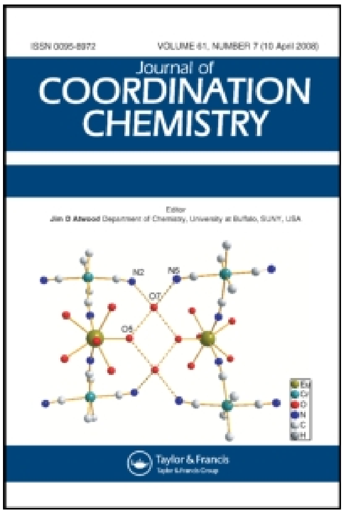

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STRUCTURAL ANALYSES OF TWO MIXED CATIONIC LANTHANIDE POTASSIUM HEXACYANOFERRATE(II) TETRAHYDRATES

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The crystal structural investigations of 1 : 1 (La/Nd)KFe(CN)$_6 \cdot 4H_2O$ (**I**) and 1 : 1 (Pr/Nd) KFe(CN)$_6 \cdot 4H_2O$ (**II**) have been determined using three-dimensional, single-crystal, X-ray diffraction data and refined by least-squares to yield final reliability (*R*) factors of 0.0180 and 0.020 based on 358 and 343 unique reflections, respectively. **I** and **II** crystallize in the hexagonal space group $P6_3/m$ (No. 176) with $a = 7.371(1)$, $c = 13.833(3)$ Å for **I** and $a = 7.362(1)$, $c = 13.799(3)$ Å for **II**. For $Z = 2$, the respective calculated densities are 2.371 and 2.388 mg m^{-3} [exp., 2.369(4) and 2.382(4) mg m^{-3}]. The coordination about the lanthanide central ions in both **I** and **II** is nine, and the geometric polyhedra are tricapped trigonal prisms (TTP). Cyanide bridging links the octahedral FeC$_6$ groups to the nine-coordinated (Ln/Nd)N$_6$(H$_2$O)$_3$ groups. The noncoordinated water molecule and the potassium ion occupy holes in the lattice along the three-fold axis above and below the lanthanide ions. Selected bond distances and angles are presented as well as discussions of the synthesis, TGA, IR, and digital SEM/EDS results, and other peripheral studies of **I** and **II**.

Keywords: Crystal structures; La/Nd and Pr/Nd complexes; ferrohexacyanides; nine-coordinate(TTP)

INTRODUCTION

Prandtl and Mohr[1] have described the syntheses of several double salts of alkali–lanthanide ferrocyanides, where the alkali metals were Na and K and the lanthanide(Ln) metals were La, Pr, Nd, Sm, ..., Er. The number (*n*) of

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water molecules that were associated with these $LnKFe(CN)_6 \cdot nH_2O$ complexes varied from 4 to 8. Obviously, the hydrate content of this series of compounds had not been described satisfactorily. However, it has now been established by means of thermal gravimetric analysis (TGA) in a crystallographic data study of $LnKFe(CN)_6 \cdot nH_2O$ where Ln = La, Ce, Pr, and Nd that $n = 4$ for this mini-series.[2]

Interest in mixed systems began in this laboratory with the crystal structure analyses of 1 : 1 $(Gd/Yb)PO_4$[3] and $Ce_{0.9}U_{0.1}PO_4$,[4] which were part of an investigation in collaboration with Oak Ridge National Laboratory. Mixed systems relative to rare-earth compositions were initiated in order to evaluate structural regulation, which may permit control of magnetic and optical properties. Structural data for the title compounds of interest are presented to provide a basis for future solid-state chemical studies dealing with structural integration and association of diverse cations so as to develop a better understanding of semipermeable membranes. Since interest in controlled hydration of zeolitic-type complexes is long standing in this laboratory, synthesis, characterization, and structural analyses of mixed lanthanide (Ln/Ln) transition metal hexacyanide hydrate systems will be continued.

