# Structural Chemistry of Chromium Compounds of $M^ICr_3O_8$ Stoicheiometry

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IN 1952 Suchow, Fankuchen, and Ward[1] demonstrated the existence of alkali-metal compounds of composition $MCr_3O_8$ (M = Li, Na, K, Rb, and Cs). Some years later, the crystal structure of the potassium compound was determined by the present author.[2] Crystals of $LiCr_3O_8$ and $CsCr_3O_8$, suitable for single-crystal *X*-ray-diffraction techniques, have now been grown and structure determinations of these substances have been completed. The results thus obtained have revealed some new interesting structural relations. For details, reference is made to the separate articles.[2–4]

The investigation has included the phases $LiCr_3O_8$, $NaCr_3O_8$, $KCr_3O_8$, $RbCr_3O_8$, $TlCr_3O_8$, and $CsCr_3O_8$ which have been found to crystallize in three different structural types and which in this paper are called the Li-, K-, and Cs-types. Information regarding space-groups and unit-cell dimensions are collected in Table 1. The *X*-ray

TABLE 1

*Crystallographic data for the compounds of the* $M^ICr_3O_8$ *family.*

| Structure type | Substance | Space group | Unit-cell dimensions (in Å) *a* | *b* | *c* | *β* | *V*(Å³) | *z* |
|---|---|---|---|---|---|---|---|---|
| Li-type | $LiCr_3O_8$ | *Cmcm* (No. 63) | 5·504 ± 0·002 | 8·289 ± 0·002 | 6·117 ± 0·003 | — | 279·1 | 2 |
| K-type | $NaCr_3O_8$ | *C*2/*m* (No. 12) | 8·492 ± 0·001 | 5·478 ± 0·002 | 6·799 ± 0·002 | 91°·44 ± 0·1 | 316·2 | 2 |
| | $KCr_3O_8$ | *C*2/*m* (No. 12) | 8·569 ± 0·001 | 5·466 ± 0·001 | 7·622 ± 0·001 | 95°·25 ± 0·1 | 355·5 | 2 |
| | $RbCr_3O_8$ | *C*2/*m* (No. 12) | 8·575 ± 0·004 | 5·450 ± 0·002 | 7·963 ± 0·003 | 95°·99 ± 0·2 | 364·6 | 2 |
| | $TlCr_3O_8$ | *C*2/*m* (No. 12) | 8·592 ± 0·001 | 5·478 ± 0·001 | 7·760 ± 0·001 | 96°·3 ± 0·2 | 370·1 | 2 |
| Cs-type | $CsCr_3O_8$ | *Pnma* (No. 62) | 15·957 ± 0·001 | 5·505 ± 0·002 | 8·264 ± 0·003 | — | 725·9 | 4 |

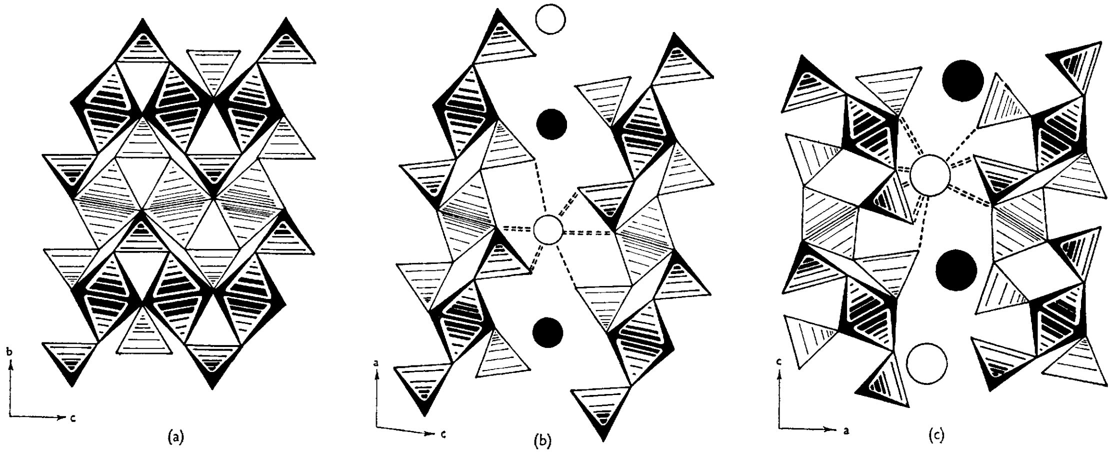

FIGURE 1

*The building schemes of* $LiCr_3O_8$ *(a),* $KCr_3O_8$ *(b), and* $CsCr_3O_8$ *(c) visualized by the coupling of co-ordinati onoctahedra and tetrahedra. The contacts between interlayer alkali atoms and oxygens are indicated by dashed lines.*

