JOURNAL OF SOLID STATE CHEMISTRY **78**, 301–306 (1989)

X-Ray Diffraction Investigations and Spectral Analyses of Monoclinic $SmKFe(CN)_6 \cdot 3H_2O$

D. F. MULLICA, E. L. SAPPENFIELD, AND H. O. PERKINS

Department of Chemistry and Physics, Baylor University, Waco, Texas 76798

Received September 6, 1988; in revised form November 1, 1988

Single-crystal and powder X-ray diffraction data, X-ray fluorescence and thermal gravimetric analyses, conoscopic results, and infrared spectral data are presented for $SmKFe(CN)_6 \cdot 3H_2O$. The compound crystallizes in the monoclinic space group $P2_1/m$ (No. 11), $a = 7.329(2)$, $b = 13.689(4)$, $c = 7.324(3)$ Å, $\beta = 119.97(3)°$, $Z = 2$, $D_m = 2.37(1)$ Mg m^{-3}, and $D_x = 2.376$ Mg m^{-3}. Final least-squares full-matrix refinement yielded $R = 0.0574$ and $R_w = 0.0568$ for 2138 unique reflections. The samarium ion is nine-coordinated forming a tricapped trigonal prism geometry. The octahedral FeC_6 groups are linked to the $SmN_6(H_2O)_3$ groups by cyanide bridging. The coordinated water molecules occupy general positions at two-thirds occupancy. The uncoordinated water molecule and the potassium ion (each at 0.5 occupancy) occupy holes in the structure. Important mean bond distances are: Sm–N = 2.478(5); Sm–O = 2.678(4); Fe–C = 1.899(5); and C≡N = 1.156(3) Å.

Introduction

Pioneer research related to the preparations and analyses of double ferrocyanide salts was initiated by Miller (*1*) in 1902. Informative preparatory studies of such compounds with potassium by Brown (*2*) lead to the foundation work of Robinson (*3*) who investigated both double and triple salts. The major emphasis of his studies (*3*) ascertained which metals formed double ferrocyanides with potassium as well as the nature, composition, and properties of the formed salts. It was Robinson (*3*) who first reported the synthesis of a double salt containing a lanthanide ion, $CeKFe(CN)_6$. There was no mention of hydration. In 1938, Prandtl and Mohr (*4*) reported the preparation of alkali–lanthanide ferrocyanides where Na and K were the alkali metals and La, Pr, Nd, Sm, Gd, Dy, and Er were the lanthanide (*Ln*) metals. The study included the number of hydrated water molecules associated with each $LnKFe(CN)_6 \cdot nH_2O$ complex. The thermal analyses and the structural characterizations were not described adequately.

It has been established that $LnKFe(CN)_6 \cdot nH_2O$ where *Ln* = La, Ce, and Nd crystallize in the hexagonal system ($P6_3/m$) and by thermal gravimetric analysis (TGA) that $n = 4$ (*5–7*). In this laboratory, X-ray powder diffraction studies of the $LnKFe(CN)_6 \cdot nH_2O$ series by comparative means of Debye–Scherrer camera film strips lead to a premature conclusion that the entire series was structurally isomorphous. A more recent IR and Mössbauer investigation of $MKFe(CN)_6 \cdot nH_2O$ complexes where *M* = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Yb has revealed the character of the outer rare-

0022-4596/89 $3.00

earth cation coordination (*8*). These results have motivated renewed concern in the lanthanide potassium ferrocyanide series.

Interest in the relations between physicochemical properties and structural arrangements of zeolitic cyanide compounds is well within the research goals in the laboratory. Therefore, X-ray characterization and structural determination of $Ln\mathrm{KT(CN)_6} \cdot n\mathrm{H_2O}$ complexes where T = Fe, Co, or Cr continues. Currently, a single-crystal structure analysis of $\mathrm{PrKFe(CN)_6 \cdot 4H_2O}$ (*9*) has been completed. The results disclosed that this compound is isomorphic with La, Ce, and $\mathrm{NdKFe(CN)_6 \cdot 4H_2O}$. However, X-ray powder characterization and single-crystal structural studies of $\mathrm{SmKFe(CN)_6 \cdot 3H_2O}$ have revealed new and informative data which now requires that other members of the $Ln\mathrm{KFe(CN)_6} \cdot n\mathrm{H_2O}$ series be more thoroughly examined.

