Structural Chemistry of Chromium Compounds of $M_2^ICr_3O_9$ Stoichiometry

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In 1966 Bither, Gillson and Young [1] demonstrated the existence of $Na_2Cr_3O_9$. The new compound was prepared by heating a mixture of CrO_3 and Na_2CrO_4 (mole ratio 1:1.25) in the temperature range 500–800°C for 3–8 h at 65 kbar pressure in a tetrahedral anvil apparatus, followed by slow cooling under pressure. The deep red, water insoluble crystals were isolated from the reaction mixture after removing unreacted Na_2CrO_4 by hot water extraction and eliminating ferromagnetic CrO_2 by magnetic separation. The colour, the chemical properties and the stoichiometry $Na_{0.67}CrO_3$, suggested, according to the authors, the compound to be a bronze. However, single crystals of $Na_2Cr_3O_9$ were reported to be insulators with a room temperature resistivity of $\sim 10^{10}$ ohm cm.

The present investigation includes the phases $Na_2Cr_3O_9$, $K_2Cr_3O_9$, and $Rb_2Cr_3O_9$. For details, reference is made to a separate article dealing with the crystal structure determination.[2] The investigation has revealed a new structure element, the $Cr_3O_9^{2-}$-chain, and also some interesting structural relations to the members of the $M^ICr_3O_8$ family.[3–6]

Crystals, suitable for single-crystal X-ray diffraction work, were grown according to Ref. 1 at 25 kbar in a girdle-apparatus.[7] At a later stage, pure specimens of the phases were obtained by a slight modification of the original preparation procedure; the CrO_3 as a starting material was replaced by CrO_2. It was also found that the slow cooling process under pressure was a prerequisite condition for the formation of the compounds $M_2^ICr_3O_9$; rapid quenching from 800°C only resulted in a mixture of CrO_2 and $M_2^ICrO_4$. This observation might indicate that the compounds $M_2^ICr_3O_9$ disproportionate reversibly at higher temperatures. Further studies on this matter are in progress.

Information regarding crystallographic data for the investigated compounds is collected in Table 1. The crystal structures

Table 1. Crystallographic data for the compounds of the $M_2^ICr_3O_9$ family. Possible space groups: $P2_1/m$ (No. 11) or $P2_1$ No. 4). $Z=2$.

	$Na_2Cr_3O_9$	$K_2Cr_3O_9$	$Rb_2Cr_3O_9$
a (Å)	8.46	9.41	9.60
b (Å)	5.99	5.99	6.11
c (Å)	7.54	7.74	7.99
β (°)	111	114	114.6
V (Å^3)	356.7	398.5	426.1

were determined from three-dimensional X-ray diffraction data and refined by the least-squares method. The structure of this isomorphous family is represented in Fig. 1 by the structure of $K_2Cr_3O_9$, which

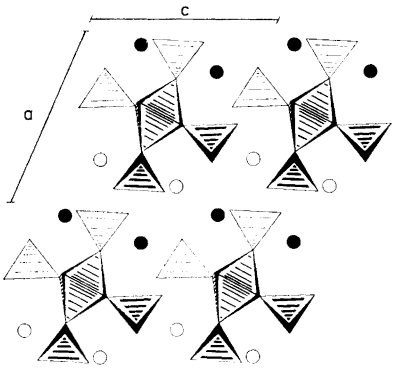

Fig. 1. The crystal structure of $K_2Cr_3O_9$ projected on (010), visualized by the coupling of coordination octahedra and tetrahedra. The octahedron at $b=\frac{1}{2}$ is shown attached to two tetrahedra at $b=1/4$ and two tetrahedra at $b=3/4$ thus forming a chain, running in the b-direction.

was determined with highest precision. From this figure it can be seen that the structure is formed of CrO_6 octahedra and CrO_4 tetrahedra, the polyhedra being arranged in chains running in the b-direction. The structure contains three crystallographically independent chromium atoms Cr(1)–Cr(3). The Cr(1) atoms are six-coordinated and situated at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and connected to another six-coordinated Cr-

Table 2. Observed chromium-oxygen distances with standard deviations (for $K_2Cr_3O_9$). The symbols (a), (b), and (c) indicate whether the oxygen atom belongs to the coordination polyhedron of one, two, or three chromium atoms.