EXPERIMENTAL

Appropriate molar ratios of the subject lanthanide (Ln) chlorides and potassium ferrohexacyanide were used to synthesize single crystals of 1 : 1 $(Ln/Nd)KFe(CN)_6 \cdot 4H_2O$ (**I** and **II**) using the U-tube slow-diffusion method. The interdiffusing constituents, $LnCl_3$ and $K_3Fe(CN)_6$, were commercially purchased (ACS grade) and used without further purification. The mixed cationic lanthanide compositions of the subject compounds (**I** and **II**) were confirmed by a semi-quantitative X-ray fluorescence analysis employing a JEOL JSM-6100 digital scanning electron microscope (SEM) equipped with an energy dispersion system (EDS). The analysis of La and Nd in **I** yielded 46.6(7)% La and 53.4(7)% Nd and that in compound **II** afforded 47.8(8)% Pr and 52.2(8)% Nd (**I** and **II** have standard correlations of 0.98). Thus, a 1 : 1 ratio in both complexes was concluded. Thermal dehydration was obtained by employing a Perkin-Elmer TGS-1 thermobalance, which was operated at $2.5°C\,min^{-1}$ while nitrogen gas purged the system $(20\,cm^3\,min^{-1})$. The TGAs of **I** and **II** yielded 4.01(2) water molecules/formula unit. Dehydration of (1 : 1) lanthanum/neodymium and praseodymium/neodymium potassium ferrohexacyanide tetrahydrate occurs in a stepwise manner. The compound loses one molecule between 80°C and 90°C and three water molecules between 125°C and 175°C indicating two types of bonding. The floatation method[5] employing bromoform ($d = 2.89\ \mathrm{mg\,m^{-3}}$) and 1,2-dibromomethane ($d = 2.18\ \mathrm{mg\,m^{-3}}$) was used to determine pycnometrically the experimental densities of **I** and **II**, 2.369(4) and 2.382(4) $\mathrm{mg\,m^{-3}}$ (calculated, 2.371 and 2.388 $\mathrm{mg\,m^{-3}}$), respectively. Infrared spectral data were obtained on a Mattson-Cygnus 100 FTIR analyzer over the frequency range of 4000–400 $\mathrm{cm^{-1}}$ using the KBr pellet technique. The spectral peaks displayed the following relevant absorptions for **I** and **II**: sharp free-stretching bands at 3620 $\mathrm{cm^{-1}}$ (unbonded, ν-OH), very strong broad bands at 3444 $\mathrm{cm^{-1}}$ with a distinct shoulder (both ν-OH bands, H-bonding), a sharp peak at 2040 $\mathrm{cm^{-1}}$ (ν-C≡N), characteristic water-stretching bands at 1615 $\mathrm{cm^{-1}}$ (scissoring, δ-HOH) and two metal–carbon peaks at 585 and 455 $\mathrm{cm^{-1}}$, which can be assigned to ν_7 [584, δ(Fe–C≡N)] and ν_8 (452, Fe–C) by comparison to the values given by Swanson and Rufalko.[6]

A conoscopic examination of **I** and **II** using crystal rotation between two crossed polarizers on a Zeiss Photomicroscope (II), provided evidence that the system was uniaxial (anisotropic in nature, birefringent) and optically homogeneous. Clear parallelepiped shaped crystals of **I** and **II** ($0.165 \times 0.187 \times 0.207$ and $0.180 \times 0.197 \times 0.213$ mm, respectively) were mounted on glass fibers which were transferred to an Enraf-Nonius CAD4-F autodiffractometer equipped with a dense graphite monochromator (take-off angle, 2.8°). The data were collected in the ω–2θ mode at a variable rate of 1.18°–4.12° $\mathrm{min^{-1}}$ and in the θ range of 1.5°–25.0° (h: $-3 \rightarrow 8$, k: $-3 \rightarrow 8$, l: $0 \rightarrow 16$). Total collected intensity data were 1358 of which 407 were independent ($R_{\mathrm{int}} = 0.044$) and 358 observed reflections with $I > 2.0\sigma(I)$ were included in the structure refinement of compound **I** and 1355 intensity data were collected for compound **II** of which 406 were independent ($R_{\mathrm{int}} = 0.041$) and 343 observed reflections with $I > 2.0\sigma(I)$ were included in the structure refinement. Intensity variations from different zones of reciprocal space were negligible during the data collection (< 1.0%). Thus electronic reliability, X-ray intensity measurements, and crystal stability were assured. All data were then corrected for Lorentz and polarization factors as well as applying semi-empirical absorption corrections using the ψ-scan program XEMP, which is within the SHELXTL-PC package[7] (min. and max. transmission factors: 0.685 and 0.941 for **I** and 0.700 and 0.941 for **II**). $N(Z)$ cumulative probability distribution tests provided evidence that the studied systems are centrosymmetric in nature.