Experimental

Clear colorless single crystals of the title compound were synthesized by employing the U-tube slow diffusion method. Both starting materials, $\mathrm{SmCl_3}$ and $\mathrm{K_4Fe(CN)_6}$, were purchased commercially (reagent grade) and were used without further purification. Aqueous dilute solutions of each were prepared with triply distilled water. The flotation method (*10*) using bromoform and iodomethane was used to determine the experimental density, 2.37(1) Mg $\mathrm{m^{-3}}$ (calcd 2.376 Mg $\mathrm{m^{-3}}$). A Perkin–Elmer TGS-1 thermobalance run at 2.5°C $\mathrm{min^{-1}}$ while being purged with nitrogen (20 cm $\mathrm{min^{-1}}$) was used to determine thermal dehydration, 3.02(4) water molecules-formula $\mathrm{unit^{-1}}$. The thermogram displayed a stepwise dehydration indicating two types of bonding, a loss of one water molecule between 70 and 90° and a loss of two water molecules between 125 and 175°. The metal constituents in $\mathrm{SmKFe(CN)_6 \cdot 3H_2O}$ were confirmed in proportional ratios required by the formula. The X-ray fluorescence analysis was carried out on a Novascan 30 scanning electron microscope (SEM) equipped with a PGT microprobe. An infrared spectrum using the KBr pressed pellet technique (pressed *in vacuo*, 15 K lb $\mathrm{in^{-2}}$) over a frequency range 4000–250 $\mathrm{cm^{-1}}$ on a Perkin–Elmer 521 grating IR spectrometer displayed the following relevant absorption peaks: 3510 (ν-OH, free $\mathrm{H_2O}$), 3480–3250 (ν-OH, very broad, H-bonding), 2065 (ν-C≡N), 1590 (δ-HOH), 605 (Fe–CN, bending), and 465 $\mathrm{cm^{-1}}$ (M–C, bending). A polystyrene film was used to calibrate selective areas of the spectrum. Finely ground crystals of samarium potassium hexacyanoferrate (II) trihydrate were placed into a thin-walled glass capillary (0.2 mm diameter). The unit cell parameters were obtained by using a Siemens Debye–Scherrer cylindrical camera (114.6 mm) under vacuum at 293 K. Copper $K\bar{\alpha}$ radiation (λ_{mean} = 1.54184 Å). A nickel (β) filter was employed. Measured S-values were placed into a least-squares program designed by Roof (*11*) for powder X-ray diffraction data. This analysis program uses the Nelson–Riley (*12*) extrapolation function to calculate the lattice constants and their estimated standard deviations, a = 7.329(2), b = 13.689(4), c = 7.324(3) Å, and β = 119.97(3)° (see Table I).

A single crystal of $\mathrm{SmKFe(CN)_6 \cdot 3H_2O}$ was selected on the basis of optical purity. A conoscopical examination using a Zeiss Photomicroscope II revealed the biaxial nature of the system. The chosen crystal was mounted on an Enraf–Nonius CAD-4F autodiffractometer which is equipped with a dense graphite monochromator (take-off angle, 5.8°). Mo$K\bar{\alpha}$ radiation (λ_{mean} = 0.71073 Å) was used for the data collection. The orientation matrix and the single-crystal lattice parameters (final unit cell parameters, high θ angles, 20 to 40°) were obtained from the refinement of 25 randomly selected reflections. These reflections were

