The Crystal Structure of LaFe(CN)$_6$.5H$_2$O*

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The crystal structure of LaFe(CN)$_6$.5H$_2$O has been determined from three-dimensional, single-crystal, X-ray diffraction data and refined by the least-squares method to give $R = 0.030$. The space group is hexagonal, $P6_3/m$, with $a = 7.554$ (1) and $c = 14.452$ (1) Å. For $Z = 2$ the calculated density is 2.09 g cm^{-3} ($\varrho_{obs} = 2.08$ g cm^{-3}). A total of 557 unique reflections were measured with Cu $K\alpha$ radiation on a three-circle diffractometer by a θ–2θ scan technique to a maximum 2θ of 160°. Cyanide bridges link octahedral FeC$_6$ groups to nine-coordinated LaN$_6$(H$_2$O)$_3$ groups. Two uncoordinated water molecules occupy holes in the structure along the threefold axis. Important bond lengths are: Fe–C, 1.931; La–N, 2.613; La–O(2), 2.585; C≡N, 1.155 Å. X-ray powder photographs show that this material is a member of an isomorphous series of compounds which includes the ferrocyanide of Th^{4+} and the ferro- and ferricyanides of Y^{3+}, $^{+3}$ and Bi all of the trivalent lanthanide metal ions except Pm^{3+} (which was unavailable).

Introduction

As part of general investigations of complex ferro- and ferricyanides (Weiser & Milligan, 1936, 1938; Weiser, Milligan & Bates, 1942; Maer, Beasley, Collins & Milligan, 1968; Beasley & Milligan, 1969), we have recently initiated studies of an isomorphous series of compounds including the ferrocyanide of Th^{4+} and the ferro- and ferricyanides of Y^{3+}, Bi^{3+} and all of the trivalent lanthanide metal ions except that of promethium (which has been unavailable to us). Powder X-ray diffraction patterns of these compounds indicate they are isomorphous, belonging to the hexagonal space group $P6_3/m$. Because of the ease with which it crystallizes we chose the lanthanum complex for our initial studies.

Prandtl & Mohr (1938) first reported the growth of single crystals of rare earth ferricyanides which were prepared in an attempt to purify the rare earth oxides. They reported that lanthanum ferricyanide which had been dried over concentrated sulfuric acid contained 4·5 moles of water per formula unit. Davies & James (1948) reported a normal composition of LaFe(CN)$_6$.5H$_2$O for this material but stated that one mole of water per formula unit could be removed by exposing the compound to a vacuum over sulfuric acid for one month. They reported a density of 2·045 g cm^{-3} at 25°C. Marsh (1947) also confirmed this density independently.

It is of special interest to determine the water content of these materials and how the water molecules are held in the crystal. If water does exist in definite crystallographic positions, it is of interest to determine whether or not it is directly coordinated to a metal ion. This could shed some light on the mechanism of semi-permeability in the related cubic ferrocyanides [see Milligan, Uda, Beasley, Dillin, Bailey & McCoy (1970) for details]. We therefore undertook the structure determination of LaFe(CN)$_6$.5H$_2$O and now report the details of this investigation.

Experimental

Bright red single crystals of LaFe(CN)$_6$.5H$_2$O were prepared by the method reported by Prandtl & Mohr (1938). The lanthanum oxide 99·99% (ACS grade) was obtained from Alfa Inorganics and potassium ferricyanide (ACS grade) was obtained from Allied Chemical. Carbon, hydrogen, nitrogen, and iron analyses were performed on these crystals by Geller Laboratories; oxygen was estimated by assuming that all the hydrogen was present as water, and lanthanum was estimated by difference. Calculated analysis for LaFe(CN)$_6$.5H$_2$O: La, 31·50; Fe, 12·67; O, 18·14; N, 19·06; C, 16·34; H, 2·29. Average analysis found for two trials: La, 31·19; Fe, 12·80; O, 18·00; N, 19·16; C, 16·59; H, 2·27. Additional analyses indicated that there was virtually no potassium or chloride ion contamination.

The lattice constants were obtained from a least-squares analysis (Roof, 1968) of the positions of 16 reflections ($2\theta = 62$–$134°$) measured with copper $K\alpha$ radiation (Cu $K\alpha_1$, $\lambda = 1.5405$ Å; Cu $K\alpha_2$, $\lambda = 1.5443$ Å) on a three-circle goniometer. The density was measured by the flotation method in a mixture of bromoform and p-xylene.