The phase problems were resolved by using the Patterson heavy atom method, which located the lanthanide(III) ions, and difference Fourier mapping.[7] All non-hydrogen atoms were refined anisotropically using the full-matrix least-squares procedure.[7] After several cycles of refinement, which included secondary extinction corrections (g), final residual index values were obtained, $R = \Sigma\Delta F/\Sigma F_o = 0.018$ and $R_w = \Sigma\sqrt{w}\Delta F/\Sigma\sqrt{w}F_o =$ 0.039 for **I** and 0.020 and 0.041 for **II** where $\Delta F = ||F_o| - |F_c||$ and $w = \sigma^{-2}(F_o)$, see Table I. The 'goodness-of-fit' value is defined as $\Sigma_2 = Gnft = [\Sigma w(\Delta F)^2/N_G]^{1/2}$ where ΔF and w have been defined above and $N_G = (N_o - N_v)$, N_o is the number of independent observations and N_v is the number of varied parameters in the refinement (see Table I). It should be noted that the occupancies of the La/Nd and Pr/Nd atoms were refined, 0.47(2)/0.53(2) and 0.49(2)/0.51(2), respectively, which are 1 : 1 ratios. The largest and smallest peaks in the final difference Fourier were 0.31 and 0.82 e Å^{-3} for **I** and 0.54 and −0.62 e Å^{-3} for **II**, all of which were located in the vicinity of the lanthanide ions. Elsewhere, the residual maps were virtually featureless revealing only random fluctuating backgrounds. Atomic scattering factors with related anomalous dispersion correction factors were obtained from the usual source.[8] Final non-hydrogen atomic coordinates with standard deviations and equivalent isotropic atomic displacement

TABLE I Crystal data and summary of compounds **I** and **II**

Compound	1 : 1 (La/Nd)KFe(CN)$_6 \cdot 4H_2O$	1 : 1 (Pr/Nd)KFe(CN)$_6 \cdot 4H_2O$
Shape	Parallelepiped	Parallelepiped
System/space group	Hexagonal/$P6_3/m$ (No. 176)	Hexagonal/$P6_3/m$ (No. 176)
Formula weight	464.71	465.71
a (Å)	7.371(1)	7.362(1)
c (Å)	13.833(3)	13.799(3)
V (Å^3)	650.9(2)	647.7(2)
Z	2	2
$D_m/(\mathrm{mg\,m^{-3}})$	2.369(4)	2.382(4)
$D_c/(\mathrm{mg\,m^{-3}})$	2.371	2.388
$F(000)(e^-)$	443	445
$\mu(\mathrm{MoK}_{\bar{\alpha}})(\mathrm{mm}^{-1})$	5.043	5.299
Temperature (°C)	19	19
Diffractometer/scan	Enraf-Nonius CAD4-F/$\omega-2\theta$	Enraf-Nonius CAD4-F/$\omega-2\theta$
Radiation Å (graphite monochromator)	$\mathrm{MoK}_{\bar{\alpha}}(\lambda = 0.71073$ Å)	$\mathrm{MoK}_{\bar{\alpha}}(\lambda = 0.71073$ Å)
Scan range, ω (°)	$1.15 + 0.34\tan\theta$	$1.15 + 0.34\tan\theta$
Reflections meas.	1358	1355
2θ range (°)	$3.0 \leq 2\theta \leq 50.0$	$3.0 \leq 2\theta \leq 50.0$
Range of h, k, l	−3 to +8, −3 to +8, 0 to +16	−3 to +8, −3 to +8, 0 to +16
Unique data	407	406
Observed data	358 $[I > 2.0\sigma(I)]$	343 $[I > 2.0\sigma(I)]$
Data to parameter ratio	11.3 : 1	11.3 : 1
GOF (Σ_2)	1.22	1.16
R, R_w	0.018, 0.039	0.020, 0.041
R_{all}, R_w, all	0.024, 0.050	0.029, 0.055
Largest diff. peak/hole	0.31, −0.82 e Å^{-3}	0.54, −0.62 e Å^{-3}
g (10^{-3} e^{-2})	8.9(11)	4.6(2)

