des contraintes stériques qui limitent les possibilités de positionnement des atomes P(1), O(E11) et O(L21) du tétraèdre en question. On observe la même déformation angulaire dans le tétraèdre P(1) de Nd(PO$_3$)$_3$.

Environnement du manganèse

Le manganèse possède un environnement octaédrique déformé d'oxygène: quatre liaisons Mn—O coplanaires de 1,90 Å environ et deux liaisons plus longues opposées de 2,16 Å perpendiculaires à leur plan (Tableau 4); l'ensemble forme en fait une bipyramide à base carrée de 2,68 Å de côté.

La distorsion tétragonale de l'octaèdre de coordination est due à l'effet Jahn–Teller. Dans le cas d'un champ cristallin octaédrique, ce phénomène agit uniquement sur les énergies des orbitales 3d^4 ou 3d^9. Il confirme donc encore la valence (+3) du manganèse (3d^4) dans notre composé.

Les octaèdres MnO$_6$ relient les quatre chaînes de la maille entre elles. Comme dans les autres polyphosphates du type Al(PO$_3$)$_3$ ou Yb(PO$_3$)$_3$ (Hong, 1974b) les octaèdres sont isolés. La plus courte distance Mn–Mn est de 5,800 Å, ce qui explique l'absence d'ordre magnétique révélée par une étude des susceptibilités magnétiques χ fonction de la température T de 6 K à l'ambiante. La pente de la droite (1/χ,T) conduit à une valeur du moment magnétique par ion Mn^{3+} de 4,98 μ_B (à 2,5% près). Cette valeur est proche de celle calculée pour l'ion libre d^4 (4,90 μ_B).

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The Crystal Structure of LaKFe(CN)$_6$.4H$_2$O

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The crystal structure of LaKFe(CN)$_6$.4H$_2$O has been determined from single-crystal X-ray diffraction data and refined by the least-squares method to give R = 2·96 and R_w = 3·32%. The space group is $P6_3/m$, with a = 7·412 (2) and c = 13·943 (2) Å. Cyanide bridges link octahedral FeC$_6$ groups to nine-coordinated LaN$_6$(O$_3$) groups. K ions occupy holes in the structure along the threefold axis. Important bond lengths are: Fe–C = 1·896 (9); La–N = 2·599 (10); La–O = 2·730 (9); C≡N = 1·154 (10) Å.

Introduction

As a continuation of a general study of a series of isomorphous hexagonal complex metal cyanides of the lanthanides, the structure of LaKFe(CN)$_6$.4H$_2$O has been determined.

Prandtl & Mohr (1938) first reported the preparation of ferri- and ferrocyanides of the lanthanides in an attempt to purify the rare-earth oxides. A single-crystal X-ray investigation of LaFe(CN)$_6$.5H$_2$O was carried out by Bailey, Williams & Milligan (1973), in which it was found that La and Fe are linked by non-linear cyanide bridges. The water coordination can be divided into two types. Three water molecules are coordinated

to the La, while the other two water molecules are contained in holes within hydrogen-bonding distance of the coordinated water. The H atoms were not located. A comparison of powder photographs of $LaFe(CN)_6 \cdot 5H_2O$ and the complex formed from lanthanum and potassium ferrocyanide suggested that the two compounds were isomorphous. Prandtl & Mohr (1938) reported the composition of the latter to be $LaKFe(CN)_6 \cdot 4H_2O$.

It is of considerable interest to determine the amount of water and the manner in which it is held in the lattice, because many of these cyanide metal complexes exhibit semi-permeable-membrane properties (Milligan, Uda, Beasley, Dillin, Bailey & McCoy, 1970). We therefore undertook this investigation of $LaKFe(CN)_6 \cdot 4H_2O$ and now report the details of the results.

Experimental

Crystals of $LaKFe(CN)_6 \cdot 4H_2O$ were grown by mixing aqueous solutions of lanthanum trichloride and potassium ferrocyanide. The clear, hexagonal prismatic crystals grew to approximately $0 \cdot 1$ mm within 2h. The crystal employed in data collection was $0 \cdot 05 \times 0 \cdot 045 \times 0 \cdot 039$ mm. The K content was confirmed by an atomic absorption analysis which yielded $8 \cdot 41$ *versus* $8 \cdot 47\%$ for the calculated value. Thermogravimetric analysis indicated $4 \cdot 08$ (10) water molecules per formula unit.

