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## Structure of ErFe(CN)<sub>6</sub>·4H<sub>2</sub>O

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**Abstract.** Erbium iron hexacyanide tetrahydrate,  $M_r = 452.28$ , orthorhombic,  $Cmcm$ ,  $a = 7.3212$  (6),  $b = 12.7576$  (8),  $c = 13.5636$  (9) Å,  $(3^{1/2}a/b) - 1 = -6.0$  (1)  $\times 10^{-3}$ ,  $V = 1266.9$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.367$ ,  $D_m = 2.333$  (5) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 77.8$  cm<sup>-1</sup>,  $F(000) = 848$ ,  $T = 295$  K,  $R = 0.020$  for 641 unique reflections. The structure of ErFe(CN)<sub>6</sub>·4H<sub>2</sub>O is of the SmFe(CN)<sub>6</sub>·4H<sub>2</sub>O type.

**Introduction.** Recently, Mullica, Perkins, Sappenfield & Leschnitzer (1989) reported on the determination of the structure of monoclinic ErFe(CN)<sub>6</sub>·4H<sub>2</sub>O. Some years ago we had ourselves (Hulliger, Landolt & Vetsch, 1976) investigated the rare-earth ferricyanides LnFe(CN)<sub>6</sub>·4H<sub>2</sub>O in powder form and assigned them the orthorhombic structure determined for SmFe(CN)<sub>6</sub>·4H<sub>2</sub>O by Kietaibl & Petter (1974). A controversy arose last year when Mullica, Perkins, Sappenfield & Grossie (1988) refined the structure of SmFe(CN)<sub>6</sub>·4H<sub>2</sub>O in the monoclinic space group  $P2_1/m$ . In our view this symmetry is too low and not compelled by the arrangement of the structural units [LnN<sub>6</sub>] and [FeC<sub>6</sub>]. Based on their own intensity data we disproved their space group assignment (Gramlich, Petter & Hulliger, 1990). We received support of our view from Marsh (1989) who independently came to the same conclusion. After we had deduced from the given lattice parameters (Gramlich, Petter & Hulliger, 1990) that Mullica's supposed ErFe(CN)<sub>6</sub>·4H<sub>2</sub>O crystal was in fact SmFe(CN)<sub>6</sub>·4H<sub>2</sub>O we decided to

start a complete structure determination on ErFe(CN)<sub>6</sub>·4H<sub>2</sub>O. Since in the meantime Mullica & Sappenfield (1989) transcribed their data for SmFe(CN)<sub>6</sub>·4H<sub>2</sub>O and SmCo(CN)<sub>6</sub>·4H<sub>2</sub>O to the orthorhombic space group  $Cmcm$  we abstain from presenting the detailed proof of the correctness of this space group by comparing the refinements in both  $P2_1/m$  and  $Cmcm$ .

**Experimental.** Single crystals were synthesized by the double-infusion technique (Huber, Hulliger & Vetsch, 1980). 1 M solutions of ErCl<sub>3</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> were infused at a speed of 0.1 ml h<sup>-1</sup> into 500 ml of a saturated aqueous solution of ErFe(CN)<sub>6</sub> kept at 335 K. Within three days small crystals grew on the walls of the growth vessel. The most perfect crystals (probably grown while floating on the surface) had the form of hexagonal plates of 0.1–0.3 mm edge length and were transparent red under the microscope. Their density was measured by the flotation method in a mixture of dibromomethane and *para*-xylene. The unit-cell dimensions of ErFe(CN)<sub>6</sub>·4H<sub>2</sub>O crystals of the same batch were derived from a Guinier powder pattern taken with Fe  $K\alpha_1$  radiation and silicon (assuming  $a = 5.43047$  Å) as calibration.

The X-ray diffraction measurements for the structure determination were performed on a Picker FACS-1 diffractometer with STOE software and encoders using monochromatic molybdenum  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation. We chose an optically perfect