	Cr(1)-Octahedron		Cr(2)-Tetrahedron		Cr(3)-Tetrahedron	
$Na_2Cr_3O_9$	Cr - 2 O (b)	1.95 Å	Cr - O (a)	1.58 Å	Cr - 2 O (a)	1.60 Å
	Cr - 2 O (b)	1.99	Cr - O (a)	1.65	Cr - O (a)	1.61
	Cr - 2 O (c)	1.97	Cr - 2 O (b)	1.66	Cr - O (b)	1.80
$K_2Cr_3O_9$	Cr - 2 O (b)	1.947 ± 10 Å	Cr - O (a)	1.611 ± 16 Å	Cr - 2 O (a)	1.591 ± 12 Å
	Cr - 2 O (b)	2.029 ± 10	Cr - O (a)	1.616 ± 16	Cr - O (a)	1.620 ± 16
	Cr - 2 O (c)	1.978 ± 11	Cr - 2 O (b)	1.638 ± 12	Cr - O (b)	1.776 ± 17
$Rb_2Cr_3O_9$	Cr - 2 O (b)	2.00 Å	Cr - O (a)	1.61 Å	Cr - O (a)	1.60 Å
	Cr - 2 O (b)	2.01	Cr - O (a)	1.62	Cr - 2 O (a)	1.63
	Cr - 2 O (c)	2.07	Cr - 2 O (b)	1.67	Cr - O (b)	1.73

atom (at $\frac{1}{2}$, 0, $\frac{1}{2}$) by sharing edges thus forming a somewhat staggered string running in the *b*-direction. To this string, the two fourcoordinated Cr(2)- and Cr(3)-atoms are attached to form a chain with the composition $\frac{1}{\infty}[Cr_3O_9^{2-}]$. The Cr(2)-tetrahedron is connected to the apices of two octahedra by sharing corners, the Cr(3)-tetrahedron is connected to the string by sharing only one corner.

In all the structures there is a significant difference between the chromium-oxygen distances found in the CrO_4 tetrahedra and in the CrO_6 octahedra (Table 2). The $(Cr-O)_{oct}$ and $(Cr-O)_{tetr}$ distances agree very well with those previously reported in compounds containing tetravalent and hexavalent chromium, respectively.[8] Thus, there appears good reason to assume that chromium has a valency of six in the tetrahedral and four in the octahedral positions.

The chains are held together by two crystallographically independent potassium atoms K(1) and K(2). The shape and the orientation of the chains of the different members are all nearly the same and the expansion of the lattice in the *a* and *c* directions when going from Na to Rb creates the necessary increase in the cation-oxygen distances (*cf.* Tables 1 and 3). The coordination around the alkali atoms is rather irregular but the influence of the cation size is clearly reflected in the number and distribution of the oxygen neighbours. The nearly constant value of the *b* axis for all the members, is also well explained by this arrangement of atoms. The structure also seems to account for the insolubility of the materials in water.

Table 3. Observed $M-O$ distances (in Å) shorter than 4 Å with standard deviations.

