

The Structure of $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and the Problem of Pseudo-hexagonal Symmetry

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Based on relations between the monoclinic site parameters as well as on the structure factors of a published structure determination, the symmetry of the pseudo-hexagonal $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ structure is shown to be orthorhombic, $Cmcm$, rather than monoclinic, $P2_1/m$. © 1989 Academic Press, Inc.

In the early seventies we started an investigation of the rare-earth ferricyanides (1). Our interest, originally, was focused on the cubic ferrimagnetic insulators like $\text{Ni}_3[\text{Mn}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$, $\text{Co}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$, etc. (2, 3). Later, we observed that crystals of the rare-earth ferricyanides appeared to grow much more easily than those of the mixed transition-element cyanides. It was, however, a magnetic hysteresis loop observed at 1.5 K on $\text{SmFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ that definitely aroused our interest in this compound family. Discrepancies in the low-temperature specific-heat data of $\text{PrCo}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ (4) pointed to variable H_2O contents ($n = 4$ or 5) depending on preparation. With smaller Ln ions only the tetrahydrates appear to be stable. The ferri- and chromicyanides are antiferromagnetic or ferrimagnetic with ordering tempera-

tures up to 11.7 K (in $\text{TbCr}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$) (5).

The structures of both forms were worked out by Kietaihl and Petter (6) on single crystals of $\text{LaFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ and $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$. For the pentahydrate the hexagonal structure described by Bailey *et al.* (7) was confirmed, while an orthorhombic structure was found for the tetrahydrate. In both structures the transition elements are octahedrally coordinated by 6 C atoms. The CN units point radially away from the central metal atom. The rare-earth cations are surrounded by 6 N atoms at the apices of a trigonal prism and by 3 (2) additional O atoms (of the hydrate molecules) lying in the equatorial plane outside the prism faces.

Kietaihl and Petter presented their crystallographic data at a meeting of the Swiss

Physical Society and published the abstract without the numerical data (6). These data, however, were used to draw Fig. 2 in Ref. (5), where the coordination of the rare-earth atom is clearly recognizable.

Based on the orthorhombic prototype $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ we determined the unit cells of all the other tetrahydrates $\text{LnT}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ with $T = \text{Cr, Fe, Co}$. It turned out that our prototype is just the representative with the smallest orthorhombic distortion, $(a\sqrt{3}/b - 1) \approx 0$, while $\text{LuCr}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ is the one with the largest distortion, $(a\sqrt{3}/b - 1) \approx -0.012$ (5). The powder pattern of $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ indeed looks hexagonal, although in the (a, b) projection of its structure the orthorhombic symmetry is evident.

Mullica *et al.* (8) argued that the hexagonal-to-orthorhombic change should occur at Gd or Tb where the f -orbitals are half filled. (However, do $4f$ electrons influence a room-temperature structure?) Therefore they reexamined the structure of $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$. Unfortunately on transforming the pseudo-hexagonal to the orthorhombic cell they chose an inappropriate setting, one that shows no symme-

tries in conventional directions (the hkl and $\bar{h}kl$ reflections of the chosen setting were nonequivalent). As a consequence they used a monoclinic cell for the structure refinement.

There is a notorious danger of ignoring the orthorhombic symmetry of pseudo-hexagonal structures. Figure 1 shows such an example. It might be possible that during an automatic search in single-crystal diffractometry the inappropriate setting $\mathbf{A}_{\text{in}}, \mathbf{B}_{\text{in}}$ is chosen. Although the metric tensor may be very nearly orthorhombic deviations from standard orthorhombic Laue symmetry can of course be substantial in this setting and an uncritical interpretation of such a situation may lead to the conclusion that the considered structure cannot be orthorhombic. If the monoclinic setting \mathbf{a}_m and \mathbf{b}_m is then chosen the lengths of these axes will not be significantly different—an important hint for the crystallographer to look for higher symmetry. The detection of the higher symmetry is less straightforward if a different monoclinic cell was chosen, for example, with $\mathbf{a}'_m = \mathbf{a}_m + \mathbf{c}_m$ and $\mathbf{c}'_m = -\mathbf{a}_m$. For a general discussion of this symmetry problem compare (9).

