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# Boundary Structures in a Series of Lanthanoid Hexacyanocobaltate(III) *n*-Hydrates and Their Raman Spectra

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Studies on $Ln[Co(CN)_6]\cdot nH_2O$ (Ln = lanthanoid ions; $n = 5, 4$) by means of thermal analysis, Raman spectroscopy, and X-ray crystallography were carried out, in order to establish the boundary structures in the series. From the thermal analyses, it was confirmed that the complexes include $Ln'[Co(CN)_6]\cdot 5H_2O$ (Ln′ = La to Nd) or $Ln''[Co(CN)_6]\cdot 4H_2O$ (Ln = Sm to Lu). Raman spectra of the complexes suggested a different classification. The complexes having five $H_2O$ molecules displayed two single bands associated with $\nu$(C−N) at around 2170 $cm^{-1}$. The complexes having four $H_2O$ molecules showed two distinct sets of bands of $\nu$(C−N): one was a singlet, and the other was split. Nevertheless, the complex with Nd, which has five $H_2O$ molecules, exhibited single and split bands. This implies that the symmetry around Nd is lower than that of other complexes having five $H_2O$ molecules. According to the X-ray crystal analysis, the Pr complex is $Pr[Co(CN)_6]\cdot 5H_2O$, hexagonal, $P6_3/m$, with $a = 7.473(1)$ Å, $c = 14.212(1)$ Å, and $Z = 2$. On the other hand, the Nd complex is $Nd[Co(CN)_6]\cdot 5H_2O$, orthorhombic, $C222_1$, with $a = 7.458(4)$ Å, $b = 12.918(3)$ Å, $c = 14.172(2)$ Å, and $Z = 4$. Although the Nd complex has five $H_2O$ molecules, the crystals are orthorhombic and belong to the space group $C222_1$. Therefore, the structure of $Nd[Co(CN)_6]\cdot 5H_2O$ is regarded as the boundary structure: one of the coordinated water molecules is disordered, although the structure is essentially the same as that of $Pr[Co(CN)_6]\cdot 5H_2O$. As Pr in $Pr[Co(CN)_6]\cdot 5H_2O$ changes into Nd, the symmetry around the metal atom is lowered and thus the bands associated with $\nu$(CN) in $Nd[Co(CN)_6]\cdot 5H_2O$ and $Sm[Co(CN)_6]\cdot 4H_2O$ outnumber those of $Pr[Co(CN)_6]\cdot 5H_2O$. The $5H_2O$ complex with Nd loses one water molecule by thermal dissociation and changes into the more stable $4H_2O$ complex, whose crystals are orthorhombic and belong to the space group *Cmcm*. $Pr[Co(CN)_6]\cdot 5H_2O$ also changes into the $4H_2O$ complex, orthorhombic and *Cmcm*, when it dehydrates.

## Introduction

Hexacyanometalate salts have been widely studied and applied to all fields. Thus, their structures and properties have been investigated for a long time. However, systematic studies on a series of the hexacyanometalate complexes have not yet been carried out. In particular, the hydration number of the complexes has been a debatable question.

The composition of lanthanoid hexacyanocobaltates(III) was reported by James and Willard in 1916:[1] they noted that the complexes possess the formula $Ln_2[Co(CN)_6]_2\cdot 9H_2O$, that is, $Ln[Co(CN)_6]\cdot 4.5H_2O$. Although similar results were published for the lanthanoid hexacyanoferrates(III), the water molecules per formula unit varied from 3 to 4.5.[2]

Hulliger *et al.*[3] reported in their investigation of $Ln[Co(CN)_6]\cdot nH_2O$ that large Ln ions in the series of the hexacyanocobaltate salts crystallize in the hexagonal system (Ln = La, ..., Nd), whereas smaller Ln ions in the series (Ln = Sm, ..., Lu) belong to an orthorhombic modification which is brought about by a gradual dehydration process. In 1979, Mullica *et al.*[4] confirmed that $La[Co(CN)_6]\cdot 5H_2O$ belonged to the hexagonal system, $P6_3/m$, by single-crystal diffractometry. Further, they stated that the $Ln[Co(CN)_6]$ series was analogous to the $Ln[Fe(CN)_6]$ series. For the crystal system of $Sm[Co(CN)_6]\cdot 4H_2O$ there was lack of agreement. Mullica *et al.*[5] reported that $Sm[Co(CN)_6]\cdot 4H_2O$ belonged to the monoclinic system, $P2_1/m$, like $Sm[Fe(CN)_6]\cdot 4H_2O$, while Hulliger *et al.*[6] stated that both belonged to the orthorhombic system, *Cmcm*. A careful reinvestigation resolved the dispute: the crystal structures of $Sm[Co(CN)_6]\cdot 4H_2O$ and $Sm[Fe(CN)_6]\cdot 4H_2O$ are orthorhombic and *Cmcm*.[7,8]

Thermal properties of the lanthanoid hexacyanometalates have also been studied. Yokobayashi[9] reported that $Ln[Co(CN)_6]\cdot 5H_2O$ (Ln = La, ..., Ce) and $Ln[Co(CN)_6]\cdot 4H_2O$ (Ln = Pr, ..., Lu) were prepared by adding $LnCl_3$ aqueous solution to $K_3[Co(CN)_6]$ aqueous solution at *ca.* 80 °C. Their thermal dehydration modes were also reported. The results did not agree with those of the series of $Ln[M(CN)_6]\cdot nH_2O$ (M = Fe or Cr,

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(1) James, C.; Willard, P. S. *J. Am. Chem. Soc.* **1916**, *38*, 1497.