Compound	M(1) - O distances		M(2) - O distances	
$Na_2Cr_3O_9$	Na - O	2.36 ± 3	Na - 2 O	2.41 ± 3
	Na - O	2.47 ± 3	Na - O	2.45 ± 3
	Na - 2 O	2.51 ± 3	Na - 2 O	2.51 ± 3
	Na - 2 O	2.73 ± 3	Na - O	2.56 ± 3
	Na - O	3.03 ± 3	Na - O	2.99 ± 3
	Na - 2 O	3.13 ± 1	Na - O	3.10 ± 3
	Na - 2 O	3.24 ± 3	Na - 2 O	3.43 ± 2
			Na - 2 O	3.59 ± 2
$K_2Cr_3O_9$	K - 2 O	2.768 ± 12	K - 2 O	2.699 ± 12
	K - O	2.820 ± 17	K - 2 O	2.718 ± 12
	K - O	2.944 ± 17	K - O	2.837 ± 16
	K - 2 O	2.951 ± 12	K - O	2.843 ± 17
	K - 2 O	2.957 ± 12	K - O	3.062 ± 16
	K - O	2.976 ± 16	K - O	3.196 ± 16
	K - 2 O	3.066 ± 4	K - 2 O	3.401 ± 8
			K - 2 O	3.564 ± 9
$Rb_2Cr_3O_9$	Rb - 2 O	2.82 ± 3	Rb - 2 O	2.82 ± 3
	Rb - 2 O	2.99 ± 3	Rb - 2 O	2.84 ± 3
	Rb - O	3.00 ± 3	Rb - O	2.90 ± 3
	Rb - 2 O	3.00 ± 3	Rb - O	2.99 ± 3
	Rb - O	3.02 ± 3	Rb - O	3.18 ± 3
	Rb - O	3.02 ± 3	Rb - O	3.22 ± 3
	Rb - 2 O	3.12 ± 1	Rb - 2 O	3.41 ± 2
			Rb - 2 O	3.59 ± 2

There are obvious structural relations between these compounds and those belonging to the $M^ICr_3O_8$ family. The structure of MCr_3O_8 (M=Na, K, Rb, Tl) is formed by CrO_4 tetrahedra and CrO_6 octahedra arranged in layers by sharing corners (*cf.* Fig. 2). The potassium atoms are situated between the layers. The alkali atoms in KCr_3O_8 are in contact with ten oxygens. The arrows in Fig. 2 indicate how, by shifting the positions of some of the oxygen atoms in the KCr_3O_8

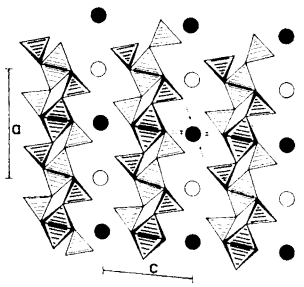

Fig. 2. The crystal structure of KCr_3O_8 projected on (010), ($a=8.569$ Å, $b=5.466$ Å, $c=7.622$ Å, $\beta=95.25°$). By shifting some of the oxygen atoms in the KCr_3O_8 type of structure in directions indicated by the arrows, rows of metal-oxygen octahedra are formed. Such octahedra are filled by Li-atoms and Cr^{III}-atoms.

structure, the coordination around the alkali atoms may be changed to an octahedral one. In the structure of $LiCr_3O_8$,[3] these positions are occupied by lithium and chromium atoms in a random way, forming somewhat staggered strings of octahedra connected by sharing edges in the *c*-direction. By sharing corners the strings are linked *via* CrO_4 tetrahedra to form a three-dimensional framework. Each CrO_4 tetrahedron is in contact with three separate octahedral strings.

From a formal point of view the structure of $M_2Cr_3O_9$ can be derived from the $(Li,Cr)Cr_2O_8$ structure by introducing a big cation in one half of the octahedral sites in an ordered way as well as adding another cation for each chain this resulting in a split up of the three-dimensional framework structure to the one-dimensional chain structure of the $M_2Cr_3O_9$ family.

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On the Crystal Structure of Phthalimidocyclohexane

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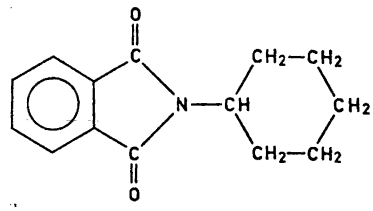
An X-ray crystallographic investigation of phthalimidocyclohexane was undertaken in order to establish to what extent the cyclohexane ring is flattened.[1]



The crystals are orthorhombic ($a=21.92_0$ Å, $b=8.04_2$ Å, $c=6.78_9$ Å) with two possible space groups: $Pnma$ and $Pna2_1$. Intensity data were obtained (at room temperature) from photometric measurements of integrated equiinclination Weissenberg diagrams (Cu$K\alpha$-radiation) corresponding to $hk0$, ··· $hk5$ and $h0l$, ··· $h5l$. The diagrams show a considerable amount of diffuse scattering. 1073 independent