Refined Crystal Structure of Lanthanum Hexacyanoferrate(III) Tetrahydrate

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Abstract

$La[Fe(CN)_6].4H_2O$ is hexagonal, space group $P6_3/m$, with $a = 7.541$ (3) and $c = 13.955$ (9) Å, $Z = 2$. The refined crystal structure has been determined from three-dimensional single-crystal X-ray diffraction data. Least-squares full-matrix refinement yielded $R = 0.068$ and $R_w = 0.069$ for 29 varied parameters. After mono-dehydration, the nine-coordinated lanthanum atom in $La[Fe(CN)_6].5H_2O$ changes to give eight-coordination in the tetrahydrated form, $La[Fe(CN)_6].4H_2O$. The eight-coordinated polyhedron is a bicapped trigonal prism, with the La atom at its center. The $La[Fe(CN)_6].4H_2O$ structure consists of an infinite array of octahedral FeC_6 groups linked by cyanide bridges to eight-coordinated $LaN_6(H_2O)_2$ groups. The important bond lengths are: $Fe-C = 1.91$ (3), $La-N = 2.56$ (3), $La-O(2) = 2.50$ (6) and $C\equiv N = 1.14$ (4) Å.

Introduction

Powder X-ray diffraction patterns of the trivalent lanthanide ferricyanides indicate the series to be isomorphous, belonging to the hexagonal space group $P6_3/m$ (Milligan, Uda, Dillin, Bailey & Williams, 1971). Early investigators of lanthanum hexacyanoferrate(III) and -cobaltate(III) have reported the hydrated content to be 4·5 water molecules per formula unit (Prandtl & Mohr, 1938; James & Willand, 1916). However, Davies & James (1948) reported that the normal composition for the ferri complex was $La[Fe(CN)_6].5H_2O$. Bailey, Williams & Milligan (1973), using single-crystal X-ray analysis, confirmed the formula unit to be $La[Fe(CN)_6].5H_2O$ and that both coordinated and uncoordinated water molecules were present, with three water molecules coordinated to the lanthanum ion and two uncoordinated water molecules occupying 'holes' in the structure. In a recent study, Morgan, Whitmore & Garner (1978) verified the removal of one molecule of water from $La[Fe-$

$(CN)_6].5H_2O$ by means of dissociation pressure measurements. The resulting $La[Fe(CN)_6].4H_2O$ form was found to be quite stable in a vacuum, but rehydrated rapidly when exposed to ambient atmospheric pressure and humidity. The heat of dissociation for the removal of one water molecule indicated fairly strong bonding for the water molecules located in the 'holes' of the crystal lattice, or that the removed water molecule was one which was bonded to the lanthanum atom.

Recently, Mullica, Milligan & Kouba (1979) have found $La[Co(CN)_6].5H_2O$ to be isomorphous with $La[Fe(CN)_6].5H_2O$. An informative study by Hulliger, Landolt & Vetsch (1976) of rare-earth cobalticyanides reported that the large lanthanide ions form a hexagonal structure for $Ln[Co(CN)_6].5H_2O$ and that the smaller lanthanide ions ($Z \geq 62$) give rise to an orthorhombic crystal system, $Ln[Co(CN)_6].4H_2O$; the loss of one molecule of water per formula unit brought about the transformation of the hexagonal pentahydrate to the orthorhombic tetrahydrate. This paper was initiated to ascertain whether a coordinated or an uncoordinated water molecule is lost in the dehydration of $La[Fe(CN)_6].5H_2O$ to $La[Fe(CN)_6].4H_2O$ and to determine whether or not a system transformation occurs.

Experimental

1 g of La_2O_3 (ACS grade, 99·99%) was dissolved in a stoichiometric quantity of dilute HCl. After filtering, the solution was cooled and diluted to a concentration of 1 g La_2O_3 per 25 ml solution (Prandtl & Mohr, 1938). A calculated volume of $K_3[Fe(CN)_6]$ (ACS grade) solution was added and the final mixture was allowed to stand at room temperature in the dark. After one week, crystallization of $La[Fe(CN)_6].5H_2O$ was complete. The bright red-orange single crystals were washed with cold water and stored in a desiccator for further treatment. One of these pentahydrated crystals was selected for X-ray analysis.

La[Fe(CN)$_6$].4H$_2$O crystals were obtained by the dehydration of La[Fe(CN)$_6$].5H$_2$O in a controlled environment at 296 K for one week (Morgan et al., 1978). The red-purple tetrahydrated crystals were then removed under vacuum to a dry container purged continuously with nitrogen passed through anhydrous CaCl$_2$. While in the dry container, the La[Fe-(CN)$_6$].4H$_2$O crystal samples were placed in degassed 0.1 mm capillaries, the ends of which were plugged with previously degassed Apiezon B grease. The capillaries were carefully removed from the dry box and permanently sealed by micro-flaming. One of the several encapillaried samples was selected to be mounted on a goniometer.