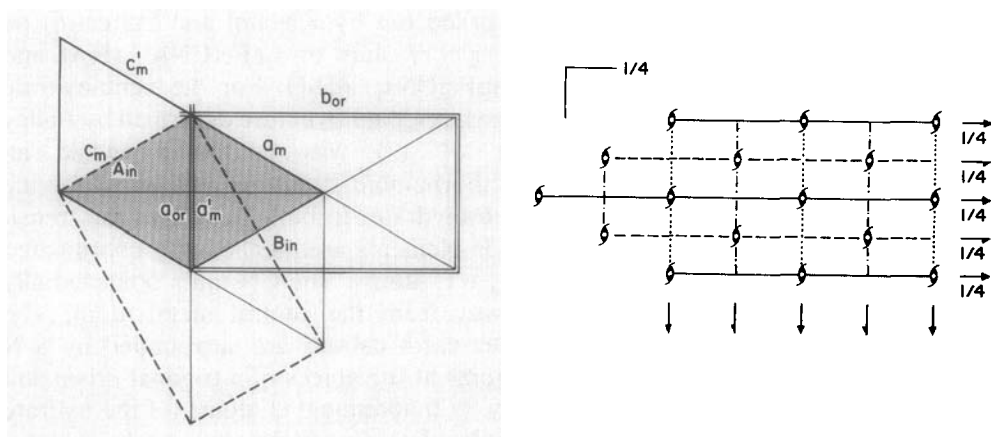


FIG. 1. Various possibilities for cells with lower symmetry when starting from a hexagonal structure (stippled cell): orthorhombic ($\mathbf{a}_{\text{or}}, \mathbf{b}_{\text{or}}$ or $\mathbf{A}_{\text{in}}, \mathbf{B}_{\text{in}}$) and monoclinic ($\mathbf{a}_m, \mathbf{c}_m$ and $\mathbf{a}'_m, \mathbf{c}'_m$). The conventional, symmetry-adapted setting for the symmetry operations defined in the right-hand part is $\mathbf{a}_{\text{or}}, \mathbf{b}_{\text{or}}$, whereas the other orthorhombic cell ($\mathbf{A}_{\text{in}}, \mathbf{B}_{\text{in}}$) as well as the monoclinic cells are inappropriate.

TABLE I

THE CRYSTAL-STRUCTURE DATA OF $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ AS DESCRIBED BY MULLICA *ET AL.* (8) IN THE MONOCLINIC CELL ($a_m, b_m, c_m; x_m, y_m, z_m$) AND IN THE TWICE AS LARGE C-CENTERED CELL ($A, B, C; X, Y, Z$)

Space group $P2_1/m$ (No. 11)

$a_m = 7.431(1)$, $b_m = 13.724(3)$, $c_m = 7.429(2)$ Å, $\beta = 119.95(1)^\circ$

Atom		x_m	y_m	z_m
Sm	2e	0.3235(6)	$\frac{1}{4}$	0.6765(6)
Fe	2a	0	0	0
C1	4f	0.2302(9)	0.5894(6)	0.1364(9)
C2	4f	0.1373(9)	0.4108(5)	0.2315(9)
C3	4f	-0.1370(9)	0.5592(5)	0.1349(9)
N1	4f	0.6255(8)	0.3598(5)	0.7771(8)
N2	4f	0.2206(8)	0.3600(5)	0.3721(8)
N3	4f	0.2177(8)	0.4035(5)	0.7849(8)
O1	4f	0.6568(7)	0.4005(4)	0.3462(8)
O2	2e	0.480(1)	$\frac{1}{4}$	0.048(1)
O3	2e	-0.048(1)	$\frac{1}{4}$	0.520(1)

Space group $C 1 1 2_1/m$

$\mathbf{A} = \mathbf{a}_m + \mathbf{c}_m$ $A = 7.436(2)$ Å $X = \frac{1}{2}(x_m + z_m)$

$\mathbf{B} = \mathbf{a}_m - \mathbf{c}_m$ $B = 12.866(3)$ Å $Y = \frac{1}{2}(x_m - z_m)$

