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Superstructure with Pseudo Translation. II. Monopotassium Pentachromium Octaselenide: a Tunnel Structure

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Abstract. KCr_5Se_8, $M_r = 930{\cdot}7$, monoclinic, $B2/m$ (c axis unique), $a = 18{\cdot}658$ (3), $b = 8{\cdot}984$ (3), $c = 3{\cdot}594$ (4) Å, $\gamma = 104{\cdot}53$ (2)°, $V = 583{\cdot}2$ (9) Å^3, $Z = 2$, $D_x = 5{\cdot}30$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 29{\cdot}444$ mm^{-1}, $F(000) = 822$, $T = 297$ K, $R = 0{\cdot}067$, $wR = 0{\cdot}047$ for the whole set of 912 reflections. The Se and the Cr atoms are in the mirror plane while the sixfold prismatically coordinated K is delocalized inside an Se-atom tunnel, in a statistical disorder along the twofold axis. Many interatomic vectors nearly equal to **a**/3 are found, giving rise to pseudo-translation superstructure effects.

Introduction. During the investigation of the quaternary system La—Cr—O—Se, single crystals were obtained using KBr flux from a mass containing these four elements at 1100 K. These crystals, in a very small quantity, could not be analyzed by usual chemical methods. Only a single-crystal X-ray diffraction study could be used to determine the chemical composition and the crystal structure of the new compound, KCr_5Se_8.

Experimental. Crystal size 50 × 80 × 210 µm. Cell dimensions from setting angles of 15 reflections on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo $K\alpha$ radiation ($7 < 2\theta < 20°$). Laue symmetry: $2/m$, B lattice with c axis unique. Data collection by ω–2θ scans, with a scan range (°) of $0{\cdot}90 + 0{\cdot}35\tan\theta$, $1 \leq \theta \leq 30°$, $0 \leq h \leq 26$, $-12 \leq k \leq 12$, $0 \leq l \leq 5$. Two standard reflections ($00\bar{2}$ and 610) were used to monitor the measuring performance; the relative standard deviation of the measurements of these reflections was $\sigma_r = 0{\cdot}002$. 912 reflections collected; 642 considered as 'observed' with $I > 4\sigma(I)$, where $\sigma^2(I) = \sigma_r^2 I^2 + \sigma_c^2$ and σ_c is set by counting statistics. Absorption correction by the analytical method of de Meulenaer & Tompa (1965): maximum and minimum transmission factors are 0·284 and 0·117. Lorentz and polarization corrections. The reflection intensities for homologous series hkl, $l = 0,2,4$, are very similar; the same is true for hkl, $l = 1,3,5$. The heavy atoms, therefore, were expected to be located in the mirror planes ($z = 0$ and $z = \frac{1}{2}$) in space group Bm or $B2/m$. Moreover, reflections are strong if $h = 3n$ (*i.e.* $h = 6n$ and $l = 2n$, or $h = 3n$ and $l = 2n+1$), which correspond to a superstructure with pseudotranslation vector **a**/3, which, because of the B centering, is equivalent to **a**/6 + **c**/2.

The most pronounced peaks in the Patterson synthesis were used as a starting point for the structure determination. As the composition was not known, we denoted these peaks as La—La vectors, La being the heaviest of the possible atoms La, Se, Cr, K and O. As the space group was not known, we used $B2$, Bm and $B2/m$ in parallel, and as the final space group appeared to be $B2/m$, and the experiments in this space group progressed better than those in the lower-symmetry space groups, we here restrict the description of our procedure to $B2/m$. Tentative La positions were input to *DIRDIF* (Beurskens *et al.*, 1983). The initial experiments had to be repeated several times to determine the scale and temperature factors, varying the assumed composition until the normalized structure factors of the unknown part of the structure showed a reasonable statistical distribution. The origin-fixation procedure of the *DIRDIF* system (Beurskens & Bosman, 1982, and references therein) then led to a Fourier synthesis in which the sublattice symmetry was destroyed and the gross features of the superstructure were present. Peak heights and interatomic distances were incompatible with the presence of either La or O, and a Fourier synthesis based on Cr—Se octahedra (with nothing on the present K^+ position) showed the presence of a disordered K atom near the mirror plane.

The position of the disordered K atom overlaps with its equivalent position. A conventional refinement of atomic positions with the *ORFLS* program (Busing,

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Table 1. *Atomic parameters*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Se(1)	0·23997 (8)	0·1577 (2)	0	0·95 (5)
Se(2)	0·16826 (9)	0·4933 (2)	0	1·04 (5)
Se(3)	0·07369 (8)	0·1615 (2)	0·5	1·14 (5)
Se(4)	0·41414 (8)	0·1772 (2)	0·5	1·07 (6)
Cr(1)	0	0	0	0·8 (1)
Cr(2)	0·7050 (1)	0·3358 (3)	0	0·83 (8)
Cr(3)	0·3427 (1)	0·0164 (3)	0	0·81 (8)
K	0	0·5	0·443 (3)	8·6 (6)

(K: occupancy factor: 0·5.)

