

## Reinvestigation of $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$

D. F. MULLICA AND E. L. SAPPENFIELD

*Department of Chemistry, Baylor University, Waco, Texas 76798*

Received May 23, 1989

The crystal structures of  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  have been determined by means of single crystal X-ray diffractometry. Both compounds refine equally well in orthorhombic *Cmcm* (No. 63) and monoclinic *P2<sub>1</sub>/m* (No. 11). Since this is the case, the higher symmetry space group should be the preferred choice. © 1989 Academic Press, Inc.

### Introduction

A recent communication (1) motivated a closer examination of the titled compounds which were published as crystallizing in the monoclinic *P2<sub>1</sub>/m* space group (2, 3). After a more careful inspection of both collected and reduced data sets and with an appropriate transformation, it was found that both data sets solve equally well in the *P2<sub>1</sub>/m* and the orthorhombic *Cmcm* space groups. Unfortunately, when we originally transferred these pseudo-hexagonal systems to orthorhombic cells, we examined the orthorhombic cells from a conventional point of view ( $hkl \neq \bar{h}kl$ ). However, the decision to reject the orthorhombic system upon these relationships was premature and inappropriate and was inherent due to the automated search routine employed for determination of cell parameters and working orientation matrices. Experimental procedures and parameters in *P2<sub>1</sub>/m* have been reported elsewhere (2, 3). Therefore, only pertinent material related to the comparison between *P2<sub>1</sub>/m* and *Cmcm* space

groups as well as coordination geometry about the samarium ion will be presented and discussed.

### Discussion

Table I presents experimental and statistical summaries for  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  differentiating *P2<sub>1</sub>/m* and *Cmcm*. Since both compounds refine equally well and to the same structure in *P2<sub>1</sub>/m* and *Cmcm*, the higher symmetry space group should be the preferred choice. The comparative fractional coordinates and equivalent isotropic thermal parameters with estimated standard deviations are given in Tables II and III for  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ , respectively, for the space group *Cmcm*. Note that Co and Fe atoms were refined isotropically. Both Co and Fe are six coordinated octahedrally by six carbon atoms ( $\text{CoC}_6$  and  $\text{FeC}_6$ ). The samarium ions are eight coordinated ( $\text{CN} = 8$ ,  $\text{SmN}_6(\text{H}_2\text{O})_2$ ) and the ligands are arranged in a square antiprism geometry (*D<sub>4d</sub>*). The square antiprismatic

TABLE I  
EXPERIMENTAL AND STATISTICAL SUMMARIES

Sp. gr.	SmCo(CN) <sub>6</sub> · 4H <sub>2</sub> O		SmFe(CN) <sub>6</sub> · 4H <sub>2</sub> O	
	<i>P</i> 2 <sub>1</sub> / <i>m</i> <sup>a</sup>	<i>Cmcm</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i> <sup>b</sup>	<i>Cmcm</i>
<i>a</i> (Å)	7.365(1)	7.366(1)	7.431(1)	7.435(1)
<i>b</i> (Å)	13.653(2)	12.780(2)	13.724(3)	12.866(3)
<i>c</i> (Å)	7.385(2)	13.653(2)	7.429(2)	13.724(3)
β(°)	120.08(2)	—	119.95(1)	—
<i>V</i> (Å <sup>3</sup> )	642.6	1285.3	656.5	1312.8
<i>D</i> <sub>c</sub> (Mg m <sup>-3</sup> )	2.261	2.261	2.197	2.198
<i>D</i> <sub>m</sub> (Mg m <sup>-3</sup> )	2.24(2)	2.24(2)	2.198(3)	2.198(3)
<i>F</i> (000)(e)	414	828	412	824
Δθ(°)	1.5–25.0	1.5–25.0	1.5–25.0	1.5–25.0
Uniq. refl.	882	595	1028	615
Sys. abs.	0 <i>kl</i> , <i>k</i> = 2 <i>n</i> + 1	<i>hkl</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> + 1 <i>h0l</i> , <i>l</i> = 2 <i>n</i> + 1	0 <i>kl</i> , <i>k</i> = 2 <i>n</i> + 1	<i>hkl</i> , <i>h</i> + <i>k</i> = 2 <i>n</i> + 1 <i>h0l</i> , <i>l</i> = 2 <i>n</i> + 1
<i>R</i> <sub>int</sub>	0.007	0.015	0.022	0.033
<i>R</i>	0.0137	0.0150	0.0292	0.0264
<i>R</i> <sub>w</sub>	0.0137	0.0165	0.0296	0.0270
GnFt(Σ <sub>2</sub> )	1.04	1.21	1.09	1.92
<i>g</i> (e <sup>-2</sup> )(10 <sup>-8</sup> )	6.84	20.6	193	207

<sup>a</sup> Ref. (3).

