

A Study of Several Mixed Cationic Systems of (Pr/La)Co(CN)₆ · 5H₂O

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Three mixed cationic (Pr/La)Co(CN)₆ · 5H₂O compounds have been synthesized where the ratios of (Pr/La) are 1:9, 2:8, and 4:6. The structural analyses of these systems using single-crystal diffractometry and full-matrix least-squares refinement yielded reliability factors of 0.036, 0.044, and 0.067 based on 643, 594, and 578 observed reflections, respectively. These complexes crystallize in the centrosymmetric hexagonal space group *P*6₃/*m* with cell parameters *a* = 7.500(1), 7.491(2), and 7.477(2) and *c* = 14.317(3), 14.297(2), and 14.265(2) Å, respectively (*Z* = 2). Observed densities, thermogravimetric results, and infrared spectroscopic data are presented, as well as X-ray powder diffraction analyses. The trivalent lanthanide (*Ln*) metal atoms are nine-coordinate in the form of (*Ln*)N₆(H₂O)₃ groups (TTP) which are linked to the octahedrally arranged CoC₆ groups by cyanide bridging. Three of the five H₂O molecules are coordinated to the *Ln* atoms and two are zeolitic in nature, occupying cavities in the polymeric array within hydrogen-bonding distances to the coordinated H₂O molecules. Selective bond distances and angles are listed and discussed as well as oxygen–oxygen intermolecular contact lengths. © 1997 Academic Press

INTRODUCTION

Microscopic crystals belonging to the hexagonal system of lanthanide (*Ln*) hexacyanides were synthesized initially by James and Willard (1). Nevertheless, it was Bonnet and Pâris (2) who studied the *Ln*Co(CN)₆ · *n*H₂O series (*n* = 4) using infrared and X-ray methods. This group assigned the series to the hexagonal (*P*6₃/*m*) LaFe(CN)₆ · 5H₂O structure proposed by Milligan *et al.* (3). In 1976, Hullinger *et al.* (4) reported an investigation of the rare earth cobaltcyanides, *Ln*Co^{III}(CN)₆ · *n*H₂O where *Ln* = La, ..., Lu. They stated that the large rare earth ions (*Ln* = La, Ce, Pr, and Nd) form a hexagonal modification and that the smaller ions conform to an orthorhombic structure with *n* = 4. Also, the cobaltcyanides of Ce, Pr, and Nd can crystallize in both hexagonal and orthorhombic lattices. Single-crystal X-ray analyses confirmed these conclusions (5–8).

Interest in mixed system (in this laboratory) started with the crystal structure analysis of 1:1 (Gd/Yb)PO₄ (9) which was part of an investigation that varied relative rare earth

compositions over a wide range. This type of structural regulation may permit control of magnetic and optical properties. In the present work, structural data for the titled compounds of interest are presented to provide a basis for future solid-state chemical studies dealing with structure integration and association of diverse cations so as to develop a better understanding of semipermeable membranes. Further, due to keen interest in controlled hydration of zeolitic type complexes, synthesis of mixed lanthanide transition hexacyanides will be continued (7, 8).

EXPERIMENTAL

Using the appropriate molar ratios of the subject lanthanide (*Ln*) chlorides, single crystals of (Pr_{0.1}La_{0.9})Co(CN)₆ · 5H₂O (**I**), (Pr_{0.2}La_{0.8})Co(CN)₆ · 5H₂O (**II**), and (Pr_{0.4}La_{0.6})Co(CN)₆ · 5H₂O (**III**) were synthesized using the U-tube slow diffusion method. The interdiffusing components, *Ln*Cl₃ and K₃Co(CN)₆, were obtained commercially (ACS grade) and used without any further purification. The respective crystal sizes used in the data collections were 0.196 × 0.246 × 0.246 mm, 0.148 × 0.246 × 0.246 mm, and 0.213 × 0.230 × 0.279 mm.

