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The Crystal Structure of $BiFe(CN)_6 \cdot 4H_2O$ and $BiCo(CN)_6 \cdot 4H_2O$

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Abstract

The structure of $BiFe(CN)_6 \cdot 4H_2O$, which is of the $SmFe(CN)_6 \cdot 4H_2O$ type, was determined by single-crystal X-ray diffraction and refined in space group *Cmcm*. Based on relations between the monoclinic site parameters of a published structure determination as well as on our psi-scans, the monoclinic symmetry, $P2_1/m$, which was proposed by D. F. Mullica, H. O. Perkins and E. L. Sappenfield, *Inorganica Chimica Acta, 142* (1988) 9, is discarded in favor of the orthorhombic symmetry, *Cmcm*. The same structure is adopted by $BiCo(CN)_6 \cdot 4H_2O$.

Several years ago we studied the rare-earth ferri-, cobalti- and chromicyanides [1]. A relationship was found between their water contents, their unit-cell volumes and the rare-earth ionic radii. Hydrates with five water molecules per formula unit are stable at room temperature with the large rare-earth elements La, Ce, Pr, while with the smaller elements Sm····Lu only four water molecules are incorporated. The pentahydrates crystallize in the hexagonal $LaFe(CN)_6 \cdot 5H_2O$ structure [2]. In this structure type the transition element is octahedrally coordinated by the carbon atoms of six radially arranged CN ions, while the rare-earth ion is surrounded by six N in trigonal-prismatic coordination and by three O of the water molecules outside the square prism faces. Two zeolitic H_2O are located above and below the two trigonal prism faces. The removal of one of the three H_2O molecules in the equatorial plane around the $[LnN_6]$ trigonal prisms reduces the symmetry of the tetrahydrates to orthorhombic according to Petter *et al.* [3, 4] or to monoclinic according to Mullica *et al.* [5].

Based on the ionic radii of Shannon and Prewitt [6, 7] we conjectured that the bismuth compounds should behave like the lanthanum analogs [1] and form pentahydrates. Some years ago we synthesized $BiFe(CN)_6 \cdot xH_2O$ and $BiCo(CN)_6 \cdot xH_2O$ and found unexpectedly small unit cells. However, the difference between the volumes of the iron and the cobalt salt was normal. The volumes were found to fall into the tetrahydrate region and thus were in accordance with the orthorhombic indexing of the Guinier patterns. A structure refinement on a $BiFe(CN)_6 \cdot 4H_2O$ single crystal confirmed the assumed space group *Cmcm*. Disappointed by the failure in an attempt to prepare $BiCr(CN)_6 \cdot 4H_2O$ the data were put aside but a recent publication of Mullica *et al.* [8] prompted their resurrection. These authors refined the structure of $BiFe(CN)_6 \cdot 4H_2O$ in space group $P2_1/m$, after they had tried the orthorhombic system (with an inadequate choice of the unit cell, leading to $hkl \neq \bar{h}kl$), in analogy to $SmFe(CN)_6 \cdot 4H_2O$ [5]. This unnecessarily low symmetry as well as some misprints in their positional parameter table – missing minus signs for x(C1), y(C2) and x(O3) – motivated us to the present note. After this manuscript was ready for being submitted notice was received of a paper by Marsh [9] who – being the expert in this field – had already given a transcription of the structure of $BiFe(CN)_6 \cdot 4H_2O$. Since Mullica and Sappenfield [10] have maintained the correctness of their monoclinic space group it was decided to repeat our structure refinement.

The preparation of $BiFe(CN)_6 \cdot 4H_2O$ was similar to that given in ref. 8 but differs in a minor point which is responsible for better crystal growth. In order to prevent hydrolysis of the Bi^{3+} ions the starting solutions, 0.05 M $Bi(NO_3)_3 \cdot 5H_2O$ and 0.05 M $K_3Fe(CN)_6$, were both prepared in 1.25 M DL-lactic acid, $CH_3CH(OH)COOH$. After filtering, the mixture of these solutions was stored in the dark at room temperature. Small dark crystals of a size up to 2 mm grew within 2–4 days. The most perfect crystals had the form of hexagons of 0.1–0.3 mm edge length and were transparent red under the microscope.