(2) Prandtl, W.; Mohr, S. *Z. Anorg. Allg. Chem.* **1938**, *236*, 243.

(3) Hulliger, F.; Landolt, M.; Vestch, H. *J. Solid State Chem.* **1976**, *18*, 307.

(4) Mullica, D. F.; Milligan, W. O.; Kouba, W. T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 967.

(5) Mullica, D. F.; Perkins, H. O.; Sappenfield, E. L. *J. Solid State Chem.* **1988**, *74*, 419.

(6) Petter, W.; Gramlich, V.; Hulliger, F. *J. Solid State Chem.* **1989**, *82*, 161.

(7) Mullica, D. F.; Sappenfield, E. L. *J. Solid State Chem.* **1989**, *82*, 168.

(8) Gramlich, V.; Petter, W.; Hulliger, F. *Acta Crystallogr., Sect. C* **1990**, *46*, 724.

(9) Yokobayashi, H. *Netsu Sokutei* **1991**, *18*, 157.

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$n = 5, 4$) proposed by Hulliger:[10] the Ce, Pr, and Nd hexacyanoferrate salts synthesized at low temperatures contained $5H_2O$ molecules per formula unit, whereas only $4H_2O$ molecules were incorporated on crystallization at high temperatures.

There are some unresolved problems about hexacyanometalate hydrates despite years of study. Where is the boundary line between $5H_2O$ and $4H_2O$ complexes in the series of $Ln[Co(CN)_6]\cdot nH_2O$? What is the structure of the boundary complex? Thus, the determination of the boundary structure between $5H_2O$ and $4H_2O$ complexes has been a longstanding question. In this work, the thermal and spectroscopic properties of the series of hexacyanocobaltate(III) hydrates were investigated. Subsequently, the crystal structures of the Pr and Nd salts were determined in order to establish the boundary structure in the series of lanthanoid hexacyanocobaltate(III) *n*-hydrates. Furthermore, the thermal dehydration process, from $5H_2O$ to $4H_2O$ complexes of the salts, was studied by means of Raman spectroscopy.

## Experimental Section

**Chemicals and Preparations.** Potassium hexacyanocobaltate(III) was prepared according to the literature:[11] $CoCl_2\cdot 6H_2O$ and KCN, which were both purchased from Waco Pure Chemical Ltd., were used in this preparation. Praseodymium, neodymium, and samarium chloride *n*-hydrates were purchased from Shin-etsu Chemical Co.

Praseodymium, neodymium, and samarium hexacyanocobaltate(III) *n*-hydrates were prepared by adding equimolar amounts of $K_3[Co(CN)_6]$ to $PrCl_3$, $NdCl_3$, or $SmCl_3$ in aqueous solution. Single crystals were obtained from each solution by keeping it for several days at room temperature.

**Measurements.** The simultaneous thermogravimetric (TGA) and differential thermal (DTA) analyses were carried out with a Rigaku Thermoflex M-8057 using a sample weighing about 10 mg; the heating rate was 5 °C $min^{-1}$ in air, and α-alumina was used as the reference.

The Raman spectra were recorded on a Jobin Yvon U-1000 spectrometer with a rotating disk, the exciting line (514.5 nm, 100 mW) being provided by an NEC GLG 3200 $Ar^+$ ion laser.

X-ray diffraction measurements were performed with a Rigaku AFC-5 automated four-circle diffractometer for the praseodymium complex and an AFC-5R for the neodymium complex with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Intensities were collected by the $\omega-2\theta$ scan technique and corrected for Lorentz and polarization factors. The structures were solved by the heavy-atom method. The positional, isotropic, and then anisotropic thermal parameters (except for hydrogen atoms) were refined by the block-diagonal least-squares method. All the calculations were carried out on a HITAC M-682H/M-880 computer at the Computer Center of The University of Tokyo, using the local version of the UNICS program.[12] Atomic scattering factors were taken from ref 13.

## Results and Discussion

Simultaneous thermogravimetric and differential thermal analyses of $Ln[Co(CN)_6]\cdot nH_2O$ (Ln = La, ..., Lu) prepared at room temperature were carried out. Thus, the composition was established: $Ln'[Co(CN)_6]\cdot 5H_2O$ (Ln′ = La, ..., Nd), and $Ln''[Co(CN)_6]\cdot 4H_2O$ (Ln = Sm, ..., Lu). Figure 1 shows the TGA and DTA curves of the Pr, Nd, and Sm complexes. For the Pr and Nd complexes, there is an endothermic peak on the DTA curve with a mass loss corresponding to one water molecule at around 100 °C. Subsequently, the DTA curve shows a pattern similar to that of the Sm complex. They do not agree with the results reported by Yokobayashi,[9] who prepared the complexes at *ca.* 80 °C. Therefore, $Pr[Co(CN)_6]\cdot 5H_2O$ and $Nd[Co(CN)_6]\cdot 5H_2O$ must be the boundary complexes in the series of $Ln[Co(CN)_6]\cdot nH_2O$ (Ln = La, ..., Lu; $n = 5, 4$).