TABLE I

EXPERIMENTAL AND STATISTICAL SUMMARIES

a (Å)	7.329(2)	7.327(1)
b (Å)	13.689(4)	13.684(1)
c (Å)	7.324(3)	7.326(1)
β (°)	119.97(3)	120.03(1)
V (Å^3)	636.54	636.93
M_r	455.46	455.46
D_x (Mg m^{-3})	2.376	2.375
D_m (Mg m^{-3})	2.37(1)	2.37(1)
Radiation	Cu$K\bar{\alpha}$	Mo$K\bar{\alpha}$
Space group		$P2_1/m$ (No. 11)
Z		2
$F(000)$		430
Cryst. Dim. (mm)		0.40 × 0.40 × 0.11
μ (Mo$K\alpha$) (mm^{-1})		6.06
Transmission range		0.858–0.998
$\Delta\omega$ (°) ($\omega - 2\theta$ scan)		$1.25 + 0.35 \tan \theta$
$\Delta\theta$ (°)		1.5–35.0
Unique relf.		2138
R		0.0574
R_w		0.0568
R_{int}		0.015
GnFt (Σ_2)		1.91
g (e^{-2}) (10^{-7})		8.26
Max $[\Delta\xi_i/\sigma(\xi_i)]$ (10^{-4})		2.35
Residual density (eÅ^{-3})		
Max.		2.5(2)
Min		−3.4(2)

automatically centered and indexed after applying subroutines SEARCH and INDEX which is part of the CAD-4F operating system. 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}. All reflections having less than 75 counts above background during the fast prescan were assumed unobserved. Data were collected in the range of $3 < 2\theta < 70°$ (h: $-11 \rightarrow 11$, k: $0 \rightarrow 11$, l: $0 \rightarrow 22$). Two check reflections ($\bar{1}\ 1\ \bar{2}$, $0\ \bar{3}\ 4$) were monitored every 2 hr of data collection. The variance in intensity throughout the entire data collection was less than 1.0% deviation. Hence, the crystal stability and the electronic and hardware reliability were verified. Lorentz, polarization, and absorption corrections (μ = 6.06 mm^{-1}) were applied to the data. After averaging redundant data, 2138 reflections were found to be unique with intensities greater than 3σ. The residual averaging error was 1.5%.

The initial cell constants obtained from the index routine appeared to belong to a hexagonal system (the same lattice parameters as reported in Table I, but with a = 7.327 Å, b = 7.326 Å, c = 13.684 Å, α = 90.0°, β = 90.0°, γ = 120.03°). After careful examination of a collected (hexagonal) data set, the hexagonal system was rejected due to noncyclic permutational conditions and the biaxial nature of $SmKFe(CN)_6 \cdot 3H_2O$. Before concluding that the system was monoclinic, the hexagonal cell was transformed to the orthorhombic system, but $h\ k\ l$, $\bar{h}\ k\ l$ intensity discrepancies were observed ($h\ k\ l \neq \bar{h}\ k\ l$). The monoclinic system was thus established by default. Systematic absences revealed a primitive cell and the $0\ k\ 0$ ($k = 2n$) condition indicated $P2_1$ or $P2_1/m$. The latter centrosymmetric space group proved to be more plausible. The initial starting atomic positions for the Sm ion were similar to those of the Pr ion in hexagonal $PrKFe(CN)_6 \cdot 4H_2O$ which were $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$(9). That is, $\frac{1}{3}$, $\frac{1}{4}$, $\frac{2}{3}$ after transformation to a monoclinic system. The atomic positions of the remaining nonhydrogen atoms were obtained from difference Fourier mapping. The model was refined by the full-matrix least-squares method (*13*). An isotropic refinement yielded a reliability index value of 0.096. After several more cycles varying anisotropic thermal parameters and applying secondary extinction corrections (g), residual factors were finalized, $R = \Sigma\Delta F/\Sigma|F_o| = 0.0574$ and $R_w = \Sigma\sqrt{w}\Delta F/\Sigma\sqrt{w}|F_o| = 0.0568$ where $\Delta F = \|F_o| - |F_c\|$ and $w = \sigma^{-2}(|F_o|)$. A final electron density map revealed some density in the vicinity of the Sm ion which is quite common for heavy metals. Elsewhere, the map was virtually featureless, revealing only a random fluctuating background (<1.0 eÅ^{-3}). Therefore, the hydrogen atom positions were not found. Atomic scattering factors and the anomalous dispersion correction factors were taken from the "International Ta-