<sup>b</sup> Ref. (2).

geometry which is the most stable arrangement (4) when comparing octacoordinated geometries (i.e., the *D*<sub>4d</sub> octacoordinated

species has the lowest qualitative energy among idealized octacoordinated structures, *D*<sub>4d</sub> < *D*<sub>2d</sub> < *C*<sub>2v</sub> < *D*<sub>3d</sub> < *D*<sub>6h</sub> < *O*<sub>h</sub>),

TABLE II  
POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH ESD'S FOR SmCo(CN)<sub>6</sub> · 4H<sub>2</sub>O IN *Cmcm*<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>b</sup>
Sm	0.000	0.32472(2)	0.250	0.0100(1)
Co	0.000	0.000	0.000	0.79(1) <sup>c</sup>
C(1)	0.3182(5)	0.4542(2)	0.0882(2)	0.015(2)
C(2)	0.000	0.1341(4)	0.0591(4)	0.015(2)
N(1)	0.2050(5)	0.4254(2)	0.1389(2)	0.024(2)
N(2)	0.000	0.2145(3)	0.0950(3)	0.023(2)
O(1)	0.2639(6)	0.2153(3)	0.250	0.032(2)
O(2)	0.000	0.6561(3)	0.0984(3)	0.033(2)

<sup>a</sup> Parameters for *P*2<sub>1</sub>/*m* are available in Ref. (3).

<sup>b</sup> Isotropic equivalent thermal parameter (*U*<sub>eq</sub>) is defined as one-third the trace of the orthogonalized *U*<sub>ij</sub> tensor.

<sup>c</sup> Co was refined isotropically and the thermal parameter is in the conventional isotropic B form.

TABLE III  
POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH ESD'S FOR SmFe(CN)<sub>6</sub> · 4H<sub>2</sub>O IN *Cmcm*<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>b</sup>
Sm	0.000	0.32353(3)	0.250	0.0104(2)
Fe	0.000	0.000	0.000	0.80(2) <sup>c</sup>
C(1)	0.3162(7)	0.4530(3)	0.0897(3)	0.017(2)
C(2)	0.000	0.1361(5)	0.0587(5)	0.017(2)
N(1)	0.2031(6)	0.4241(2)	0.1408(3)	0.025(2)
N(2)	0.000	0.2162(4)	0.0957(4)	0.026(2)
O(1)	0.2623(8)	0.2147(4)	0.250	0.033(2)
O(2)	0.000	0.6553(4)	0.0999(4)	0.035(2)

<sup>a</sup> Parameters for *P*2<sub>1</sub>/*m* are available in Ref. (2).

<sup>b</sup> Isotropic equivalent thermal parameter (*U*<sub>eq</sub>) is defined as one-third the trace of the orthogonalized *U*<sub>ij</sub> tensor.

<sup>c</sup> Fe was refined isotropically and the thermal parameter is in the conventional isotropic B form.

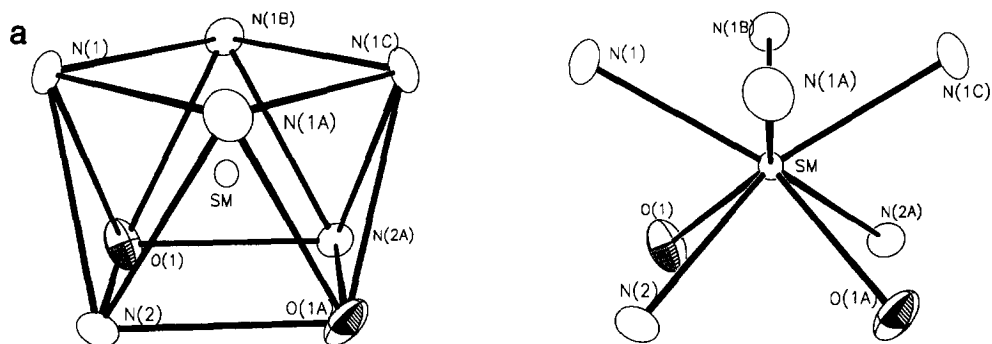


FIG. 1a.  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ . The square antiprismatic arrangement about the central Sm atom for the  $Cmcm$  system; note parallelism between opposing square faces.