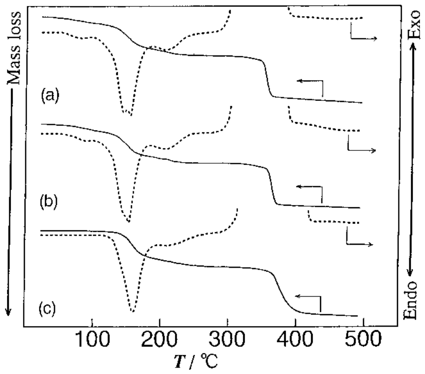

**Figure 1.** Thermogravimetric and differential thermal analysis curves of (a) $Pr[Co(CN)_6]\cdot 5H_2O$, (b) $Nd[Co(CN)_6]\cdot 5H_2O$, and (c) $Sm[Co(CN)_6]\cdot 4H_2O$.

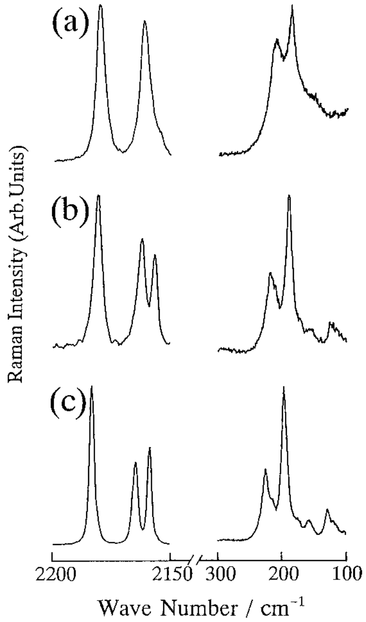

**Figure 2.** Raman spectra of (a) $Pr[Co(CN)_6]\cdot 5H_2O$, (b) $Nd[Co(CN)_6]\cdot 5H_2O$, and (c) $Sm[Co(CN)_6]\cdot 4H_2O$.

Powder X-ray diffraction data for the complexes were measured in order to obtain structural information. However, no informative data were obtained: data for both complexes were very similar to each other, since the frameworks ($Ln[Co(CN)_6]$) of the complexes are the same. In contrast, Raman spectra of the series $Ln[Co(CN)_6]\cdot nH_2O$ (Ln = La, ..., Lu; $n = 5, 4$) exhibit the characteristic patterns. The complexes having five $H_2O$ molecules; displayed two single bands associated with $\nu$(C−N) at around 2170 $cm^{-1}$. On the other hand, complexes having four $H_2O$ molecules showed two distinct $\nu$(C−N) bands: one was a singlet, and the other was split. Figure 2 shows the Raman spectra of Pr, Nd, and Sm complexes. The spectrum of the Pr complex is the typical one for $5H_2O$ complexes, and that of the Sm complex is typical for $4H_2O$. Although the Nd complex has five $H_2O$ molecules, the spectrum exhibited single and split bands in the region 2200−2150 $cm^{-1}$ (the intensities of the bands are different from those of the Sm complex) and were similar to the spectra of the Sm complex in the region 300−100 $cm^{-1}$. This implies that, in spite of having

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(10) Hulliger, F.; Landolt, M.; Vetsch, H. *J. Solid State Chem.* **1976**, *18*, 283.

(11) Blanchard, A. A.; Coleman, G. W. *Inorganic Synthesis*; McGraw-Hill: New York, 1946; Vol. II.

(12) *UNICS, Universal Crystallographic Computation Program System*; Sakurai, T., Ed.; Crystallographic Society of Japan: Tokyo, 1967.

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**Table 1.** Crystal Data for $Pr[Co(CN)_6]\cdot 5H_2O$ and $Nd[Co(CN)_6]\cdot 5H_2O$

| | $Pr[Co(CN)_6]\cdot 5H_2O$ | $Nd[Co(CN)_6]\cdot 5H_2O$ |
|---|---|---|
| fw | 446.022 | 449.355 |
| cryst syst | hexagonal | orthorhombic |
| space group | $P6_3/m$ | $C222_1$ |
| $a$, Å | 7.473(1) | 7.458(4) |
| $b$, Å | | 12.918(3) |
| $c$, Å | 14.212(1) | 14.172(2) |
| $V$, Å$^3$ | 687.2 | 1365.3 |
| $Z$ | 2 | 4 |
| $\rho_{obsd}$, g cm$^{-3}$ | 2.1471(9) | 2.1763(9) |
| $\rho_{calcd}$, g cm$^{-3}$ | 2.155 56 | 2.164 64 |
| $\mu$(Mo Kα), cm$^{-1}$ | 47.9 | 50.8 |
| radiation ($\lambda_\alpha$, Å) | 0.71069 (Mo Kα) | |
| $T$, °C | 25 | |
| $R^a$ | 0.042 | 0.069 |
| $R_w{}^a$ | 0.052 | 0.077 |

$^a$ $R$ and $R_w$ are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, with $w = 1/[\{\sigma(|F_o|)\}^2 + (0.02|F_o|)^2]$.