TABLE II

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH E.S.D.'S

Atom	*x*	*y*	*z*	Occupancy	U_{eq}[a]
Sm	0.33398(8)	0.25	0.66706(8)	1	0.01151(9)
Fe	0.00	0.00	0.00	1	0.84(2)[b]
C(1)	0.2410(12)	0.5800(7)	0.0791(13)	1	0.024(2)
C(2)	0.0793(1)	0.4193(7)	0.8404(11)	1	0.022(2)
C(3)	0.1587(13)	0.4197(7)	0.2390(11)	1	0.025(2)
N(1)	0.3905(12)	0.6268(7)	0.1318(12)	1	0.036(2)
N(2)	0.1298(12)	0.3717(7)	0.7425(11)	1	0.038(2)
N(3)	0.2568(13)	0.3730(7)	0.3884(11)	1	0.037(2)
O(1)	0.3444(18)	0.5816(9)	0.6664(20)	0.50	0.037(2)
K	0.3274(9)	0.5825(5)	0.6670(8)	0.50	0.056(2)
O(2)	0.363(2)	0.75	0.435(1)	0.667	0.015(2)
O(3)	0.436(2)	0.25	0.073(1)	0.667	0.015(3)
O(4)	0.072(2)	0.75	0.637(1)	0.667	0.015(3)

[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.

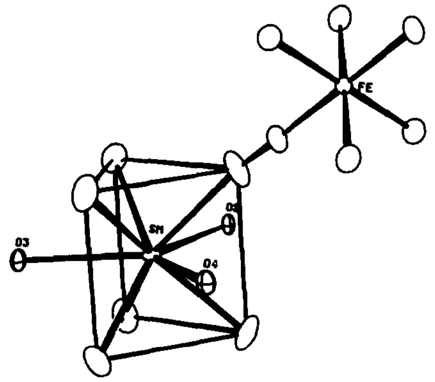

FIG. 1. A projected view of the $SmN_6(H_2O)_3$ (tricapped trigonal prism, TTP) and the octahedral FeC_6 group. The Sm–N C–Fe linkage is emphasized (see Table III for bond angles).

bles" (*14*). Final atomic positions and equivalent isotropic thermal factors are presented in Table II. Full listings of anisotropic thermal parameters and observed and calculated structure factors are available from the authors (D.F.M.).

Discussion

Samarium potassium ferrohexacyanide trihydrate crystallizes in the monoclinic space group $P2_1/m$. The experimental data was also refined in space group $P2_1$ in order to determine if the two models were significantly different. The data refined as well in $P2_1$. The $P2_1$ model converged at a final reliability index of 0.055 for 163 variables versus the $P2_1/m$ model at 0.057 for 90 variables. According to Hamilton (*15*), the $P2_1$ model is not significantly better than $P2_1/m$. The hypothesis that the correct space group is $P2_1/m$ rather than acentric $P2_1$ was tested. The ratio $[R(P2_1/m)]/[R(P2_1)]$ was much less than the Hamilton $\mathcal{R}$ at the 0.005 significance level. Consequently, the null hypothesis (H_0) was accepted. Further, the cyanide bond lengths obtained from the $P2_1$ solution were extremely large ranging from 1.18(2) to 1.22(3) Å; see Table III for a comparison. Selective interatomic bond distances and angles are presented in Table III. The $Fe(CN)_6^{-4}$ complex ion is octahedral with a mean Fe–C distance of 1.899(5) Å and C–Fe–C angles ranging from 89.8(3)

