A Structural Investigation of Praseodymium Potassium Hexacyanoferrate (II) Tetrahydrate, PrKFe(CN)₆ · 4H₂O

D. F. MULLICA, E. L. SAPPENFIELD, AND H. O. PERKINS

Departments of Chemistry and Physics, Baylor University, Waco, Texas 76798

Single-crystal and powder X-ray diffraction data, thermal gravimetric analysis, and infrared spectral data are present for $PrKFe(CN)_6 \cdot 4H_2O$. The crystal structure has been determined by single-crystal diffractometry and refined by the least-squares method to yield $R = 0.0149$ and $R_w = 0.0155$. The praseodymium ions are linked nonlinearly to the FeC_6 octahedra by cyanide bridges. Cavities within the structure are occupied by potassium ions and zeolitic water molecules which are within hydrogen bonding distance to the water molecules which are bonded to the nine-coordinated praseodymium ions, $PrN_6(H_2O)_3$. The powder diffraction data obtained by employing a Siemens Debye–Scherrer camera have yielded cell parameters of $a = 7.374(2)$ and $c = 13.816(3)$ Å. The compound is hexagonal, $P6_3/m$ (No. 176), $D_M = 2.34(3)$ Mg m^{-3}, and $D_X = 2.368$ Mg m^{-3}. The powder diffraction data have been evaluated and the resultant quantitative figures of merit are $F_{30} = 30(0.021, 48)$ and $M20 = 29.7$. Important bond lengths are: Pr–N = 2.540(3); Fe–C = 1.908(3); Pr–O = 2.704(4); and C≡N = 1.159(4) Å. © 1988 Academic Press, Inc.

Introduction

Much work has been done to elucidate the structural properties of many ferri- and ferrocyanides (1–4). Of particular interest are the double salt ferrocyanides of the lanthanide series because of their possible semipermeable membrane (5) and ion-exchange properties (6). These properties are considered to be related to the nature of the zeolitic water molecules held in cavities in the structure of the double salt ferrocyanides by hydrogen bonding. It is of considerable interest to determine the size and physical characteristics of the cavities in the structure of the double salt ferrocyanides. A single-crystal X-ray study of LaKFe(CN)₆ · 4H₂O by Beall *et al.* (7) indicated that the structure was isomorphous with LaFe(CN)₆ · 5H₂O (8). It was found that the La and Fe ions are linked by nonlinear bridges and that there are two types of water molecules within the unit cell. Three water molecules are coordinated to the La ion and two zeolitic water molecules are held in cavities within hydrogen bonding distance to the coordinated water molecules. In the LaK Fe(CN)₆ · 4H₂O compound, one of the zeolitic water molecules is replaced by a potassium atom. Understanding the manner in which the K atom is held within the cavity can lead to elucidating the origin of the semipermeable and ion-exchange properties of the double salt ferrocyanides of the lanthanides.

As a continuation of the investigation into the structure of the double salt ferro-

hexacyanides of the lanthanid series, the single-crystal structural analysis, X-ray powder diffraction data, and physical characterization of praseodymium potassium hexacyanoferrate (II) tetrahydrate are presented.

Synthesis and Physical Analysis

Clear green crystals were obtained by precipitation from a mixture of slightly acidic 0.5 M $K_4Fe(CN)_6$ and 0.5 M $PrCl_3$. After mixing, the solution was filtered and stored in the dark at 10°C overnight. Both potassium ferrocyanide and praseodymium trichloride were purchased commercially and used without further purification. The single crystal used in the single-crystal analysis data collection was an optically clear hexagonal prism, 0.12 × 0.12 × 0.15 mm. The experimental density for $PrKFe(CN)_6 \cdot 4H_2O$ is 2.34(3) Mg m^{-3} by the flotation technique (calculated density, 2.368 Mg m^{-3}).

Thermal dehydration of the title compound was determined using a Perkin–Elmer TGS-1 thermobalance. Thermogravimetric analysis indicated 4.0(1) water molecules per formula unit. Dehydration of the praseodymium potassium ferrohexacyanide occurs in a stepwise manner. The compound loses one molecule between 80 and 90°C and three water molecules between 125 and 175°C indicating two types of bonding. $PrKFe(CN)_6 \cdot 4H_2O$ appears stable both as the tetrahydrate and the trihydrate.

