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Synthesis, Spectroscopic Studies, and Crystal and Molecular Structure of Bismuth Hexacyanoferrate(III) Tetrahydrate, $BiFe(CN)_6 \cdot 4H_2O$

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Hexacyano-cobaltates and ferrates of tripositive metal ions have been a subject of investigation for many years. Original research was directed at the separation of the lanthanides. Prandtl and Mohr [1] reported a detailed study on the crystallization of ferri- and ferro-hexacyanides in 1938. Further interest in these zeolitic materials stemmed from the importance of semipermeable membranes. This is the area of study that prompted the first complete structural analysis of a lanthanide ferrihexacyanide, $LaFe(CN)_6 \cdot 5H_2O$, by Bailey *et al.* [2]. $LaFe(CN)_6 \cdot 5H_2O$ was found to crystallize in the hexagonal space group $P6_3/m$. It appeared that all the other large tripositive metal ions were analogs to this hexagonal system. However, the work by Hulliger *et al.* [3–5] revealed discrepancies in the specific-heat and X-ray intensity data in some lanthanide cations. This work showed that a second crystal modification existed, and that a change in hydration number occurred along with the change in system. Further, Hulliger *et al.* [3–5] found that magnetic ordering occurred for some of the lanthanide compounds along long super exchange paths [4]. Structural investigations by means of single-crystal analyses of presupposed isomorphous compounds (other large tripositive ions with completed 4f and 5d orbitals) should reveal additional information about the properties of these zeolitic materials. More recently, it was reported that $SmFe(CN)_6 \cdot 4H_2O$ crystallizes in the monoclinic space group $P2_1/m$ [6]. It was of interest to determine the structure of $BiFe(CN)_6 \cdot 4H_2O$ in order to compare it to the lanthanide hexacyanide complexes, particularly $LaFe(CN)_6 \cdot 5H_2O$ because the La^{3+} ion has approximately the same ionic radius as the Bi^{3+} ion.

Experimental

A solution of 0.05 M $Bi(NO_3)_3$, reagent grade, was prepared in 0.15 M HNO_3 in order to prevent the hydrolysis of the Bi^{3+} ion. The $Bi(NO_3)_3$ solution was then added to an aqueous solution of 0.05 M $K_3Fe(CN)_6$ which had previously been acidified with HNO_3 to a pH of 3.0. The water used in the preparation of solutions was degassed. The mixture was then filtered and stored in the dark at room temperature. Small red crystals formed after four to six days.

The metal constituents in the titled compound were confirmed by X-ray fluorescence analysis, using a Novascan 30 scanning electron microscope (SEM) equipped with a PGT microprobe. Thermal dehydration results of 4.01(3) water molecules-formula $unit^{-1}$ were obtained on a Perkin-Elmer TGS-1 thermobalance which was run at 2.5 °C min^{-1} while nitrogen gas purged the system at 20 cm^3 min^{-1}. The flotation method using iodomethane and bromoform was employed to determine the experimental density, 2.502(9) Mg m^{-3} (calc.: 2.504 Mg m^{-3}). A Perkin-Elmer 521 grating IR spectrometer utilizing a frequency range of 4000–250 cm^{-1} (KBr pressed pellet) was used to obtain spectral results. Absorption maxima are observed in the vicinities of 3620 (ν(OH) free hydroxyl), 3410 (ν(OH), very broad, intermolecular hydrogen bonding), 2160 (ν(CN), cyanide stretching), 1620 (δ(HOH), water of hydration), 550 (M–CN, bending), and 440 (M–C, stretching) cm^{-1}. A conoscopic examination of the studied compound was performed by crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II. The biaxial character of the $BiFe(CN)_6 \cdot 4H_2O$ crystals was determined by the number of extinctions occurring in a 360° rotation.