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for compounds **I** and **II**

Atom	*Occ.*	*x*	*y*	*z*	U_{eq}[a]
1 : 1 (La/Nd)KFe(CN)$_6\cdot 4H_2O$					
La(1)	0.50	6667	3333	2500	12(1)
Nd(1)	0.50	6667	3333	2500	12(1)
Fe(1)	1.00	0000	0000	0000	13(1)
C(1)	1.00	2388(5)	1662(5)	784(2)	19(1)
N(1)	1.00	3857(5)	2656(5)	1253(2)	34(1)
O(1)	1.00	10 699(5)	4256(5)	2500	30(1)
O(2)	0.50	3333	6667	730(3)	72(3)
K(1)	0.50	3333	6667	860(9)	41(2)
1 : 1 (Pr/Nd)KFe(CN)$_6\cdot 4H_2O$					
Pr(1)	0.50	6667	3333	2500	12(1)
Nd(1)	0.50	6667	3333	2500	12(1)
Fe(1)	1.00	0000	0000	0000	12(1)
C(1)	1.00	2394(5)	1662(6)	788(2)	17(1)
N(1)	1.00	3863(5)	2642(6)	1257(2)	32(1)
O(1)	1.00	10 683(6)	4267(7)	2500	28(1)
O(2)	0.50	3333	6667	692(4)	54(2)
K(1)	0.50	3333	6667	882(2)	39(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

parameters are provided in Table II. The presence of any additional symmetry in **I** and **II** was ruled out by employing the program MISSYM.[9] Tables of observed and calculated structure factors are available from the authors (JMF).

DISCUSSION

All bond lengths presented in Table III are internally consistent with the model and are in good agreement with experimental literature values listed in BIDICS.[10] The respective mean (La/Nd)–N and (Pr/Nd)–N bond distances of 2.546(3) and 2.532(3) Å and the respective mean (La/Nd)–O and (Pr/Nd)–O bond distances of 2.697(3) and 2.680(4) Å are quite reasonable when compared to the average values (within standard deviations) found in the structural analyses of LnKFe(CN)$_6\cdot 4H_2O$[11–13], Ln = La, Pr, Nd. The mean bond distance in **I** and **II** of Fe–C, 1.904(3) Å, is in accord with bond distances determined in the structural investigations of Taylor and Mueller[14] on $K_4Fe(CN)_6\cdot 3D_2O$ (1.906 Å), Buser *et al.*[15] on Prussian blue (1.906 Å), and Morosin[16] on $(NH_4)_4Fe(CN)_6\cdot 1.5H_2O$ (1.902 Å). The carbon to nitrogen bond lengths listed in Table III, 1.156(3) and 1.153(3) Å, are consistent with the C≡N distances found in the X-ray studies by Revegg[17] and Peters and Eagen.[18] There is strong directional bonding