$BiCo(CN)_6 \cdot 4H_2O$ can easily be synthesized in aqueous solutions since $K_3Co(CN)_6$ is more stable than its iron analog. Thus, a solution of 0.01 M $Bi(NO_3)_3 \cdot 5H_2O$ in 1 M HNO_3 was mixed with an

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aqueous 0.02 M $K_3Co(CN)_6$ solution in the volume ratio 2:1, and kept at room temperature. Within one day small crystals (0.1–0.4 mm) grew, which are transparent with a rosy tinge.

The experimental difficulties increase enormously if we proceed to the opposite direction, towards Mn and Cr. The acidification of the solutions, necessary to prevent Bi^{3+} from transforming to $(BiO)^+$, favors the decomposition of $K_3Cr(CN)_6$. Up to now attempts to prepare $BiCr(CN)_6 \cdot 4H_2O$ have not been successful.

Magnetic measurements proved that Fe^{III} and Co^{III} are in a low-spin state as they are in the rare-earth analogs. No indication of magnetic order was detected in the iron compound down to 1.6 K.

The structure determination was carried out on single crystals which looked optically perfect. The intensity data were collected on a Picker FACS-I diffractometer with STOE software and encoders, using Mo Kα radiation monochromatized with a graphite monochromator. The intensities of three standard reflections, (4,0,0), (0,6,0) and (0,0,6), were checked every 2 h. In a first step all eight octants were measured on a very small crystal of 65 μm X 65 μm X 80 μm to test the arguments of Mullica *et al.* [8] about the low symmetry. The intensities we measured in the range $2\theta = 3 \cdots 40°$ in the positive as well as in the negative 2θ range. By performing measurements in the full sphere it was possible to scrutinize the symmetry conditions on equivalent reflections. For 35 reflections at $\chi > 60°$ that showed deviations from the orthorhombic symmetry ψ-scans were performed. A thorough analysis proved (see Fig. 1) that all discrepancies can be explained by absorption effects. Thus, there is no reason to abandon the orthorhombic symmetry. In spite of the effort (8384 reflections were measured) this data set was not used for the evaluation of the structure since several attempts to obtain a data set of sufficient quality by numerical correction procedures failed. Therefore, in order to avoid all problems connected with absorption corrections, an even smaller single crystal of dimensions 30 μm X 30 μm X 50 μm was selected to reduce the difficulties due to absorption, accepting the considerably longer measuring times. On this tiny crystal in one octant from $2\theta = 3$–$50°$, 691 reflections (of which 570 had intensities greater than 2σ) were measured. The structure refinement was done with the SHELXTL PLUS, XLS-Structure Refinement Package (Nicolet Instruments Corporation, 1988). As starting model the data of $SmFe(CN)_6 \cdot 4H_2O$ were used. The extreme smallness of the crystal allowed to an absorption correction ($\mu = 14.46$ mm^{-1}, $r = 0.036$ mm, $\mu r = 0.52$) to be neglected. For all atoms the thermal parameters were refined anisotropically. The full-matrix least-squares refinement of the 52 variables on F_{hkl} yielded the reliability values $R = 0.028$ and $R_w = 0.028$. A difference Fourier map showed no deviations from the proposed structure. Similar site parameters have been obtained with the other two crystals though with larger R values and less realistic U values as a consequence of the absorption. These R values are one of the main arguments of Mullica *et al.* [8] in favor of the monoclinic space group. Due to the large absorption of the Bi atoms it is very delicate to calculate a good absorption correction. A doubling of the number of variables required by a lower-symmetry space group leads in general to a reduction of the R value. An insufficient absorption correction does not completely remove the systematic error in the data set so that the Hamilton significance test [11], which was also used to defend the monoclinic symmetry, is no longer reliable. Taking these facts into account it is by no means justified to deduce a lower symmetry from the actual experimental data. In this connection it might be worthwhile remembering the clarifying paper of Donohue and Trueblood [12] about the 'unreliability' of R values.

