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Synthesis and Structural Study of Samarium Hexacyanoferrate (III) Tetrahydrate, $SmFe(CN)_6 \cdot 4H_2O$

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Single crystals of $SmFe(CN)_6 \cdot 4H_2O$ prepared from an aqueous solution under ambient conditions have been used for single-crystal diffraction, thermal gravimetric analysis, and infrared spectrometric studies. This characterized compound is compared to previously reported $LnT(CN)_6$ (T = Cr, Fe, Co) structures. Samarium hexacyanoferrate (III) tetrahydrate is found to be monoclinic, not hexagonal or orthorhombic as presupposed. $SmFe(CN)_6 \cdot 4H_2O$ crystallizes in space group $P2_1/m$ (No. 11), a = 7.431(1), b = 13.724(3), c = 7.429(2) Å, β = 119.95(1)°, Z = 2. Full-matrix least-squares refinement has yielded the final values of $R = 0.0292$ and $R_w = 0.0296$ for 1028 unique reflections. The observed and calculated densities are 2.198(3) and 2.197 Mg m^{-3}, respectively. The dominant feature of the structure is that the samarium ion is eight-coordinated, not nine as previously believed. The samarium ion is bonded to six cyanonitrogen atoms and two water molecules in a square antiprism geometry (D_{4d}), the $SmN_6(H_2O)_2$ group. The FeC_6 group is octahedrally arranged. Cyanide bridging links these groups to build an infinite polymeric array. Additional water molecules are trapped in distorted cubic cages within the structure. The important averaged bond lengths are: Sm–N = 2.505(15); Sm–O = 2.402(1); Fe–C = 1.931(3); and C≡N = 1.156(10) Å. © 1988 Academic Press, Inc.

Introduction

Rare-earth hexacyanoferrates (III) and cobaltates (III) have been a subject of investigation for over a century. Cleve and Hoegland (*1*) prepared the first rare-earth (RE) cobaltic cyanide in 1873. In 1915, Bonardi and James (*2*) used potassium hexacyanocobaltate in the separation of yttrium and erbium. However, James and Willand (*3*) were the first group to prepare rare-earth hexacyanocobaltate hydrates, $(RE)Co(CN)_6 \cdot nH_2O$ where RE = Y, La, Ce, Nd, Gd, and Yb. These researchers also examined the solubilities of these compounds and reported that each studied compound contained 4.5 water molecules per formula unit and that these crystalline materials belonged to the hexagonal system. Grant and James (*4*), in 1917, precipitated Y, La, and $NdFe(CN)_6 \cdot nH_2O$ where $n = 4$. Prandtl and Mohr (*5*) did an extensive study on the preparation of single crystals of lanthanide (Ln) ferro- and ferrihexacyanide hydrates in 1938. In the latter series, Ln = La, Pr, Nd, Sm, Gd, Dy, and Er, n was equal to 3 for Pr, 4 for Nd, Sm, Gd, and Er, and 4.5 for La and Dy.

It was not until Gallagher (*6*) suggested the preparation of $LnFeO_3$ and $LnCoO_3$ through the decomposition of $LnT(CN)_6 \cdot nH_2O$, where T = Fe and Co, that the cor-

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rect lanthanide–solvent ratios were established. Bailey *et al.* (*7*) employing single-crystal X-ray diffraction analysis reported the crystal structure of $LaFe(CN)_6 \cdot 5H_2O$ in 1973. The structure is hexagonal ($P6_3/m$); there are five water molecules per formula unit (not 4.5); and the nine-coordinated lanthanum ion (tricapped trigonal prism) has D_{3h} symmetry. In the same year, Hulliger *et al.* (*8*) described the $LnT(CN)_6 \cdot 4H_2O$ (T = Fe, Co) as having orthorhombic symmetry which is nearly pseudo-hexagonal. A "double-infusion" technique used in the preparation of these hexacyanides and some magnetic properties were also reported. Kietaible *et al.* (*9*) followed up the work of Hulliger *et al.* (*8*) using their single crystals to confirm the structural analysis of Bailey *et al.* (*7*), but instead reported that SmFe $(CN)_6 \cdot 4H_2O$ was orthorhombic, *Cmcm* with a = 7.425, b = 12.850, c = 13.711 Å, and Z = 4. In 1975, Bonnet *et al.* (*10, 11*), using the hexagonal model proposed by Bailey (*7*), reported cell parameters of all $LnT(CN)_6 \cdot nH_2O$ where T = Co, Fe, and n = 4, 5. Finally, in 1976, Hulliger *et al.* (*12, 13*) reported more structural and magnetic data on $LnT(CN)_6 \cdot nH_2O$ (T = Cr, Co, Fe; n = 4, 5). The pentahydrates were classified as hexagonal and the tetrahydrates as orthorhombic.

