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Structure of the Elpasolite Dicesium Potassium Hexacyanochromate(III), $Cs_2K[Cr(CN)_6]$, at 295 K

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Abstract. $M_r = 513{\cdot}0$, monoclinic, $P2_1/n$, $a = 11{\cdot}302\,(2)$, $b = 8{\cdot}303\,(2)$, $c = 7{\cdot}761\,(2)$ Å, $\beta = 90{\cdot}30\,(2)°$, $V = 728{\cdot}3$ Å^3, $D_m = 2{\cdot}33\,(1)$, $D_x = 2{\cdot}34$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}1$ mm^{-1}, $F(000) = 462$, 295 K, $R(F) = 0{\cdot}042$ for 2364 reflections with $I > 3\sigma(I)$. The compound is isomorphous with other elpasolites $Cs_2M^IM^{III}(CN)_6$ in their monoclinic phases. Mean distances are Cr—C = 2·072 (2) and C—N = 1·138 (6) Å. Residual difference maps show peaks consistent with the anharmonicity expected from a transition to the higher-symmetry phases characteristic of elpasolites.

Introduction. In a search for crystals containing the $Cr(CN)_6^{3-}$ ion suitable for both spin and charge-density studies we have examined certain elpasolites. These salts, $Cs_2M^IM^{III}(CN)_6$, have a low-temperature $P2_1/n$ phase (III), many have an intermediate tetragonal $P4/mnc$ phase (II), while at high temperatures the structure is $Fm3m$ (Swanson & Lucas, 1978). Of the known salts (M^{III} = Cr, Mn, Fe, Co, Ir) the chromicyanides have the most suitable magnetic properties for a polarized neutron diffraction study to examine the spin distribution in the *M*—C—N bonding system. The II→III phase transition is second order and precursive effects extend far down in temperature (Ryan & Swanson, 1976). Accordingly, we require a crystal with a high III→II phase-transition temperature. It appears that this requires a heavier rather than a lighter non-cesium alkali metal. We prepared $Cs_2KCr(CN)_6$ and examined its structure in the monoclinic phase III. An attempt to prepare $Cs_2RbCr(CN)_6$ failed.

Experimental. Large crystals were easily grown by slow cooling of a warm solution containing Cs^+, K^+ and $Cr(CN)_6^{3-}$ in 2:1:1 ratio. A solution containing Cs^+, Rb^+, $Cr(CN)_6^{3-}$ and K^+ in the ratio 2:1:1:0·1 yielded only $Cs_2KCr(CN)_6$. $Cs_2RbCr(CN)_6$ is obviously far less stable, if it does exist, than is the potassium salt. All crystals obtained could be indexed on an *A*-centered triclinic cell with axes **a**, **b + c** and **b − c** in X-ray Weissenberg photographs. Any departure from a monoclinic $P2_1/n$, *a,b,c* cell was small, if present, as has been reported in other elpasolites (Ryan, Smyth & Swanson, 1979). Crystal of near cubic shape, 0·25 × 0·24 × 0·26 mm perpendicular to (100), (011) and (0$\bar{1}$1), respectively; long exposures revealed no superlattice reflections, and no apparent departure from monoclinic symmetry; D_m by flotation; six reflections used for measuring lattice parameters. Syntex $P2_1$ diffractometer, hemisphere of data measured to $2\theta \leq 75°$, outside that sphere the data were too weak to be observed; including some repeat measurements, 7570 reflections studied; four standards measured every 200 reflections, no systematic change in intensity with time; analytical absorption correction, averaging of reflections equivalent in monoclinic symmetry, 3860 unique reflections obtained, $0 \leq h \leq 19$, $0 \leq k \leq 14$, $-13 \leq l \leq 13$, $R_{\rm int} = 0{\cdot}016$, 2364 with $I > 3\sigma(I)$ used in refinement; $\sigma(I)$ assigned as the counting statistic, an estimate from $R_{\rm int}$, or 1% of *I*, whichever was the largest; least-squares refinement of atomic coordinates, anisotropic thermal parameters, *CRYLSQ* of XRAY76 in the full-matrix mode (Stewart, 1976); $\sum\sigma^{-2}(F) \times (|F_{\rm obs}| - |F_{\rm calc}|)^2$ minimized, neutral-atom scattering factors (Cromer & Mann, 1968) modified for anomalous dispersion (Cromer & Liberman, 1970), starting parameters taken from $Cs_2KFe(CN)_6$ structure (Fletcher & Gibb, 1977), $R = 0{\cdot}042$, $R_w = 0{\cdot}037$, $w = 1/\sigma^2(F)$. Table 1 lists the fractional atomic coordinates and the trace of the thermal motion tensor, $\bar{U}$.* Extinction effects were small, $[g = 0{\cdot}60\,(4) \times 10^{-3}$ cm$^{-1}]$, corresponding to a maximum reduction of about 6% in any reflection.