A routine application of the Si(Li) solid-state detector, which has been installed on the Enraf–Nonius CAD-4 diffractometer in this laboratory, is to obtain X-ray fluorescence data on the same single crystal from which X-ray diffraction data will be collected (Mullica, Beall, Milligan & Oliver, 1979). Qualitative determinations of the metal constituents in both the tetra- and pentahydrated forms of La[Fe(CN)$_6$] were quickly verified and quantitative results at the expected ratio of 1:1 were obtained within 1 h of exposure time. Lattice constants for La[Fe(CN)$_6$].5H$_2$O, which were equivalent to the work of Bailey et al. (1973), and for La[Fe(CN)$_6$].4H$_2$O were obtained on the automated CAD-4 diffractometer. Intensities for both data sets were measured by the ω–2θ scan technique with a variable scan rate of 0.4–3.3° min^{-1} determined by a fast prescan (3.3° min^{-1}). Using Mo $K\bar{\alpha}$ radiation (λ mean = 0.71073 Å) at 290 K, data were collected in the ranges $3 < 2\theta < 50°$ and $3 < 2\theta < 60°$ for La[Fe(CN)$_6$].4H$_2$O and La[Fe(CN)$_6$].5H$_2$O, respectively. The intensities of two check reflections from each data set were monitored every 2 h of exposure time so as to check the reliability of the electronic hardware, X-ray intensity measurements and the stability of the crystal. Only random variations from the mean intensity values were observed in both sets of data (<2.1% deviation) which did not constitute any trend. Reflections placed in the structural refinement obeyed the respective conditions $I_{net} > 3\sigma(I)$ and $I_{net} > 2\sigma(I)$ for the tetra- and pentahydrated compounds. The data were corrected for Lorentz and polarization effects. Analytical absorption corrections were applied to each experimental data set and the resultant residual averaging error for each was 0.032 and 0.014 determined according to $R' = \sum |F_o| - |F_{av}|/\sum |F_o|$. The standard deviations of the average data were calculated according to Peterson & Levy (1957), $\sigma_{(F)} = N^{-1} \sum 1.02\sigma_{F_i}$ where N = number of redundant reflections and σ_{F_i} = standard deviation for each individual reflection. Crystal data and experimental conditions are presented in Table 1.

Structural determination and refinement

The initial metal positional parameters for La[Fe(CN)$_6$].4H$_2$O were taken from the crystallographic model established by Bailey et al. (1973) for penta-hydrated lanthanum hexacyanoferrate(III). A three-dimensional difference Fourier map disclosed the cyanide groups to be in general positions and a subsequent electron density map phased from the established metal and cyanide group positions revealed approximate positions for the two independent O atoms, O(1) at $\frac{1}{3}$, $\frac{2}{3}$, 0.9 and O(2) at 0.51, 0.46, $\frac{1}{4}$. Isotropic refinement, using a full-matrix general least-squares program (GENLES, Larson, 1967), yielded residual indices of $R = 0.105$ and $R_w = 0.113$. R and R_w are defined as $R = \sum (\Delta F)/\sum |F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2}$, where $w = \sigma^{-2}(|F_o|)$ and $\Delta F = ||F_o| - |F_c||$. At this point a difference density map revealed excess negative density in the vicinity of the O(2) atom. Consequently, several more cycles of isotropic refinement varying the population parameter for the O(2) atom yielded an R of 0.088 and an O(2) atom occupancy of $\frac{2}{3}$. After varying anisotropic thermal parameters for all atoms except O(2), final reliability factors were obtained ($R = 0.068$ and $R_w = 0.069$). A final difference electron density map revealed only a randomly fluctuating background. Therefore, no attempt was made to assign H atom positions.

The refinement of La[Fe(CN)$_6$].5H$_2$O presented no problem. All positional parameters were taken directly from the work of Bailey et al. (1973) and an immediate anisotropic refinement yielded final residual indices of 0.032 for both R and R_w. The applied correlation matrix in both refinements showed no unusual relationships between variables (ξ_i). The maximum absolute average values of convergence $[\Delta\xi_i/\sigma(\xi_i)]$ for the tetra- and pentahydrated forms of lanthanum hexacyanoferrate(III) were 9.6 × 10^{-2} and 2.6 × 10^{-3}, respectively. Atomic scattering factors and the applied anomalous-dispersion corrections were taken from Ibers & Hamilton (1974). Table 2 lists the final refined atomic and thermal parameters with their estimated