TABLE III Bond distances (Å) and angle (°) for compounds **I** and **II**

Atoms	*Distance*	*Atoms*	*Angle*
1 : 1 (La/Nd)KFe$(CN)_6 \cdot 4H_2O$			
Ln(1)–N(1)	2.546(3)	N(1)–Ln–N(1)#1	79.1(1)
Ln(1)–O(1)	2.697(3)	N(1)–Ln–N(1)#7	85.3(2)
Fe(1)–C(1)	1.902(3)	O(1)–Ln–N(1)	137.33(8)
C(1)–N(1)	1.156(3)	O(1)–Ln–N(1)#1	67.92(9)
O(1)···O(2)	3.088(3)	O(1)–Ln–N(1)#2	68.93(9)
O(1)···N(1)#1	2.930(3)	O(1)–Ln–O(1)#1	120.0
O(1)#1···N(1)	2.970(3)	C(1)–Fe(1)–C(1)#3	89.3(1)
		C(1)–Fe(1)–C(1)#8	180.0
		C(1)–Fe(1)–C(1)#9	90.7(1)
		N(1)–C(1)–Fe(1)	178.8(3)
		C(1)–N(1)–Ln(1)	156.5(3)

Ln = La or Nd
Symmetry transformations used to generate equivalent atoms:
#1 $-y+1, x-y, z$; #2 $-x+y+1, -x+1, z$; #3 $y, -x+y, -z$; #7 $x, y, -z+0.5$; #8 $-x, -y, -z$; #9 $-x+y, -x, z$.

Atoms	*Distance*	*Atoms*	*Angle*
1 : 1 (Pr/Nd)KFe$(CN)_6 \cdot 4H_2O$			
Ln(1)–N(1)	2.532(3)	N(1)–Ln–N(1)#1	79.1(1)
Ln(1)–O(1)	2.680(4)	N(1)–Ln–N(1)#5	85.3(2)
Fe(1)–C(1)	1.905(3)	O(1)–Ln–N(1)	137.35(8)
C(1)–N(1)	1.153(3)	O(1)–Ln–N(1)#1	67.83(10)
O(1)···O(2)	3.115(3)	O(1)–Ln–N(1)#2	69.01(10)
O(1)···N(1)#1	2.911(3)	O(1)–Ln–O(1)#2	120.0
O(1)#1···N(1)	2.955(3)	C(1)–Fe(1)–C(1)#8	89.3(2)
		C(1)–Fe(1)–C(1)#6	180.0
		C(1)–Fe(1)–C(1)#9	90.7(2)
		N(1)–C(1)–Fe(1)	178.4(3)
		C(1)–N(1)–Ln(1)	157.2(3)

Ln = Pr or Nd
Symmetry transformations used to generate equivalent atoms:
#1 $-y+1, x-y, z$; #2 $-x+y+1, -x+1, z$; #5 $x, y, -z+0.5$; #6 $-x, -y, -z$; #8 $y, -x+y, -z$; #9 $-y, x-y, z$.

related to the interaction of Fe 3*d* orbitals and cyanide π orbitals, which is evidenced by the Fe–C≡N bond angle of 178.8(3)° in **I** and 178.4(3)° in **II**. There is little or no directional influence in the electrostatic bonding of the Ln ions, which is denoted by the Ln–N≡C bond angle of 156.5(3)° and 157.2(3)° respectively.

The mixed (1 : 1) La/Nd and Pr/Nd ions are nine-coordinate, which is quite common in complexes of the lanthanide and actinide series.[2,19–22] The nine-coordinate $LnN_6(H_2O)_3$ groups are symmetrical tricapped trigonal prisms (TTP, D_{3h}) where the centrally located Ln ions are bonded to six nitrogen atoms in apical positions (three above and three below the lanthanide atoms) and to three oxygen atoms (H_2O molecules) equatorially positioned so as to centrally cap the three square faces of the trigonal prism, see

Figure 1. The iron ions are six-coordinate, forming octahedral FeC_6 groups. Figures 1 and 2 show the cyanide bridging that links the FeC_6 and the $LnN_6(H_2O)_3$ groups. The potassium ions and noncoordinated water molecules are located within holes in the crystal lattice directly above and