The structural change, hexagonal ($P6_3/m$) to orthorhombic (*Cmcm*), if based solely on size considerations, appears to occur too early in the $LnT(CN)_6$ series. Generally, these changes occur at Gd or Tb where the *f*-orbitals are half filled. Since no complete structural study was reported and most of the conjecture on this is based on powder work, we decided to prepare and reexamine $SmFe(CN)_6 \cdot 4H_2O$.

Experimental

Single-crystals were synthesized by a procedure similar to that of Prandtl and Mohr (*5*). A 0.05 *M* aqueous solution of $SmCl_3$, made by dissolving the appropriate oxide in hydrochloric acid, was mixed with 15 ml of 0.05 *M* $K_3Fe(CN)_6$. The solution was immediately filtered and then approximately 1 ml of 0.1 *M* HCl was added to this solution so as to maintain an acidic medium. This mixture was then stored in the dark. Bright red single crystals formed after 4 days.

The density of $SmFe(CN)_6 \cdot 4H_2O$ was measured by the flotation method in a mixture of bromobenzene and 1,1,2,2 tetrabromoethane. The observed density is 2.198(3) Mg m^{-3}. Qualititative X-ray fluorescence analysis of the metal constituents verified the presence of both samarium and iron. Thermal gravimetric analysis was carried out in order to determine the number of associated water molecules per formula unit, 4.0(1). A Perkin-Elmer TGS-1 thermal balance operated at 1.25° min^{-1} with a nitrogen atmosphere was employed. A stable dihydrate was found at approximately 135°C. The structure and properties of this stable dihydrate will be the subject of a later report. A Perkin-Elmer 521 grating IR spectrometer utilizing a frequency range of 4000–250 cm^{-1} was used to obtain an infrared spectrum of the title compound. Using the pressed-disk method (KBr pellet), the following relevant absorption peaks were observed: 3619 (ν, OH); 3410 (ν, OH, H-bonding); 2135 (ν, $C\equiv N$); 1630 (δ, HOH); 540 (δ, Fe–CN); and 439 cm^{-1} (ν, Fe–C).

A clear, red single crystal with well-defined edges was chosen for the crystallographic analysis. A conoscopical study verified its biaxial nature. The crystal was mounted on a thin glass fiber and transferred to an Enraf-Nonius CAD-4 fully automated diffractometer which was equipped with a dense graphite monochromator (take-off angle, 5.8°). All X-ray measurements were made at 290°K using Mo$K\bar{\alpha}$ radiation (λ_{mean} = 0.71073 Å). The working orientation matrix and the unit cell parameters were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The initial cell obtained from the index routine appeared hexagonal (the same lattice constants as reported here for monoclinic cell), but the conoscopical study together with the noncyclic permutational conditions suggested a less symmetric system. The hexagonal cell was then transformed to the orthorhombic cell, as reported by Hulliger (*8, 12, 13*). The orthorhombic system is biaxial, but the hkl and $\bar{h}kl$ reflections were nonequivalent. The monoclinic cell $a = 7.431(1)$, $b = 13.724(3)$, $c = 7.429(2)$ Å, and $\beta = 119.95(1)°$ was chosen. Crystal data, experimental conditions, and statistical data are summarized in Table I. Intensity data were collected using the ω-2θ technique with a variable scan rate (0.38–$3.35°$ min^{-1}) determined by a fast prescan of $3.35°$ min^{-1}. Data were collected in the range $3.0 < 2\theta < 50°$ (h: $-9 \rightarrow 9$, k: $0 \rightarrow 17$, l: $0 \rightarrow 9$). Two standard reflections ($\bar{1}\bar{2}\bar{2}$ and $0\bar{6}0$) were monitored every 2 hr of collection time (56 hr exposure) and revealed no systematic variation in intensity which verified hardware and crystal stability. Lorentz and polarization corrections were applied. An empirical absorption correction based on high χ angle ψ scans of five reflections was performed (avg. correction factor 0.9593). Systematic absences revealed a primitive cell and the $0k0$ ($k = 2n$) condition indicated $P2_1$ or $P2_1/m$. After applying the zero-moment test (NZ-test) proposed by Howell *et al.* (*14*) to the observed data, the result was then compared to the theoretical centric and acentric distributions and a centrosymmetric system was indicated. Further, $SmFe(CN)_6 \cdot 4H_2O$ did not produce an electric moment by the change of temperature. Although a negative pryoelectricity test is a rather weak check for centrosymmetry, it helped choose centrosymmetric $P2_1/m$ over the noncentrosymmetric $P2_1$. Equivalent reflections were averaged ($R_{\mathrm{int.}} = 0.022$), yielding 1058 reflections, of which 1028 had intensities greater than 3σ.