A single crystal was selected on the basis of size and optical clarity ($0.092 \times 0.092 \times 0.368$ mm) and mounted on an Enraf-Nonius CAD-4F diffractometer. Graphite monochromatized Mo Kα (λ_{mean} = 0.71073 Å) radiation was used. Lattice constants were determined from 25 centered reflections, $a = 7.420(1)$, $b = 13.678(2)$, $c = 7.421(1)$ Å, $\beta = 119.76(1)°$, $V = 653.81$ Å^3, $Z = 2$, monoclinic, $P2_1/m$. Initially, a hexagonal cell was considered but, was finally rejected due to non-cyclic permutational conditions and the biaxial nature of the studied compound. This initial hexagonal cell was transformed to the orthorhombic system, similar to the cells reported by Hulliger *et al.* [4, 5] but hkl, $\bar{h}kl$ intensity discrepancies were found ($hkl \neq \bar{h}kl$).

Finally, a monoclinic cell ($P2_1/m$) with $\beta = 119.76(1)$ and $a \approx c$ was chosen. 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 $3 < 2\theta < 50°$ (h: $-8 \rightarrow 8$, k: $0 \rightarrow 16$, l: $0 \rightarrow 8$). Two standard reflections (054, 232) were

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monitored every 2 h of collection time and revealed no systematic intensity variation. Lorentz, polarization, and an empirical high chi angle absorption correction (trans. range, 0.706–0.998) were applied to the data as well as secondary extinction corrections ($g = 1.6 \times 10^{-6}$ e^{-2}). Equivalent reflections were averaged ($R_{int} = 0.020$) yielding 1036 reflections with intensities greater than 3σ. The initial starting model was the $SmFe(CN)_6 \cdot 4H_2O$ structure [6]. After refining Bi and Fe positions, the carbon, nitrogen, and oxygen atoms were located by difference Fourier mapping. A full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$, with a weighting factor (w) of σ^{-2} (F_o) was employed [7]. All atoms, with the exception of Fe^{3+}, were refined anisotropically. Final R values are: $R = \Sigma\Delta F/\Sigma F_o$ = 0.030 and $R_w = \Sigma\sqrt{w}\Delta F/\Sigma\sqrt{w}F_o = 0.031$, where $\Delta F = [|F_o| - |F_c|]$. The 'goodness of fit' value (Σ_2) was 1.68 and the maximum absolute value of convergence [$\Delta\xi_i/\sigma(\xi_i)$ where ξ_i values are varied parameters] was 6.3×10^{-5}. Scattering factors and anomalous dispersion terms were obtained from the usual source [8]. Atomic coordinates and bond distances and angles are given in Tables I and II.

TABLE I. Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2$)[a]

Atom	x	y	z	U_{eq}[b]
Bi	0.32371(8)	0.250	0.67635(8)	0.0130(1)
Fe	0.000	0.500	0.000	0.94(4)[c]
C(1)	0.137(2)	0.5583(9)	0.137(2)	0.019(3)
C(2)	0.238(2)	0.4125(9)	0.140(2)	0.021(3)
C(3)	0.139(2)	0.4117(9)	0.233(2)	0.019(3)
N(1)	0.220(2)	0.4064(9)	0.783(1)	0.032(3)
N(2)	0.627(1)	0.3610(9)	0.777(1)	0.029(3)
N(3)	0.222(2)	0.3611(9)	0.372(1)	0.032(3)
O(1)	0.657(1)	0.4023(8)	1.342(1)	0.033(3)
O(2)	0.475(2)	0.250	1.050(2)	0.040(5)
O(3)	0.049(2)	0.250	0.524(2)	0.043(5)

[a] e.s.d.s given in parentheses. [b] Isotropic equivalent thermal parameter (U_{eq}) defined as 1/3 the trace of the orthogonalized U_{ij} tensor. [c] Refined isotropically.

TABLE II. Interatomic Distances (Å) and Bond Angles (°) for $BiFe(CN)_6 \cdot 4H_2O$[a]

