2.66 – 3.10 Å. The coordination polyhedra $K(1)O_{11}$ and $K(2)O_8$ both consist of oxygen atoms

Table 8. Bond angles with standard deviation in the structures $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$.

	$Na_2Cr_3O_8OH$		$K_2Cr_3O_8OH$	
Bond angles O – Cr – O in the chromate tetrahedra	O(1) – Cr(2) – O(1)	108.8 ± 7	O(1) – Cr(2) – O(1)	109.5 ± 6
	O(1) – Cr(2) – O(4)	110.4 ± 5	O(1) – Cr(2) – O(4)	109.5 ± 4
	O(1) – Cr(2) – O(5)	108.7 ± 4	O(1) – Cr(2) – O(5)	109.9 ± 4
	O(1) – Cr(2) – O(4)	110.4 ± 5	O(1) – Cr(2) – O(4)	109.5 ± 4
	O(1) – Cr(2) – O(5)	108.7 ± 4	O(1) – Cr(2) – O(5)	109.9 ± 4
	O(4) – Cr(2) – O(5)	109.9 ± 8	O(4) – Cr(2) – O(5)	108.4 ± 6
	O(2) – Cr(3) – O(6)	110.2 ± 5	O(2) – Cr(3) – O(6)	109.0 ± 4
	O(2) – Cr(3) – O(6)	110.2 ± 5	O(2) – Cr(3) – O(6)	109.0 ± 4
	O(2) – Cr(3) – O(7)	108.1 ± 7	O(2) – Cr(3) – O(7)	111.6 ± 6
	O(6) – Cr(3) – O(6)	108.6 ± 8	O(6) – Cr(3) – O(6)	107.3 ± 7
	O(6) – Cr(3) – O(7)	109.9 ± 5	O(6) – Cr(3) – O(7)	109.9 ± 4
	O(6) – Cr(3) – O(7)	109.9 ± 5	O(6) – Cr(3) – O(7)	109.9 ± 4
Bond angles O – Cr – O in the chromate octahedra	O(1) – Cr(1) – O(1)	179.9 ± 0	O(1) – Cr(1) – O(1)	179.9 ± 0
	O(1) – Cr(1) – O(2)	89.9 ± 5	O(1) – Cr(1) – O(2)	89.1 ± 4
	O(1) – Cr(1) – O(2)	90.0 ± 5	O(1) – Cr(1) – O(2)	90.9 ± 4
	O(1) – Cr(1) – O(3)	91.0 ± 5	O(1) – Cr(1) – O(3)	91.9 ± 4
	O(1) – Cr(1) – O(3)	89.0 ± 5	O(1) – Cr(1) – O(3)	88.1 ± 4
	O(1) – Cr(1) – O(2)	90.0 ± 5	O(1) – Cr(1) – O(2)	90.9 ± 4
	O(1) – Cr(1) – O(2)	90.0 ± 5	O(1) – Cr(1) – O(2)	89.1 ± 4
	O(1) – Cr(1) – O(3)	90.0 ± 5	O(1) – Cr(1) – O(3)	88.1 ± 4
	O(1) – Cr(1) – O(3)	91.0 ± 5	O(1) – Cr(1) – O(3)	91.9 ± 4
	O(2) – Cr(1) – O(2)	180.0 ± 0	O(2) – Cr(1) – O(2)	180.0 ± 0
	O(2) – Cr(1) – O(3)	98.8 ± 4	O(2) – Cr(1) – O(3)	99.9 ± 4
	O(2) – Cr(1) – O(3)	81.2 ± 4	O(2) – Cr(1) – O(3)	80.0 ± 4
	O(2) – Cr(1) – O(3)	81.2 ± 4	O(2) – Cr(1) – O(3)	80.0 ± 4
	O(2) – Cr(1) – O(3)	98.8 ± 4	O(2) – Cr(1) – O(3)	100.0 ± 4
	O(2) – Cr(1) – O(3)	179.9 ± 0	O(3) – Cr(1) – O(3)	179.9 ± 0