An infrared spectrum using the KBr press disk method over the frequency range 4000 to 250 cm^{-1} on a Perkin–Elmer 521 spectrophotometer displays a sharp –OH peak at 3606 cm^{-1} and a broad –OH peak between 3540 and 3360 cm^{-1}. The sharp peak is due to the coordinated water and the broad peak is a result of the zeolitic water. A sharp C≡N band is located at 2061 cm^{-1} and two metal carbon peaks are

positioned at 592 and 452 cm^{-1}. The two metal carbon peaks can be assigned to ν_7 (529, δ(Fe–C≡N)) and ν_8 (452, Fe–C stretch) by comparison to the values given by Swanson and Rafalko (2). There is also the characteristic water peak at 1602 cm^{-1}.

Powder Diffraction Analysis

The X-ray powder diffraction data was obtained by employing a Debye–Scherrer cylindrical camera having a radius of 114.6 mm at room temperature (~295 K) and under vacuum. The powder pattern was taken using nickel filtered copper $K\bar{\alpha}$ radiation (λ_{mean} = 1.54184 Å). The praseodymium potassium ferrohexacyanide crystals were finely ground and placed in a 0.2-mm-diameter capillary.

All lines were attributed to the hexagonal system which was determined by preliminary single-crystal analysis. Cell parameters were refined by placing measured S values (back-reflection ring diameters) into a least-squares program (9) designed for X-ray powder diffraction data. This powder diffraction analysis program employs the Nelson–Riley extrapolation function to calculate lattice constants and their standard deviations. The lattice parameters were determined to be a = 7.374(2) and c = 13.816(3) Å with figures of merit of F_{30} = 30(0.021,48) (10) and $M20$ = 29.7 (11). The observed and calculated d-spacing values (in Å) for $PrKFe(CN)_6 \cdot 4H_2O$ and the visually estimated relative intensities, based on 100 as the intensity for the strongest observed reflection, are given in Table I.

Single-Crystal Analysis

The crystal used in the X-ray analysis was selected on the basis of optical quality and mounted on an Enraf–Nonious CAD-4F automated diffractometer equipped with a dense graphite monochromator (take-off angle, 5.8°; $MoK\bar{\alpha}$, λ_{mean} = 0.71073 Å). The

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR PrKFe(CN)₆ · 4H₂O

2θ (exp)	Intensity (I/I_0)	Observed d space	h	k	l	Δ2θ	Figure of merit $(F_N)^a$
12.800	5	6.916	0	0	2	−0.015	67(0.015, 1)
13.875	5	6.383	1	0	0	0.008	68(0.011, 2)
15.300	90	5.791	1	0	1	0.015	79(0.013, 3)
18.925	100	4.689	1	0	2	0.000	104(0.010, 4)
23.825	80	3.735	1	0	3	0.003	120(0.008, 5)
24.125	80	3.689	1	1	0	0.002	138(0.007, 6)
25.775	5	3.457	0	0	4	−0.019	98(0.009, 8)
27.400	5	3.255	1	1	2	−0.021	86(0.010, 9)
27.925	5	3.195	2	0	0	−0.018	80(0.011,10)
28.675	5	3.113	2	0	1	−0.021	75(0.012,11)
30.875	30	2.8962	2	0	2	0.024	64(0.016,13)
34.125	80	2.6274	2	0	3	−0.045	50(0.016,15)
35.599	50	2.5219	1	1	4	−0.018	48(0.016,17)
37.249	5	2.4139	2	1	0	−0.003	51(0.015,18)
37.849	20	2.3770	2	1	1	0.012	53(0.015,19)
39.075	5	2.3052	0	0	6	−0.042	46(0.017,21)
39.576	20	2.2772	2	1	2	0.025	45(0.017,22)
41.700	10	2.1660	1	0	6	0.004	46(0.016,24)
42.301	40	2.1366	2	1	3	0.027	45(0.017,25)
43.276	5	2.0907	2	0	5	−0.028	41(0.018,28)
44.525	5	2.0349	3	0	2	−0.014	42(0.017,29)
46.499	5	1.9530	1	1	6	0.003	43(0.017,31)
48.224	5	1.8871	1	0	7	−0.038	40[0.018,33)
48.749	5	1.8680	2	0	6	−0.008	41(0.017,34)
49.400	10	1.8449	2	2	0	−0.040	39(0.018,35)
50.249	30	1.8157	2	1	5	0.062	35(0.020,37)
52.076	5	1.7562	3	1	1	0.019	33(0.020,41)
53.051	5	1.7262	0	0	8	0.027	33(0.020,43)
53.425	10	1.7150	3	1	2	0.024	33(0.020,44)
55.049	10	1.6682	1	0	8	−0.039	30(0.021,48)

