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A Structural Investigation of Monoclinic $SmCo(CN)_6 \cdot 4H_2O$

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The crystal structure of $SmCo(CN)_6 \cdot 4H_2O$ has been determined from three-dimensional, single-crystal, X-ray diffraction data and refined by the full-matrix least-squares method to give $R = 0.0137$ ($R_w = 0.0137$) and $\Sigma_2 = 1.04$. The compound crystallizes in the monoclinic space group $P2_1/m$, $a = 7.365(1)$, $b = 13.653(2)$, $c = 7.385(2)$ Å, and $\beta = 120.08(2)°$. For $Z = 2$, the calculated density is 2.261 Mg m^{-3} ($D_m = 2.24(2)$ Mg m^{-3}). A total of 882 unique reflections were measured with Mo$K\alpha$ radiation by the ω-2θ scan technique. The Sm ion is eight-coordinated in a square antiprism geometry, the $SmN_6(H_2O)_2$ group. The Co ion is octahedrally coordinated to six carbon atoms, the CoC_6 group. These groups are connected by cyanide bridges. Two uncoordinated water molecules occupy holes in the structure. Important mean bond distances are: Sm–N = 2.512, Sm–O = 2.404, Co–C = 1.890, and C≡N = 1.146 Å. Dehydration, fluorescence, and infrared data are reported.

Introduction

In 1916, James and Willard (*1*) reported that the rare-earth cobalticyanides possess the formula $(RE)_2[Co(CN)_6]_2 \cdot 9H_2O$, i.e., $RECo(CN)_6 \cdot 4.5H_2O$. Similar results were published for the lanthanide (*Ln*) hexacyanoferrates, but the water molecules per formula unit varied from 3 to 4.5 (*2*). The preparation and magnetic properties of several members of the lanthanide cobalticyanide series were presented by Karantassis *et al.* (*3*). These investigations were followed by conductance studies of several $LnCo(CN)_6$ (*4*).

It was not until 1975 with the work of Bonnet and Paris (*5*) using infrared and X-ray diffraction methods that the hexacyanocobaltates (III) of the lanthanide series were classified as belonging to the hexagonal system. The characterization of $LaCo(CN)_6 \cdot 5H_2O$ by single-crystal diffractometry (*6*) showed that this compound was indeed in the hexagonal system, $P6_3/m$. An informative investigation of $LnCo(CN)_6 \cdot nH_2O$ was conducted by Hulliger *et al.* (*7*). In their report, large *Ln* ions in the cobalticyanide series crystallize in the hexagonal system (*Ln* = La . . . Nd) whereas smaller *Ln* ions in the series (*Ln* = Sm . . . Lu) belong to an orthorhombic modification which is brought about by a gradual dehydration process. Further, it was stated that the $LnCo(CN)_6$ series was analogous to the $LnFe(CN)_6$ series. With this in mind and the recent discovery that $SmFe(CN)_6 \cdot 4H_2O$ crystallizes in the monoclinic system ($P2_1/m$) and not in the orthorhombic system

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(*8*), it was deemed necessary to examine samarium hexacyanocobaltate (III).

Experimental

Starting materials were of reagent-grade quality. An aqueous acidic solution (pH 4) of 0.2 *M* $SmCl_3$ was added to 15 ml of 0.1 *M* $K_3Co(CN)_6$. The mixture was filtered and stored in the dark at room temperature. Clear and colorless single crystals formed after 2 to 5 days and, after harvesting, the crystals were washed several times with triple-distilled water. The crystals of $SmCo(CN)_6 \cdot 4H_2O$ are indefinitely stable at room temperature. The flotation method was used to obtain the experimental density, 2.24(2) Mg m^{-3} (calcd, 2.261 Mg m^{-3}). X-ray fluorescence analysis verified the metal constituents and a thermal gravimetric analysis (Perkin–Elmer TGS-1) revealed the water content, 4.03 (*8*) water molecules per formula unit. A Perkin–Elmer 521 grating ir spectrometer using the KBr pressed-pellet method was employed to obtain pertinent spectral data. Absorption maxima are in the vicinities of 3615 (ν-OH, free hydroxyl); 3415 (ν-OH, very broad, intermolecular hydrogen bonding); 2150 (ν-CN, stretching); 1615 (δ-HOH, water of hydration); 600 (*M*-CN, bending); and 440 cm^{-1} (*M*–C, stretching). The biaxial character of the titled compound was determined by a conoscopic rotational examination using two crossed polarizers on a Zeiss Photomicroscope II.