TABLE I

Experimental and Statistical Summary for $SmFe(CN)_6 \cdot 4H_2O$

Monoclinic, $P2_1/m$ (No. 11)	
Crystal size (mm^3)	$0.21 \times 0.20 \times 0.41$
Cell parameters (Å)	
a	7.431(1)
b	13.724(3)
c	7.429(2)
β(°)	119.95(1)
V ($\mathrm{Å}^3$)	656.46
M_r	434.37
Z	2
D_c ($\mathrm{Mg\ m^{-3}}$)	2.197
D_m ($\mathrm{Mg\ m^{-3}}$)	2.198(3)
$F(000)$	412 e
μ (Mo $K\bar{\alpha}$, cm^{-1})	55.7
Transmission range	0.871–0.999
R_{int}	0.022
$\Delta\theta$ (°)	1.5–25.0
Unique reflections [$I > 3\sigma(I)$]	1028
Sys. abs.	0k0, k = 2n + 1
R	0.0292
R_w	0.0296
$GnFt$ (Σ_2)	1.09
g (e^{-2})	$1.93(4) \times 10^{-6}$
Shift/error [$\Delta\xi_i/\sigma(\xi_i)$] ($10^{-5}$)	
Max.	23.9
Avg.	1.5
Residual (e $\mathrm{Å}^{-3}$)	
Max.	1.2(2)
Min.	−1.1(2)

The initial position of the samarium ion was determined from a Patterson map (0.32, $\frac{1}{4}$, 0.67). This is essentially the same site for the lanthanum atom in $LaFe(CN)_6 \cdot 5H_2O$ [$\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$] (*7*), if it were transformed into this hexagonal cell. The positions of the remaining nonhydrogen atoms were determined by difference Fourier mapping. The model was then refined by the full-matrix least-squares method (*15*) employing anisotropic thermal parameters (except for Fe which was kept isotropic). Secondary extinction corrections were applied. The corrections were in the form $|F_o| = |F_c|/(1 + gI_c)$ where F_o and F_c are the observed and calculated structure factors, I_c is the calculated intensity, and g is the extinction parameter. After several cycles of full-matrix refinement, final residual index values were obtained, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0292$ and $R_w = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2} = 0.0296$ where $w = \sigma^{-2}(F_o)$. The final "goodness-of-fit value" was $\Sigma_2 = 1.09$ and the largest value of abscission $[\Delta\xi_i/\sigma(\xi_i)]$ was 2.39×10^{-4} (average is 1.5×10^{-5}) where ξ_i values are varied parameters. A final difference Fourier map was virtually featureless revealing only a random fluctuating background. Atomic scattering factors and anomalous dispersion correction factors for all atoms were taken from the usual source (*16*). Final atomic positions, equivalent isotropic thermal factors, selected bond and contact distances, and bond angles are presented in Tables II and III. Full listings of anisotropic thermal parameters and observed and calculated structure factors are available from D.F.M.

Results and Discussion

$SmFe(CN)_6 \cdot 4H_2O$ is monoclinic ($P2_1/m$, No. 11) and the local arrangement of water and cyanide groups about the samarium ion is quite different than that previously reported (*8, 9*). The Sm^{3+} ion in $SmFe(CN)_6 \cdot 4H_2O$ is eight-coordinated and its ligands form a square antiprism, D_{4d} point group (see Figs. 1 and 2). This square-antiprismatic arrangement is the most stable system when comparing energy relationships among octacoordinated geometries (*17*). The two water-oxygen atoms are located *trans* to each other on one of the square-antiprism faces (see Fig. 1a). Six nitrogen atoms from cyano groups complete the eight-atom polyhedron. The four atoms: O(2); O(3); N(3); and N(3)′ are planar to within 0.003 Å, using the least-squares planes method (*15*). The other four nitrogen atoms in the opposing square face form a perfect plane. The dihedral angle between these square planes is 0.0°. The averaged Sm–N bond distance is 2.502(15) Å and the