To minimize error due to absorption a crystal was ground into a sphere of radius 0·104 mm. Spherical absorption corrections according to Bond (1959) were applied for $\mu R = 3.26$.

Systematic absences 000l, $l = 2n + 1$ are consistent with space groups $P6_3$ and $P6_3/m$. Successful refine-

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ment based on space group $P6_3/m$ indicates that the non-hydrogen atoms occupy positions in this centro-symmetric space group.

Intensities were measured by θ–2θ scans with a G.E. XRD-5 diffractometer equipped with a three-circle goniometer and using nickel-filtered copper radiation. The rate of scanning was $2°/$min and the normal scan range was $3\cdot33°$. The background was measured for 20 sec on either side of the scan range. For some of the broad, high-angle reflections the scan range had to be increased. Reflections were measured to a maximum 2θ of 160°. A standard was measured periodically and the data were linearly corrected between standards for instrumental drift. An estimated standard deviation for the intensity of each reflection was calculated as:

$$\sigma_I = [I + B + (0\cdot02I)^2]^{1/2} \qquad (1)$$

where I is the total integrated peak intensity and B is the normalized background count (Stout & Jensen, 1968). A total of 557 unique reflections was measured and 518 were recorded as observed according to the criterion:

$(I - B) \geq 2\sigma_I$, where σ_I is defined in equation (1).

Crystal data

LaFe(CN)$_6$.5H$_2$O   F.W. 440·964
$a = 7\cdot554 \pm 0\cdot001$ Å $c = 14\cdot452 \pm 0\cdot001$ Å
$\varrho_{obs} = 2\cdot08$ g cm^{-3} $\varrho_{calc} = 2\cdot09$ g cm^{-3}
$V = 714\cdot24$ Å^3 $Z = 2$
System: hexagonal
Systematic absences: $000l$, $l = 2n + 1$
Space group: $P6_3/m$.

Structure determination

Patterson sections at $Z = 0$, $\frac{1}{4}$ and $\frac{1}{2}$ revealed the two heavy metal atom positions; the iron atom in position set 2(b) and the lanthanum ion in position set 2(c). A three-dimensional electron-density map phased from this partial model revealed a carbon atom and a nitrogen atom in general positions and two independent oxygen atom positions; one in position set 4(f) and one in position set 6(h). This model was refined isotropically with a full-matrix least-squares refinement program (Stemple, 1971) and gave disagreement indices: $R = 0\cdot049$ and $R_w = 0\cdot051$ where

$$R = \sum \||F_o| - |F_c|\|/\sum|F_o|$$

and

$$R_w = \sum w\||F_o| - |F_c|\|/\sum w|F_o| .$$

A difference Fourier map calculated at this time indicated that there was some anisotropy in the thermal motion of some of the atoms in this structure, especially in the nitrogen atom and the two oxygen atoms. It was decided, therefore, to refine the structure anisotropically, where anisotropic temperature factors were of the form

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)] .$$

Several cycles of full-matrix anisotropic refinement yielded final values of $R = 0\cdot0296$ and $R_w = 0\cdot0258$. A subsequent difference Fourier map had very little detail except at $z = 0\cdot25$. There were two peaks, $-1\cdot31$ e Å^{-3} and $1\cdot05$ e Å^{-3} near the lanthanum ion position. Elsewhere the largest peaks ranged from $0\cdot86$ e Å^{-3} to $-1\cdot04$ e Å^{-3}. None of the positive peaks was at a suitable position for a hydrogen atom. The hydrogen atoms bonded to O(1) are required by symmetry to be disordered since O(1) is on a threefold axis. The hydrogen atoms on O(2) may lie in the mirror at $z = 0\cdot25$ or above and below the mirror if they are ordered. Also there are no contact distances involving these oxygen atoms which are short enough to allow hydrogen bonding. Therefore, no attempt was made to assign or refine hydrogen atom positions in this structure.

The quantity minimized in the least-squares refinement procedure was $\sum w(|F_o| - |kF_c|)^2$, where k is a scale factor and $w = 1/\sigma^2(F_o)$ is the weight derived from equation (1) (Stout & Jensen, 1968). For all unobserved reflections $w = 0$.