$\mathbf{C} = \mathbf{b}_m$ $C = 13.724(3)$ Å $Z = y_m$

$\gamma = \angle(\mathbf{A}, \mathbf{B})$ $\gamma = 89.98(2)^\circ$

Atom	X	Y	Z	Symp. op. ^a	b
Sm	0.5000(6)	-0.1765(6)	$\frac{1}{4}$	$X - \frac{1}{2}, Y + \frac{1}{2}, Z$	Sm
Fe	0	0	0	X, Y, Z	Fe
C1	0.1833(9)	0.0469(9)	0.5894(6)	$\frac{1}{2} - X, \frac{1}{2} - Y, Z - \frac{1}{2}$	C1
C2	0.1844(9)	-0.0471(9)	0.4108(5)	$\frac{1}{2} - X, \frac{1}{2} + Y, \frac{1}{2} - Z$	C1
C3	-0.0011(10)	-0.1360(9)	0.5592(5)	$X, -Y, Z - \frac{1}{2}$	C2
N1	0.7013(8)	-0.0758(8)	0.3598(5)	$X - \frac{1}{2}, \frac{1}{2} + Y, \frac{1}{2} - Z$	N1
N2	0.2964(9)	-0.0758(9)	0.3600(5)	$\frac{1}{2} - X, \frac{1}{2} + Y, \frac{1}{2} - Z$	N1
N3	0.5013(8)	-0.2836(8)	0.4035(5)	$\frac{1}{2} - X, \frac{1}{2} + Y, \frac{1}{2} - Z$	N2
O1	0.5015(8)	0.1553(8)	0.4005(4)	$\frac{1}{2} - X, \frac{1}{2} + Y, \frac{1}{2} - Z$	O2
O2	0.264(1)	0.216(1)	$\frac{1}{4}$	X, Y, Z	O1
O3	0.236(1)	-0.284(1)	$\frac{1}{4}$	$\frac{1}{2} - X, \frac{1}{2} + Y, Z$	O1

^a $Cmcm$ symmetry operations [10] transforming the X, Y, Z coordinates into the standard coordinates of Table III.

^b Corresponding designation of the atoms in Table III.

In order to prove the correctness of the orthorhombic space group $Cmcm$ introduced by Kietaihl and Petter (6) we discuss in the following the data of Mullica *et al.* (8) reproduced in Table I. A first glance already reveals that the structure is at least pseudo-orthorhombic: $a_m - c_m = 0.002(3)$

Å. Moreover, within (or virtually within) the assumed experimental errors Sm, C3, N3, and O1 lie in the diagonal plane (101) since for these atoms $x_m + z_m = 1.00010(12)$, $-0.0021(18)$, $1.0026(16)$, and $1.0030(15)$, respectively. Furthermore, the diagonal plane (101) obviously is a mirror

TABLE II

THE CRYSTALLOGRAPHIC DATA OF KIETAIBL AND PETTER (6) FOR $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, SPACE GROUP $Cmcm$ (NO. 63) (LEFT-HAND PART), IN COMPARISON WITH THE DATA OF MULLICA *ET AL.* (8) AFTER TRANSFORMATION TO THE ORTHORHOMBIC CELL (RIGHT-HAND PART)

Atom site		x	y	z	x	y	z
Sm	4c	0	0.3236(1)	$\frac{1}{4}$	0	0.3235(6)	$\frac{1}{4}$
Fe	4a	0	0	0	0	0	0
C1	16h	0.3159(3)	0.4532(2)	0.0888(2)	0.3161(9)	0.4530(9)	0.0893(6)
C2	8f	0	0.1357(3)	0.0592(2)	0	0.1360(9)	0.0592(5)
N1	16h	0.2024(3)	0.4244(2)	0.1398(2)	0.2025(9)	0.4242(9)	0.1401(6)
N2	8f	0	0.2161(3)	0.0956(2)	0	0.2164(8)	0.0965(5)
O1	8g	0.2634(5)	0.2153(3)	$\frac{1}{4}$	0.264(1)	0.216(1)	$\frac{1}{4}$
O2	8f	0	0.6558(3)	0.0999(2)	0	0.6553(8)	0.0995(4)
		$a = 7.433(3) \text{ \AA} (5)$			$a = 7.436(2) \text{ \AA}$		
		$b = 12.875(4) = \sqrt{3} \times 7.433 \text{ \AA}$			$b = 12.866(3) = \sqrt{3} \times 7.428 \text{ \AA}$		
		$c = 13.730(5) \text{ \AA}$			$c = 13.724(3) \text{ \AA}$		

plane: The relations

$$x_m(\text{O2}) = -z_m(\text{O3}); \quad y_m(\text{O2}) = y_m(\text{O3}); \\ z_m(\text{O2}) = -x_m(\text{O3})$$

for the oxygen atoms hold exactly, while for the nitrogen atoms we have

$$x_m(\text{N1}) + z_m(\text{N2}) = 0.9976(16) \\ y_m(\text{N1}) - y_m(\text{N2}) = -0.0002(10) \\ z_m(\text{N1}) + x_m(\text{N2}) = 0.9977(16).$$

For the carbon atoms C1 and C2 the correspondence is recognizable only after the transformation $C2 \rightarrow C2' = -x_{m2}, y_{m2}, -z_{m2}$:

$$x_m(\text{C1}) - z_m(\text{C2}') = -0.0013(18) \\ y_m(\text{C1}) + y_m(\text{C2}) = 1.0002(11) \\ z_m(\text{C1}) - x_m(\text{C2}) = -0.0013(18).$$