from 3 different chains. The coordination spheres of the potassium atoms are apparently determined to a considerable extent from the space demands of the $^1_\infty|Cr_3O_8OH^{2-}|$ chain. In Ref. 6 a comparison was made between the Na-, K-, and Rb-phases (*cf.* also Tables 6 and 7). It was shown that the shape and the orientation of the chains are the same for all the different members, and the expansion of the lattice in the *a* and *c* directions when going from Na to Rb creates the necessary enlargement of the interstitial voids to accommodate the cations.

From Table 7 can be seen that the coordination number is six for the Na compound, the range of the distances for Na(1) – O is 2.36 – 2.74 Å, and for Na(2) – O 2.41 – 2.55 Å. The ranges are in agreement with the values 2.25 – 2.78 Å, given in Ref. 14 for 6-fold coordination.

The nearly constant value of the *b* axis for the members of the $A_2Cr_3O_8OH$ family investigated is well explained by the arrangement of polyhedra given above. The structure also seems to account for the insolubility of the materials in water. With regard to the red colour of the compounds and the room temperature resistivity of $\sim 10^{10}$ ohm cm reported for the Na compound,[5] there seem to be good reasons for assuming a strictly ordered arrangement of the metal atom valencies.

The absorption band at 3400 cm^{-1} indicates an OH stretching frequency of a hydrogen bond of medium strength with an oxygen-oxygen distance in the range 2.7 – 3.0 Å. It seems reasonable to assume that the hydrogen atoms are attached to the oxygen atom O(3) in a two-fold position which belongs solely to the strings of octahedra and which does not form any bridges between tetrahedra and octahedra. The oxygen-oxygen distances give no indication of a plausible oxygen counterpart in the hydrogen bridge.

The formula of the family of compounds might then be written $A_2Cr^{III}OH(Cr^{VI}O_4)_2$.

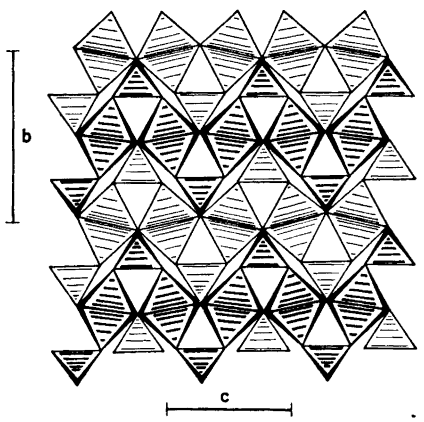

Fig. 2. The crystal structure of $LiCr_3O_8$ projected on (100). $a = 5.504$ Å, $b = 8.289$ Å, $c = 6.117$ Å.

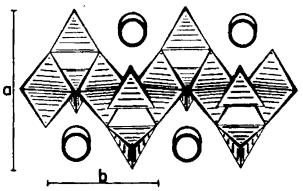

Fig. 3. The crystal structure of $K_2Cr_3O_8OH$ projected on (001) showing the coupling of the CrO_6-octahedra and CrO_4-tetrahedra. The K atoms are indicated as large circles.

From a formal point of view the structure of the family can be derived from the $LiCr_3O_8$ structure (of $CrVO_4$ structure type). The structure of $LiCr_3O_8$ is built up of slightly staggered strings of $(Li_{0.5},Cr_{0.5})O_6$ octahedra connected in the *c* direction by edge sharing. By sharing of corners the strings are linked *via* CrO_4 tetrahedra to form a three-dimensional framework (Fig. 2). Each CrO_4 tetrahedron is in contact with three separate octahedral chains. By the introduction of large cations, the three-dimensional structure is split up into onedimensional chains, with the composition $^1_\infty|Cr_3O_8OH^{2-}|$. Such a chain is visualized in Fig. 3.

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