The Structural Analysis of $NdKFe(CN)_6 \cdot 4H_2O$

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The title compound crystallizes in the hexagonal space group $P6_3/m(C_{6h}^2$, *No. 176), with* $a = 7.358(1)$ *Å and* $c = 13.780(2)$ *Å. The experimental density for two molecules in the unit cell is 2.399(5) Mg* m^{-3} *(calculated, 2.402 Mg* m^{-3}*). The single-crystal X-ray diffraction data refined by a full-matrix least-squares method have yielded* $R_1 = 0.0160$ *and* $R_2 = 0.0165$, *based on 858 unique reflections. The octahedral* FeC_6 *groups are linked to the nine-coordinated* $NdN_6(H_2O)_3$ *groups via cyanide bridging. The uncoordinated water molecule and the potassium ion occupy holes in the structure along a threefold axis above and below the Nd ion. Important bond lengths are:* $Nd–N = 2.518(3)$; $Fe–C = 1.903(3)$; $Nd–O = 2.685(3)$; *and* $C{\equiv} = 1.166(4)$ *Å.*

Introduction

Double ferrocyanides with potassium were prepared and analyzed by Robinson [1] at the turn of the century. Double salts of ferrocyanides containing potassium and lanthanide (Ln) metals were reported by Prandtl and Mohr [2] in 1938. The number (n) of water molecules associated with $LnKFe(CN)_6 \cdot 4H_2O$ compounds varied from 4 to 8. The thermal analysis and the structural composition of these alkali–lanthanide ferrocyanides had not been satisfactorily described. Recently, Milligan *et al.* [3, 4] completed single crystal studies of two lanthanide potassium hexacyanoferrates(II). As a continuation of general investigations of series of isomorphous hexagonal complex metal cyanides of the lanthanides and since research on double salts of ferrocyanide compounds is needed to help resolve problems related to semi-permeable membranes, it was deemed necessary to undertake the structural study of the title compound.

Experimental

The U-tube slow diffusion method using stoichiometric amounts of aqueous solutions of $NdCl_3$ and $K_4Fe(CN)_6$ produced single crystals of neodymium potassium ferrocyanide tetrahydrate. Both starting compounds were obtained commercially and were used without any further purification. The flotation method [5] was employed to determine the observed density, 2.399(5) Mg m^{-3} (calculated, 2.402 Mg

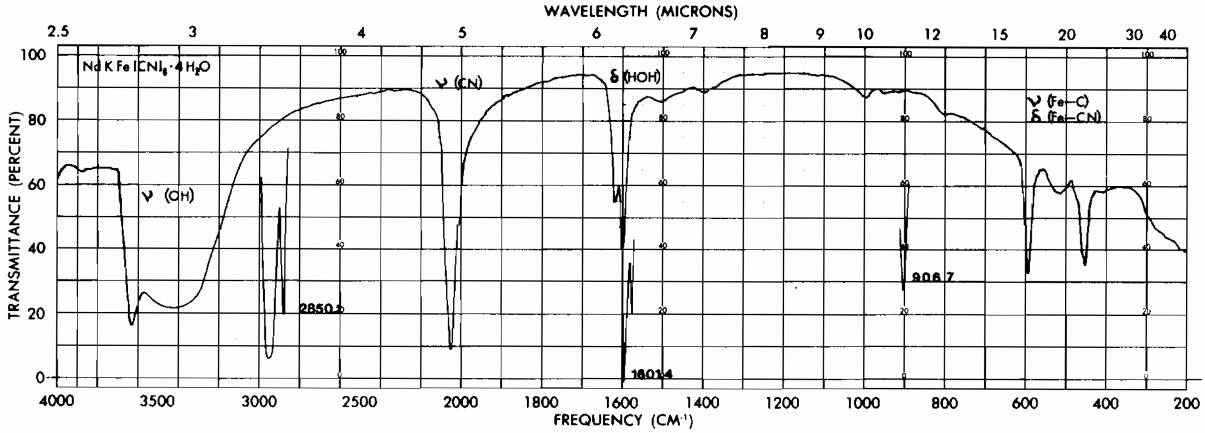

Fig. 1. IR spectra of $NdKFe(CN)_6 \cdot 4H_2O$ and polystyrene film calibration points.

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m^{-3}). A Perkin-Elmer 521 grating IR spectrometer using the press–disc technique was used to obtain an infrared spectrum of $NdKFe(CN)_6 \cdot 4H_2O$ over the frequency range of 4000–250 cm^{-1}, see Fig. 1. The thermal dehydration was obtained by employing a Perkin-Elmer TGS-1 thermobalance which was operated at 2.5 °C min^{-1} while nitrogen purged the system (20 cm^3 min^{-1}). The analysis yielded the dehydration of 4.09(10) water molecules per formula unit. A routine application of the Si(Li) solid-state detector which is mounted on the Enraf-Nonius CAD-4 automated diffractometer in this laboratory, is to secure X-ray fluorescence data on the same single crystal from which single-crystal X-ray diffraction data will be collected [6]. Qualitative determinations of the metal constituents (Nd and Fe) were verified in approximately 1 h of exposure time.

