

SHORT COMMUNICATIONS

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Acta Cryst. (1990). **C46**, 724–726

The space group of the structure of $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and its analogs $\text{LnT}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm} \cdots \text{Lu}$, $T = \text{Fe}, \text{Cr}, \text{Co}$). By V. GRAMLICH and W. PETTER, *Institut für Kristallographie und Petrographie, ETH, CH-8092 Zürich, Switzerland* and F. HULLIGER, *Laboratorium für Festkörperphysik, ETH, CH-8093 Zürich, Switzerland*

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Abstract

Based on relationships between the site parameters and the given structure factors, the structure reported for ' $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ ' [which almost certainly was $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$] is shown to be orthorhombic rather than monoclinic as claimed by Mullica, Perkins, Sappenfield & Leschnitzer [*Acta Cryst.* (1989), **C45**, 330–331]. Since no line splitting was detectable on the diffraction patterns of its analogs it is highly probable that their structures are also orthorhombic.

A couple of years ago we synthesized the rare-earth ferri-, cobalti- and chromicyanides which, with the heavier rare-earth elements, all crystallize with four water molecules per formula unit, $\text{LnT}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ (Hulliger, Landolt & Vetsch, 1976). Based on the Guinier patterns and intensity calculations with *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) we assigned the orthorhombic $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ structure to all these compounds. This structure type (space group *Cmcm*) had been determined on single crystals by Kietaihl & Petter (1974), but the structural details remained unpublished. In order to compensate for this lack and to characterize the orthorhombic arrangement we included a projection of this structure in our first publication.

Some time ago, the orthorhombic space group *Cmcm* was questioned by Mullica, Perkins, Sappenfield & Grossie (1988). These authors interpreted their own single-crystal diffraction measurements on $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ with the monoclinic space group $P2_1/m$. In a reply (Petter, Gramlich & Hulliger, 1989) we showed up their error and pointed out various possibilities for an incorrect choice of a monoclinic unit cell. In their latest structure determination on $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, Mullica, Perkins, Sappenfield & Leschnitzer (1989) have indeed chosen another monoclinic cell. The following is to discard this possibility and to prove the correctness of our orthorhombic structure assignment.

In Fig. 1 we show the relationship between the monoclinic cell (a_m, b_m, c_m, β) chosen by Mullica *et al.* (1989) and our orthorhombic cell (a_{or}, b_{or}, c_{or}). In a first step we

transcribe the monoclinic coordinates to the (twice as large) cell that will finally turn out to be orthorhombic:

$$x' = \frac{1}{2} + x_m/2 - z_m, y' = \frac{1}{2} - x_m/2, z' = y_m.$$

The resulting data are listed in the upper part of Table 1. It is easily seen that within the given experimental inaccuracies we can proceed to the orthorhombic cell, analogous to the one derived by Kietaihl & Petter (1974) for $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$.

As a further confirmation of the orthorhombic space group we present in Table 2 a reinterpretation of the data of Mullica *et al.* (1989) that clearly demonstrates the correctness of our assignments.

While preparing the present paper we became aware of a recent debate, concerning the same problem. Marsh (1989a) reported on the incorrect monoclinic space group of the isostructural $\text{BiFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and confirmed the

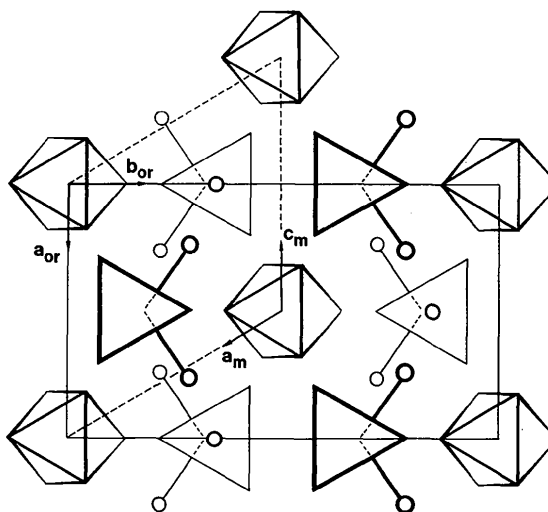


Fig. 1. An *ab* projection of the structure of $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ showing the relationship between the monoclinic cell (a_m, b_m, c_m, β) chosen by Mullica *et al.* (1989) and the true orthorhombic unit cell (a_{or}, b_{or}, c_{or}).