The single crystal used in the structural analysis was chosen on the basis of optical quality and was mounted on an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator (Mo$K\bar{\alpha}$, λ = 0.71073 Å). The available system routines (search, index, and least squares) yielded the orientation matrix and the lattice constants, a = 7.365 (1), b = 13.653 (2), c = 7.385 (2) Å, β = 120.08 (2)° (monoclinic, $P2_1/m$, $Z = 2$). The initial cell obtained from the index program was hexagonal ($a \approx b$, γ = 120.08). However, after examining a short data set, the hexagonal system was rejected due to noncyclic permutational conditions which were presupposed from the biaxial behavior of the system. The hexagonal cell was transformed using a theoretical extension of the reduced-cell concept (Niggli matrix) to the orthorhombic system, similar to the orthorhombic cell (*Cmcm*) reported by Hulliger *et al.* (*7*). Since *hkl*, $\bar{h}kl$ intensity discrepancies were found ($hkl \neq \bar{h}kl$), this system was also rejected especially after observing the averaged data, $R_{int.}$ = 0.17. After much effort and work, a monoclinic cell ($P2_1/m$) with $a \approx c$ and β = 120.08 (2) was chosen. The ω-2θ technique was used to collect intensity data. The monitored standard reflections showed no systematic intensity variation, thereby assuring crystal and hardware stability. Lorentz and polarization corrections were made as well as secondary extinction corrections ($g = 6.84 \times 10^{-8}$ e^{-2}). Equivalent reflections were averaged ($R_{int.}$ = 0.007) yielding 882 reflections with intensities greater than 3σ. The Sm atomic position was obtained from patterson mapping (0.35, 0.25, 0.67) which is essentially the same site for La in hexagonal $LaCo(CN)_6 \cdot 5H_2O$ (*6*), [$\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$]. Cobalt, carbon, nitrogen, and oxygen atoms were obtained by the difference Fourier method. A full-matrix least-matrix refinement package was employed (*9*). All atoms, except Co, were refined anisotropically which lead to final index values of R = 0.0137 and R_w = 0.0137 and a "goodness-of-fit" of 1.04. The maximum value of abscission was 5×10^{-4}. A final residual density map revealed only a random fluctuating background. Scattering factors and anomalous dispersion terms were obtained from the usual source (*10*). Atomic coordinates, equivalent isotropic thermal parameters, interatomic and contact lengths, and bond angles are presented in Tables I and II. Tables of observed and calculated structure factors are available from the authors.

TABLE I

POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR $SmCo(CN)_6 \cdot 4H_2O$

Atom	x	y	z	U_{eq}[a]
Sm	0.35054(4)	0.250	0.67529(4)	0.00973(6)
Co	0.000	0.500	0.000	0.78(1)*
C1	0.0911(5)	0.4123(3)	0.8635(5)	0.015(1)
C2	0.2678(5)	0.5597(3)	0.1337(5)	0.016(1)
C3	0.0912(5)	0.4125(3)	0.2275(5)	0.015(1)
N1	0.1491(5)	0.3616(3)	0.7796(5)	0.024(1)
N2	0.4300(5)	0.5953(3)	0.2148(5)	0.0223(9)
N3	0.1489(5)	0.3165(3)	0.3697(5)	0.024(1)
O1	0.3116(4)	0.5984(2)	0.6553(5)	0.0321(9)
O2	0.4304(7)	0.750	0.9504(6)	0.033(1)
O3	0.4306(6)	0.750	0.4805(6)	0.033(1)

Note. Starred atoms were refined isotropically.

[a] $U_{eq} = (U_{11} + U_{22} + U_{33} + U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha)/3$.

* Refined isotropically.