^{a} $F_N = (1/|\overline{\Delta 2\theta}|)(N/N_{poss})$, where $\Delta 2\theta = 2\theta_{calc}$.

setting angles of 25 accurately centered reflections were used to obtain the orientation matrix and the cell parameters (see Table II). Intensity data were measured using the ω-2θ scan technique in range 3° <2θ <66° with a scan rate of 0.39 to 3.35° min⁻¹. All reflections having less than 75 counts above background during a fast pre-scan (3.35° min⁻¹) were assumed to be unobserved. Two reflections ($1\overline{1}6$ and 220) were chosen as standards and were monitored periodically (2h) in order to check crystal stability and reliability of the elec-tronic hardware. The two standard reflections revealed no appreciable variance in intensity throughout the entire data collection (<0.1% deviation). Of the 910 total reflections (h: 0 → 9; k: 0 → 9; l: 0 → 21) collected, 810 reflections fitted $I_{net} > 3\sigma(I)$ with $I_{net} = (P\text{-}2B)$ 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 (0.03). Lorentz and polarization corrections were applied and equivalent reflections averaged leaving 623

unique reflections to be used in the structural refinement. Systematic absences ($000l$, $l = 2n + 1$) were consistent with space groups $P6_3$ and $P6_3/m$. Successful refinement in the latter space group indicates that the nonhydrogen atoms occupy positions in this centrosymmetric space group.

The heavy lanthanoid atoms were located by assuming a structure isomorphous to $LaKFe(CN)_6 \cdot 4H_2O$ (8). The remaining atomic positions were determined by difference Fourier mapping. The model was then refined by the full-matrix least-squares technique employing anisotropic thermal parameters and a secondary extinction correction ($g = 3.6 \times 10^{-6} \, e^{-2}$). The refinement was terminated when all parameters had stabilized and the maximum shift-to-error

TABLE III

TABLE OF POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS ($\times 10^{-4}$)

Atom	x	y	z	$U_{eq}{}^a$ (Å^2)
PR	333	6667	2500	98.0(4)
FE	0000	0000	0000	101(1)
N	2670(4)	8809(4)	1259(2)	295(7)
C	727(4)	2390(4)	790(2)	175(6)
O1	4256(4)	3550(4)	2500	274(8)
O2	6667	3333	745(5)	50(2)
K	6667	3333	877(2)	403(5)

^{a} $U_{eq} = (U_{11} + U_{22} + U_{33} + U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha)/3$.

ratio was less than 0.001. The refinement program (12) yielded final R factors for $PrKFe(CN)_6 \cdot 4H_2O$ of $R = 0.0149$ and $R_w = 0.0155$, where $R = \Sigma| \, |F_o| - |F_c| \, |/\Sigma|F_o|$ and $R_w = \Sigma\sqrt{w}||F_o| - |F_c||/\Sigma\sqrt{w}|F_o|$. Final difference Fourier maps revealed only a random fluctuating background with a maximum density of $+0.521e$ Å^{-3} and a minimum of $-0.614e$ Å^{-3} in the vicinity of the lanthanoid atom site, a feature quite common to compounds of the heavy lanthanides. Atomic scattering factors and anomalous dispersion factors were taken from the International Tables (13). Single crystal and powder diffraction data, experimental conditions, and statistical data are listed in Table II. Final atomic positions and thermal parameters are presented in Table III.[1]