crystal of dimensions  $0.06 \times 0.05 \times 0.08$  mm ( $\mu = 77.8$  cm<sup>-1</sup>). By the  $\omega/\theta$  scan method (learned profile version) we measured in four octants in the range  $2\theta = 6-43^\circ$  ( $h: 0-8, k: 0-15, l: 0-16$ ) 2686 reflections of which 124 reflections with intensities  $I < 2\sigma$  were finally omitted in the calculations (641 unique reflections). The intensities of three standard reflections, 400, 060 and 008, were checked every two hours revealing variations of less than 1%. The symmetry conditions were tested on equivalent reflections. Experimental absorption corrections were made with the empirical absorption correction program *EMPIR* revision 1.2 of the *XLS Structure Refinement Package* (Nicolet Instrument Corporation, 1988) based on  $\psi$  scans on 18 reflections with  $\chi > 60^\circ$  (maximum and minimum correction values 0.4318 and 0.6908). The structure refinement was calculated with the *SHELXTL-Plus* program of the same package. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No extinction corrections were applied. As starting parameters we used the values of  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ , neglecting the H atoms completely. The full-matrix least-squares refinement of 52 variables on  $F_{hkl}$  values yielded the reliability values  $R = 0.0202$ ,  $wR = 0.0221$ , goodness of fit = 1.33;  $w = [\sigma^2(F) + 0.0016F^2]^{-1}$ ; maximum shift/e.s.d. = 0.47. A difference Fourier map showed no additional peaks ( $\Delta\rho_{\text{max}} = 1.53$ ,  $\Delta\rho_{\text{min}} = -0.66$  e Å<sup>-3</sup>). The hydrogen atoms were thus not detectable.

**Discussion.** The resulting structure data are listed in Table 1. A projection of the structure is given in our preceding paper (Gramlich, Petter & Hulliger, 1990). The interatomic distances in  $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  are compiled in Table 2.\* In addition to the bonding distances we have also listed some longer distances that might be of interest, e.g. for a discussion of the geometrical arrangement or of the magnetic properties. The distances obtained are similar to those found in  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ . As can be deduced from Table 2 the oxygen atoms O2 only form hydrogen bridges to the O1 atoms of the coordinated  $\text{H}_2\text{O}$  molecules. Discussions of all the other structural details can be found in the publications cited above.

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\* Lists of the structure factors and the anisotropic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53076 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positions and thermal parameters* ( $\text{\AA}^2 \times 10^2$ ) of  $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  at 295 K

Estimated statistical standard deviations of the last figures are added in parentheses.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	Site	x	y	z	$U_{eq}$
Er	4(c)	0	0.3234 (1)	$\frac{1}{4}$	1.0 (2)
Fe	4(a)	0	0	0	1.0 (2)
Cl	16(h)	0.3112 (5)	0.4517 (3)	0.0900 (3)	1.9 (3)
C2	8(f)	0	0.1366 (5)	0.0602 (4)	1.6 (4)
N1	16(h)	0.1987 (5)	0.4208 (2)	0.1417 (3)	2.4 (4)
N2	8(f)	0	0.2179 (4)	0.1004 (3)	2.4 (4)
O1	8(g)	0.2593 (5)	0.2190 (3)	$\frac{1}{4}$	3.3 (4)
O2	8(f)	0	0.6561 (4)	0.0997 (4)	3.3 (5)

Table 2. *Interatomic distances* ( $\text{\AA}$ ) and *bond angles* ( $^\circ$ ) in  $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$

Uncertainties of the last digits (estimated standard deviations) are added in parentheses.

Er—2O1	2.319 (4)	N1—1C1	1.151 (5)
4N1	2.412 (4)	1Er	2.412 (4)
2N2	2.435 (5)	1N1	2.909 (6)
4O2	4.702 (4)	1N1	2.938 (6)
2O2	4.709 (5)	1O1	2.997 (5)
2O2	4.750 (6)	1N2	3.022 (6)
Fe—2C2	1.925 (7)	N2—1C2	1.172 (8)
4C1	1.944 (4)	1Er	2.435 (5)
2Er	5.3405 (9)	2O1	2.779 (4)
4Er	5.4749 (8)	2N2	3.022 (6)
2Fe	6.7818 (5)	O1—1Er	2.319 (4)
2Fe	7.3212 (6)	2N2	2.779 (4)
4Fe	7.3545 (5)	2O2	2.812 (5)
Cl—1N1	1.151 (5)	2N2	2.997 (5)
1Fe	1.944 (4)	1O1	3.524 (6)
1C2	2.707 (7)	1O1	3.797 (5)
1C1	2.735 (6)	O2—2O1	2.812 (5)
1C2	2.764 (7)	1N2	3.154 (7)
1C1	2.765 (5)	2N1	3.384 (6)
1O2	3.465 (6)	1C2	3.420 (8)
C2—1N2	1.172 (8)	2C1	3.465 (6)
1Fe	1.925 (7)	1O2	4.077 (8)
2C1	2.707 (7)		
2C1	2.764 (7)		
2O1	3.367 (5)		
1O2	3.420 (8)		
O1—Er—O1	109.9 (2)	C2—Fe—C2	180.0 (2)
N1—Er—N1	118.0 (1)	Cl—Fe—C2	91.2 (2)
	74.2 (1)		88.8 (2)
	75.0 (1)	Fe—Cl—N1	178.2 (4)
N1—Er—N2	142.4 (1)	Fe—C2—N2	177.4 (5)
	77.1 (1)	Er—N1—C1	168.2 (3)
N2—Er—N2	112.9 (2)	Er—N2—C2	151.3 (4)
Cl—Fe—Cl	180.0 (2)		
	89.4 (2)		
	90.6 (2)		