**Table 2.** Positional ($\times 10^3$) and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for $Pr[Co(CN)_6]\cdot 5H_2O$ and $Nd[Co(CN)_6]\cdot 5H_2O$

| atom | $x$ | $y$ | $z$ | $B_{eq}{}^a$/Å$^2$ |
|---|---|---|---|---|
| | | $Pr[Co(CN)_6]\cdot 5H_2O$ | | |
| Pr | $^1/_3$ | $^2/_3$ | $^1/_4$ | 1.0 |
| Co | 0 | 0 | 0 | 1.0 |
| C | 120(1) | 238(1) | 77.1(7) | 1.5 |
| N | 192(1) | 809(2) | 123.3(7) | 2.6 |
| O(1) | $^1/_3$ | $^2/_3$ | 917(1) | 3.8 |
| O(2) | 535(3) | 475(3) | $^1/_4$ | 4.9 |
| | | $Nd[Co(CN)_6]\cdot 5H_2O$ | | |
| Nd | 0 | 666.72(5) | $^1/_4$ | 1.0 |
| Co | −10.6(3) | 0 | 0 | 0.9 |
| C(1) | 11(2) | 882.4(8) | 76.5(8) | 1.6 |
| C(2) | 330(2) | 570.7(7) | 79(1) | 1.4 |
| C(3) | −316(1) | 549.7(7) | 76.3(9) | 1.2 |
| N(1) | 20(2) | 809.1(7) | 124.0(8) | 1.6 |
| N(2) | 220(1) | 607.7(7) | 123.9(9) | 1.7 |
| N(3) | −203(1) | 583.9(7) | 122.8(8) | 1.5 |
| O(1) | −25(1) | 666.4(8) | 583.4(8) | 2.7 |
| O(2)$^b$ | 31(4) | 470(1) | 235(2) | 1.6 |
| O(3) | 293(1) | 765(1) | 254(2) | 4.1 |

$^a$ Equivalent temperature factor: $B_{eq} = {}^4/_3\ \{\sum_i\sum_j B_{ij}\mathbf{a}_i\cdot\mathbf{a}_j\}$. $^b$ Disordered $H_2O$: occupancy of the atom is 0.5.

**Table 3.** Selected Bond Distances (Å) in $Pr[Co(CN)_6]\cdot 5H_2O$ and $Nd[Co(CN)_6]\cdot 5H_2O^a$

| $Pr[Co(CN)_6]\cdot 5H_2O$ | | $Nd[Co(CN)_6]\cdot 5H_2O$ | |
|---|---|---|---|
| Pr−N | 2.573(13) | Nd−N(1) | 2.56(1) |
| | | Nd−N(2) | 2.54(1) |
| | | Nd−N(3) | 2.58(1) |
| Pr−O(2) | 2.527(17) | Nd−O(2) | 2.53(1) |
| | | Nd−O(3) | 2.56(1) |
| Co−C | 1.882(9) | Co−C(1) | 1.87(1) |
| | | Co−C(2) | 1.87(1) |
| | | Co−C(3) | 1.92(1) |
| C−N | 1.154(15) | C(1)−N(1) | 1.16(2) |
| | | C(2)−N(2) | 1.15(2) |
| | | C(3)−N(3) | 1.16(2) |
| O(2)···O(1)$^I$ | 2.97(3) | O(3)···O(1)$^{II}$ | 2.82(3) |
| | | O(2)···O(1)$^{III}$ | 2.78(3) |

$^a$ Key to symmetry operations: (I) $1 - x$, $1 - y$, $1 - z$: (II) $0.5 + x$, $1.5 - y$, $1 - z$; (III) $x$, $1 - y$, $1 - z$.