Table 2. *Interatomic distances* (Å)

Cr(1)–Se(3)	2·495 (1) × 4*	K–K$^{\rm vii}$	0·41 (2)
–Se(4$^{\rm ii}$)	2·525 (2) × 2	–K$^{\rm viii}$	3·18 (2)
Cr(2)–Se(2$^{\rm iii}$)	2·476 (3)	–Se(4$^{\rm ix}$)	3·344 (5) × 2
–Se(2$^{\rm iv}$)	2·487 (2) × 2	–Se(2)	3·534 (5) × 2
–Se(3$^{\rm v}$)	2·556 (3)	–Se(4$^{\rm x}$)	3·557 (6) × 2
–Se(1$^{\rm iv}$)	2·596 (2) × 2	–Se(3)	3·643 (2) × 2
Cr(3)–Se(4)	2·475 (2) × 2	–Se(2$^{\rm xi}$)	3·737 (6) × 2
–Se(3$^{\rm ii}$)	2·497 (3)		
–Se(1)	2·550 (3)		
–Se(1$^{\rm ii}$)	2·617 (2) × 2		

Symmetry code: (i) $1-x, -y, -z$; (ii) $\frac{1}{2}-x, -y, \frac{1}{2}-z$; (iii) $1-x, 1-y, -z$; (iv) $\frac{1}{2}+x, y, \frac{1}{2}+z$; (v) $\frac{1}{2}+x, y, z-\frac{1}{2}$; (vii) $x, y, 1-z$; (viii) $-x, 1-y, -z$; (ix) $x-\frac{1}{2}, y, z-\frac{1}{2}$; (x) $x-\frac{1}{2}, y, \frac{1}{2}+z$; (xi) $x, y, 1+z$.

* Multiplicity of this bond.

1971) leads to a position of the K atom out of the mirror plane (in a site partially occupied on the twofold axis along the z direction) with an occupancy factor of 0·42 instead of 0·5. Introducing third- and fourth-rank tensors leads to a correct weight of 0·50 but the off-centering remains. The site potential of the K$^+$ ion is therefore rather distorted with respect to a harmonic distribution. An attempt to refine in the noncentrosymmetric space group $B2$ did not introduce any improvement. At the end of the refinement on F, $R = 0{\cdot}067$ and $wR = 0{\cdot}047$ for the whole set of 912 reflections and $wR = 0{\cdot}046$ for the 642 'observed' reflections [$w = 1/\sigma^2(F)$]. Minimum and maximum electron densities in final difference map: $-0{\cdot}10$ and $0{\cdot}15$ e Å^{-3}. $\Delta/\sigma = 0{\cdot}1$. Scattering factors with corrections for dispersion are taken from *International Tables for X-ray Crystallography* (1974). Bond distances and angles are calculated using the program *ORFFE*3 (Busing, Martin & Levy, 1971). Computer used: Sperry 1100.

Final atomic parameters with equivalent isotropic temperature factors are given in Table 1.† Main bond distances are listed in Table 2.

Discussion. We can see (Fig. 1) that the interatomic vectors with the same z coordinates Cr(1)–Cr(3), Cr(3)–Cr(3$^{\rm i}$), Se(3)–Se(4) are nearly equal to **a**/3 [symmetry code: (i) $1-x, -y, -z$].

All Cr atoms are coordinated by six Se atoms. Cr(1) is at the center of a slightly distorted octahedron of Se(3) and Se(4) atoms. The coordination octahedra around the Cr(2) and Cr(3) atoms are slightly more distorted: for example, the distances Cr(3)–Se vary from 2·476 (2) to 2·617 (2) Å. The structure can be described as intersecting layers of edge-sharing CrSe$_6$ octahedra, leaving channels along [001] which contain the K atoms. One layer is defined by the stacking sequence [Cr(1)–Cr(3)–Cr(3$^{\rm i}$)]$_n$ which extends along [100] and is connected along [001] by the lattice translation. A different, less planar layer of edge or face sharing octahedra is defined by the stacking sequence [Cr(3)–Cr(2$^{\rm i}$)–Cr(2)–Cr(3$^{\rm i}$)]$_n$ which extends along [010], also connected along [001] by the lattice translation: Cr(2) and Cr(2$^{\rm i}$) share edges; Cr(2) and Cr(3$^{\rm i}$) share faces. [Alternatively, one may consider the Cr(1)–Cr(3)–Cr(3$^{\rm i}$) layer of edge-sharing octahedra as being bridged by the Cr(2)–Cr(2$^{\rm i}$) double chain of edge-sharing octahedra, the junctions being made *via* Se-atom faces.]