The largest $\Delta\xi_i/\sigma(\xi_i)$ after the final cycle of refinement was $0\cdot12$, and the average value was approximately $0\cdot01$ for all parameters. No secondary extinction

Table 1. *Observed and calculated structure factors for* LaFe(CN)$_6$.5H$_2$O

corrections were applied. Scattering factors for La and Fe were obtained from Cromer & Waber (1965), and those for O, N and C were from Ibers (1962). Anomalous dispersion corrections were applied to the scattering factors of La and Fe (Cromer, 1965). The final observed and calculated structure factors are given in Table 1 and the final atomic positions and thermal parameters are shown in Table 2.

Discussion

A drawing of the structure viewed perpendicular to the *ac* plane is shown in Fig. 1, including the important bond lengths and bond angles. A complete list of bond lengths, contact distances and bond angles is given in Table 3. The structure consists of an infinite

polymeric array of octahedral FeC_6 groups bridged through cyanide linkages to nine-coordinated $LaN_6(H_2O)_3$ groups. There are also two uncoordinated water molecules in the asymmetric unit which are located in 'holes' on the threefold axis above or below the lanthanum atom.

The FeC_6 group is required by space-group symmetry to be octahedral. The Fe–C bond length of 1·931(3) Å is slightly longer than those previously reported for the $Fe(CN)_6^{3-}$ complex ion in some titanium, iron, and cobalt ferro- and ferricyanides (Maer, Beasley, Collins & Milligan, 1968) and in hydroferrocyanic acid (Peirrot, Kern & Weiss, 1966). These Fe–C distances ranged from 1·87 to 1·89 Å.

Nine-coordination is not too uncommon with lanthanide ion compounds. Many of the lanthanide

Table 2. *Atomic position and thermal parameters* ($\times 10^4$) *for* $LaFe(CN)_6.5H_2O$*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La	0·3333	0·6667	0·2500	62 (1)		11·2 (3)		0	0
Fe	0·0000	0·0000	0·0000	64 (3)		11·3 (6)		0	0
O(1)	0·3333	0·6667	0·9136 (6)	340 (24)		48 (4)		0	0
O(2)	0·4863 (12)	0·4276 (11)	0·2500	373 (23)	342 (21)	72 (4)	621 (41)	0	0
N	0·2202 (8)	0·8358 (7)	0·1229 (3)	233 (13)	240 (13)	44 (2)	301 (22)	−56 (9)	54 (9)
C	0·1020 (7)	0·2401 (6)	0·0772 (3)	126 (8)	119 (8)	24 (1)	118 (14)	−17 (7)	−22 (7)

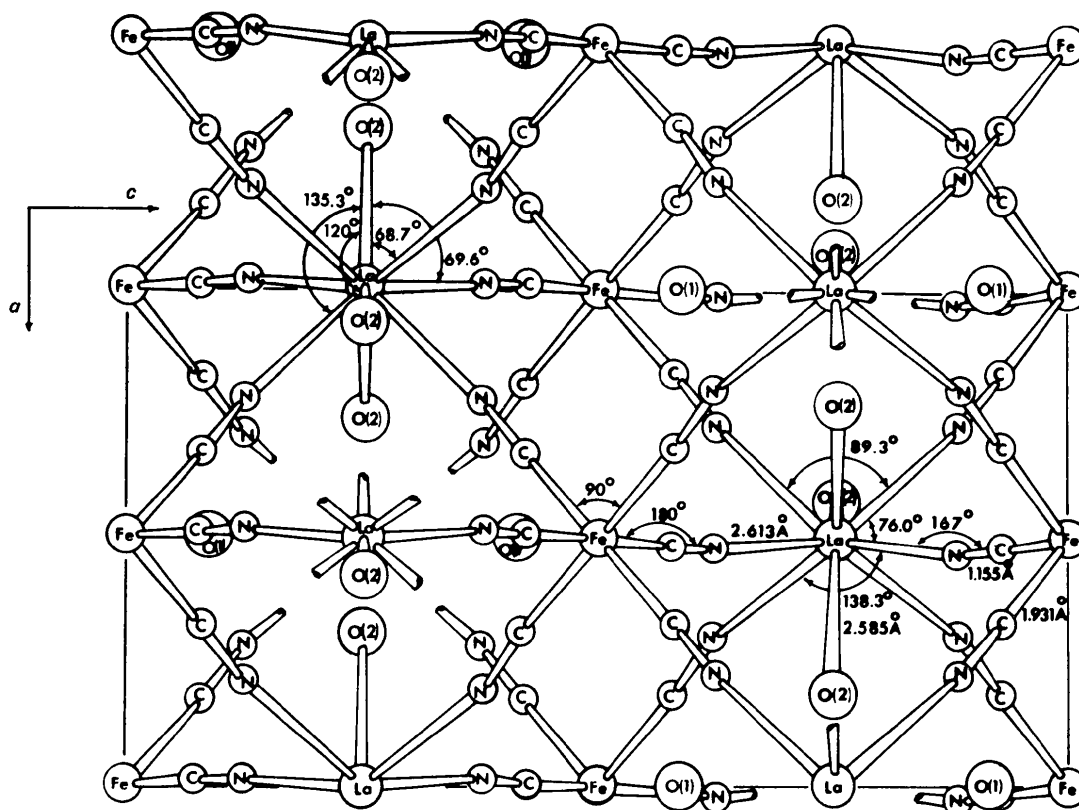* Estimated standard deviations of last significant digits are in parentheses.