**Table 4.** Selected Bond Angles (deg) in $Pr[Co(CN)_6]\cdot 5H_2O$ and $Nd[Co(CN)_6]\cdot 5H_2O^a$

| $Pr[Co(CN)_6]\cdot 5H_2O$ | | $Nd[Co(CN)_6]\cdot 5H_2O$ | |
|---|---|---|---|
| N−Pr−N | 76.2(4) | N(1)−Nd−N(2) | 71.9(4) |
| N(1)−Nd−N(3) | 81.1(4) | | |
| | | N(2)−Nd−N(3) | 76.3(4) |
| N−Pr−N | 89.1(3) | N(1)−Nd−N(1)$^I$ | 88.5(4) |
| | | N(2)−Nd−N(3)$^I$ | 89.3(4) |
| N−Pr−N | 138.3(4) | N(1)−Nd−N(2)$^I$ | 137.8(4) |
| | | N(1)−Nd−N(3)$^I$ | 138.4(4) |
| | | N(2)−Nd−N(2)$^I$ | 145.1(4) |
| | | N(3)−Nd−N(3)$^I$ | 131.1(4) |
| N−Pr−O(2) | 135.4(5) | N(1)−Nd−O(2) | 130.4(4) |
| | | N(3)−Nd−O(3) | 136.8(4) |
| | | N(1)−Nd−O(2)$^I$ | 140.7(4) |
| | | N(2)−Nd−O(3)$^I$ | 133.8(4) |
| N−Pr−O(2) | 69.0(5) | N(2)−Nd−O(2) | 65.5(4) |
| | | N(3)−Nd−O(2) | 65.4(4) |
| | | N(1)−Nd−O(3) | 66.9(4) |
| | | N(2)−Nd−O(3) | 66.9(4) |
| N−Pr−O(2) | 69.2(4) | N(2)−Nd−O(2)$^I$ | 79.6(4) |
| | | N(3)−Nd−O(2)$^I$ | 66.1(4) |
| | | N(1)−Nd−O(3)$^I$ | 71.0(4) |
| | | N(3)−Nd−O(3)$^I$ | 71.7(4) |
| Co−C−N | 179.4(9) | Co−C(1)$^{II}$−N(1)$^{II}$ | 177(1) |
| | | Co−C(2)$^{III}$−N(2)$^{III}$ | 177(1) |
| | | Co−C(3)$^{IV}$−N(3)$^{IV}$ | 178(1) |
| C−N−Pr | 170.2(9) | C(1)−N(1)−Nd | 169(1) |
| | | C(2)−N(2)−Nd | 169(1) |
| | | C(3)−N(3)−Nd | 169(1) |
| C−Co−C | 89.9(4) | C(1)$^{II}$−Co−C(2)$^V$ | 87.3(5) |
| C−Co−C | 90.1(4) | C(1)$^{II}$−Co−C(3)$^{VI}$ | 93.3(6) |
| | | C(2)$^V$−Co−C(3)$^{VI}$ | 89.2(6) |
| O(2)−Pr−O(2) | 120 | O(2)−Nd−O(3) | 114.9(4) |
| | | O(2)$^I$−Nd−O(3) | 125.0(4) |

$^a$ Key to symmetry operations: (I) $-x$, $y$, $0.5 - z$; (II) $-x$, $-y$, $-z$; (III) $0.5 - x$, $-0.5 + y$, $-z$; (IV) $-0.5 - x$, $-0.5 + y$, $-z$; (V) $0.5 - x$, $0.5 - y$, $z$; (VI) $-0.5 - x$, $0.5 - y$, $z$.

five $H_2O$ molecules, the symmetry around the Nd atom in the complex is lower than that of other $5H_2O$ complexes.

The X-ray structure determinations of the Pr and Nd complexes, which are likely to have boundary structures, have not yet been carried out. To confirm the interpretation of the results of the Raman spectroscopy, the X-ray crystal analyses of the complexes with Pr and Nd were carried out. If the crystals of the complex having $5H_2O$ molecules are isomorphous with those of $La[Co(CN)_6]\cdot 5H_2O$, they are hexagonal and $P6_3/m$. However, the symmetry of the boundary complexes must be lower than that of $La[Co(CN)_6]\cdot 5H_2O$. Therefore, X-ray diffraction measurements for the Pr and Nd complexes were carried out on the assumption that they were monoclinic, the lowest symmetry for the crystals. Then, the data sets were solved in a suitable space group with an appropriate transformation.

The structure of $Pr[Co(CN)_6]\cdot 5H_2O$ was refined with reduced data sets and with an appropriate transformation to $P6_3/m$, since it was found that the complex has the same symmetry as $La[Co(CN)_6]\cdot 5H_2O$. The crystal data for $Pr[Co(CN)_6]\cdot 5H_2O$ are listed in Table 1. The final atomic parameters are listed in Table 2, interatomic distances in Table 3, and bond angles in Table 4. A perspective drawing of the complex and the atom-numbering scheme are shown in Figure 3. The crystal and molecular structures are almost the same as those for $La[Co(CN)_6]\cdot 5H_2O$[4] and $La[Fe(CN)_6]\cdot 5H_2O$.[14] The structural characteristics of $Pr[Co(CN)_6]\cdot 5H_2O$ are as follows: praseodymium is nine-coordinated in the form of the $PrN_6(H_2O)_3$ group; cobalt is six-coordinated in the form of an octahedral $CoC_6$ group; cyanide linkages between the $PrN_6(H_2O)_3$ and $CoC_6$ groups build an infinite polymeric array; two uncoordinated water molecules occupy zeolitic holes in the structure on a 6-fold rotatory inversion axis above and below the Pr atom. The praseodymium atom has coordinated to three waters in the mirror plane and

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(14) Bailey, W. E.; Williams, R. J.; Milligan, W. O. *Acta Crystallogr. Sect. B* **1973**, *29*, 1365.

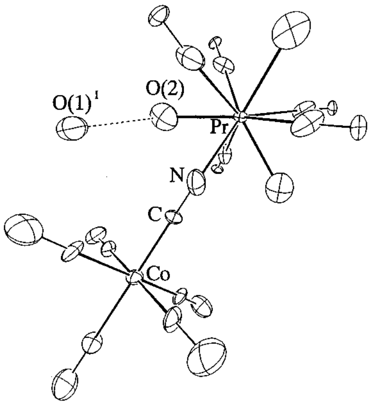

**Figure 3.** Perspective drawing of $Pr[Co(CN)_6]\cdot 5H_2O$ showing 50% thermal ellipsoids and the atom-numbering scheme. Key to symmetry operations: (I) $1 - x$, $1 - y$, $1 - z$. The dashed line indicates hydrogen bonding.