TABLE II

EXPERIMENTAL AND STATISTICAL SUMMARIES

	Powder	Single crystal
a (Å)	7.374(2)	7.374(2)
c (Å)	13.816(3)	13.826(2)
V (Å^3)	650.6	651.1
D_m (Mg m^{-3})	2.34(3)	2.34(3)
D_x (Mg m^{-3})	2.368	2.367
Radiation	Cu$K\alpha$	Mo$K\alpha$
Space Group	$P6_3/m$ (No. 176)	
Z	2	
MW	464.02	
$F(000)$	396	
Cryst. Dim. (mm)	$0.12 \times 0.12 \times 0.15$	
μ (Mo$K\alpha$)(mm^{-1})	5.14	
$\Delta\omega$ (°)($\omega-2\theta$ scan)	$1.30 + 0.35 \tan\theta$	
$\Delta\theta$ (°)	1.5 to 33.0	
scan limits (°min^{-1})	0.39 to 3.35	
Unique refl.	623	
Systematic abs	$000l = 2n + 1$	
R	0.0149	
R_w	0.0155	
R_{int}	0.018	
GnFt(Σ_2)	0.738	
$g(e^{-2})(10^{-6})$	3.60	
Max[$\Delta\zeta i/\sigma(\zeta i)$]($10^{-3}$)	0.12	
Residual density (e Å^{-3})		
Maximum	+0.521	
Minimum	−0.614	

Discussion

The nine-coordinate praseodymium ion is bonded to six nitrogen atoms and three water molecules. This nine-coordinated arrangement is quite common for lanthanide compounds *(7, 8, 14, 15)*. The $PrN_6(H_2O)_3$ system is arranged in a tricapped trigonal prism (D_{3h}) with the water molecules occupying equatorial capping positions of the trigonal prism. An additional uncoordinated water molecule is contained within cavities in the structure and is within the range of hydrogen bonding (3.06 Å) from the coordinated water molecule. The potassium ion is also contained in these holes in the lattice. Both are located along the three-fold axis directly above and below the Pr atom. Figure 1 shows the arrangement of the nitrogen and water molecules around the praseodymium. The ferrocyanide octahedra are linked to the $PrN_6(H_2O)_3$ groups by cyanide bridges. Pr–N≡C–Fe is nonlinear.

Selected bond and contact distances and bond angles are listed in Table IV. The $Fe(CN)_6^{-4}$ complex ion is octahedral with Fe–C bond distances of 1.908(3) Å and C–Fe–C bond angles of 90.5(1) and 89.5(1)°. The C–N bond distance is 1.159(4) Å. The distances and angles are in complete agreement with the isostructural LaK $Fe(CN)_6$ · 4H₂O and with experimental literature values found in BIDICS *(16)*.

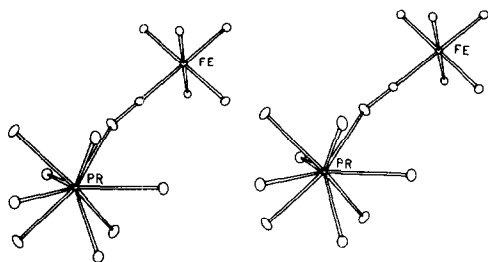
FIG. 1. A stereoview of the nine-coordinated praseodymium atom and the FeC₆ octahedral arrangement.

TABLE IV

TABLE OF BOND DISTANCES (Å) AND ANGLES (°)

PR–N	2.540(3)	N–O2	3.239(11)
PR–O1	2.704(4)	N–O2	3.34(4)
C–N	1.159(4)	C–O2	3.397(3)
FE–C	1.908(3)	C–O2	3.48(3)
		O1–O2	3.06(4)
N–PR–N	79.4(1)	N–PR–O1	68.7(1)
N–PR–N	85.0(2)	N–PR–O1	68.0(1)
N–PR–N	136.74(6)	N–PR–O1	137.50(8)
C–FE–C	180.00(0)	O1–PR–O1	120.00(0)
C–FE–C	90.5(1)	PR–N–C	155.8(3)
C–FE–C	89.5(1)	FE–C–N	178.9(3)

Note. Numbers in parentheses are estimated standard deviations in the least-significant digits.