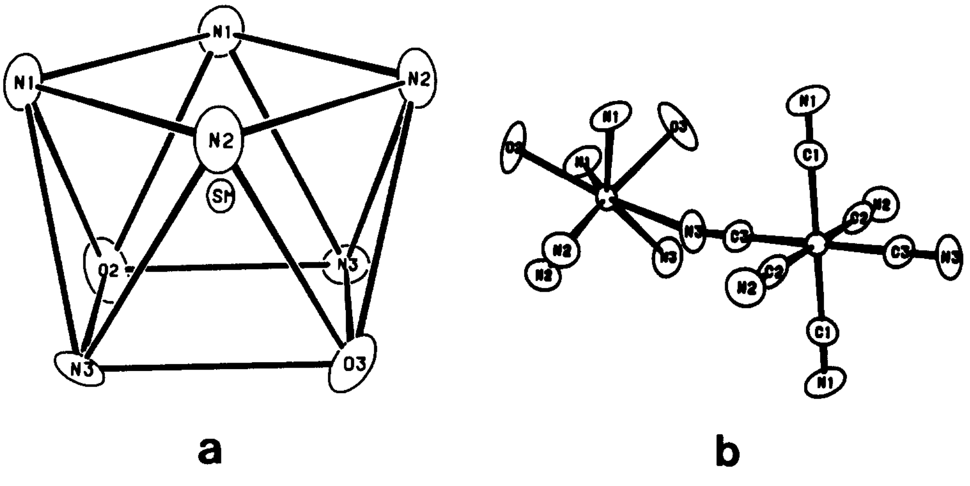
TABLE II

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS FOR $SmCo(CN)_6 \cdot 4H_2O$

Sm–N (1)	2.504(3)	Co–C(1)–N(1)	177.9(2)
Sm–N (2)	2.534(3)	Co–C(2)–N(2)	179.7(2)
Sm–N (3)	2.501(3)	Co–C(3)–N(3)	178.0(2)
Avg.	2.513	Avg.	178.5
Sm–O (2)	2.403(4)		
Sm–O (3)	2.405(4)		
Avg.	2.404		
		Sm–N(1)–C(1)	167.0(2)
Co–C(1)	1.891(4)	Sm–N(2)–C(2)	148.7(2)
Co–C(2)	1.891(4)	Sm–N(3)–C(3)	166.8(2)
Co–C(3)	1.889(4)	Avg.	160.8
Avg.	1.890		
C(1)–N(1)	1.145(5)		
C(2)–N(2)	1.142(5)		
C(3)–N(3)	1.150(5)	C(1)–Co–C(2)	89.7(2)
Avg.	1.146	C(1)–Co–C(3)	90.6(2)
		C(2)–Co–C(3)	89.7(2)
O(1)–O(3)	2.802(5)	Avg.	90.0

Results and Discussion

Samarium cobaltic hexacyanide tetrahydrate is monoclinic and isostructural with its ferricyanide analog (*8*). The samarium ion is eight-coordinated (CN = 8) and its ligands are arranged in a square antiprism geometry (D_{4d}), forming the $SmN_6(H_2O)_2$ group (see Fig. 1) which is linked to the octahedrally arranged CoC_6 (Co, CN = 6) group by cyanide bridging. The infinite polymeric array has additional water mole-



a b

FIG. 1. $SmCo(CN)_6 \cdot 4H_2O$. (a) The square antiprism geometry and (b) the octahedrally arranged cyano groups about the iron atom and the cyanide bridging which links the $SmN_2(H_2O)_2$ and FeC_6 groups.