Unit-cell parameters were determined on an Enraf–Nonius CAD-4 diffractometer using the subroutines *SEARCH, INDEX*, and *DETCELL*.* The unit cell and orientation matrix for data collection were determined from 15 centered reflections (Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å). The diffractometer was equipped with a dense graphite monochromator set at a $5 \cdot 85°$ take-off angle. Data were collected using the θ–2θ technique with the scan rate determined by a fast prescan ($5 \cdot 0°$ min^{-1}). All reflections having less than 75 counts above background during the prescan were deemed to be unobserved. Reflections with more than 75 counts above background in the prescan were measured at a rate such that a minimum of 2000 counts above background was achieved at the estimated scan rate, which varied from $0 \cdot 4$ to about $5°$ min^{-1}. Standard deviations for I were estimated from: $\sigma^2(I) = I + 2B + (0 \cdot 02\ I)^2$, where I = integrated intensity, B = background. The 2% contribution of the integrated intensity was added in to allow for inconsistency of the beam, errors in absorption correction, *etc.* (Peterson & Levy, 1957). Several sets of redundant data were collected and, upon averaging, a residual error of $R' = 1 \cdot 5\%$ was obtained, where $R' = \sum |F_o - F_{av}|/\sum|F_o|$. The standard deviations of the average data were obtained from: $\sigma_{\langle F \rangle} = 1(1/n)\sum 1 \cdot 02\sigma_{F_i}$, where n = number of re-

* CAD-4 Operating System, Enraf Nonius, Inc., Delft, Holland.

dundant reflections and σ_{F_i} = standard deviation for each individual reflection.

For any given intensity measurement, the width of the scan was determined by: total scan width $= A + B \times \tan\theta$, with $A = 1 \cdot 90$ and $B = 0 \cdot 70$. Backgrounds were measured by extending the scan range 25% on either side. The crystal to source distance was 216 mm and the crystal to detector distance was set at 173 mm. The counter entrance slit was set at 4 mm, and the lower and upper discriminators for pulse-height analysis were set to obtain 95% of the Mo $K\alpha$ peak. As a reliability check of the electronics and of crystal stability, two reflections, 410 and 216, were recorded every 30 data points. No significant variation in intensity was noticed during the entire period of data collection. The maximum variation was $2 \cdot 5\%$. 1381 reflections were collected in the range of $3° \leq 2\theta \leq 85°$, of which 540 were independent and had net intensities greater than $3\sigma(I)$. There were 754 reflections with $I < 3\sigma(I)$. All reflections were corrected for Lorentz and polarization effects. An absorption correction employing crystal shape was also made.* The maximum and minimum transmission factors were $71 \cdot 5$ and $68 \cdot 9\%$.

Structural determination

Patterson sections at $z = 0$, $\frac{1}{4}$ and $\frac{1}{2}$ revealed the two heavy-metal positions: the Fe atom in position set $2(b)$ and the La ion in position set $2(c)$. A difference Fourier map phased with these metal positions revealed that the C and N atoms were in general positions. Electron density was also observed in position sets $4(f)$ and $6(h)$. The density in the $4(f)$ position was divided equally between K and H_2O. This model was refined anisotropically with a full-matrix least-squares program† and gave disagreement indices: $R = 0 \cdot 03$ and $R_w = 0 \cdot 033$, where $R = \sum \|F_o| - |F_c\||/\sum F_o|$ and $R_w = \sum w^{1/2}\|F_o| - |F_c\||/\sum w^{1/2}|F_o|$, where $w = 1/\sigma^2$.

In the final cycles of refinement the anisotropic thermal parameters on the water molecules in $4(f)$ were held constant at the values obtained in the study of $LaFe(CN)_6 \cdot 5H_2O$ by Bailey, Williams & Milligan.

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* The program employed in the absorption correction was a modified version of an original program by Busing and Levy.
† The programs used in this refinement were written primarily by A. C. Larson, Government Reports LA Nos. 3198, 3259, 3309.