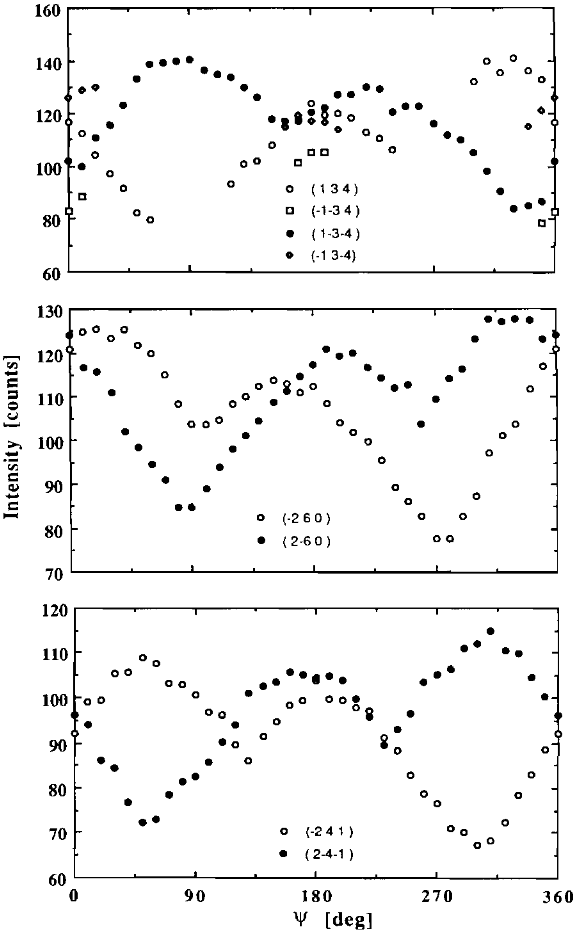

Fig. 1. Three representative examples of the ψ-scans which demonstrate that seeming intensity differences of equivalent reflections are due to geometrical and absorption effects.

TABLE 1. Crystallographic data of $BiFe(CN)_6 \cdot 4H_2O$ and $BiCo(CN)_6 \cdot 4H_2O$. Orthorhombic $SmFe(CN)_6 \cdot 4H_2O$ type, space group *Cmcm* (No. 63); C1 and N1 in 16h, O1 in 8g, C2, N2 and O2 in 8f, Bi in 4c, and Fe or Co in 4a. Atomic positions in the structure of $BiFe(CN)_6 \cdot 4H_2O$[a]

Atom	Site	x	y	z	$100\ U_{11}$	$100\ U_{22}$	$100\ U_{33}$	$100\ U_{12}$	$100\ U_{13}$	$100\ U_{23}$
Bi	4c	0	0.32379(5)	$\frac{1}{4}$	1.65(4)	1.71(4)	1.17(4)	0	0	0
Fe	4a	0	0	0	1.34(10)	1.57(10)	1.36(10)	0	0	0.12(8)
C1	16h	0.1843(11)	0.0473(6)	0.5879(6)	1.7(4)	2.5(4)	1.8(4)	0.0(3)	0.0(3)	0.2(3)
C2	8f	0	0.1365(9)	0.0598(8)	1.8(6)	2.7(6)	1.5(6)	0	0	0.3(5)
N1	16h	0.2014(10)	0.4253(6)	0.1405(6)	2.2(5)	4.4(4)	3.3(4)	−0.4(4)	0.8(3)	0.9(4)
N2	8f	0	0.2173(8)	0.0938(8)	4.5(7)	1.7(5)	2.0(5)	0	0	−1.3(4)
O1	8g	0.2641(14)	0.2123(8)	$\frac{1}{4}$	3.9(6)	7.0(6)	2.6(4)	2.6(5)	0	0
O2	8f	0	0.3449(8)	0.5997(7)	4.0(6)	4.6(6)	3.5(5)	0	0	0.9(4)

$BiFe(CN)_6 \cdot 4H_2O$: $a = 7.449(1)$, $b = 12.853(2)$, $c = 13.679(2)$ Å; $(a\sqrt{3}/b - 1) = +0.0041(6)$; $V/Z = 327.4$ Å^3; $d_x = 2.509(2)$ g/cm^3. $BiCo(CN)_6 \cdot 4H_2O$: $a = 7.401(1)$, $b = 12.729(2)$, $c = 13.622(2)$ Å; $(a\sqrt{3}/b - 1) = +0.0070(7)$; $V/Z = 320.8$ Å^3; $d_x = 2.546(2)$ g/cm^3.