TABLE III

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) WITH E.S.D.'S

Sm–N(1)	2.472(6)	N(1)–Sm–N(1)′	86.0(4)
Sm–N(2)	2.479(6)	N(2)–Sm–N(2)′	84.4(4)
Sm–N(3)	2.483(6)	N(3)–Sm–N(3)′	85.4(4)
Avg.	2.478(5)	N(1)–Sm–N(2)	79.2(2)
		N(1)–Sm–N(3)	79.0(2)
Fe–C(1)	1.905(7)	N(2)–Sm–N(3)	79.2(2)
Fe–C(2)	1.899(6)		
Fe–C(3)	1.894(6)	N(1)–Sm–O(2)	67.8(2)
Avg.	1.899(5)	N(2)–Sm–O(3)	67.5(2)
		N(3)–Sm–O(4)	67.4(2)
Sm–O(2)	2.674(8)	N(1)–Sm–O(3)	69.3(2)
Sm–O(3)	2.681(8)	N(2)–Sm–O(4)	69.1(2)
Sm–O(4)	2.679(8)	N(3)–Sm–O(2)	69.5(2)
Avg.	2.678(4)		
		C(1)–Fe–C(2)	89.9(3)
C(1)–N(1)	1.155(9)	C(1)–Fe–C(3)	90.3(3)
C(2)–N(2)	1.158(8)	C(2)–Fe–C(3)	89.8(3)
C(3)–N(3)	1.156(8)	Avg.	90.0(2)
Avg.	1.156(3)		
		Fe–C(1)–N(1)	178.1(6)
O(1)–O(2)	2.905(8)	Fe–C(2)–N(2)	178.6(7)
O(1)–O(3)	2.909(8)	Fe–C(3)–N(3)	178.0(7)
O(1)–O(4)	2.984(8)	Avg.	178.2(3)
O(2)–Sm–O(3)	120.0(3)	Sm–N(1)–C(1)	158.8(6)
O(2)–Sm–O(4)	120.0(2)	Sm–N(2)–C(2)	158.7(6)
O(3)–Sm–O(4)	120.0(3)	Sm–N(3)–C(3)	158.7(6)
Avg.	120.0(1)	Avg.	158.7(1)

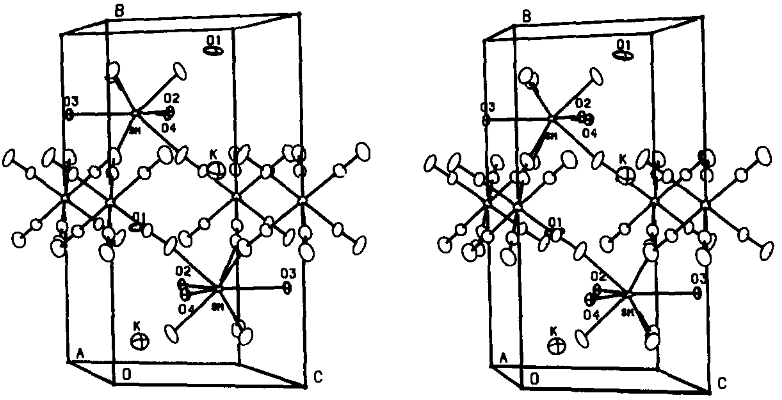

Fig. 2. A stereodrawing of the unit cell and its contents. Note the location of the uncoordinated water molecules and potassium ions.