Conoscopic examinations of single crystals of **I**, **II**, and **III** verified the uniaxial nature (birefringent) of each complex. Crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II was used for the optical surveys. A Perkin–Elmer TGS-1 Thermobalance (TGA) was employed to determine the thermal dehydrations of **I**, **II**, and **III**, run at 2.5°C min⁻¹ while purging the balance with N₂ (20 cm³ min⁻¹). The analyses yielded the value of 5.0 water molecules per formula unit for each compound. Infrared spectral data were obtained on a Mattson Cygnus 100 FTIR analyzer over the frequency range 4000–400 cm⁻¹ using the KBr pellet technique. The spectral peaks displayed the following relevant absorptions for **I**, **II**, and **III**: sharp free OH stretching bands at approximately 3630 cm⁻¹, very broad, strong bands at 3420 cm⁻¹ with distinct and well pronounced shoulders at approximately 3230 cm⁻¹ (*ν*-OH bands, H-bonding), very sharp peaks at about 2150 cm⁻¹ (*ν*-C≡N) and 1610 cm⁻¹ (*δ*-HOH), and Co–CN bonding frequencies at approximately 438 cm⁻¹. X-ray powder

diffraction data were obtained by the use of a Siemens Debye–Scherrer cylindrical camera (114.6 mm, 292 K, under vacuum). CuK α ($\lambda_{\text{mean}} = 1.54184 \text{ \AA}$) radiation was used with a Ni filter. Crystals of **I**, **II**, and **III** were finely ground and placed into thin-walled glass capillaries (0.2 mm). Ring diameter measurements (S values) were entered into a least-squares program (10) designed for X-ray powder diffraction data. This analysis program uses the Nelson–Riley extrapolation function (11) to calculate lattice parameters and their estimated standard deviations. The refined lattice constants for **I**, **II**, and **III** (using the powder method) are $a = 7.500(2)$, $7.493(2)$, and $7.482(1)$, and $c = 14.316(7)$, $14.298(3)$, and $14.263(3) \text{ \AA}$, respectively (see Table 1). The respective figures-of-merit values associated with each studied system are: $F_{19} = 61(0.006, 50)$, $F_{20} = 53(0.007, 50)$, $F_{20} = 54(0.008, 48)$, and $M_{20} = 54.4, 47.9$ (compounds **II** and **III**, respectively) (12, 13). Table 2 presents the observed and calculated 2θ values ($^\circ$) with the average percentage deviation, the visually estimated relative intensities based on 100 as the strongest observed reflection, and the observed and calculated d spacings (\AA) for compound **I**. The average percentage deviation between observed and calculated d spacings is also presented in Table 2. Tables and powder data results for **II** and **III** are available from the authors (DFM).

TABLE 1
Experimental and Statistical Data Summaries

	I	II	III
System	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$
$a/\text{\AA}$, single crystal	7.500(1)	7.491(2)	7.477(2)
$c/\text{\AA}$, single crystal	14.317(3)	14.296(2)	14.265(3)
$V/\text{\AA}^3$, single crystal	697.4	694.7	690.8
$a/\text{\AA}$, powder	7.500(2)	7.493(2)	7.482(1)
$c/\text{\AA}$, powder	14.316(7)	14.298(3)	14.263(3)
$V/\text{\AA}^3$, powder	697.4	695.2	691.5
M_r	444.2	444.4	444.8
Z	2	2	2
$D_c/\text{Mg m}^{-3}$	2.115	2.125	2.139
$D_o/\text{Mg m}^{-3}$	2.121(8)	2.125(8)	2.136(8)
$F(000)/(e^-)$	424.4	424.8	425.6
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	4.29	4.34	4.45
Transmission Range			
min.	0.8707	0.9237	0.8441
max.	0.9993	0.9990	0.9977
$\Delta\theta/^\circ$	1.5–30.0	1.5–30.0	1.5–30.0
T/K	292	292	292
R_{int}	0.051	0.036	0.051
R	0.036	0.044	0.067
$R_w(R_{\text{all}})$	0.043(0.041)	0.054(0.051)	0.086(0.079)
$g/(10^{-3}e^{-2})$	1.4(7)	3.4(12)	7(3)
Unique refl.	643	594	578
GOF (\sum_2)	1.31	1.02	1.52