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

TABLE 2. Contact distances (Å) up to 3.5 Å and bond angles (°) in the structure of $BiFe(CN)_6 \cdot 4H_2O$[a]

Bi–2O1	2.434(10)	{2.425(10) and 2.412(10)}
Bi–4N1	2.489(8)	{2.499(8) and 2.508(8)}
Bi–2N2	2.538(11)	{2.531(9)}
Fe–4C1	1.924(8)	{1.933(9) and 1.945(9)}
Fe–2C2	1.936(12)	{1.932(9)}
C1–1N1	1.169(11)	{1.134(12) and 1.137(12)}
C1–1Fe	1.924(6)	{1.933(9) and 1.945(9)}
C1–1C1	2.695(12)	{2.702(19)*}
C1–1C2	2.698(13)	{2.690(19)* and 2.697(19)*}
C1–1C1	2.746(12)	{2.793(15)*}
C1–1C2	2.759(12)	{2.769(23)* and 2.800(23)}
C1–1O2	3.511(11)	{3.515(17)* and 3.526(17)*}
C2–1N2	1.138(16)	{1.135(12)}
C2–1Fe	1.936(12)	{1.932(9)}
C2–2C1	2.698(13)	{2.690(19)* and 2.697(19)*}
C2–2C1	2.759(12)	{2.769(23)* and 2.800(23)*}
C2–2O1	3.404(11)	{3.411(15)* and 3.415(19)*}
C2–1O2	3.455(15)	{3.393(19)*}
N1–1C1	1.169(11)	{1.134(12) and 1.137(12)}
N1–1Bi	2.489(8)	{2.499(8) and 2.508(8)}
N1–1N1	2.996(12)	{3.016(10)*}
N1–1N1	3.001(11)	{3.037(17)* and 3.039(17)*}
N1–1N2	3.132(12)	{3.105(19)* and 3.120(20)*}
N1–1O1	3.156(12)	{3.143(21)* and 3.154(19)*}
N1–1O2	3.360(12)	{3.391(12)* and 3.392(12)*}
N2–1C2	1.138(16)	{1.153(12)}
N2–1Bi	2.538(11)	{2.531(9)}
N2–2O1	2.905(11)	{2.892(14)* and 2.906(14)*}
N2–1O2	3.114(15)	{3.063(18)*}
N2–2N1	3.132(12)	{3.105(19)* and 3.120(20)*}
O1–1Bi	2.434(10)	{2.412(10) and 2.425(10)}
O1–2O2	2.803(10)	{2.820(12)* and 2.828(12)*}
O1–2N2	2.905(11)	{2.893(13)* and 2.906(14)*}
O1–2N1	3.156(12)	{3.143(21)* and 3.154(19)*}
O1–2C2	3.404(11)	{3.411(15)* and 3.415(15)*}
O2–2O1	2.803(10)	{2.830(10)}
O2–1N2	3.114(15)	{3.063(18)*}
O2–2N1	3.360(12)	{3.391(18)* and 3.392(12)*}
O2–1C2	3.455(15)	{3.393(19)*}
Fe–C1–N1	178.7(6)	{178.7(9) and 178.8(8)}
Fe–C2–N2	179.1(10)	{179.0(9)}

(continued)

TABLE 2. *(continued)*

Bi–N1–C1	165.3(7)	{165.7(8) and 166.4(8)}
Bi–N2–C2	146.8(9)	{146.8(8)}
C1–Fe–C1	91.1(3)	{91.9(4)}
C1–Fe–C2	91.3(4)	{91.6(4)}
	88.7(4)	{87.7(4)}
N1–Bi–N1	116.8(3)	{117.4(4)*}
	74.0(3)	{74.0(3)* and 74.6(4)*}
	74.1(3)	{74.7(4)*}
N1–Bi–N2	142.1(2)	{143.0(3)* and 142.4(4)*}
	77.1(3)	{76.2(4)* and 76.5(4)*}
N2–Bi–N2	114.7(4)	{115.5(5)*}
O1–Bi–O1	107.9(4)	{108.0(5)*}

[a] Our values are compared with those of Mullica *et al.* [8] (in { }; those with an asterisk are our calculations based on the parameters given in ref. 8). Estimated standard deviations are given in parentheses.

The structure data of $BiFe(CN)_6 \cdot 4H_2O$ crystal are listed in Table 1 (see also 'Supplementary Material'). The interatomic distances are compared in Table 2 with the corresponding values of Mullica *et al.* [8]. Their values coincide with ours within the experimental accuracy which was to be expected since the monoclinic description differs from the orthorhombic one by a lowered Laue symmetry only. It is noteworthy that the C–N distances are as reasonable as in the monoclinic model. And of course, there is a very satisfactory agreement between our structure parameters and those obtained by transforming the monoclinic data of Mullica *et al.* [8] as listed in Table 3. A stereoview of the coordinations can be found in their publication [8] while a [0, 0, 1] projection of the structure is shown in Fig. 2.