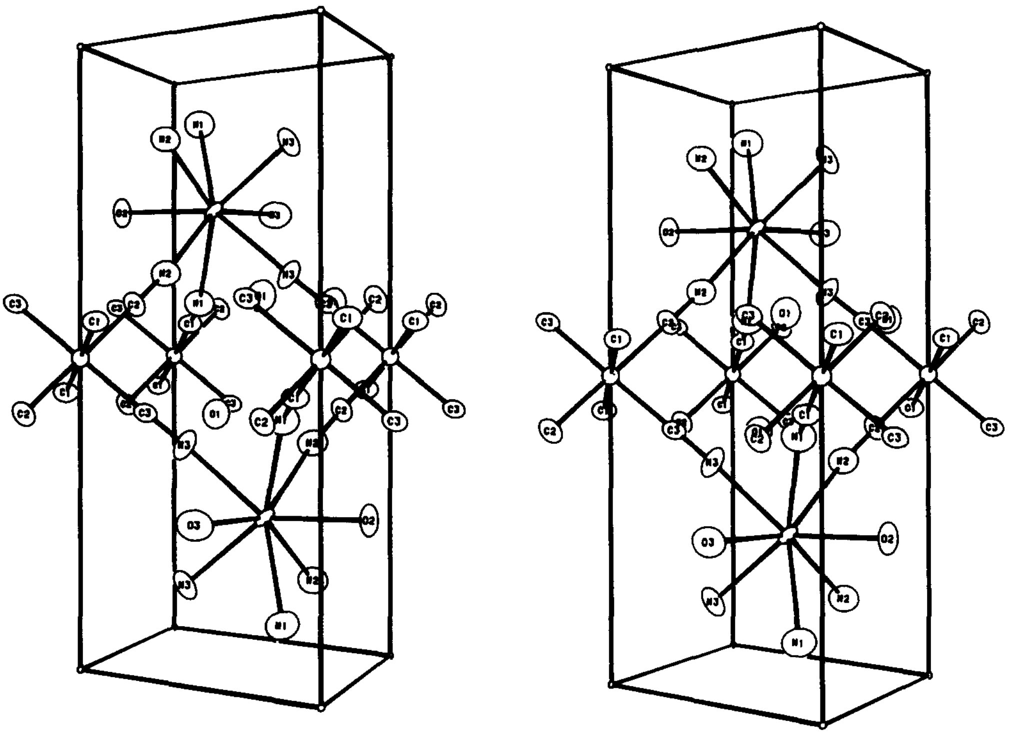


FIG. 2. $SmCo(CN)_6 \cdot 4H_2O$. A stereoscopic view of the contents of the unit cell. The fully coordinated Sm^{3+} (CN = 8) and Co^{3+} (CN = 6) ions are presented. The zeolitic trapped water molecules, O(1), are seen within the Sm–N≡C–Co network.

cules trapped in cubic-like cages within the structure (see Fig. 2). The two bonded water molecules are arranged trans to one another on one of the square faces of the square antiprism. Both faces of the polyhedron are planar to within 0.008 Å (least-squares plane refinement) and the dihedral angle between the planes is 0.1°, verifying parallelism. The zeolitic water molecules can be removed from the cages by careful heating of the crystal to 135°, very slowly. A stable dihydrate is formed which is expected to be the topic of future work.

The averaged Sm–N and Sm–O distances of 2.513 and 2.404 Å, respectively, are in good agreement with published bond lengths found in BIDICS (*11*). The averaged cobalt to carbon bond distance of 1.890 Å is in excellent agreement with the Co–C bond length calculated by Curry and Runiciman (*12*), 1.89 Å, and with the experimental work of Vannerberg (*13*), 1.896(11) Å, and that of Reynhardt and Boeyens (*14*), 1.89(1) Å, on the crystal structure of $K_3Co(CN)_6$. The averaged C≡N bond distance of 1.146 Å is in very good agreement with values found in the literature related to cyanide bridging (*12–17*). The interaction of Co 3*d* orbitals and the cyanide orbitals shows strong directional bonding; the average Co–C≡N bond angle is 178.5°. Directional influences are not observed when considering electrostatic binding of the samarium ion, Sm–N≡C bond angles vary between 148.7 and 167.0°. The zeolite water molecule, O(1), which is found within the Sm–N≡C–Co network, is within hydrogen bonding distances (2.802 Å) to the coordinated water molecule, O(3). The work of Brown (*18*) on the geometry of hydrogen bonds has shown that O . . . O contact distances of approximately 2.73 Å relate to strong hydrogen bonding and as the contact distances increase, hydrogen bonding becomes progressively weaker. Infrared data demonstrates that hydrogen bonding prevails in the $SmCo(CN)_6 \cdot 4H_2O$ system, a very strong and broad ν-OH in the vicinity of 3415 cm^{-1}. The zeolitic property of O(1) and its stability within the structure can be attributed to the hydrogen bonding. For many years, researchers have believed the LnCo(CN)$_6 \cdot n$H$_2$O series belonged to the hexagonal system (Ln = La . . . Nd) or to the orthorhombic system (Ln = Sm . . . Lu). Only $LaCo(CN)_6 \cdot 5H_2O$, by means of single-crystal X-ray diffraction (*6*), was truly verified (hexagonal, $P6_3/m$). Much work is needed in this area, since it has been shown that $SmCo(CN)_6 \cdot 4H_2O$ is neither hexagonal nor orthorhombic. The structural analyses of other heavier Ln Co(CN)$_6 \cdot n$H$_2$O compounds are in progress.

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