TABLE II

FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH e.s.d.'s

Atom	x	y	z	U_{eq}[a]
Sm	0.32355(6)	0.250	0.67655(6)	0.0102(1)
Fe	0.000	0.500	0.000	0.83(2)[b]
C(1)	0.2302(9)	0.5894(6)	0.1364(9)	0.020(2)
C(2)	0.1373(9)	0.4108(5)	0.2315(9)	0.016(2)
C(3)	−0.1370(9)	0.5592(5)	0.1349(9)	0.017(2)
N(1)	0.6255(8)	0.3598(5)	0.7771(8)	0.027(2)
N(2)	0.2206(8)	0.3600(5)	0.3721(8)	0.026(2)
N(3)	0.2177(8)	0.4035(5)	0.7849(8)	0.024(2)
O(1)	0.6568(7)	0.4005(4)	0.3462(8)	0.037(2)
O(2)	0.480(1)	0.250	1.048(1)	0.035(2)
O(3)	−0.048(1)	0.250	0.520(1)	0.033(2)

[a] Isotropic equivalent thermal parameter (U_{eq}) is defined as one-third the trace of the orthogonalized U_{ij} tensor.

[b] Fe was refined isotropically and the thermal parameter is in the conventional isotropic B form.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) WITH e.s.d.'s FOR $SmFe(CN)_6 \cdot 4H_2O$

Sm–N(1)	2.488(6)	N(1)–Sm–N(1)′	74.5(3)
Sm–N(2)	2.501(6)	N(1)–Sm–N(2)	74.3(2)
Sm–N(3)	2.518(6)	N(2)–Sm–N(2)′	74.3(3)
Avg.	2.502(15)	N(2)′–Sm–N(1)′	74.3(2)
		N(3)–Sm–O(2)	71.5(2)
Sm–O(2)	2.403(7)	N(3)–Sm–O(3)	71.8(1)
Sm–O(3)	2.401(7)	O(3)–Sm–N(3)′	71.5(2)
Avg.	2.402(1)	N(3)′–Sm–O(2)	71.5(2)
Fe–C(1)	1.930(7)	Fe–C(1)–N(1)	177.1(3)
Fe–C(2)	1.935(7)	Fe–C(2)–N(2)	178.1(3)
Fe–C(3)	1.929(7)	Fe–C(3)–N(3)	178.7(3)
Avg.	1.931(3)	Avg.	178.0(8)
C(1)–N(1)	1.167(9)	Sm–N(1)–C(1)	166.1(3)
C(2)–N(2)	1.146(9)	Sm–N(2)–C(2)	166.7(3)
C(3)–N(3)	1.154(8)	Sm–N(3)–C(3)	149.5(3)
Avg.	1.156(10)	Avg.	160(8)
O(1)–O(3)	2.815(7)	C(1)–Fe–C(2)	90.0(3)
		C(1)–Fe–C(3)	88.9(3)
		C(2)–Fe–C(3)	89.3(3)
		Avg.	89.4(5)

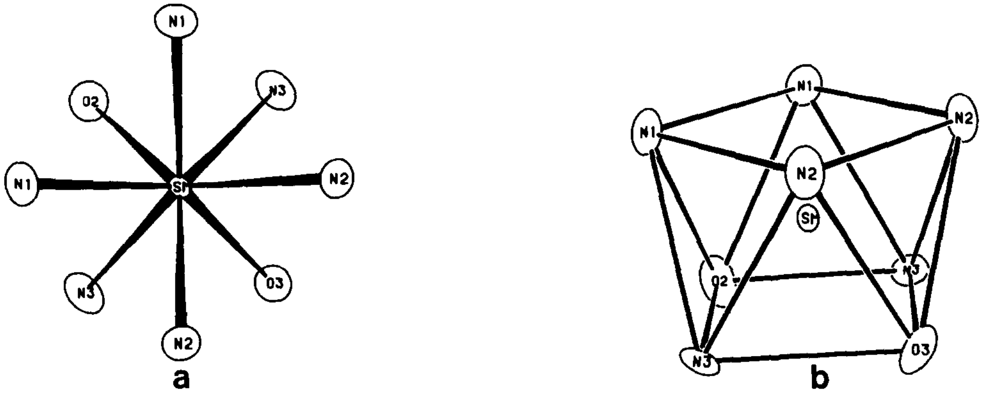

FIG. 1. $SmFe(CN)_6 \cdot 4H_2O$. The atoms Sm, O(2), and O(3) occupy a crystallographic mirror plane. (a) A top view of the square antiprismatic geometry (D_{4d}). (b) A regular presentation of a square antiprism.

average Sm–O distance is 2.402(1) Å. Both values are well within the range of values compiled in BIDICS (*18*). A water molecule, O(1), is trapped in a distorted cubic cage consisting of Sm–N–C–Fe edges (see Fig. 2). A note of interest, water O(1) is approximately 4.0 Å from the Sm^{3+} ion, completely out of bonding range. This water molecule is however within hydrogen bonding distance, 2.815(7) Å, to another water molecule, O(3), which is bonded to the Sm^{3+} ion. Hydrogen bonding is evidenced by an infrared study which was mentioned in the experimental section of this paper. A neutron diffraction study on this zeolitic type compound would clear up any questions related to hydrogen bonding. Such a project will hopefully be realized in the near future.