TABLE 2
X-ray Powder Diffraction Data for
(1:9)(Pr/Ln)Co(CN)₆ · 5H₂O

h	k	l	$2\theta_0(\text{deg})$	$2\theta_0(\text{deg})$	I/I_0	$d_0(\text{\AA})$	$d_c(\text{\AA})$
1	0	1	14.975	14.980	100	5.92	5.91
1	0	2	18.446	18.446	80	4.81	4.81
1	0	3	23.163	23.163	80	3.84	3.84
1	1	0	23.727	23.727	10	3.75	3.75
1	1	2	26.854	26.854	60	3.32	3.32
1	1	3	30.298	30.298	3	2.95	2.95
2	0	3	33.359	33.371	3	2.686	2.685
1	0	5	34.198	34.224	5	2.622	2.620
1	1	4	34.647	34.647	40	2.589	2.589
2	1	0	36.603	36.603	7	2.455	2.455
2	1	1	37.168	37.168	20	2.419	2.419
2	1	2	38.781	38.781	30	2.322	2.322
3	0	0	41.720	41.719	25	2.165	2.165
3	0	2	43.708	43.686	25	2.071	2.072
2	2	0	48.550	48.555	5	1.875	1.875
3	0	4	49.201	49.184	5	1.8519	1.8525
3	1	1	51.101	51.104	5	1.7874	1.7873
2	2	3	52.452	52.433	5	1.7445	1.7451
3	1	3	54.451	54.444	3	1.6851	1.6853

Note. Average percentage deviation ($\Delta 2\theta$) in $2\theta = 0.015$. Average percentage deviation (Δd) in d spacing = 0.036.

Single crystals of **I**, **II**, and **III**, selected on the basis of optical purity and homogeneity, were mounted on glass fibers and transferred to goniometer heads which, in turn, were placed on an Enraf–Nonius diffractometer equipped with a dense graphite monochromator (take-off angle 2.8°). The orientation matrices and unit cell parameters for each data set (using MoK α radiation, $\lambda = 0.71073 \text{ \AA}$) were obtained from the least-squares refinements of 25 randomly selected and accurately centered reflections. Data were then collected over the range $3.0^\circ < 2\theta < 60.0^\circ$ using the ω - 2θ scan technique at a variable scan rate between 0.56 and $5.17^\circ \text{ min}^{-1}$ in ω which was determined by a fast prescan of $5.17^\circ \text{ min}^{-1}$. Three standard reflections for each data set showed no significant intensity changes over the duration of the data collection. Therefore, the reliability and stability of the electronic hardware and the crystal were declared true. Reflections having less than 75 counts above the background during the prescan were considered to be unobserved. Experimental and statistical summaries are presented in Table 1 for complexes **I**, **II**, and **III**. All resultant data sets were corrected for Lorentz and polarization effects and absorption corrections were applied; see Table 1 for transmission ranges. All redundant data were averaged. Systematic absences ($000l$, $l = 2n + 1$) were consistent with space groups $P6_3$ and $P6_3/m$. However, $N(Z)$ analyses (cumulative probability distribution relative to centrosymmetric test) provided evidence that the studied compounds are centrosymmetric in nature. Hence, $P6_3/m$ was the logical space

group choice. The heavy atom Patterson method located the *Ln* and Co atoms and difference Fourier mapping positioned all other nonhydrogen atoms. Each structure was initially refined isotropically using a full-matrix least-squares program (14). Secondary extinction corrections were applied (see Table 1). After several cycles of anisotropic refinement of **I**, **II**, and **III**, final reliability factors based on $R = \sum \Delta F / \sum F_0$ and $R_w = \sum \sqrt{w} \Delta F / \sum \sqrt{w} F_0$ were obtained. ΔF is defined as $\|F_0| - |F_c\|$ and the weighting function w is denoted as the reciprocal of the square of the standard deviation of F_0 , $\sigma^{-2}(F_0)$. Respective R values are 0.036, 0.044, and 0.067 and the "goodness-of-fit" values (GOF, \sum_2) are 1.31, 1.02, and 1.52. Final electron density maps revealed some density in the vicinity of the lanthanide metal atoms which is quite reasonable for heavy metal atoms. Elsewhere, only random fluctuating backgrounds were observed. Atomic scattering factors and associated anomalous dispersion correction factors for all atoms were taken from the usual source (15). Final atomic position and equivalent isotropic thermal parameters with estimated standard deviations are listed in Table 3. Tables of observed and calculated structure factor are available from DFM.