Table 1. *Crystal and experimental data*

Compound	La[Fe(CN)$_6$].4H$_2$O	La[Fe(CN)$_6$].5H$_2$O
M_r	422.92	440.94
Space group	$P6_3/m$	$P6_3/m$
a (Å)	7.541 (3)	7.554 (1)
c (Å)	13.955 (9)	14.452 (1)
V (Å^3)	687.26	714.19
ρ_{calc} (Mg m^{-3})	2.04	2.05
Z	2	2
μ(Mo $K\bar{\alpha}$) (mm^{-1})	4.15	4.00
Crystal size (mm)	0.14 × 0.14 × 0.11	0.13 × 0.13 × 0.11
Scan width (°)	1.4 + 0.35 tan θ	1.2 + 0.35 tan θ
$\sigma(I)/I$ ratio in final scan	0.02	0.02
Fixed aperture (mm)	2.0	2.0
Maximum scan time (s)	300	300
Number of reflections	190	502

Table 2. *Atomic positions* (×10³) *and thermal parameters*

La[Fe(CN)₆].4H₂O

	x	y	z	U*_eq (Å²)	U (Å²)	Occupancy
La	¼	¼	¼	14·6		1
Fe	0	0	0	13·0		1
C	121 (6)	240 (5)	79 (2)	22·1		1
N	197 (6)	805 (6)	119 (3)	28·7		1
O(1)	¼	¼	904 (3)	25·0		1
O(2)	518 (9)	468 (9)	¼		5·3	½

La[Fe(CN)₆].5H₂O

	x	y	z	U*_eq (Å²)	Occupancy
La	¼	¼	¼	12·0	1
Fe	0	0	0	12·2	1
C	107·5 (9)	240·1 (9)	76·9 (3)	16·6	1
N	217·4 (8)	833·1 (8)	122·8 (3)	20·6	1
O(1)	¼	¼	914·8 (6)	25·3	1
O(2)	491·3 (12)	429·9 (12)	¼	24·5	1

* Equivalent isotropic U values (×10²).

standard deviations for La[Fe(CN)₆].4H₂O and La[Fe(CN)₆].5H₂O.*

Discussion

The loss of one water molecule in the dehydration process did not bring about a system transformation [hexagonal to orthorhombic, as suggested by Hulliger *et al.* (1976) in rare-earth cobalticyanides]. Like the pentahydrated complex, La[Fe(CN)₆].4H₂O proved to be hexagonal ($P6_3/m$). During the early indexing and orientation stages of La[Fe(CN)₆].4H₂O on the Enraf–Nonius CAD-4 diffractometer, all attempts to convert the found hexagonal lattice to an orthorhombic cell using transformation matrices from a report on theoretical extensions of the reduced-cell concept in crystallography (Roof, 1969) failed. Further, both general multiplicity factors and space-group extinctions were employed to bring about the appropriate Laue-symmetry and space-group assignments. Space groups $P6_3$ and $P6_3/m$ were consistent with systematic absences 000*l*, $l = 2n + 1$, but successful refinement of the non-hydrogen atoms in $P6_3/m$ indicated that this centrosymmetric model was correct.

The obvious differences between the tetra- and pentahydrated forms were the reductions of the lattice constants, especially the c_0 axes (Δ0·5 Å), which brought about the concurrent shortening of bond lengths La–N, La–O(2), Fe–C, and the contact distance O(1)···O(2). The dissociation work by Morgan *et al.* (1978) helped guide our crystallographic

options. Their findings, which were deduced from the magnitude of the heat of dissociation, evidenced the existence of strong hydrogen bonds, if the removed water molecule was one of the independent uncoordinated molecules, or the removal of a coordinated water molecule. Our crystallographic investigation verified the latter conclusion. It is well known that the dehydration of the classical compound CuSO₄.5H₂O has three successive stages of dehydration. In the pentahydrated copper sulfate structure, four of the water molecules are coordinated with the copper atom, Cu(H₂O)₄; the fifth occupies a hole in the structure remote from the metallic atoms and is held in position by hydrogen bonding (O···O contact distances 2·68 to 2·99 Å). An X-ray diffraction analysis by Beevers & Lipson (1934) has shown that the first break in the dehydration curve of CuSO₄.5H₂O corresponds to the breaking up of the group around one of the Cu atoms (two coordinated O atoms), then dehydration of the remaining associated O atoms, and finally the expulsion of the odd water molecule. A neutron diffraction analysis by Bacon & Curry (1962) verified the earlier X-ray investigation and supported Beevers & Lipson's conclusions.