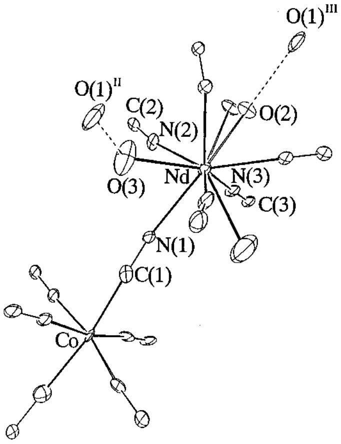

**Figure 4.** Perspective drawing of $Nd[Co(CN)_6]\cdot 5H_2O$ showing 50% thermal ellipsoids and the atom-numbering scheme. Key to symmetry operations: (II) $0.5 + x$, $1.5 - y$, $1 - z$; (III) $x$, $1 - y$, $1 - z$. Dashed lines indicate hydrogen bonding.

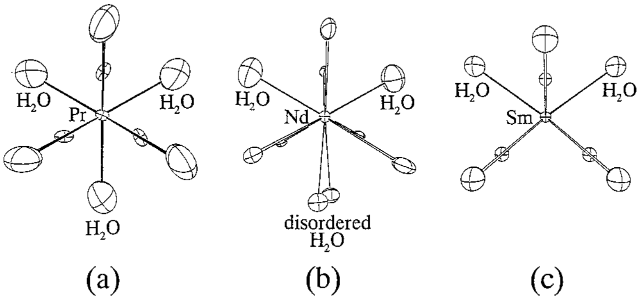

**Figure 5.** Metal coordination geometries in (a) $Pr[Co(CN)_6]\cdot 5H_2O$, (b) $Nd[Co(CN)_6]\cdot 5H_2O$, and (c) $Sm[Co(CN)_6]\cdot 4H_2O$. (a) is represented by $D_{3h}$, (b) is approximately $C_{2v}$, and (c) is $C_{2v}$. The structure of (c) was obtained from refs 6 and 7.

the nitrogen ends of six cyanides, three on either side of the mirror plane. The coordination geometry is approximately $D_{3h}$. The uncoordinated water molecule, O(1), is very weakly hydrogen-bonded to the coordinated water molecule, O(2): O(1)···O(2) = 2.96(4) Å. This is consistent with $La[Co(CN)_6]\cdot 5H_2O$[4] and $La[Fe(CN)_6]\cdot 5H_2O$.[14,15]

In the data sets for $Nd[Co(CN)_6]\cdot 5H_2O$, the hexagonal system was rejected due to noncyclic permutational conditions which were presupposed from the biaxial behavior of the system. Then, the cell was transformed to the orthorhombic system. There are systematic absences for a *C* face-centered lattice. Weak reflections of (*h*0*l*) were retained when *l* was odd: the reflections should be absent if the space group is *Cmcm*. The result implies that the space group of the system lacks the mirror plane which is induced in *Cmcm* (*i.e.*, the space group is $C222_1$). The crystal data for $Nd[Co(CN)_6]\cdot 5H_2O$ are listed in Table 1. Since the space group, $C222_1$, is noncentrosymmetric, there are two absolute configurations. At the stage of locating all of the atoms except for hydrogen ones, the *R* factor for the better of the two absolute configurations was 0.0765; that for the alternative absolute configuration was 0.0767. Thereafter, the refinement was continued with the better absolute configuration. The final atomic parameters are listed in Table 2, interatomic distances in Table 3, and bond angles in Table 4. A perspective drawing of the complex and the atom-numbering scheme are shown in Figure 4. The structure is essentially the same as that for $Pr[Co(CN)_6]\cdot 5H_2O$: it consists of an infinite polymeric array of octahedral $CoC_6$ groups bridged through cyanide linkages to nine-coordinated $NdN_6(H_2O)_3$ groups. There are two uncoordinated water molecules occupying zeolitic holes in the structure on a 2-fold screw axis, which cooresponds to the 6-fold rotatory inversion axis in $Pr[Co(CN)_6]\cdot 5H_2O$, above and below the Nd atom. One of three coordinated water molecules, O(2), is disordered: O(2) is in a position ($x = 0.031(4)$, $y = 0.470(1)$, $z = 0.235(2)$) with occupancy 0.5, and the water molecule is disordered because of a 2-fold axis. The disordered water molecule is distinct from the other water molecules. Thus, the symmetry around the Nd atom is lower than that of Pr in $Pr[Co(CN)_6]\cdot 5H_2O$, as shown in Figure 5. The Nd coordination geometry is approximately $C_{2v}$. The symmetry is equivalent to that of Sm in $Sm[Co(CN)_6]\cdot 4H_2O$:[6,7] the samarium atom is eight-coordinated and its ligands form the $SmN_6(H_2O)_2$ group, which is linked to the octahedrally arranged $CoC_6$ (Co is six-coordinated) group by cyanide bridging. The uncoordinated water molecule, O(1), is hydrogen-bonded to the coordinated water molecules O(3): O(1)···O(3) = 2.82(3) Å. In the $4H_2O$ complexes $Sm[Fe(CN)_6]\cdot 4H_2O$, $Sm[Co(CN)_6]\cdot 4H_2O$,[7] and $La[Fe(CN)_6]\cdot 4H_2O$ (a monodehydrated product of $La[Fe(CN)_6]\cdot 5H_2O$),[15] the uncoordinated water molecule is also hydrogen-bonded to the coordinated one. Moreover, in $Nd[Co(CN)_6]\cdot 5H_2O$, there is another hydrogen bond between O(1) and the disordered O(2): O(1)···O(2) = 2.78(3) Å. The hydrogen bonding is rather strong. Due to such hydrogen bonds, the structure of $Nd[Co(CN)_6]\cdot 5H_2O$ deviates from the typical structure for a $5H_2O$ complex, hexagonal and $P6_3/m$, to that of a $4H_2O$ complex, orthorhombic. Therefore, the structure of $Nd[Co(CN)_6]\cdot 5H_2O$ is regarded as a transient structure from a $5H_2O$ to a $4H_2O$ complex.