TABLE 3
Atomic Coordination ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in Parentheses

Atom	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)^a$
Compound I					
Pr	0.10	3333	6667	2500	10(1)
La	0.90	3333	6667	2500	10(1)
Co	1.00	0000	0000	0000	11(1)
C	1.00	1347(5)	2363(5)	763(3)	20(1)
N	1.00	2162(5)	3812(5)	1215(4)	38(1)
O(1)	1.00	4920(8)	10597(6)	2500	54(2)
O(2)	1.00	3333	6667	-857(7)	56(3)
Compound II					
Pr	0.20	3333	6667	2500	13(2)
La	0.80	3333	6667	2500	11(1)
Co	1.00	0000	0000	0000	12(1)
C	1.00	1325(7)	2357(7)	761(4)	25(2)
N	1.00	2143(8)	3813(7)	1211(5)	40(2)
O(1)	1.00	4910(12)	10614(10)	2500	56(3)
O(2)	1.00	3333	6667	-832(9)	69(5)
Compound III					
Pr	0.40	3333	6667	2500	16(1)
La	0.60	3333	6667	2500	6(1)
Co	1.00	0000	0000	0000	15(1)
C	1.00	1182(14)	2446(9)	756(7)	27(3)
N	1.00	1989(17)	3891(16)	1221(9)	63(6)
O(1)	1.00	5409(20)	10641(16)	2500	68(7)
O(2)	1.00	3333	6667	-843(14)	41(5)

^aEquivalent isotropic thermal parameters (U_{eq}) is defined as one-third the trace of orthogonalized U_{ij} tensor.

TABLE 4
Bond and Contact Distances (\AA) with e.s.d.'s in Parentheses

Compound I			
<i>Ln</i> ^a -N	2.619(5)	C-N	1.144(5)
<i>Ln</i> -O(1)	2.568(4)	O(1) ... O(2)	2.970(8)
Co-C	1.888(3)	O(2) ... N	3.495
Compound II			
<i>Ln</i> ^a -N	2.618(6)	C-N	1.145(5)
<i>Ln</i> -O(1)	2.578(7)	O(1) ... O(2)	2.981(11)
Co-C	1.879(5)	O(2) ... N	3.462
Compound III			
<i>Ln</i> ^a -N	2.561(12)	C-N	1.148(14)
<i>Ln</i> -O(1)	2.574(11)	O(1) ... O(2)	2.938(17)
Co-C	1.916(8)	O(2) ... N	3.449

^a*Ln* = Pr or La.

DISCUSSION

Figure 1 is a representative projected view of the $LnN_6(H_2O)_3$ group displaying a tricapped trigonal prism (TTP, D_{3h}) geometry. The octahedral CoC_6 group is also viewed in Fig. 1, as well as the $Ln-N \equiv C-Co$ cyanide bridging; see Tables 4 and 5 for bond distances and angles. The cyanide linkages between the $LnN_6(H_2O)_3$ and CoC_6