Anisotropy of thermal motion was not large, although U_{22} was consistently found to be smaller than U_{11} or U_{33}. The final *R* factors seem to be rather high in the light of the good quality of the data. Unlike the case of $Cs_2LiCr(CN)_6$ (Ryan & Swanson, 1976), twinning on (011) was not present. Examination of difference Fourier maps showed substantial residual densities only around the Cs, K and Cr atoms. Use of Cs^+, K^+ and

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38736 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cr^{3+} ion form factors did not reduce these features significantly. Restricting the data used to the range $0 < \sin\theta/\lambda < 0{\cdot}5$ Å^{-1} improved R to 0·023. We, therefore, tentatively ascribe the residues to the effects of anharmonicity in thermal motion. Around the potassium atom there is an almost spherical shell of excess density peaking at 1·1 e Å^{-3} at about 0·5 Å from the atom center, while at the chromium atom there is a more diffuse spherical shell reaching −0·5 e Å^{-3}. However, the most striking feature is around the cesium atom where, besides a small peak at the atom itself, the major density, reaching 1·3 e Å^{-3}, occurs at $\frac{1}{4}$, $\frac{1}{2}$, 0, which is approximately 0·6 Å from the atom along **b**.

Discussion. Inter- and intramolecular bond lengths and angles are listed in Table 2. The $Cr(CN)_6^{3-}$ ion is close to ideal octahedral stereochemistry, with bond lengths not significantly different from those in $Cs_2LiCr(CN)_6$ (Ryan & Swanson, 1976) and $K_3Cr(CN)_6$ (Figgis, Reynolds & Williams, 1981). The intermolecular Cs···N and K···N distances differ little from those in $Cs_2KFe(CN)_6$ (Fletcher & Gibb, 1977) with a maximum difference of 0·030 Å and a mean value of 0·013 Å, in spite of much larger changes in cell size and $[M(CN)_6]^{3-}$ size.

These observations lend support to the supposition of Fletcher & Gibb that both Cs···N and K···N contacts determine details of these K-containing structures, unlike $Cs_2LiCr(CN)_6$, where the Cs atom appears to be in a hole too large for it (Cs···N = 3·762 Å). This larger hole size was used (Ryan & Swanson, 1976) to explain the high Cs motion (0·060 Å^2) compared to that of C (0·036 Å^2) and of N (0·064 Å^2) in $Cs_2LiCr(CN)_6$. Our values for these thermal motions in $Cs_2KCr(CN)_6$ are virtually identical to those in $Cs_2LiCr(CN)_6$. This implies that a simple correlation of hole size with thermal motion is not appropriate. Even in $Cs_2KCr(CN)_6$ the Cs motion remains anomalously high compared to that of the other atoms. The III→II phase transition almost certainly involves, mainly, a Cs shift from its general position to ($\frac{1}{4}$, $\frac{1}{2}$, 0) (Ryan & Swanson, 1976). This is essentially a translation along **b**. Our data show a rather lower value for U_{22} [0·0456 (5) Å^2] than for U_{33} [0·0547 (5) Å^2] or for U_{11} [0·0621 (5) Å^2]. This suggests that the Cs-displacive transition III→II in $Cs_2KCr(CN)_6$ at 295 K is still quite far away in temperature and that the translational mode observed to soften by Ryan & Swanson is still quite high in frequency. Even so, the fact that our difference Fourier map shows a strong peak at ($\frac{1}{4}$, $\frac{1}{2}$, 0) implies that the mode is already substantially anharmonic and that we are seeing a precursive effect of the III→II transition. A low-temperature study of $Cs_2KCr(CN)_6$ has been commenced to examine this supposition.

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Table 1. *Fractional atomic coordinates* (×10^4) *and mean thermal parameter* (Å^2 × 10^4)

$$\bar{U} = \tfrac{1}{3}\textstyle\sum_i U_{ii}.$$

	x	y	z	$\bar{U}$
Cr(1)	0	0	0	278
K(1)	0	5000	5000	298
Cs(1)	2511 (1)	4277 (1)	−228 (1)	524
C(1)	352 (3)	1327 (5)	−2204 (5)	380
C(2)	447 (4)	−2099 (5)	−1286 (5)	370
C(3)	1742 (4)	257 (5)	783 (5)	384
N(1)	570 (4)	2049 (5)	−3407 (5)	652
N(2)	697 (4)	−3245 (5)	−1999 (5)	593
N(3)	2690 (3)	451 (5)	1237 (6)	605

Table 2. *Interatomic distances* (Å) *and angles* (°)

(i) Bonding contacts			
Cr(1)–C(1)	2·075 (4)	C(1)–N(1)	1·138 (6)
Cr(1)–C(2)	2·072 (4)	C(2)–N(2)	1·138 (6)
Cr(1)–C(3)	2·068 (4)	C(3)–N(3)	1·137 (6)
(ii) Angles			
C(1)–Cr(1)–C(2)	90·1 (2)	Cr(1)–C(1)–N(1)	178·5 (6)
C(1)–Cr(1)–C(3)	90·1 (2)	Cr(1)–C(2)–N(2)	179·5 (8)
C(2)–Cr(1)–C(3)	89·7 (2)	Cr(1)–C(3)–N(3)	177·6 (4)
(iii) Non-bonding contacts			
Cs(1)···N(2^{i})	3·208 (4)	K(1)···N(2^{iv})	2·855 (4)
Cs(1)···N(3)	3·379 (5)	K(1)···N(1^{v})	2·817 (4)
Cs(1)···N(3^{ii})	3·256 (4)	K(1)···N(3^{ii})	2·812 (4)
Cs(1)···N(1^{iii})	3·340 (4)		

Transformations of the asymmetric unit

(i) $x, 1+y, z$ (iv) $x, 1+y, 1+z$
(ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ (v) $x, y, 1+z$
(iii) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$

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