This particular arrangement of coordination octahedra gives rise to tunnels with diamond-shaped cross sections and space (room, cavities) centered around

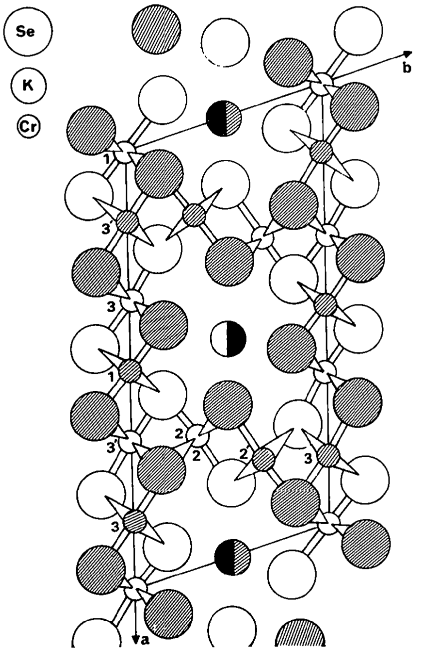

Fig. 1. Projection of the structure along **c**. The K$^+$ ion is indicated by half circles in black and white (indicating nearby disordered positions). The K–Se bonds are omitted. Shaded atoms are positioned at $z = \frac{1}{2}$; other atoms at $z = 0$. The numbering of the Cr atoms is given.

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† Lists of structure factors, anisotropic thermal parameters and coefficients of third- and fourth-rank tensors for the K$^+$ ion have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44304 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

position $2(d)$ (0, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0, symmetry $2/m$) in which the K^+ ion is off-centered (positioned on the binary axis, out of the mirror) and occupies, in a statistical disorder, one of the two positions related by the mirror plane and 0·41 (2) Å apart. The coordination of this ion is triangular base-prismatic, if we consider only Se—K distances less than 3·56 Å. Two of them are much shorter than the four others. The off-centering of the K^+ gives rise to a lengthening of some of the K—Se distances. This kind of coordination was also found in KIn_5S_8 (Carré & Pardo, 1983), in which, however, the K^+ ion remains in a mirror plane of the space group, in a different statistical disorder. The K—K distances are then longer [0·912 (12) Å].

In spite of several similarities, the KCr_5Se_8 and KIn_5S_8 compounds are not isostructural. In KIn_5S_8, the atoms In(1) and In(2) [which are homologues of Cr(1) and Cr(2) in KCr_5Se_8] are octahedrally coordinated while In(3) [homologous to Cr(3)] is only tetrahedrally coordinated. Moreover, in KIn_5S_8, no pseudo translation is present. Finally, the KIn_5S_8 structure is well defined by the stacking sequence $[\mathrm{In(1)–octahedron–In(3)–tetrahedron–In(3')–tetrahedron}]_n$. Thus, two layers related by the [010] translation are linked by the vertices (S atoms) of the dioctahedra around In(2): the cavity is then occupied by the K^+ ion in the mirror plane, in a statistical disorder.

To conclude, the KCr_5Se_8 structure is characterized by the existence of a tunnel of Se atoms in which a K^+ ion occupies the site along the binary axis in a statistical disorder.

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Refinement of the Structure of Orthorhombic Sulfur, α-S_8

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Abstract. α-Sulfur, S_8, $M_r = 256{\cdot}51$, orthorhombic, *Fddd*, $a = 10{\cdot}4646\,(1)$, $b = 12{\cdot}8660\,(1)$, $c = 24{\cdot}4860\,(3)$ Å, $V = 3296{\cdot}7$ Å^3, $Z = 16$, $D_x = 2{\cdot}067$ g cm^{-3}, Mo $K\alpha$, $\lambda\alpha_1 = 0{\cdot}70930$ Å, $\mu = 19{\cdot}90$ cm^{-1}, $F(000) = 2048$, $T = 298$ K, $R = 0{\cdot}019$, $wR = 0{\cdot}023$ for 851 reflections with $I \geq 3\sigma(I)$, $R = 0{\cdot}019$ ($wR = 0{\cdot}020$) for 506 reflections with $I \geq 3\sigma(I)$ and $(\sin\theta)/\lambda \geq 0{\cdot}481$ Å^{-1}. Mean structural parameters are the same for both refinements: S—S = 2·046 (3) (uncorrected) and 2·055 (2) Å (corrected for libration), S—S—S = 108·2 (6) and S—S—S—S = 98·5 (19)°.

Introduction. Although orthorhombic sulfur (α-S) is the most familiar form of the element and was the first to be subjected to a crystallographic analysis, it remains the least-precisely determined structure of elemental sulfur. Structural studies have been elegantly summarized by Donohue (1982), the most recent studies of α-S all being based on the data of Abrahams (1955). The lowest R value in the literature (0·126) is that of Pawley & Rinaldi (1972), who stated that efforts to obtain higher-quality data were in progress at that time. Since no further work on α-S has appeared to date, it must be assumed that no significantly better data set had been obtained. We report here a redetermination of the α-S structure based on a new room-temperature data set, which has resulted in a substantial improvement in the precision of the derived structural parameters.

Experimental. High-quality crystals of α-S were isolated from the reaction mixture of $[\mathrm{Fe\{C_5H_3(PPh_2)\text{-}Li\}_2}]$.TMED and elemental sulfur along with those of the desired product $[\mathrm{Fe\{C_5H_3(PPh_2)\}_2}]S_3$ (Butler, Cullen, Einstein, Herring, Jagannathan & Willis, 1987). The crystals were octahedral in shape with faces of the form {111} developed, distances between parallel faces ranging from 0·31 to 0·35 mm. The unusual pale-violet

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