contains two water-oxygen atoms located *trans* to each other on one of the square antiprism faces and six cyanonitrogen atoms (2, 3). The four atoms O(2), O(3), N(3), N(3)' (see Refs. (2, 3)) for the  $P2_1/m$  system and O(1), O(1A), N(2), N(2A) for the  $Cmcm$  system (see Fig. 1a) are planar to within 0.003 and 0.009 Å, respectively, using the least-squares planes method (5) for both systems. The other four nitrogen atoms in

the opposing square face form a perfect plane (see Fig. 1a). The dihedral angles between these opposing square planes in the square antiprism polyhedron in both systems are 0.0°. There is a question, however, of whether or not the polyhedron about the metal ions in the  $Cmcm$  system can be described as a bicapped trigonal prism as seen in Fig. 1b. When examining the dihedral angles between the apical trigonal planes (if a bicapped trigonal prism is assumed) in both compounds, it is found that they are greater than 25.0° which obviously demonstrates nonparallelism. Parallelism within 7–10° is

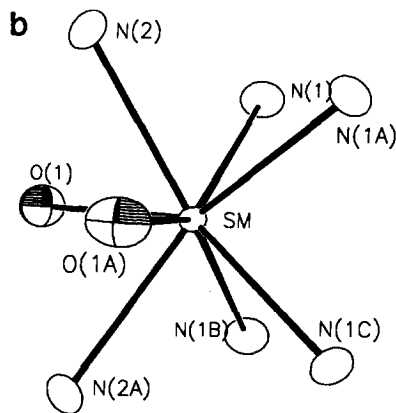


FIG. 1b.  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ . The polyhedron about the Sm atom in a bicapped trigonal arrangement; note the obvious nonparallelism between the apical trigonal planes. The polyhedron could be described as a severely distorted bicapped trigonal prism, but the word distorted ceases to have meaning when another ideal geometry is observed (square antiprism polyhedron).

TABLE IV  
BOND DISTANCES (Å) WITH  
ESD'S FOR  $\text{SmCo}(\text{CN})_6$   
 $4\text{H}_2\text{O}$  IN  $Cmcm^a$

Sm–N(1)	2.498(3)
Sm–N(2)	2.540(4)
Avg.	2.519
Sm–O(1)	2.396(4)
Co–C(1)	1.896(3)
Co–C(2)	1.890(4)
Avg.	1.893
C(1)–N(1)	1.145(4)
C(2)–N(2)	1.136(6)
Avg.	1.141
O(1)–O(2)	2.809(4)

<sup>a</sup> Bond distances for  $P2_1/m$  are available in Ref. (3).

TABLE V

BOND DISTANCES (Å) WITH  
ESD'S FOR  $\text{SmFeCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$   
IN  $Cmcm^a$

Sm-N(1)	2.492(3)
Sm-N(2)	2.529(4)
Avg.	2.510
Sm-O(1)	2.403(4)
Fe-C(1)	1.935(4)
Fe-C(2)	1.926(5)
Avg.	1.931
C(1)-N(1)	1.156(4)
C(2)-N(2)	1.151(7)
Avg.	1.153
O(1)-O(2)	2.819(4)

<sup>a</sup> Bond distances for  $P2_1/m$   
are available in Ref. (2).

needed in order to establish a trigonal prism geometry. Further, when examining the dihedral angles between both apical trigonal planes and the plane formed by the central atom and the equatorial atoms in both compounds, all such angles are greater than  $12.5^\circ$ . With all of this in mind, there should be little doubt that the polyhedron about the central metal ions in  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  and  $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ , whether the considered space group is  $P2_1/m$  or  $Cmcm$ , is a square antiprism geometry. Comparative bond distances are presented in Tables IV and V and comparative selected bond angles are listed in Table VI. Finally, that which applies to the titled compounds regarding the assignment of a space group (i.e.,  $Cmcm$ ) also applies to  $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  (6).

### Acknowledgment

The authors gratefully acknowledge the financial support of this work by the Robert A. Welch Foundation (Grant AA-668).

TABLE VI

BOND ANGLES ( $^\circ$ ) WITH ESD'S  
for  $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$  AND  
 $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}^a$

$\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$	
Co-C(1)-N(1)	177.7(3)
Co-C(2)-N(2)	179.7(6)
Avg.	178.7
Sm-N(1)-C(1)	166.9(3)
Sm-N(2)-C(2)	149.2(4)
Avg.	158.1
C(1)-Co-C(1)'	89.8(1)
C(1)-Co-C(2)	89.6(1)
C(1)'-Co-C(2)	90.4(1)
Avg.	89.9
$\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$	
Fe-C(1)-N(1)	177.8(3)
Fe-C(2)-N(2)	178.4(4)
Avg.	178.1
Sm-N(1)-C(1)	166.6(3)
Sm-N(2)-C(2)	149.3(4)
Avg.	158.0
C(1)-Fe-C(1)'	89.8(2)
C(1)-Fe-C(2)	89.0(1)
C(1)'-Fe-C(2)	89.0(1)
Avg.	89.3

<sup>a</sup> Comparative bond angles for  $P2_1/m$   
are available in Refs. (2, 3).

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