TABLE 5
Bond Angles ($^\circ$) with e.s.d.'s in Parentheses

Compound I				
<i>N-Ln</i> ^a - <i>N</i> ⁱ	76.1(1)	O(1)- <i>Ln</i> -O(1)	120.0(1)	
<i>N-Ln</i> - <i>N</i> ⁱⁱ	89.3(2)	C-Co-C ^{iv}	180.0(1)	
<i>N-Ln</i> - <i>N</i> ⁱⁱⁱ	138.3(1)	C-Co-C ^v	90.1(1)	
<i>N-Ln</i> -O(1)	135.4(1)	C-Co-C ^{vi}	89.9(1)	
<i>N-Ln</i> -O(1) ^{vii}	69.4(1)	<i>Ln</i> -N-C	167.2(3)	
<i>N-Ln</i> -O(1) ⁱ	68.9(1)	Co-C-N	178.9(4)	
Compound II				
<i>N-Ln</i> ^a - <i>N</i> ⁱ	75.9(2)	O(1)- <i>Ln</i> -O(1)	120.0(2)	
<i>N-Ln</i> - <i>N</i> ⁱⁱ	89.5(3)	C-Co-C ^{iv}	180.0(1)	
<i>N-Ln</i> - <i>N</i> ⁱⁱⁱ	138.4(2)	C-Co-C ^v	90.1(2)	
<i>N-Ln</i> -O(1)	135.2(1)	C-Co-C ^{vi}	89.9(2)	
<i>N-Ln</i> -O(1) ^{vii}	70.0(2)	<i>Ln</i> -N-C	167.1(5)	
<i>N-Ln</i> -O(1) ⁱ	68.4(2)	Co-C-N	178.8(6)	
Compound III				
<i>N-Ln</i> ^a - <i>N</i> ⁱ	74.9(3)	O(1)- <i>Ln</i> -O(1)	120.0(3)	
<i>N-Ln</i> - <i>N</i> ⁱⁱ	90.3(5)	C-Co-C ^{iv}	180.0(1)	
<i>N-Ln</i> - <i>N</i> ⁱⁱⁱ	138.9(4)	C-Co-C ^v	91.4(4)	
<i>N-Ln</i> -O(1)	134.5(3)	C-Co-C ^{vi}	88.6(4)	
<i>N-Ln</i> -O(1) ^{vii}	67.8(4)	<i>Ln</i> -N-C	169.2(9)	
<i>N-Ln</i> -O(1) ⁱ	71.1(4)	Co-C-N	175.8(12)	
Symmetry operators:	i	1 - <i>y</i> , 1 + <i>x</i> - <i>y</i> , <i>z</i>	v	<i>y</i> , <i>y</i> - <i>x</i> , - <i>z</i>
	ii	<i>x</i> , <i>y</i> , $\frac{1}{2}$ - <i>z</i>	vi	- <i>y</i> , <i>x</i> - <i>y</i> , <i>z</i>
	iii	1 - <i>y</i> , 1 + <i>x</i> - <i>y</i> , $\frac{1}{2}$ - <i>z</i>	vii	<i>y</i> - <i>x</i> , 1 - <i>x</i> , <i>z</i>
	iv	- <i>x</i> , - <i>y</i> , - <i>z</i>		

^a*Ln* = Pr or La.

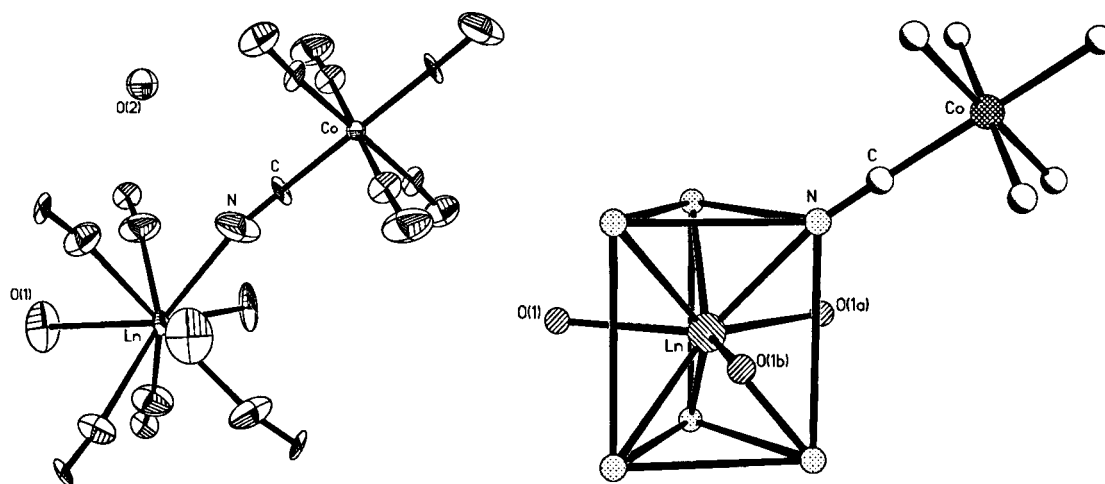


FIG. 1. (a) A representative view of **I**, **II**, and **III** displaying the 9-coordination and 6-coordination about *Ln* and Co, respectively. (b) A projected view of the TTP and octahedral geometries. Note the cyanide bridging connecting *Ln* and Co atoms.