Our argumentations are summed up in Tables I and II. The former gives first the crystal structure data of Mullica *et al.*, then the data transformed to the appropriate doubled cell. We emphasize that the angle γ in this new cell differs at the outmost by one standard deviation from 90° (corre-

sponding to the fact that a_m and c_m of Mullica *et al.* are not significantly different). Thus we are entitled to put $\gamma = 90^\circ$, i.e., to describe the structure in the orthorhombic space group $Cmcm$. The resulting averaged standardized orthorhombic coordinates are listed in Table II. The average deviation of the monoclinic coordinates from the corresponding orthorhombic coordinates is 0.6 standard deviations (0.6σ) with a maximum deviation of 1.9σ at $X(\text{O1})$. This analysis of the structure data of Mullica *et al.* shows that the deviation of their structure from orthorhombic symmetry is not significant since all differences are smaller than 3σ .

In order to support our deductions we list in Table III the low-angle part of the diffraction pattern with the corresponding single-crystal data of Mullica *et al.* (8) and our orthorhombic assignments. The diffraction angles calculated from the monoclinic cell appear generally in groups of three almost equal θ values. Two of them are evidently symmetry equivalent as shown by the given orthorhombic transformation. As is to be expected the observed F values for h_m, k_m, l_m and l_m, k_m, h_m pairs differ in a few cases by slightly more than the standard devia-

TABLE III

DIFFRACTION DATA FOR $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ SIMULATED FOR IRON RADIATION WITH THE MONOCLINIC CELL OF MULLICA *ET AL.* (8) AND THEIR SINGLE-CRYSTAL F VALUES (THOSE WITH AN ASTERISK WERE OMITTED IN THEIR CALCULATIONS) JUXTAPOSED TO THE DATA BASED ON THE ORTHORHOMBIC CELL OF KIETAIBL AND PETTER

Monoclinic cell				Orthorhombic cell					
h_m	k_m	l_m	$4\theta_m$ (°)	$10F_{\text{obs}}$	$10F_{\text{calc}}$	h_{or}	k_{or}	l_{or}	$4\theta_{\text{or}}$ (°)
0	2	0	32.44	517(6)	512	0	0	2	32.42
1	0	0	34.59	11 ^a (61)	34	1	1	0	34.60
0	0	1	34.60	—	—	1	1	0	
1	0	1	34.62	245(6)	197	0	2	0	34.59
1	1	0	38.24	940(6)	916	1	1	1	38.24
0	1	1	38.25	923(6)	915	1	1	1	
1	1	1	38.27	815(6)	826	0	2	1	38.24
1	2	0	47.59	1013(7)	970	1	1	2	47.59
0	2	1	47.60	1012(7)	970	1	1	2	
1	2	1	47.61	1219(7)	1101	0	2	2	47.59
1	3	0	60.18	797(8)	778	1	1	3	60.17
0	3	1	60.19	803(8)	781	1	1	3	
1	3	1	60.20	859(8)	803	0	2	3	60.17
1	0	1	60.37	1056(8)	1120	2	0	0	60.39
2	0	1	60.41	1281(7)	1255	1	3	0	60.39
1	0	2	60.42	1258(7)	1248	1	3	0	
1	1	1	62.60	21 ^a (49)	9	2	0	1	Extincted
2	1	1	62.64	211(9)	233	1	3	1	62.62
1	1	2	62.65	225(8)	234	1	3	1	
0	4	0	65.55	761(8)	763	0	0	4	65.52
1	2	1	68.90	100(13)	148	2	0	2	68.91
2	2	1	68.94	623(8)	611	1	3	2	68.91
1	2	2	68.95	610(8)	614	1	3	2	
2	0	0	70.00	626(8)	632	2	2	0	70.01
0	0	2	70.02	606(8)	624	2	2	0	
2	0	2	70.06	95(13)	104	0	4	0	70.01
2	1	0	71.96	417(8)	421	2	2	1	71.97
0	1	2	71.98	405(8)	420	2	2	1	
2	1	2	72.02	136(11)	195	0	4	1	71.97
1	4	0	74.58	85 ^a (15)	63	1	1	4	74.56
0	4	1	74.58	83 ^a (15)	62	1	1	4	
1	4	1	74.59	610(9)	564	0	2	4	74.56
2	2	0	77.59	634(9)	661	2	2	2	77.60
0	2	2	77.61	673(9)	669	2	2	2	
2	2	2	77.65	494(9)	502	0	4	2	77.60
2	3	0	86.29	1349(9)	1282	2	2	3	86.29
0	3	2	86.31	1234(9)	1281	2	2	3	
2	3	2	86.35	1217(9)	1309	0	4	3	86.29
1	5	0	90.17	897(9)	879	1	1	5	90.14
0	5	1	90.18	868(9)	876	1	1	5	
1	5	1	90.19	325(10)	346	0	2	5	90.14