Single Crystal Analysis

After a preliminary optical examination, a single crystal of the title compound was selected and mounted on a glass fiber which was transferred to a goniometer head on the CAD-4 autodiffractometer. The diffractometer is equipped with a dense graphite monochromator (take-off angle, 5.8°). All X-ray measurements were made at 290 K using MoK_α radiation (λ mean = 0.71073 Å). A least-squares fit of 25 accurately centered reflections was used to obtain the working orientation matrix and the unit cell dimensions, see Table I. Intensities were measured using the $\Omega - 2\theta$ scan technique at a rate of 0.38–3.35° min^{-1} (determined by a fast prescan, 3.35° min^{-1}) over a range of $3° < 2\theta < 90°$. During the prescan, all reflections having less than 75 counts above background were considered unobserved. Two check reflections were monitored every 2 h of data collection and both revealed only random variations (<1.2%). Thus, the stability of the crystal and the electronic and hardware reliability were verified. Of the total 2111 collected reflections, 1003 reflections conformed to the condition $I_{net} > 3\sigma(I)$ with $I_{net} = (P - 2B)$ and $\sigma(I) = (P + 2B + p^2 I_{net}^2)^{1/2}$, where P is the peak intensity, B is the sum of the time-scaled background counts on both sides of the peak and p is the ignorance factor (0.02). Lorentz and polarization corrections were made on the resultant data. After averaging redundant data, 858 reflections were found to be unique. The residual averaging error was 0.8%, according to $R' = \Sigma\Delta|F|/\Sigma F_o$ where $\Delta|F| = |F_o - F_{avg.}|$. Crystal data, experimental conditions, and statistical summary are presented in Table I..

Structural Refinement

After verifying the hexagonal 6/m Laue group according to *hki0* C ≠ *hik0* C and *hkil* C ≠ *hikl* C, space groups $P6_3$ and $P6_3/m$ were the possible choices due to 000*l* where *l* = 2n. Due to successful refinement in previous work [3, 4], $P6_3/m$ (C_{6h}^2, No. 176) with the origin at its center became the starting model. The Nd and Fe atoms were placed in 2c and 2b (1/3, 2/3, 1/4 and 0, 0, 0 respectively). Both carbon and nitrogen atoms were positioned in general locations (12*i*). A difference Fourier map then yielded the needed information necessary to assign the proper coordinates to the K atom and the coordinated and uncoordinated water molecules. The coordinated water molecule, O(1), was placed into positional set *6h* and the potassium ion and the uncoordinated water molecule, O(2), were positioned into number set 4*f* (each at 0.5 occupancy). Both populations were refined to 0.51(1) and 0.51(1), respectively (See, Table II). An isotropic refinement using a full-matrix least-squares program [7] yielded a reliability factor of 0.039. Several more cycles varying anisotropic thermal parameters and applying secondary extinction corrections (*g*) produced final residual index values (R_1 and R_2) of 0.0160 and 0.0165. The reliability factors are defined as: $R_1 = \Sigma\Delta F/\Sigma|F_o|$ and $R_2 = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$ where $\Delta F = (|F_o| - |F_c|)$ and $w = \sigma^{-2}(|F_o|)$. The quantity minimized in the refinement was $\Sigma w(|F_o| - |F_c|)^2$. The largest value of abscission $[\Delta\xi_i/\sigma(\xi_i)]$ where ξ_i values are varied parameters, was 2.7×10^{-3} (see Table I for average value). A final electron density map was virtually featureless revealing only a random fluctuating background. Atomic scattering factors with appropriate anomalous dispersion correction factors were taken from the usual source, Ibers and Hamilton [8]. Final positional and thermal parameters with their estimated standard deviations (e.s. d. s) are presented in Table II.

TABLE I. Experimental and Statistical Summary for $NdKFe(CN)_6 \cdot 4H_2O$.

$a_o = 7.358(1)$; $c_o = 13.780(2)$ Å
Volume: 646.08 $Å^3$
M.W.: 467.36 g mol^{-1}
Observed density: 2.399(5) Mg m^{-3}
Space group: $P6_3/m$; $Z = 2$
$\Delta\omega(°)(\omega - 2\theta$ scan): $1.25 + 0.35 \tan\theta$
$\Delta\theta$: 1.5–45.0

Unique reflections: 858
$R_1 = 0.0160$; $R_2 = 0.0165$
Average value of $\Delta\xi_i/\sigma(\xi_i)$: 1.2×10^{-4}
No. of variables (ξ_i): 33
$g = 9.3(2) \times 10^{-6}$ c^{-2}
Residual density: max. 0.5(8) e $Å^{-3}$
min. 0.5(8) e $Å^{-3}$

TABLE II. Atomic Positions (×10^4) and Thermal Parameters (Å^2 × 10^2) with e.s.d.'s.[a]