powder patterns of these substances as well as the single-crystal diffraction data of $LiCr_3O_8$ and $CsCr_3O_8$ are included in a document, copies of which may be obtained by request from the Secretary of this Institute.[5]

The structure of $KCr_3O_8$, Figure 1b, is formed of $CrO_6$ octahedra and $CrO_4$ tetrahedra, the polyhedra being arranged in layers by sharing corners. The layers are held together by K atoms which have ten nearest oxygen neighbours. The lattice expansion in the isomorphous series of the Na, K, Rb, and Tl phases, reflected in the length of the *c*-axis, is mainly due to the increase in size of the interlayer alkali-metal atoms.

The atomic arrangement of $CsCr_3O_8$ contains layers formed of $CrO_6$ octahedra and $CrO_4$ tetrahedra joined by corners essentially in the same way as in the K-type. The orientation of half of the tetrahedra is, however, different (*cf.* Figure 1c) and every second layer of the Cs-type is rotated by 180° as compared with the K-type. This results in a doubling of the repeat distance normal to the layers in the Cs-type structure. The shift of the atoms and the change of the layer orientation create the increase in co-ordination number from ten (in the K-type) to fourteen required by the large interlayer Cs atoms.

The structure of $LiCr_3O_8$, Figure 1a, is built up of somewhat staggered strings of $(Li,Cr)O_6$ octahedra connected by sharing edges in the *c*-direction. The lithium and one third of the chromium atoms randomly occupy the octahedral sites in the strings. 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 strings. The arrangement of octahedra and tetrahedra is the same as found by Brandt[6] in $CrVO_4$(o-rh) and also occurs in several chromates, phosphates and sulphates of $MXO_4$ stoicheiometry.

There is also an obvious structural relation between the Li- and K-types. If the layers of the latter are packed close together it is possible to reduce the co-ordination polyhedron around the interlayer atom to an octahedron. The metal–oxygen arrangement thus arrived at is actually the one present in the Li-type, not taking into account

TABLE 2

*Observed chromium–oxygen distances in chromium compounds of* $M^ICr_3O_8$ *stoicheiometry*

| | Octahedra | | Tetrahedra | | | |
|---|---|---|---|---|---|---|
| $LiCr_3O_8$ | (Li, Cr)–2 O | 2·05 Å | Cr–2 O | 1·62 Å | | |
| | (Li, Cr)–4 O | 2·05 Å | Cr–2 O | 1·68 Å | | |
| $KCr_3O_8$ | Cr–2 O | 1·93 Å | Cr–O | 1·65 Å | | |
| | Cr–4 O | 1·99 Å | Cr–O | 1·55 Å | | |
| | | | Cr–2 O | 1·64 Å | | |
| $CsCr_3O_8$ | Cr–O | 1·98 Å | Cr–O | 1·58 Å | Cr–O | 1·57 Å |
| | Cr–O | 2·02 Å | Cr–O | 1·69 Å | Cr–O | 1·68 Å |
| | Cr–2 O | 2·00 Å | Cr–2 O | 1·64 Å | Cr–2 O | 1·71 Å |
| | Cr–2 O | 1·89 Å | | | | |

the randomization of Li and Cr atoms within the octahedra.

In all the three different structure types there is a significant difference between the chromium–oxygen distances found in the $CrO_4$ tetrahedra and 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 ter- and sexi-valent chromium respectively. Thus, there appears good reason to assume that chromium has a valency of six in the tetrahedral and three in octahedral positions. This is also supported by magnetic susceptibility data ($KCr_3O_8$)[7] and electric resistivity data ($LiCr_3O_8$ and $KCr_3O_8$).[8] It is thus possible to formulate these compounds as $M^ICr^{III}(Cr^{VI}O_4)_2$. In this respect the present group of compounds clearly deviates from several chromates containing $Cr^V$ atoms as demonstrated by recent structural studies.[9,10]

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