Table 1. Transcription of the monoclinic data of Mullica *et al.* (1989) to the twice as large cell (upper part) and final parameters (lower part)

	x'	y'	z'	Symmetry operations
'Er'	0.0005 (10)	0.32353 (3)	$\frac{1}{4}$	x, y, z
Fe	0	0	$\frac{1}{2}$	$x, y, \frac{1}{2} - z$
C(1)	0.3154 (14)	0.4534 (5)	0.4105 (5)	$x, y, \frac{1}{2} - z$
C(3)	-0.3158 (14)	0.4534 (5)	0.4114 (5)	$-x, y, \frac{1}{2} - z$
C(2)	0.0000 (13)	0.1362 (5)	0.4404 (5)	$x, y, \frac{1}{2} - z$
N(1)	0.2032 (12)	0.4242 (4)	0.3608 (5)	$x, y, \frac{1}{2} - z$
N(3)	-0.2039 (12)	0.4246 (4)	0.3608 (5)	$-x, y, \frac{1}{2} - z$
N(2)	0.0006 (13)	0.2160 (4)	0.4036 (4)	$x, y, \frac{1}{2} - z$
O(2)	-0.2645 (15)	0.2155 (5)	$\frac{1}{4}$	$-x, y, z$
O(3)	0.2660 (15)	0.2150 (5)	$\frac{1}{4}$	x, y, z
O(1)	-0.0008 (13)	0.3447 (4)	0.5999 (4)	$x, -y, z - \frac{1}{2}$

Final orthorhombic site parameters				
'Er'	4(c)	0	0.32353 (3)	$\frac{1}{4}$
Fe	4(a)	0	0	0
C(1)	16(h)	0.3156 (9)	0.4534 (4)	0.0891 (4)
C(2)	8(f)	0	0.1362 (5)	0.0596 (5)
N(1)	16(h)	0.2035 (9)	0.4244 (3)	0.1392 (4)
N(2)	8(f)	0	0.2161 (3)	0.0964 (4)
O(1)	8(g)	0.2653 (12)	0.2152 (4)	$\frac{1}{4}$
O(2)	8(f)	0	0.6553 (4)	0.0999 (4)

The symmetry operations transform the x', y', z' coordinates into the orthorhombic standard coordinates used for $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ (Petter, Gramlich & Hulliger, 1989).

$$a' = 7.435 (2), b' = 12.868 (3), c' = 13.729 (2) \text{ \AA}, \gamma = 90.00 (3)^\circ.$$

$$a = 7.435 (2), b = 12.868 (3), c = 13.729 (2) \text{ \AA},$$

$$(3^{1/2}a/b - 1) = +8 (5) \times 10^{-4}.$$

orthorhombic one. Mullica & Sappenfield (1989) justified their monoclinic assignment with a better R value and a Hamilton significance test which, formally, strongly rejected the orthorhombic symmetry. However, Hamilton (1965) himself recommended great care in case of systematic errors: 'Statistical tests demand the assumption of random errors in the data, and systematic errors can lead one to make gross errors in the application of hypothesis tests' (end of p. 606). Since the coordinates obtained by the monoclinic refinements do not significantly deviate from the corresponding orthorhombic values, the Hamilton test may alternatively be interpreted in the way that the hypothesis of a completely successful absorption correction has to be rejected.

One discrepancy is left, nevertheless. The orthorhombic unit cell that we derive for $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ from Mullica's data (Table 1) is considerably larger than the one that we published in our previous work. It is, however, conspicuously similar to the one we found for $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ [$a = 7.433 (3)$, $b = 12.875 (4)$, $c = 13.730 (5) \text{ \AA}$]. Since the orthorhombic distortion ($3^{1/2}a/b - 1$) varies characteristically within the rare-earth series we dare speculate - based on Figs. 3 and 4 of our first report (Hulliger *et al.*, 1976), as summarized in Fig. 2 of the present paper - that the so called $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ single crystal was in fact an $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ crystal from an earlier batch, but certainly not the Er analog. Our conjecture also follows from the monoclinic setting of Mullica *et al.* (1989). If we transform the ' $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ ' monoclinic cell into the unit cell used by Mullica *et al.* (1988) for $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ we obtain nearly coinciding values for a , b , c , β [$a = 7.431 (4)$, $b = 13.729 (2)$, $c = 7.431 (1) \text{ \AA}$, $\beta =$