Table 1. *Atomic positions for* $LaKFe(CN)_6 \cdot 4H_2O$

	Occupancy	x	y	z
Fe	1	0	0	0
La	1	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
K	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{3}$	0·0874 (8)
C	1	0·0703 (9)	0·2358 (5)	0·0778 (5)
N	1	0·2669 (12)	0·8856 (13)	0·1241 (5)
O(1)	1	0·4216 (13)	0·3506 (12)	$\frac{1}{4}$
O(2)	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{3}$	0·0726 (47)

This was done because of the high correlation of the thermal parameters between the K and the zeolitic-type water. A difference Fourier map after the final cycle of refinement revealed a maximum peak of 0·7 e Å^{-3}, located close to La. None of the peaks was in a suitable position to be a H atom.

The quantity minimized in the least-squares refinement procedure was $\sum w(|F_o| - |F_c|)^2$. A secondary-extinction coefficient was refined, but proved to be of no significance according to the Hamilton (1965) test of R values. Scattering factors for all atoms were obtained from Cromer & Waber (1965). Anomalous dispersion corrections were applied for all atoms. Atomic positions are listed in Table 1.*

Discussion

The structure consists of ferrocyanide octahedra linked to nine-coordinate La ions. The La ion has three water molecules coordinated to it, and an additional water molecule is contained in holes in the structure that are close to hydrogen-bonding distance away from the co-ordinated water. The K ion is also contained in these same holes in the lattice. Fig. 1 shows the arrangement of the Fe(CN)$_6^{4-}$ octahedra.

The bond distances and angles are listed in Table 2. The Fe^{II} ion is octahedrally coordinated to the cyanides as evidenced by the C—Fe—C angles in Table 2 and the Fe—C bond distances of 1·896 (9) Å. The Fe—C bond distance of 1·896 (9) Å is in complete agreement with that found by Pierrot, Kern & Weiss (1966) of 1·89 Å.

The nine-coordinate La is quite common. This coordination has been previously reported for both the trihydroxides and trihalides of the lanthanides (Schubert & Seitz, 1947; Zachariasen, 1948; Atoji & Williams, 1959; Christensen, Hazell & Nilsson, 1967; Beall, Wolcott & Milligan, 1977). In the present structure some differences appear in the coordination around the La compared with LaFe(CN)$_6$.5H$_2$O. The La—nitrogen bond distance of 2·599 (10) Å is not significantly different from that of 2·613 (4) Å observed in LaFe(CN)$_6$.5H$_2$O. However, the O—N distances of 2·972 (17) and 3·019 (10) Å and the La—O distance of 2·730 (9) Å are all considerably longer than those seen in LaFe(CN)$_6$.5H$_2$O. These changes are also reflected in the change in La—N—C angle that has decreased from 167·1° in LaFe(CN)$_6$.5H$_2$O to 155·2°. The result of the N atoms moving closer to each other in the z direction is that the O atoms are being forced out of the polyhedron. This phenomenon has been observed previously in the LnCo(CN)$_6$.nH$_2$O system by Hulliger, Landolt & Vetsch (1976) where the water molecules were actually forced out of the coordination sphere. Fig. 2 shows the coordination polyhedron of LaKFe(CN)$_6$.4H$_2$O viewed along c.