Atoms	x	y	z	Occupancy	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd	1/3	2/3	1/4	1	1.12(1)	–	0.97(1)	0.56	0	0
Fe	0	0	0	1	1.13(2)	–	0.92(4)	0.56	0	0
K	2/3	1/3	816(5)	0.49(1)	6.4(2)	–	3.1(4)	3.19	0	0
C	733(4)	2388(5)	791(2)	1	1.6(1)	1.9(1)	1.7(1)	0.9(1)	−0.2(1)	−0.2(1)
N	2657(5)	8787(5)	1268(2)	1	2.5(1)	2.7(2)	3.7(2)	1.3(1)	−0.7(1)	1.0(1)
O(1)	4269(6)	3576(5)	1/4	1	2.8(2)	2.7(2)	2.8(2)	1.7(1)	0	0
O(2)	2/3	1/3	893(6)	0.49(1)	1.9(2)	–	3.5(4)	1.0	0	0

[a] The anisotropic temperature factors are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$ where U_{ij} values are the thermal parameters denoted in terms of mean-squre amplitudes of vibration.

Discussion

The Nd ion is nonacoordinated. This is fairly common in molecular complexes of the lanthanide and actinide series [9, 10, 11]. The nine-coordinated NdN$_6$(H$_2$O)$_3$ group is a symmetrical tricapped trigonal prism (D_{3h}) where the centrally located Nd atom is bonded to six nitrogen atoms in apical sites (three above and three below the metal atom) and to three water molecules equatorially positioned so as to cap centrally the three square faces of the trigonal prism. The iron ion is 6-coordinated forming a FeC$_6$ octahedral group which is linked to the 9-coordinated NdN$_6$(H$_2$O)$_3$ group by cyanide bridges. The uncoordinated water molecule and the potassium atom are contained in holes in the structure above and below the Nd atom along the three-fold axis. The uncoordinated H$_2$O molecules, O(2), and the coordinated H$_2$O molecules, O(1), have a contact distance well within the range of hydrogen bonding, 2.892(6) Å (see Table III). The infrared spectra (Fig. 1) displays two pronounced O–H stretching frequencies, a very sharp peak at approximately 3600 cm^{-1} assigned to the coordinated water molecule and a rather broad peak between 3550–3400 cm^{-1} that verifies the existance of hydrogen bonding. Other pertinent peaks are labeled on the I.R. spectra. Table III lists bond and contact distances as well as bond angles.

TABLE III. Bond and Contact Distances (Å) and Bond Angles (°) with e.s.d.s.

Fe–C	1.903(3)	Fe–C–N	178.89(28)
Nd–N	2.518(3)	Nd–N–C	147.50(12)
Nd–O(1)	2.685(3)	N–Nd–N	79.53(11)
C–N	1.166(4)	N–Nd–N	136.66(5)
O–N	2.910(4)	N–Nd–O	67.93(9)
O–N	2.940(4)	N–Nd–O	68.73(9)
O–K	2.974(2)	N–Nd–O	137.61(7)
O(1)–O(2)	2.892(6)	C–Fe–C	89.59(12)
		C–Fe–C	90.41(12)

All listed bond lengths in Table III are internally consistent with the model and are also in good agreement with experimental literature values found in BIDICS [12]. Specifically, the Fe–C bond distance of 1.903(3) Å is in direct accord with the work of Taylor and Mueller [13] on K$_4$Fe(CN)$_6$·3D$_2$O (1.906 Å), Buser *et al.* [14] on prussian blue (1.906 Å), and Morosin [15] on (NH$_4$)$_4$Fe(CN)$_6$·1.5H$_2$O (1.902 Å). The carbon to nitrogen bond length list in Table III is consistent with the C–N distances found in the X-ray studies by Revegg [16], 1.163 Å,

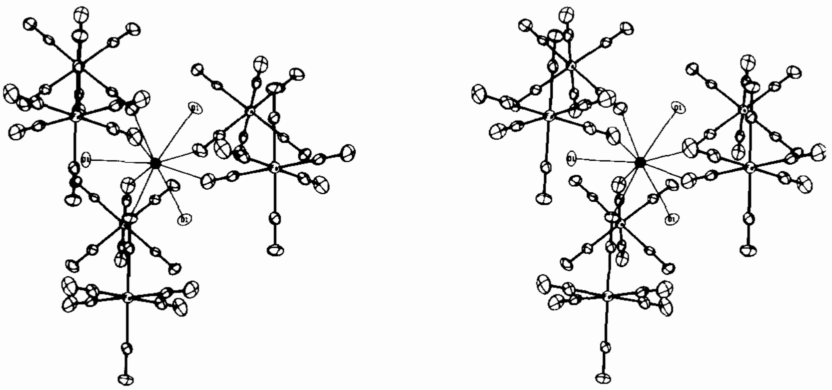

Fig. 2. NdKFe(CH)$_6$·4H$_2$O, a representative stereoview along the *c*-axis.

and Peters and Eagen [17], 1.164 Å. Figure 2 is a stereoscopic view of the coordination polyhedron of $NdKFe(CN)_6 \cdot 4H_2O$ viewed along the *c*-axis.

Acknowledgement

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