$119.96 (9)^\circ$, as compared with $a = 7.431 (1)$, $b = 13.724 (3)$, $c = 7.429 (2) \text{ \AA}$, $\beta = 119.95 (1)^\circ$ given by Mullica *et al.* (1988) for $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$] as well as for the x, y, z parameters. Since the $[\text{LnN}_6]$ trigonal prisms are shrinking while the $[\text{FeC}_6]$ octahedra remain unchanged we expect not only a smaller unit cell but also slightly different atomic site parameters. As a consequence, the given Ln—N bond distances are fairly similar for both $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and ' $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ ':

$$\text{Sm—N} = 2.488 (6), 2.501 (6), 2.518 (6) \text{ \AA} \rightarrow \text{av. } 2.502 (15) \text{ \AA}$$

$$\text{'Er'—N} = 2.505 (4), 2.511 (4), 2.522 (4) \text{ \AA} \rightarrow \text{av. } 2.513 (7) \text{ \AA}$$

The average distances differ by 0.011 \AA , which means they are equal within the experimental accuracy, whereas the covalent as well as the ionic radii of Sm and Er (Shannon, 1976) differ by roughly 0.07 \AA (Sm: 1.098 and 0.958 \AA , Er: 1.030 and 0.890 \AA , respectively).

Whatever is the case, it is highly improbable that the structures of the tetrahydrates $\text{LnT}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ ($T = \text{Cr}, \text{Fe}, \text{Co}$) are monoclinic (rather than orthorhombic, as we assumed) since a careful inspection of their powder diffraction patterns did not reveal any line splittings. However, as Mullica *et al.* (1989) stated, $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ is isotopic with $\text{BiFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ that we recently confirmed to be orthorhombic too (Petter, Dommann, Vetsch & Hulliger, 1989).

The loss of one water molecule in the $\text{LnT}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ series on going from the large Ln ions La^{3+} , $\text{Ce}^{3+} \dots (n = 5)$ to the smaller ones, Sm^{3+} , $\text{Gd}^{3+} \dots (n = 4)$ gives rise to a symmetry reduction of the coordination polyhedra around the rare-earth ions from trigonal, $[\text{LnN}_6\text{O}_3]$, to orthorhombic, $[\text{LnN}_6\text{O}_2]$. These reduced units are distinctly

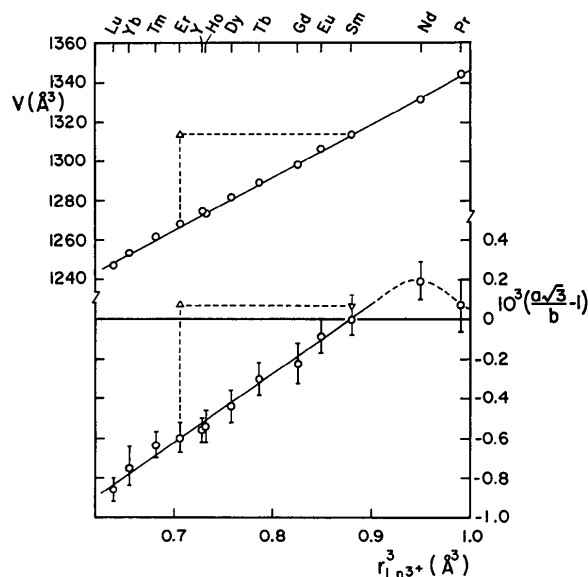


Fig. 2. Unit-cell volume and orthorhombic distortion ($3^{1/2}a/b - 1$) vs cube of the Ln^{3+} ionic radii for the rare-earth representatives of the $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ structure type. Triangles indicate data due to Mullica *et al.* (1988) (∇) and (1989) (Δ) after transformation of their monoclinic cells.