Table 2. *Bond distances* (Å) *and angles* (°) *for*
LaKFe(CN)$_6$.4H$_2$O

Fe—C	1·896 (9)	Fe—C—N	179·1 (7)
La—N	2·599 (10)	La—N—C	155·2 (7)
La—O(1)	2·730 (9)	N—La—N	79·4 (3)
C—N	1·154 (10)	N—La—O	136·7 (3)
O—N	2·972 (17)	N—La—O	137·5 (2)
O—N	3·019 (10)	N—La—O	69·0 (4)
O—K	2·947 (13)	N—La—O	67·8 (4)
		C—Fe—C	89·5 (4)
		C—Fe—C	90·5 (4)
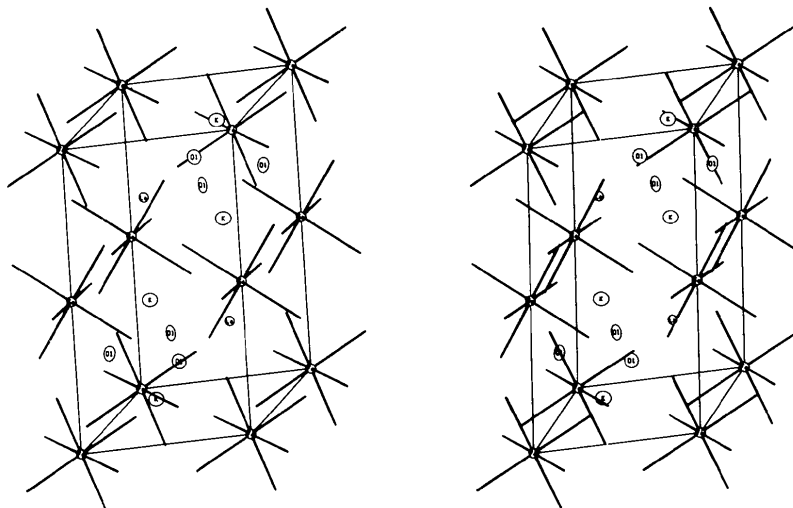
Fig. 1. Stereoview of Fe(CN)$_6^{4-}$ octahedra arrangement.
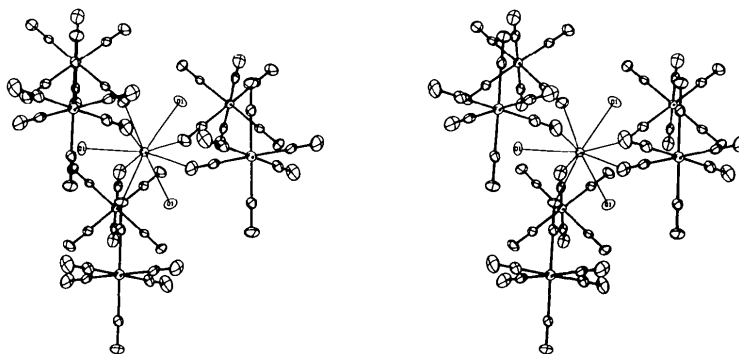
Fig. 2. Coordination polyhedron of $LaKFe(CN)_6.4H_2O$ viewed along c.

The cyanide bond of 1·154 (10) Å is quite consistent with many other structures in the literature. As mentioned earlier, the FeC_6 is an essentially regular octahedron, which is shown by the C—Fe—C angles of 89·5 (4) and 90·5 (4)°. The Fe—C—N angle is 179·1 (7)°. This angle is a reflection of the directional covalent character of the C end of the cyanide. The N end of the cyanide exhibits a more ionic non-directional interaction manifested in a La—N—C angle of 155·2 (7)° compared with 167·1° in $LaFe(CN)_6.5H_2O$. This larger distortion in the La—N—C angle from 180° contributes to the difference in the lattice constant between $LaKFe(CN)_6.4H_2O$ and $LaFe(CN)_6.5H_2O$, $c = 13·943$ (2) and $c = 14·452$ (1) Å respectively.

The structure up to this point is identical with that of $LaFe(CN)_6.5H_2O$, with small distortions around La. As mentioned earlier, the electron density observed in the difference Fourier map in the $4(f)$ position set was divided equally between two K atoms and two water molecules. In contrast, $LaFe(CN)_6.5H_2O$ had four water molecules in this position set. Essentially the structures are isomorphous, with two K atoms replacing two water molecules. This would explain why the powder photographs are almost identical. The zeolitic-type water is marginally close enough to being within hydrogen-bond distance of the coordinated water (3·1 Å). However, this distance may not be significant, since there was high correlation between the positional parameters of the K and water molecules. Thermal gravimetric analysis exhibits almost continuous dehydration curves, and the IR O—H stretching frequency around 3500 cm^{-1} indicates that a weak hydrogen bond may exist. This suggests that neutron diffraction work on these structures is necessary to further elucidate the origin of the semi-permeable properties of these compounds.

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