The data and arguments presented here convincingly prove that the symmetry of the crystal structure of $BiFe(CN)_6 \cdot 4H_2O$ need not be reduced to monoclinic and that *Cmcm* is the correct space group. This is also plausible because elimination of one of three equatorial H_2O molecules around the $[LnN_6]$ trigonal prisms on going from the hexagonal $LaFe(CN)_6 \cdot 5H_2O$ type to the $SmFe(CN)_6 \cdot 4H_2O$ type leads to an intrinsically orthorhombic arrangement, as is striking to the eye as soon as one looks at a [001] projection (Fig. 2). There is no obvious energy gain on distorting the structure and nature will certainly not reduce the symmetry without a compelling reason.

Based on the similar Guinier pattern and intensity calculations with LAZY PULVERIX [13] the same $SmFe(CN)_6 \cdot 4H_2O$-type structure can be assigned to the cobalt analog $BiCo(CN)_6 \cdot 4H_2O$. Its unit-cell data are included in Table 1.

Acknowledgement

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TABLE 3. The *C*-centered monoclinic cell (derived from the monoclinic cell of Mullica *et al.* [8] by doubling: $a' = a + c$, $b' = a - c$, $c' = b$) that transforms to the orthorhombic *Cmcm* cell. The notation used for the orthorhombic $SmFe(CN)_6 \cdot 4H_2O$ type is added on the right-hand side

Atom	*x*	*y*	*z*	Atom site in *Cmcm*	
Bi	0.00003(8)	0.32368(8)	$\frac{1}{4}$	Bi	4c
Fe	0	0	0	Fe	4a
C1	0.000(2)	0.137(2)	0.0583(9)	C2	8f
C2	0.189(2)	0.049(2)	0.5875(9)	C1	16h
C3	0.186(2)	0.047(2)	0.5883(9)		
N1	0.0015(15)	0.2185(15)	0.0936(9)	N2	8f
N2	0.202(1)	0.425(1)	0.1390(9)	N1	16h
N3	0.2030(9)	0.425(1)	0.1389(9)		
O1	0.0005(10)	0.3425(10)	0.5977(8)	O2	8f
O2	0.2625(20)	0.2125(20)	$\frac{1}{4}$	O1	8g
O3	0.2625(20)	0.2135(20)	$\frac{1}{4}$		

$a = 7.447(2)$, $b = 12.837(3)$, $c = 13.678(2)$ Å, $\gamma = 90.01(2)°$.

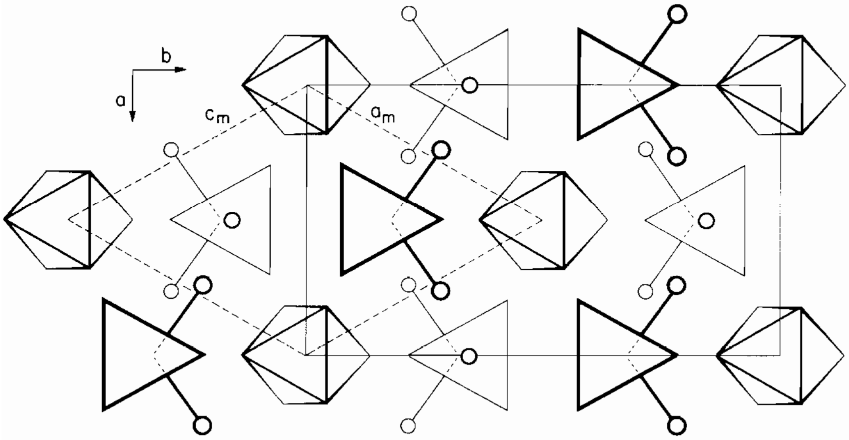

Fig. 2. Projection of the orthorhombic $SmFe(CN)_6 \cdot 4H_2O$-type structure of $BiFe(CN)_6 \cdot 4H_2O$ onto the (*a*, *b*) plane. The water molecules are given as small circles. The bonded H_2O molecules are connected with the Bi atoms. The zeolitic H_2O molecules above and below each trigonal N prism (near the center of the triangles) are partly omitted. The positions of the Fe and C atoms are defined by the octahedra, those of N and Bi by the deformed trigonal prisms and the Bi–O bonds (6N + 2O together form a slightly deformed square antiprism). The monoclinic cell (a_m, c_m) used by Mullica *et al.* [8] is indicated by broken lines.

Supplementary Material

Lists of the structure factor amplitudes and anisotropic thermal parameters may be obtained from authors W.P. and V.G.

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