Such results are not contradictory to those of Raman spectra. The factor group of the Bravais unit cell is $C_{6h}$, and the site symmetries[16] for Pr and Co, which are bridged by $-CN-$, in $Pr[Co(CN)_6]\cdot 5H_2O$ are both $C_{3h}$. Both the Pr and Co atoms are associated with $E_{2g}$, $E_{1u}$, $B_g$, and $A_u$ as the active modes. Of these modes only $E_{2g}$ is Raman-active. Thus, in $Pr[Co(CN)_6]\cdot 5H_2O$, there are two $E_{2g}$ Raman-active modes. On the other hand, in $Sm[Co(CN)_6]\cdot 4H_2O$, the factor group is $D_{2h}$, and the site symmetries for Sm and Co are $C_{2v}$ and $C_{2h}$, respectively. The Sm atom is associated with $A_g$, $B_{2u}$, $B_{3g}$, $B_{1u}$, $B_{1g}$, and $B_{3u}$ modes, and Co has $A_u$, $2B_{1u}$, and $2B_{3u}$ modes, of which $A_g$, $B_{1g}$, and $B_{3g}$ are Raman-active modes. Since the Raman-active modes in $Sm[Co(CN)_6]\cdot 4H_2O$ are higher than those modes in $Pr[Co(CN)_6]\cdot 5H_2O$, the vibrations of the bridging $-CN-$ between Sm and Co, $\nu$(CN), must be split. The site symmetries

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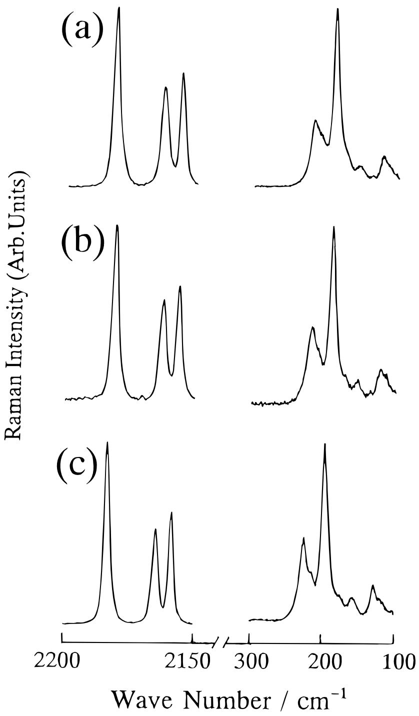

**Figure 6.** Raman spectra of monodehydrated products of $\mathrm{Pr[Co(CN)_6]\cdot 5H_2O}$, $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$, and $\mathrm{Sm[Co(CN)_6]\cdot 4H_2O}$: (a) $\mathrm{Pr[Co(CN)_6]\cdot 4H_2O}$; (b) $\mathrm{Nd[Co(CN)_6]\cdot 4H_2O}$; (c) $\mathrm{Sm[Co(CN)_6]\cdot 4H_2O}$.

for Nd and Co in $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$ (space group $C222_1$) are, to be exact, both $C_2$, which is lower symmetry than $C_{3h}$, $C_{2v}$, or $C_{2h}$, and their factor group is $D_2$. The reflections of ($h0l$) in the data sets for $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$ were rather weak when $l$ was odd, as mentioned above. This fact implies that the heavy atoms are arranged in the equivalent positions for $Cmcm$, whose reflections of ($h0l$) were absent when $l$ was odd; the site symmetries for Nd and Co are approximately $C_{2v}$ and $C_{2h}$, respectively, and the factor group is $D_{2h}$. The fact that the split pattern of $\nu$(CN) in $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$ is similar to that in $\mathrm{Sm[Co(CN)_6]\cdot 4H_2O}$ must be caused by the similarity between the site symmetries for Nd and Co and for Sm and Co.

It is impossible to discuss the local structure around the metal in the series $\mathrm{Ln[Co(CN)_6]\cdot}n\mathrm{H_2O}$ by means of X-ray powder diffraction results, since the frameworks ($\mathrm{Ln[Co(CN)_6]}$) of the complexes are the same. In contrast, the symmetry around the metal can be described by Raman spectroscopy. Thus, Raman spectroscpoy is one effective method to investigate the local structural change of the series $\mathrm{Ln[Co(CN)_6]\cdot}n\mathrm{H_2O}$.