to 90.3(3)°. The interaction of Fe 3*d* orbitals and the CN^- orbitals leads to strong directional bonding (averaged Fe–C≡N, 178.2°). Little or no directional influence is observed relating to electrostatic bonding of the samarium ion to the CN^- group (Sm–N≡C angle, 158.7°). The samarium ion is nine-coordinated which is quite common in molecular complexes of the lanthanide and actinide series. The nine-coordinated $SmN_6(H_2O)_3$ group forms a symmetrical tricapped trigonal prism (D_{3h}) where the centrally located Sm atom is bonded to six nitrogen atoms in apical positions and equatorially to three H_2O molecules; see Figs. 1 and 2. The dihedral angles between the two apical trigonal planes is 1.0° and the dihedral angle between the equatorial oxygen trigonal plane and either apical plane is less than 2.0°. The uncoordinated water molecule, O(1), and the potassium ion are found within cativities in the structure. The uncoordinated water molecule is within hydrogen bonding distance to the coordinated water molecules. Intermoiety oxygen–oxygen contact distances are O(1)· · ·O(2) = 2.905(8), O(1)· · ·O(3) = 2.909(8), and O(1)· · ·O(4) = 2.984(8) Å; see Table III. The strength of hydrogen bonds has been shown by Brown (*16*) to be dependent upon the O· · ·O interatomic distances, assuming no geometric constraints. In the structure of interest, only moderate to weak hydrogen bonding can exist. Infrared data presented in the experimental section and the TGA results lend credence to the X-ray diffraction analysis. All listed bond distances and angles are internally consistent with the model and in good agreement with experimental literature values found in BIDICS (*17*). Specifically, the carbon to nitrogen bond length listed in Table III is in direct accord with the work of Danford and Livingston (*18*), 1.156 Å, and Sheridan and Thomas (*19*), 1.157 Å, and with the summation of triple-bond radii tabularized by Pauling (*20*), 0.603 for carbon and 0.55 for nitrogen. This laboratory has initiated structural investigations pertaining to other members of the $LnKT(CN)_6 \cdot nH_2O$ series (Ln = Eu, . . . , Lu, and T = Fe, Co, and Cr).

Acknowledgment

The authors acknowledge the financial support of this work by The Robert A. Welch Foundation, Grant No. AA-668.

References

1. E. H. Miller, *J. Amer. Chem. Soc.* **24,** 226 (1902).
2. J. C. Brown, *J. Chem. Soc.* **91,** 1826 (1907).

3. F. W. Robinson, *J. Chem. Soc.* **95,** 1353 (1907).
4. W. Prandtl and S. Mohr, *Z. Anorg. Allg. Chem.* **236,** 243 (1938).
5. G. W. Beall, D. F. Mullica, W. O. Milligan, J. Korp, and I. Bernal, *Acta Crystallogr. Sect. B* **34,** 1446 (1978).
6. D. F. Mullica, W. O. Milligan, and J. D. Oliver, *Inorg. Nucl. Chem. Lett.* **15,** 1 (1979).
7. W. O. Milligan, D. F. Mullica, and H. O. Perkins, *Inorg. Chim. Acta* **60,** 35 (1982).
8. O. Zakharieva-Pencheva and V. A. Dementiev, *J. Mol. Struct.* **115,** 75 (1984).
9. D. F. Mullica, E. L. Sappenfield, and H. O. Perkins, *J. Solid State Chem.* **73,** 65 (1988).
10. J. W. Retgers, *Z. Phys. Chem.* **3,** 289 (1889).
11. R. B. Roof, Jr., LASL Report, Los Alamos Scientific Laboratory (1968).
12. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. (London)* **57,** 477 (1945).
13. Enraf-Nonius, "Enraf-Nonius VAX Structure Determination Package," Delft (1982).
14. J. A. Ibers and W. C. Hamilton, Eds., "International Tables for X-Ray Crystallography," Vol. IV, p. 72, Kynoch Press, Birmingham (1974).
15. W. C. Hamilton, *Acta Crystallogr.* **18,** 502 (1965).
16. I. D. Brown, *Acta Crystallogr. Sect. A* **32,** 24 (1976).
17. "Bond Index to the Determinations of Inorganic Crystal Structures," BIDICS, Institute for Material Research, Hamilton (1969–1981).
18. M. D. Danford and R. L. Livingston, *J. Amer. Chem. Soc.* **77,** 2944 (1955).
19. J. Sheridan and L. F. Thomas, *Nature (London)* **174,** 798 (1954).
20. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., p. 228, Cornell Univ. Press, Ithaca, NY (1960).