Table 2. Comparison of the diffraction data for the monoclinic (*m*) and the orthorhombic (*or*) cell of $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$. The Guinier diffraction pattern calculated for Cu $K\alpha$ radiation for the monoclinic cell is listed in the left-hand part, the corresponding data for the orthorhombic cell are given in the right-hand part. The middle part contains the observed and calculated structure factors of Mullica *et al.* (1989) assigned to the monoclinic cell

$$h_{or} = |l_m|, k_{or} = 2h_m + l_m, l_{or} = k_m.$$

$4\theta_m$	h_m	k_m	l_m	Intensity	$10 F_{obs}$	$10 F_{calc}$	$(10\sigma F)$	$4\theta_{or}$	h_{or}	k_{or}	l_{or}	Intensity
25.79	0	2	0	218	607	655	(25)	25.79	0	0	2	219
27.51	1	0	1	0.5	0*	33	(96)	27.51	1	1	0	1
27.51	0	0	1	0.6	0*	34	(101)					
27.53	1	0	0	34	279	268	(34)	27.53	0	2	0	34
30.40	1	1	1	1000	1113	1186	(25)	30.40	1	1	1	2000
30.40	0	1	1	998	1111	1186	(25)					
30.41	1	1	0	750	971	1029	(25)	30.42	0	2	1	751
37.80	1	2	1	611	1186	1176	(28)	37.80	1	1	2	1225
37.80	0	2	1	613	1216	1179	(28)					
37.81	1	2	0	910	1470	1429	(28)	37.81	0	2	2	910
47.71	1	3	1	243	940	938	(32)	47.71	1	1	3	487
47.71	0	3	1	244	921	938	(32)					
47.72	1	3	0	251	941	950	(32)	47.72	0	2	3	251
47.87	1	0	2	280	1411	1434	(31)	47.87	2	0	0	281
47.90	2	0	1	386	1657	1666	(31)	47.90	1	3	0	773
47.90	1	0	1	386	1662	1666	(31)					
49.62	1	1	2	0	0*	2	(135)	49.62	2	0	1	extincted
49.65	2	1	1	17	262	257	(47)	49.65	1	3	1	34
49.65	1	1	1	17	258	256	(47)					
51.92	0	4	0	95	889	920	(33)	51.92	0	0	4	95
54.56	1	2	2	15	0*	267	(145)	54.56	2	0	2	15
54.58	2	2	1	126	711	752	(35)	54.59	1	3	2	251
54.59	1	2	1	125	688	749	(35)					
55.43	2	0	2	57	735	732	(35)	55.43	2	2	0	114
55.43	0	0	2	57	735	736	(35)					
55.46	2	0	0	0.3	0*	76	(?)	55.46	0	4	0	0.2
56.96	2	1	2	51	458	518	(40)	56.96	2	2	1	101
56.96	0	1	2	51	466	517	(39)					
56.99	2	1	0	15	145	295	(72)	56.99	0	4	1	14
58.98	1	4	1	0	0*	30	(143)	58.98	1	1	4	0.0
58.98	0	4	1	0	108*	32	(90)					
58.99	1	4	0	81	690	655	(36)	58.99	0	2	4	81
61.35	2	2	2	90	725	764	(37)	61.35	2	2	2	180
61.35	0	2	2	89	727	760	(37)					
61.38	2	2	0	46	566	550	(38)	61.38	0	4	2	46
61.98	1	3	2	0.0	0*	5	(139)	61.98	2	0	3	extincted
62.00	2	3	1	0.1	0*	30	(121)	62.01	1	3	3	0.2
62.01	1	3	1	0.2	63*	33	(133)					
68.10	2	3	2	346	1671	1588	(37)	68.10	2	2	3	691
68.10	0	3	2	344	1649	1583	(37)					
68.13	2	3	0	362	1635	1632	(37)	68.13	0	4	3	362

*These reflections were considered unobserved in the structure refinement of Mullica *et al.* (1989).

rotated with respect to the hexagonal $\text{LaFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ structure (Bailey, Williams & Milligan, 1973) to attain an overall orthorhombic arrangement, and there is no physical reason for tiny atomic shifts which destroy the symmetry plane (Fig. 1).

Note: After submitting our manuscript we received notice of a paper by Marsh (1989b) who came to the same conclusion as regards the space group. His Table 1 corresponds to the second part of our Table 1 after trivial transformations.

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