The bond distances determined in both data sets (see Table 3) were found to be in excellent agreement with previously reported bond lengths listed in *Bond Index of the Determinations of Inorganic Crystal Structures* (1969–1977). An important observation is the contraction of O(1)···O(2). Prior to the loss of one molecule of water, this contact distance (2·99 Å) suggested that the uncoordinated water molecule, O(1), could only be weakly hydrogen bonded to the coordinated water molecule, O(2). In the La[Fe(CN)₆].4H₂O structure the contraction of O(1)···O(2) to 2·83 (5) Å indicates that

Table 3. *Comparative bond lengths* (Å) *and angles* (°)

	La[Fe(CN)₆].4H₂O	La[Fe(CN)₆].5H₂O
La–N	2·56 (3)	2·612 (5)
La–O(2)	2·50 (6)	2·599 (6)
Fe–C	1·91 (3)	1·926 (6)
C–N	1·14 (4)	1·158 (7)
O(1)···O(2)	2·83 (5)	2·987 (6)
C···C	2·71 (6)	2·725 (10)
O(2)···N	2·85 (6)	2·942 (8)
O(2)···N	2·91 (6)	2·976 (8)
O(1)···N	3·50 (5)	3·534 (9)
O(1)···N	3·81 (4)	3·642 (5)
C–Fe–C	89·8 (1·4)	89·95 (21)
C–Fe–C	90·2 (1·4)	90·05 (21)
C–Fe–C	179·99	179·99
N–La–N	90·9 (1·9)	89·4 (2)
N–La–N	74·8 (1·5)	76·0 (2)
N–La–N	138·9 (8)	138·4 (1)
Fe–C–N	174·4 (3·7)	178·0 (6)
C–N–La	164·2 (3·8)	166·8 (5)
N–La–O(2)	68·8 (1·2)	68·7 (2)
N–La–O(2)	70·2 (1·2)	69·6 (2)
N–La–O(2)	134·5 (9)	135·3 (1)
O(2)–La–O(2)	120·0	120·0

not only strengthening of the hydrogen bonding but the definite existence of such bonds. Brown (1976), on the geometry of hydrogen bonds, has demonstrated that the strongest hydrogen bond is found when the $O \cdots O$ contact length is 2·73 Å and that hydrogen bonding becomes progressively stronger as the contact length shortens (3·1 towards 2·7 Å).

A stereoscopic view of $La[Fe(CN)_6].5H_2O$ and $La[Fe(CN)_6].4H_2O$ is presented in Fig. 1. An infinite polymeric array of octahedral FeC_6 groups, required by space-group symmetry, are linked by cyanide bridges to the nine-coordinated $LaN_6(H_2O)_3$ group in the pentahydrate form and to the eight-coordinated $LaN_6(H_2O)_2$ group in the tetrahydrate form. In both forms, the two uncoordinated water molecules are found in 'holes' above and below the La^{3+} ion on a threefold axis. The nine-coordinated $LaN_6(H_2O)_3$ group, having slightly distorted D_{3h} symmetry, is a tricapped trigonal prism with the La atom located at its center, the six N atoms in apical positions and the three H_2O molecules equatorially positioned near the centers of the rectangular faces. Helmholtz (1939), Zachariasen (1948) and Christensen, Hazell & Nilsson (1967) have previously described this type of coordination geometry. The eight-coordinated $LaN_6(H_2O)_2$ group in the tetrahydrate complex can be described as a trigonal prism with two of the square faces capped. Some lanthanide and actinide halides have been observed to have this bicapped-trigonal-prism lattice, a hendecahedron with C_{2v} symmetry which is a hybrid of D_{4d} symmetry (Demitras, Russ, Salmon, Weber & Weiss, 1972). Hulliger et al. (1976) characterized this eight-coordination geometry for orthorhombic $Sm[Fe(CN)_6].4H_2O$. The water molecules form trigonal bipyramidal (D_{3h}) polyhedra in $La[Fe(CN)_6].5H_2O$, whereas in $La[Fe(CN)_6].4H_2O$ they form a tetrahedral cluster.

In summary, the mono-dehydration of $La[Fe(CN)_6].5H_2O$ to $La[Fe(CN)_6].4H_2O$ did not bring about a system or space-group change, but did significantly shorten the cell parameters and some bond distances. Also, the nine-coordinated La atom grouping (a tetradecahedron) changed to an eight-coordinated $LaN_6(H_2O)_2$ group (a hendecahedron). Studies of continued dehydration of $La[Fe(CN)_6].5H_2O$ to $La[Fe(CN)_6].nH_2O$ $(n < 4)$ and dehydration of $Ln[M(CN)_6].nH_2O$ (where Ln = a lanthanide and M = a transition metal) have been initiated.

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Fig. 1. Stereoscopic drawing of $La[Fe(CN)_6].5H_2O$ with three coordinated water molecules, O(2). The drawing emphasizes the coordinated array of atoms about the centered La atom. The removal of one O(2) atom [O(2)---La] yields the eight-coordinated $LaN_6(H_2O)_2$ group found in mono-dehydrated $La[Fe(CN)_6].4H_2O$. Filled circles represent Fe atoms.