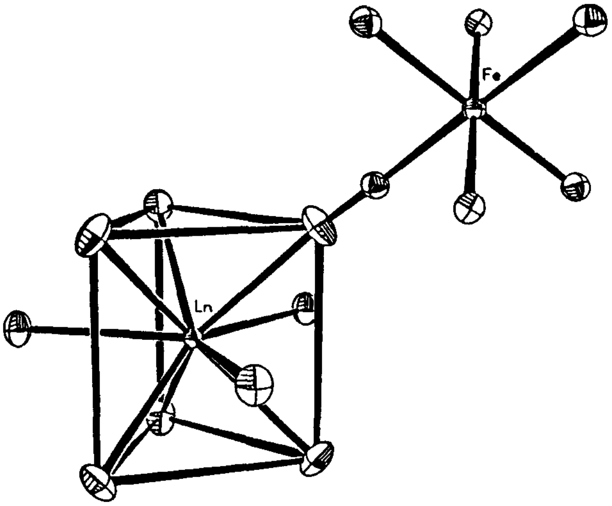

FIGURE 1 A projected view of the $LnN_6(H_2O)_3$ group displaying the nine-coordination about the central Ln ions in complexes I and II. The geometry is a TTP. The octahedral FeC_6 groups and the $LnN_6(H_2O)_3$ groups are linked by cyanide bridging (see Table III for bond angles).

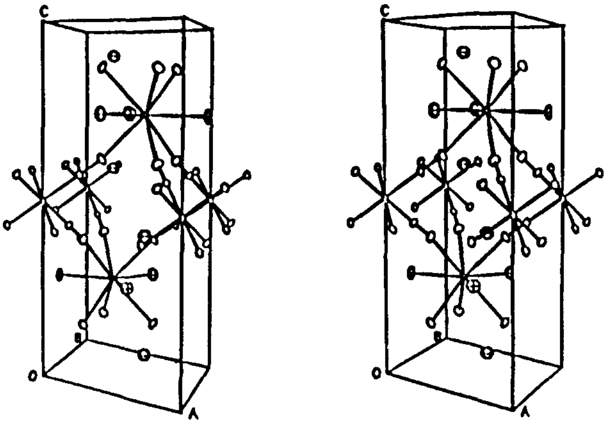

FIGURE 2 A stereoview of the unit cell showing the C≡N linkage between the Ln and Fe ions and the positioning of the noncoordinated water molecules, O(2), and the potassium atoms in I and II.

below the Ln ions along the three-fold axis in both **I** and **II**. In each compound (**I** and **II**), the noncoordinated H_2O molecules, O(2), and the coordinated H_2O molecules, O(1), have contact distances well within the range of hydrogen bonding, 3.088(3) and 3.115(3) Å, respectively (see Table III). Hydrogen bonding and electrostatic cohesive forces are important in the network of these type complexes. Studies by Brown[23] have shown that the strength of hydrogen bonds is dependent upon the $O\cdots O$ interatomic contact distance, assuming no geometric constraints. Strong H-bonds have $O\cdots O$ contact lengths of 2.73 Å or less and as the contact distance increases, the H-bonding becomes progressively weaker. Note the different intermoiety oxygen–oxygen and oxygen–nitrogen contact distances in Table III. Beyond a contact distance of 3.4 Å, hydrogen-bonding probably does not exist. The infrared studies lend credence to our crystallographic conclusions (see section Experimental). Recall, a very broad band with a distinct shoulder, both of which relate to H-bonding and possibly to two modes of H-bonding. This inferential conclusion could be substantiated by a neutron diffraction study if and when large crystals of the title compound are obtained.

The results of this present crystallographic study suggest that there is need for further structural work on these zeolitic-type complexes. This paper is part of a series of research investigations on properties of hydrated mixed lanthanide and transition metal complexes of cyanides so that weak aspects in the theories of semipermeable membranes and hydrogen bonding can be partially resolved.

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Supplementary Materials

Anisotropic thermal parameters, complete bond distance and angles, and structure factor data for complexes **I** and **II** are available from the authors (JMF).

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