coplanar with 3—2—14—15 = 8·1 (3)°. The two phenyl rings make a dihedral angle of about 24° while the methylenedioxy group is coplanar with the attached phenyl ring. Least-squares enantiomorph refinement indicates a slight preference for the (4*R*,6a*S*) configuration; however, the statistics are not unequivocal.

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SHORT COMMUNICATION

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Single-crystal neutron diffraction of Cs₂KFe(CN)₆ at 4·2 K.

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Abstract

The structure of $Cs_2KFe(CN)_6$ at 4·2 K has been determined by a neutron diffraction study of single-crystal and powder samples. The unit cell is monoclinic, $P2_1/n$, with $a = 10.976\,(7)$, $b = 8.118\,(4)$, $c = 7.542\,(5)$ Å, $\beta = 90.71\,(1)°$, $Z = 2$. Corresponding to $R = 7.95\%$ for 307 reflections, the mean distances are Fe—C 1·93 (1) and C—N 1·15 (1) Å. The low-temperature structure does not differ essentially from the room-temperature configuration determined by X-ray diffraction.

Introduction

The salts $Cs_2LiM(CN)_6$ ($M = Cr$, Mn, Fe, Co, Ir) crystallize at high temperatures in the cubic elpasolite structure ($Fm3m$). On cooling, a first phase transformation produces a tetragonal structure (phase II) while a second leads to a monoclinic phase (III) with space group $P2_1/n$ (Swanson & Lucas, 1978). Two analogous salts, $Cs_2NaFe(CN)_6$ and $Cs_2KFe(CN)_6$, crystallize in the same monoclinic space group at room temperature (Fletcher & Gibb, 1977). A study of the optical properties of $Cs_2NaFe(CN)_6$, however, presented evidence that the symmetry of the room-temperature structure may be lower than monoclinic (Ryan, Smyth & Swanson, 1979). Our neutron diffraction study at 4·2 K was undertaken to investigate the possibility of a phase change occurring below room temperature.

Experimental

Suitable crystals of $Cs_2KFe(CN)_6$ were grown by cooling a saturated aqueous solution from 308 to 298 K. A crystal $2.5 \times 1.5 \times 1$ mm was oriented by precession photographs, sealed under He in a vanadium container, and placed on a two-axis spectrometer at the Saphir reactor in Würenlingen. The neutron wavelength was 1.050 ± 0.005 Å (graphite monochromator). Powder patterns of $Cs_2KFe(CN)_6$ and $Cs_2LiFe(CN)_6$ were recorded with a neutron wavelength of 2.346 ± 0.005 Å (graphite monochromator). The crystal was oriented with the reflections 202, 20$\bar{2}$, $\bar{2}$02, and $\bar{2}$0$\bar{2}$, *b* being perpendicular to the scattering plane. 307 unique reflections were measured with the θ–2θ scan technique by tilting the counter around the horizontal axis (111 *h0l*, 140 *h1l*, 56 *h2l*). 248 reflections had $I > \sigma(I)$. Typical peak half-widths were 0·3° (θ). No reflections disobeying the extinction rule *h0l*, $h + l \neq 2n$ were observed. Accurate lattice constants were determined from powder patterns (53 lines) recorded at 293 and 4·2 K, by profile analysis (Rietveld, 1969) based on the structural parameters given in Table 1. Structural calculations based on F^2 were performed with a local version of *ORFLS* (Busing, Martin & Levy, 1962). The following scattering lengths (in 10^{-11} mm) were taken from Koester (1977): C 0·665, N 0·936, K 0·371, Fe 0·954, Cs 0·542. Isotropic least-squares refinement with the results of Fletcher & Gibb (1977) as starting parameters gave a rather high R_w of 12·1%. Introduction of corrections for absorption and for primary and secondary extinction (Zachariasen, 1967) led to

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and isotropic temperature factors at* 4·2 K

	x	y	z	B (Å^2)
Fe	0	0	0	0·23 (5)
K	0	5000	5000	0·26 (12)
Cs	2522 (3)	4190 (17)	−273 (4)	0·31 (6)
C(1)	331 (3)	1270 (14)	−2088 (4)	0·37 (6)
C(2)	425 (3)	−2030 (16)	−1236 (4)	0·47 (6)
C(3)	1666 (2)	250 (14)	772 (3)	0·41 (5)
N(1)	560 (2)	2000 (10)	−3344 (3)	0·70 (4)
N(2)	697 (2)	−3200 (11)	−1996 (3)	0·60 (4)
N(3)	2669 (2)	430 (10)	1255 (2)	0·60 (4)

a significant improvement. The extinction parameters r and g were $1·90 \times 10^{-2}$ mm and $1·98 \times 10^3$ respectively. The final $R = 7·95\%$ and $R_w = 4·40\%$. The corresponding values for only those reflections with $I > \sigma$ were 4·24 and 4·34% respectively. The maximum shift-to-error ratio in the final cycle was 0·05. Table 1 lists the positional and thermal parameters.*

Results

The present neutron diffraction studies of both a single crystal and a powder sample show that $Cs_2KFe(CN)_6$ does not undergo a phase change in the range from 4·2 to 293 K. Qualitative evidence for the absence of phase transformations is furnished by the powder pattern which shows no additional lines upon cooling from room temperature to 4·2 K, in contrast to $Cs_2LiFe(CN)_6$. The new lines appearing at low temperatures in the powder pattern of the latter can be assigned to a cubic primitive cell but are also consistent with the proposed space groups (Ryan, Smyth & Swanson, 1979) for phase (II) ($220 < T < 170$ K, $P4/mnc$) and phase (III) ($T < 170$ K, $P2_1/n$). The 4·2 K structure of $Cs_2KFe(CN)_6$ is, within standard deviations, identical to the room-temperature X-ray structure (Fletcher & Gibb, 1977), corresponding to

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34756 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

N denotes the present 4·2 K neutron results, X the X-ray structure at room temperature (Fletcher & Gibb, 1977).

	N	X
Fe—C(1)	1·92 (1)	1·930 (11)
Fe—C(2)	1·96 (1)	1·924 (11)
Fe—C(3)	1·92 (1)	1·921 (11)
C(1)—N(1)	1·147 (9)	1·158 (16)
C(2)—N(2)	1·15 (1)	1·159 (17)
C(3)—N(3)	1·164 (7)	1·146 (16)
C(1)—Fe—C(2)	90·8 (5)	90·6 (5)
C(1)—Fe—C(3)	90·1 (3)	90·8 (5)
C(2)—Fe—C(3)	90·1 (3)	89·2 (5)
Fe—C(1)—N(1)	177·9 (6)	178·5 (11)
Fe—C(2)—N(2)	177·9 (6)	179·2 (11)
Fe—C(3)—N(3)	178·8 (8)	177·4 (11)

space group $P2_1/n$. The interatomic distances and angles (Table 2) prove that no essential distortions of the coordination unit occur on cooling the crystal from 293 to 4·2 K. The $Cs_2KFe(CN)_6$ structure may be considered to represent the general low-temperature structure of the elpasolite-related cyanides $Cs_2M^IM^{III}(CN)_6$.

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