groups build an infinite polymeric array. The two uncoordinated zeolitic water molecules occupy holes in the structure on a threefold axis above and below the rare earth metal ions; see Fig. 2. Nonaccordinated geometries are quite common in ionic lattices of the larger lanthanide complexes and have been reported for *Ln*(OH)₃ and *Ln*Cl₃ systems (16, 17). The interaction of Co 3*d* orbitals and the C≡N⁻ orbitals leads to strong directional bonding; the Co–C≡N⁻ angles are approximately 179° in **I**, **II**, and **III**, (see Table 5). However, little or no directional influences are observed concerning electrostatic bonding of the *Ln* ions to the C≡N⁻ groups; the *Ln*–N≡C angles are about 167° in the studied cyanide complexes. The Co–C bond distances of 1.888(3), 1.879(5), and 1.916(8) Å in **I**, **II**, and **III**, respectively, are in good agreement with the calculated bond length

by Curry and Runciman (18) and with the experimental Co–C bond length of 1.887(9) Å determined in the crystal structure of LaCo(CN)₆ · 5H₂O (5). All other bond lengths are internally consistent and are in good agreement with published values found in the Cambridge Structure Database (19) and BIDICS (20). The uncoordinated water molecules [O(2)] are zeolitic in nature and are within hydrogen bonding distance to the coordinated water molecule, O(1). In this work, the hydrogen bonding would be considered moderate to weak, since the intermoeity contact distances between O(1) and O(2) are 2.970(8), 2.981(11), and 2.938(17) Å for compounds **I**, **II**, and **III**; see Table 4. The strength of a hydrogen bond has been indicated by Brown (21) to be dependent upon the O...O interatomic distances, assuming no geometric constants. O...O contact distances

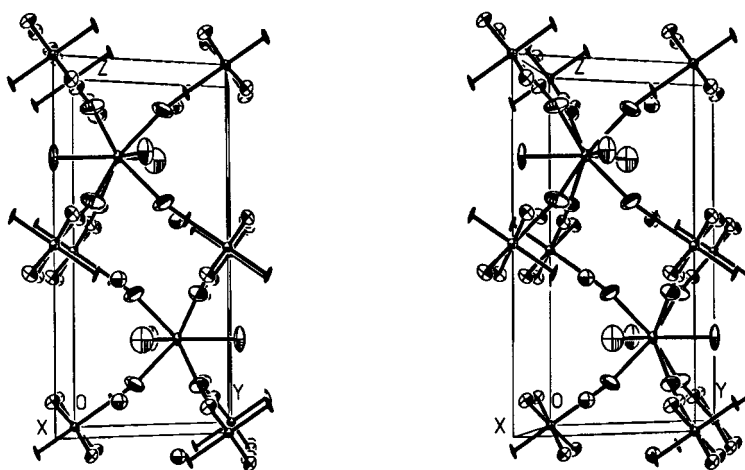


FIG. 2. A stereoview of the unit cell and its contents. Note the locations of the uncoordinated water molecules.

of 2.73 Å or less can be associated with strong hydrogen bonds. However, as the contact length increases, the hydrogen bonding becomes progressively weaker and beyond 3.3–3.4 Å H-bonding does not occur. The infrared studies (mentioned in the experiment section) also lend credence to the involvement of hydrogen bonding. The position and stability of the uncoordinated water molecules in all three structures can be attributed to hydrogen bond energy and moderate to weak H-bonds would allow easy removal of the zeolitic O(2) water molecules (22). Mixed systems have become of interest to the scientific community at large. Therefore, structural investigations dealing with mixed cationic lanthanide hexacyano-transition metallate (II or III) complexes will be advanced in this laboratory. Much effort is being placed on growing crystals large enough for neutron diffraction analysis which would help clarify any questions related to hydrogen atom positioning and, in turn, hydrogen bonding, as well as yield informative results regarding controlled hydration of zeolitic type complexes.

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