The bond length from the praseodymium ion to the three oxygen atoms in the coordinated water is 2.704(4) Å. These atoms (Pr and O's) lie in the equatorial mirror plane. Six cyanides are linked to the praseodymium through the nitrogen with a Pr–N distance of 2.540(3) Å. The Pr–O and Pr–N bond distances are shorter than those in the lanthanum analog as a result of the smaller Pr ionic radius. The bond angles around the praseodymium atom are also listed in Table IV and are in good agreement with analogous structures found in the literature. Figure 2 shows the arrangement in the unit cell of the uncoordinated water molecule and potassium ion. This zeolitic-type water molecule and the K ion occupy basically the same site which is evidenced by an occupancy refinement for each, 0.50(1) and 0.50(1). Figure 2 also shows the C–N linkage between the Pr and Fe. In addition, the connection between the two praseodymium ions present in the unit cell by way of two Fe ions through the C–N linkage is represented.

The O–H stretching frequency around 3500 cm⁻¹ indicates a weak hydrogen bond and the $O(1)–O(2)$ bond length of 3.06(4) Å indicates the possible presence of weak hydrogen bonding. This inferential conclusion could be substantiated by a neutron diffraction study. The water molecules in
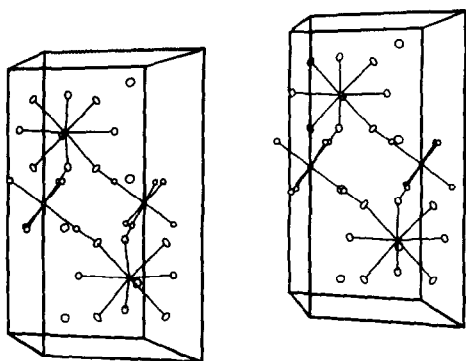
FIG. 2. A stereodrawing of the unit cell showing the C≡N linkage between the Pr and Fe and the arrangement between the uncoordinated water molecules and potassium ions.

the cavities are loosely held as evidenced by the large thermal parameters. The results of this structural study suggest that there is a need for further structural work on these zeolitic-type complexes. This paper is part of a series of research investigations on zeolitic properties of hydrated lanthanide and transition metal complexes of cyanides so that weak aspects in the theories of semipermeable membranes and hydrogen bonding can be partially resolved as well as the origin of the ion-exchange properties which are associated with double salt ferrocyanides.

Acknowledgment

References

1. D. F. MULLICA, W. O. MILLIGAN, AND J. D. OLIVER, Inorg. Nucl. Chem. Lett. 15, 1 (1979).
2. B. I. SWANSON AND J. J. RAFALKO, Inorg. Chem. 15, 249 (1976).
3. P. GRAVEREAU, E. GARNIER, AND A. HARDY, Acta Crystallogr. B 35, 2843 (1979).
4. P. GRAVEREAU AND E. GARNIER, Acta Crystallogr. C 40, 1306 (1984).
5. W. O. MILLIGAN, M. UDA, M. L. BEASLEY, D. R. DILLIN, W. E. BAILEY, AND J. J. McCOY, "Office of Saline Water Research and Development Progress Report No. 594" (1970).
6. A. K. JAIN, R. P. SINGH, AND C. BALA, Analyst 107, 770 (1982).
7. G. W. BEALL, D. F. MULLICA, W. O. MILLIGAN, J. KORP, AND I. BERNAL, Acta Crystallogr. B 34, 1446 (1978).
8. W. E. BAILEY, R. J. WILLIAMS, AND W. O. MILLIGAN, Acta Crystallogr. B 29, 1365 (1973).
9. R. B. ROOF, JR., LASL Report, Los Alamos-Scientific Laboratory, (1968).
10. G. S. SMITH AND R. L. SNYDER, J. Appl. Crystallogr. 12, 60 (1979).
11. P. M. DeWOLFF, J. Appl. Crystallogr. 1, 108 (1968).
12. Enraf-Nonius, "Enraf-Nonius VAX Structure Determination Package," Delft (1982).
13. J. A. IBERS AND W. C. HAMILTON, Eds. "International Tables for X-ray Crystallography," Vol. IV, p. 72, Kynoch Press, Birmingham (1974).
14. L. HELMHOTZ, J. Amer. Chem. Soc. 61, 1544 (1939).
15. D. R. FITZWATER AND R. E. RANDLE, Z. Kristallogr. 112, 362 (1959).
16. "Bond Index of the Determination of Inorganic Crystal Structures," BIDICS, Institute for Materials Research, Hamilton (1969–1981).