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## Structure of $\text{LaCr}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$

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**Abstract.** Lanthanum chromium hexacyanide pentahydrate,  $M_r = 437.09$ , hexagonal,  $P6_3/m$ ,  $a = 7.7053$  (4),  $c = 14.8155$  (9) Å,  $V = 761.8$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.909$  (8),  $D_m = 1.897$  (4) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 34.9$  cm<sup>-1</sup>,  $F(000) = 398$ ,  $T = 295$  K, final  $R = 0.024$  for 430 unique reflections. The structure is of the  $\text{LaFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$  type. The La atom is nine coordinated by six N atoms, forming a trigonal prism, and three H<sub>2</sub>O molecules in the equatorial plane of the N prism. The Cr atom is located at the center of a C octahedron. Two uncoordinated H<sub>2</sub>O molecules occupy holes above and below the triangular N prism faces. Bonding distances are: La—N 2.619 (5), La—O 2.591 (5), Cr—C 2.065 (4), C—N 1.138 (6) Å.

**Introduction.** Some years ago we reported on the synthesis of the series  $\text{LnCr}(\text{CN})_6 \cdot n\text{H}_2\text{O}$  (Ln = La–Lu, Y;  $n = 4$  or 5) (Hulliger, Landolt & Vetsch, 1976). These compounds are of some theoretical interest due to their relatively high magnetic ordering temperatures (11.7 K in the case of the Tb compound). The hexagonal modification with five water molecules per formula unit ( $n = 5$ ) is stable at room temperature only with the larger rare-earth elements while from Ln = Sm through to Lu the orthorhombic modification with four water molecules ( $n = 4$ ) is formed, in analogy to the corresponding iron and cobalt compounds (orthorhombic structure, see Petter, Gramlich & Hulliger, 1989; Mullica & Sappenfield, 1989). Based on the similarity of their X-ray powder diffraction patterns with those of the iron and cobalt analogs we assigned to them the same crystal structures. To place our assignment for the whole series on safer ground we decided to carry out a full structure determination for one representative of each modification. In the following we report the data obtained for hexagonal  $\text{LaCr}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ .

**Experimental.** As starting materials for the synthesis of  $\text{LaCr}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$  we used purified  $\text{K}_3\text{Cr}(\text{CN})_6$ , prepared according to Brauer (1981) from  $\text{CrO}_3$  (p. A., Fluka, Buchs), and  $\text{LaCl}_3$  prepared from  $\text{La}_2\text{O}_3$  (4N; Research Chemicals, Phoenix, AZ) and hydrochloric acid. The growth procedure is as follows. A 1–2 M neutral aqueous solution of  $\text{LaCl}_3$  is added to an equal volume of clear, light yellow 1 M  $\text{K}_3\text{Cr}(\text{CN})_6$  solution saturated at room temperature. After keeping the mixture in the dark at room temperature for 1–2 days small crystals can be filtered from the solution. High-quality crystals can be obtained only if the growth proceeds very slowly. The crystallization time, however, is limited by the gradual decomposition of  $\text{K}_3\text{Cr}(\text{CN})_6$  to  $\text{Cr}(\text{OH})_3$ . The resulting crystals of size 0.1–1 mm have the shape of squat hexagonal prisms, in most cases with pyramids on both ends. Their density was measured by the flotation method in a mixture of *para*-xylene and bromoform. The water content was checked by thermogravimetric measurements to be 4.9 (2) H<sub>2</sub>O per formula unit. The unit-cell dimensions of  $\text{LaCr}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$  crystals of the same batch were derived from a Guinier powder pattern taken with Fe  $K\alpha_1$  radiation and silicon (assuming  $a = 5.43047$  Å) as internal calibration. For the structure determination a small, nearly spherical and optically perfect crystal with edge length 0.04 mm and height 0.05 mm was chosen.

The X-ray diffraction measurements for the structure determination were performed on a Picker FACS-1 diffractometer with STOE software and encoders using monochromatic molybdenum  $K\alpha$  radiation. By the  $\omega/\theta$  scan method (learned profile version) we measured in four octants in the range  $2\theta = 3$ – $50^\circ$  (range of  $h, k, l$ :  $-7$ – $0, 0$ – $9, 0$ – $17$ ) 2377 reflections of which 40 reflections with intensities  $I < 2\sigma$  were finally omitted in the calculations (430