Fig. 1. A view of the structure of $LaFe(CN)_6.5H_2O$ perpendicular to the *ac* plane. Bond lengths and angles are indicated on the drawing.

Table 3. *Bond lengths, contact distances and bond angles for* LaFe(CN)$_6$.5H$_2$O*

La–N	2·613 (4) Å	N–La–N	89·3 (1)°
La–O(2)	2·585 (5)	N–La–N	76·0 (1)
Fe–C	1·913 (3)	N–La–N	138·3 (2)
C—N	1·155 (5)	N–La–O(2)	135·3 (1)
		N–La–O(2)	68·7 (1)
		N–La–O(2)	69·6 (1)
		O(2)–La–O(2)	120·0
		Fe–C–N	179·5 (4)
O(1)···O(2)	2·988 (8) Å	C–N–La	167·1 (4)
C·····C	2·731 (5)		
O(2)···N	2·934 (7)		
O(2)···N	2·968 (5)		
O(1)···N	3·550 (8)		
O(1)···C	3·660 (7)		
O(1)···C	3·694 (5)		
O(1)···N	3·620 (5)		

* Estimated standard deviations of last significant digits are in parentheses.

trihydroxides and trihalides have been prepared in a crystalline form which is hexagonal and has a nine-coordinated lanthanide ion with a slightly distorted D_{3h} symmetry (Schubert & Seitz, 1947: Zachariasen, 1948; Atoji & Williams, 1959; Christensen, Hazell & Nilsson, 1967). A similar geometry has also been shown to exist for [Nd(H$_2$O)$_9$] (BrO$_3$)$_3$ (Helmholtz, 1939) and the ethyl sulfate salts of erbium(III), yttrium(III) and praseodymium(III) nonahydrates (Fitzwater & Rundle, 1959).

The lanthanum atom in the present structure has coordinated to it three waters in the mirror at 2·585 (5) Å and the nitrogen ends of six cyanides, three on either side of the mirror, at a distance of 2·61 Å. The coordination geometry is only slightly less than D_{3h} as evidenced by the two nearly equal O(2)–N distances within the LaN$_6$(H$_2$O)$_3$ group of 2·934 (7) and 2·968 (5) Å.

The C≡N bond length is 1·155 (5) Å, which is normal. The assignment of the carbon and nitrogen ends of the cyanide group was based on chemical principles and the behavior of the thermal parameters. The present assignment yields the more reasonable temperature factors and is consistent with known structure information on cyanide bridges (Cromer, 1957; Cromer & Larson, 1962; Cromer, Larson & Roof, 1965, 1966). These past studies indicate that the carbon end of the bridge forms a directional or covalent bond while the nitrogen end has a nondirectional type of interaction. This is manifested by the fact that M–C–N angles are consistently ~180° while C–N–M angles range from ~150–180°. With the present assignment the Fe–C–N angle is 180° while the C–N–La angle is 167°.

The other water molecules in the structure, those designated O(1), are uncoordinated. The closest contact distance is with O(2), 2·988 (8) Å, and this is too large even for hydrogen bonding. Some of the

other relatively close contact distances with O(1) are given in Table 3. The 'looseness' of this water molecule is further evidenced by its large thermal parameters, and it is this water, no doubt, that was removed by Davies & James (1948) under stringent drying conditions.

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