Note. For the correct orthorhombic cell $h_{\text{or}} = h_m + l_m$, $k_{\text{or}} = h_m - l_m$, $l_{\text{or}} = k_m$ (whereas the assignment $h'_{\text{or}} = l_m$, $k'_{\text{or}} = 2h_m + l_m$, $l'_{\text{or}} = k_m$ leads to the inadequate orthorhombic cell).

^a Considered as unobserved in the calculations (8).

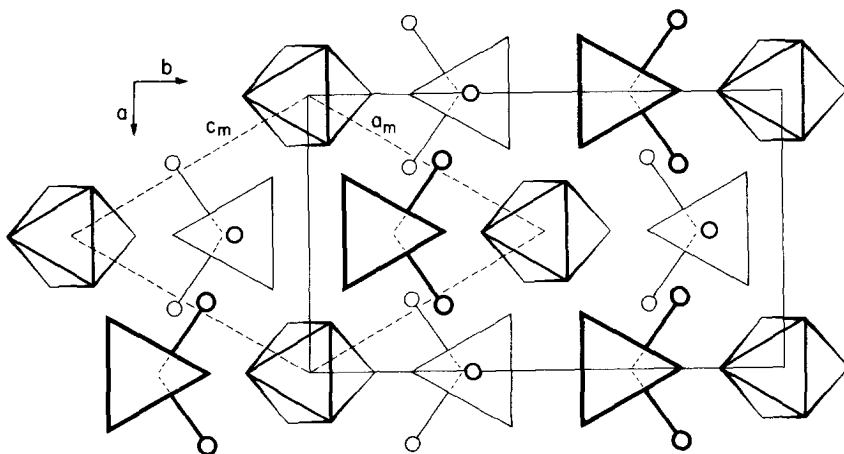


FIG. 2. Projection of the orthorhombic $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ structure onto the (a, b) plane. The water molecules are given as small circles. The bonded H_2O molecules are connected with the Sm atoms. The zeolitic H_2O molecules above and below each trigonal N prism (near the centers of the triangles) are partly omitted. The positions of the Fe and C atoms by the octahedra, those of N and Sm by the deformed trigonal prisms and the Sm-O bonds ($6\text{N} + 2\text{O}$ together form a slightly deformed square antiprism). The monoclinic cell (a_m, c_m) used by Mullica *et al.* (8) is indicated by broken lines.

tions while the calculated F values almost coincide. We have in fact checked the full θ range with similar results and we think that the agreement between the intensities of the pertinent reflection pairs is convincing.

The symmetrized orthorhombic atomic site parameters are compared with the parameters of Kietaihl and Petter in Table II. It is evident that both structure determinations are virtually identical and within the experimental accuracy the interatomic distances are the same. As discussed by Mullica *et al.* (8) the trigonal-prismatic $6\text{N} + 3\text{O}$ coordination of the rare-earth atom in hexagonal $\text{LaFe}(\text{CN})_6 \cdot 5\text{H}_2\text{O}$ is transformed to a nearly square-antiprismatic $6\text{N} + 2\text{O}$ coordination in $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ through the shift of the two remaining equatorial oxygen atoms and the elongation of the N2 prism edge. However, D_{4d} is certainly not its correct point group, though the two nitrogen atoms N2 of the particular prism edge and the two equatorial oxygen atoms O1 virtually lie in a plane (within the experimental resolution $y(\text{N}2) = y(\text{O}1)$) and

the opposite square N1 prism face indeed is surprisingly well quadratic ($2x_{\text{N}1}a = 3.012(7) \text{ \AA}$ and $(\frac{1}{2} - 2z_{\text{N}1})c = 3.018(12) \text{ \AA}$). The relative orientation of the pseudo-monoclinic and the orthorhombic cell can be seen in Fig. 2, where a projection of the structure is shown.

We were not able to detect any line splitting in the high-angle range of the Guinier patterns of the other tetrahydrates $\text{LnCr}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, $\text{LnFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, and $\text{LnCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, so that we think there is no reason to reduce the orthorhombic symmetry to monoclinic.

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