Bi–N(1)	2.531(9)	Fe–C(1)–N(1)	179.0(9)
Bi–N(2)	2.499(8)	Fe–C(2)–N(2)	178.7(9)
Bi–N(3)	2.508(8)	Fe–C(3)–N(3)	178.8(8)
Average	2.513		178.8
Bi–O(2)	2.425(10)		
Bi–O(3)	2.412(10)		
Average	2.418		
Fe–C(1)	1.932(9)	Bi–N(1)–C(1)	146.8(8)
Fe–C(2)	1.945(9)	Bi–N(2)–C(2)	165.7(8)
Fe–C(3)	1.933(9)	Bi–N(3)–C(3)	166.4(8)
Average	1.937		159.6
C(1)–N(1)	1.153(12)	C–(1)–Fe–C(2)	87.7(4)
C(2)–N(2)	1.134(12)	C–(1)–Fe–C(3)	91.6(4)
C(3)–N(3)	1.137(12)	C–(2)–Fe–C(3)	91.9(4)
Average	1.141		90.4
O(1)–O(3)	2.830(10)		

[a] e.s.d.s given in parentheses.

Results and Discussion

A stereoview of the fully coordinated Bi^{3+} (CN = 8) and Fe^{3+} ($CN = 6$) ions is given in Fig. 1. The long cyanide bridging pathways of Bi–N–C–Fe are easily seen in the stereoscopic view of the molecular packing within the unit cell, see Fig. 2. Bismuth having a completely filled 5d orbital, should therefore be spherically symmetric, which is evidenced by the thermal parameters. The atomic radii of Bi^{3+} and La^{3+} ions are approximately equal [9] and Hulliger *et al.* [4, 5] have suggested that hydrous bismuth(III) ferricyanide would crystallize in a hexagonal cell isomorphous to hydrous lanthanum ferricyanide.

$BiFe(CN)_6 \cdot 4H_2O$ crystallizes in the monoclinic space group $P2_1/m$ (No. 11). The Fe^{3+} ion is octahedrally coordinated with an averaged Fe–C bond distance of 1.937 Å. The averaged bond angle for Fe–C≡N is 178.8°, essentially linear. The Bi^{3+} cation

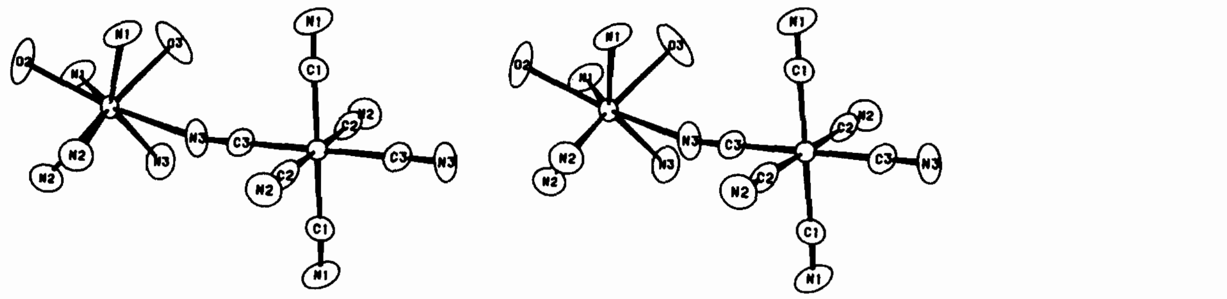

Fig. 1. $BiFe(CN)_6 \cdot 4H_2O$. A stereoview of the fully coordinated Bi^{3+} and Fe^{3+} ions. The eighth coordination about the Bi^{3+} ion forms a square antiprism geometry. The cyano groups about the iron atom form an octahedral geometry.