It is reported that the number of water molecules in the series $\mathrm{Ln[M(CN)_6]\cdot}n\mathrm{H_2O}$ changed according to the preparation temperature.[10] A few studies on the thermal dissociation of $\mathrm{La[Co(CN)_6]\cdot 5H_2O}$ were reported.[15,17] In such investigations, X-ray diffraction methods were employed. It is often difficult, however, to obtain local structural information. Thus, we applied Raman spectroscopy to confirm the structure of the thermal dissociation products of $\mathrm{Pr[Co(CN)_6]\cdot 5H_2O}$ and $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$. As shown in Figure 1, the complexes lose one water molecule around 100 °C. Raman spectra of the dehydrated complexes are shown in Figure 6 along with that of $\mathrm{[Co(CN)_6]\cdot 4H_2O}$. In all of the spectra, the two regions ($\nu$(CN) and librational modes of lattice waters and/or lattice vibrations) are the same. It is clear that the symmetries around the metal atoms in the dehydrated Pr and Nd complexes are identical with that of $\mathrm{Sm[Co(CN)_6]\cdot 4H_2O}$. This implies that the symmetry around the Pr or Nd atom completely changes into $C_{2v}$; *i.e.*, the space groups of the Pr and Nd complexes, $P6_3/m$ and $C222_1$, respectively, change into $Cmcm$, when the $\mathrm{5H_2O}$ complexes lose one water molecule. The results are essentially consistent with those for $\mathrm{La[Fe(CN)_6]\cdot 5H_2O}$. Mullica *et al.*[15] reported that, after monodehydration, the nine-coordinated La atom in $\mathrm{La[Fe(CN)_6]\cdot 5H_2O}$ changes to give eight-coordination in the tetrahydrated form, $\mathrm{La[Fe(CN)_6]\cdot 4H_2O}$, and the eight-coordinated polyhedron is a bicapped trigonal prism, with the La atom at its center. Hulliger *et al.*[17] stated that at atmospheric pressure the hexagonal $\mathrm{La[Fe(CN)_6]\cdot 5H_2O}$ loses the first $\mathrm{H_2O}$ molecule near 70 °C, and this first-order transition to the orthorhombic phase is accompanied by a marked volume jump. Hulliger *et al.* speculated that the gradually lost water stems from the zeolitic cavities and that the structure collapses as soon as 1.0 $\mathrm{H_2O}$ is given off. After the structural rearrangement, both zeolitic holes are again completely filled and the procedure can restart. In contrast with such speculation, we propose from the aforementioned results another explanation for the dehydration process. At the first-order $n = 5$ to $n = 4$ transition on the TGA curve of $\mathrm{Pr[Co(CN)_6]\cdot 5H_2O}$, the framework deviates and the structure changes into the less symmetrical one, a transient structure such as $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$. Thereupon, the disordered coordinated water molecule is removed and then the structural rearrangement occurs.

## Conclusion

The composition of the series of lanthanoid hexacyanocobaltate(III) *n*-hydrates prepared at room temperature was as follows: $\mathrm{Ln'[Co(CN)_6]\cdot 5H_2O}$ (Ln′ = La, ..., Nd), and $\mathrm{Ln''[Co(CN)_6]\cdot 4H_2O}$ (Ln″ = Sm, ..., Lu). The complexes with a lanthanoid ligher than Nd are $\mathrm{5H_2O}$ complexes, hexagonal and $P6_3$/m, and those with a lanthanoid heavier than Nd are $\mathrm{4H_2O}$ complexes, orthorhombic and $Cmcm$. Although the Nd complex is a $\mathrm{5H_2O}$ complex, the crystals are orthorhombic and $C222_1$. Therefore, $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$ has the boundary structure: one of the coordinated water molecules is disordered, although the structure is essentially the same as that of $\mathrm{Pr[Co(CN)_6]\cdot 5H_2O}$. The structure of $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$ is considered to be metastable because the crystals easily lose water molecules: even in the aqueous solution the single crystals lose water molecules in several weeks and decompose. The $\mathrm{5H_2O}$ complex with Nd loses one water molecule and changes into the more stable $\mathrm{4H_2O}$ complex, whose crystals must be orthorhombic and $Cmcm$. $\mathrm{Pr[Co(CN)_6]\cdot 5H_2O}$ also changes into the $\mathrm{4H_2O}$ complex, orthorhombic and $Cmcm$, when it dehydrates. The hydration of the series of lanthanoid hexacyanocobaltate(III) *n*-hydrates should be based on the size effect of the lanthanoids. In this case, the boundary atom in the series is Nd.

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**Supporting Information Available:** Details of the X-ray diffraction analyses, including tables of experimental details, thermal parameters, bond lengths, and bond angles and Figures S1 and S2, showing stereoscopic views of the crystal packing of $\mathrm{Pr[Co(CN)_6]\cdot 5H_2O}$ and $\mathrm{Nd[Co(CN)_6]\cdot 5H_2O}$ (7 pages). Ordering information is given on any current masthead page.

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