The low spin Fe^{3+} ion is octahedrally coordinated to six cyano groups. The average Fe–C bond distance is 1.931(3) Å, which compares well with literature values (*18*). The interaction of Fe 3*d* orbitals and the

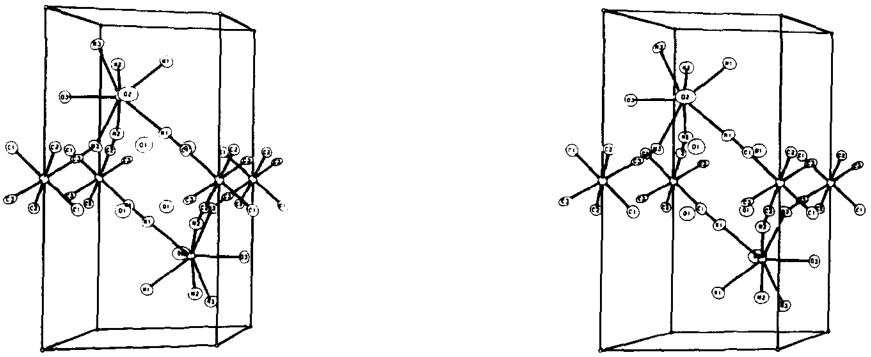

FIG. 2. $SmFe(CN)_6 \cdot 4H_2O$. A sterodrawing of the unit cell and its contents. The metal ions are shown fully coordinated. The Sm—N≡C—Fe linkages from the edges of distorted cubic cages in which water molecules O(1)'s are trapped.

CN^- orbitals leads to strong directional bonding as attested to by the averaged Fe—C≡N bond angle of 178.0°. There is very little directional influence in the electrostatic bonding of the lanthanide ion; the Sm–N–C bond angles range from 149.5 to 166.7°. The average C≡N bond distance is 1.156(10) Å.

The early lanthanide ferrihexacyanides (La and Nd) crystallize at room temperature with five associated waters per formula unit. $LaFe(CN)_6 \cdot 5H_2O$ (*7*) was the first of these compounds completely characterized crystallographically. The lanthanum compound is hexagonal ($P6_3/m$) and has D_{3h} (tricapped trigonal prism) symmetry about the central lanthanide ion. Further work proved that both Nd and Pr ferrihexacyanide complexes also crystallize initially as pentahydrates but readily convert to the tetrahydrate after several days. These dehydrated crystals are opaque and often fracture. It has been found that clear, well-formed crystals of Pr and Nd ferri- and cobaltic hexacyanide tetrahydrate form at elevated temperatures in the vicinity of 80°C. Samarium ferri- or cobaltic hexacyanide forms only the tetrahydrate between room temperatures and 80°C. It appears that the size of the lanthanide ion plays a major role in determining the hydration number and the resultant structure of these compounds. Pr^{3+} and Nd^{3+} central ions are large enough so that a coordination of nine may be realized, six cyano-nitrogens and three water molecules, only if it is in the presence of an aqueous medium (mother liquor). Removal of these cyrstals from the mother liquor decreases the external pressure on the lanthanide ion and internal pressure from the crowding of ligands, and forces one coordinated water away from the metal ion. Spedding *et al.* (*19*) compared the partial molal volumes of hydrated Ln^{3+} ions and deduced the coordination number of these ions. It is interesting that the larger Nd^{3+} ion has a smaller partial molal volume than the Tb^{3+} ion and that the change from nine to eight-coordination occurs at Gd^{3+}. It appears that the repulsion between ligands in the *Ln* coordination sphere increases from La to Nd and finally becomes large enough to make the structure energetically unstable. This structural change is also seen in the lanthanide tribromides. Recently, it has been found by preliminary crystallographic techniques that the ferri- and cobaltichexacyanides of Sm, Er, and Bi are also monoclinic and with all probability, are isostructural with $SmFe(CN)_6 \cdot 4H_2O$ (*20*). The structures of these cyanide complexes will be the subject of later reports.

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