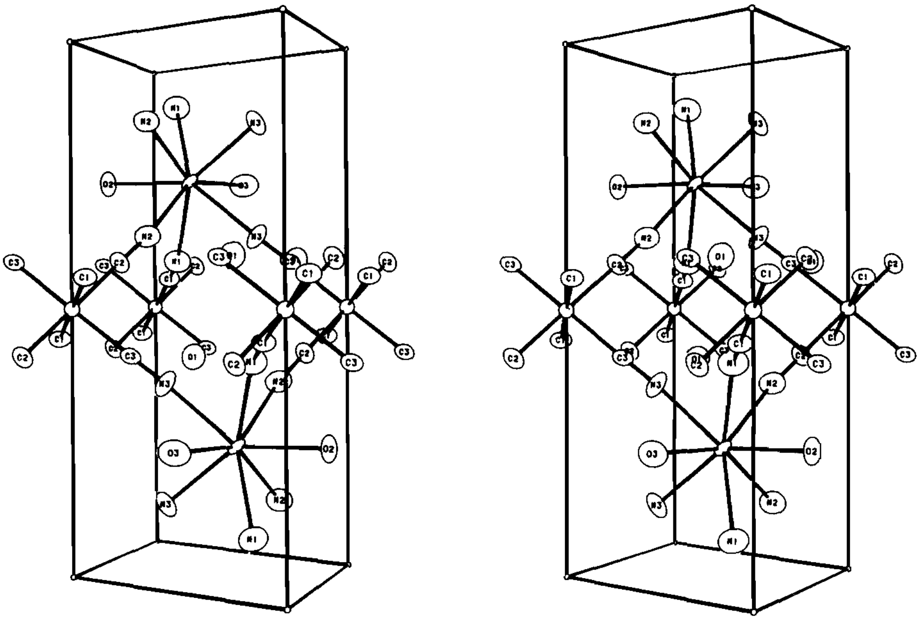

Fig. 2. $BiFe(CN)_6 \cdot 4H_2O$. A stereoview of the unit cell. The Bi^{3+} and Fe^{3+} ions are drawn fully coordinated. O(1) atoms associated with the zeolitic water molecules are seen within the Bi–N–C–Fe network.

is eight-coordinated to two oxygen atoms from the water molecules and six nitrogen atoms from cyano groups. The eight atoms are arranged as a square antiprism about the central Bi^{3+} ion, see Fig. 1. Both water molecules lie in the same plane, *trans* to one another. The four nitrogen atoms, N(2), N(2′), N(3), and N(3′), are planar to within 0.001 Å (least-squares plane refinement). The two oxygen atoms, O(2) and O(3), and two other nitrogen atoms, N(1) and N(1′), are planar to within 0.036 Å. These two planes have a dihedral angle of 0.3° which verifies parallelism. The averaged Bi–N and Bi–O bond distances are 2.513 and 2.418 Å, respectively. These averaged bond lengths and that of F–C are in good agreement with other published distances found in BIDICS [10]. The Bi–N≡C bond angles range from 146.8 to 166.4°, which implies that there is very little directional influence due to electrostatic binding of the bismuth ion. However, there is strong directional bonding related to the interaction of Fe 3d orbitals and the CN^- orbitals as attested to by the averaged F–C≡N bond angle of 178.8°. The averaged C≡N bond distance is 1.141 Å. The zeolitic water molecule, O(1), is trapped in distorted cages composed of a Bi–N–C–Fe network. This water molecule, is within hydrogen bonding to the coordinated water molecule, O(3). The contact distance between O(1) and O(3) is 2.830 Å [11].

Shannon [8] has stated that when the Bi^{3+} cation is forced into high symmetry, the Bi^{3+} compound has a smaller volume than that of the corresponding La^{3+} compound. The difference depends on the lone pair character. Generally, a lone pair repulsion in the Bi^{3+} coordination sphere would result in longer bond lengths for those bonds adjacent to the lone pair and short lengths for those more remote. In a high symmetry coordination sphere, the lone pair has little interaction and the Bi^{3+} ion tends to be smaller. The cell volume of $BiFe(CN)_6 \cdot 4H_2O$ is smaller than that of $LaFe(CN)_6 \cdot 5H_2O$ (653.86 compared to 714.24 $Å^3$). This difference is due to the loss of one water molecule and the decreased Bi^{3+} ion size. The respective Bi–N and Bi–O bond lengths 2.513 and 2.418 Å are shorter than those of La–N and La–O, 2.613 and 2.585 Å.

This contraction is also seen in the cell volumes of the corresponding hexacyanide cobaltates, $BiCo(CN)_6 \cdot 4H_2O$ is 640.8 $Å^3$ and $LaCo(CN)_6 \cdot 5H_2O$ is 699.99 $Å^3$ [12]. The analyses of heavy lanthanide ferri- and cobaltichexacyanide systems are forthcoming.

Supplementary Material

Full listings of anisotropic thermal parameters and observed and calculated structure factors are available. Copies may be obtained from D.F.M.

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