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# A THERMAL AND STRUCTURAL STUDY ON LANTHANUM HEXACYANOCOBALTATE(III) PENTAHYDRATE, La[Co(CN)$_6$]·5H$_2$O. PART III

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## Abstract

On dehydration of $La[Co(CN)_6]\cdot 5H_2O$, the color of the complex, changes from white to pale blue at around 230°C. Heating the pale blue specimen, the color changes to deep blue at around 290°C. This deep blue specimen is easily rehydrated to a pink one. As reported previously, in the pale blue specimen, $Co^{3+}$ ions are situated in the center of the $D_{4h}$ crystal field formed by six $CN^-$ ions.

The deep blue specimen is due to the presence of $[Co(CN)_4]^{2-}$ ions in which $Co^{2+}$ was situated in a $T_d$ coordination field formed by four $CN^-$ ions and the Co–C bond length is 1.67 Å. The pink species corresponded to *trans*-$[Co(CN)_4(H_2O)_2]^{2-}$ and the bond lengths of Co–C and Co–O are 1.89 and 1.85 Å, respectively.

The Raman spectra of the complex observed at 25°C displays two bands at 2157 and 2176 cm$^{-1}$ associated with the vibration of C–N bond, and the band of 2157 cm$^{-1}$ was split into two bands, 2150 and 2156 cm$^{-1}$, at around 100°C. When the complex was heated to around 230°C, three new bands were observed at 2103, 2116 and 2141 cm$^{-1}$. The bands of 2103 and 2116 cm$^{-1}$ were assigned to the stretching vibration of C≡N bonding to $Co^{2+}$. The band of 2141 cm$^{-1}$ was assigned to the stretching vibration of the inverted $CN^-$ as follows: $Co–C≡N–La \rightarrow Co–N≡C–La$. The activation energy for the inversion of $CN^-$ was estimated as 67 kJ mol$^{-1}$.

**Keywords:** crystal structures, dehydration, $La[Co(CN)_6]\cdot 5H_2O$

## Introduction

The crystal structures and the thermal properties of a series of complexes $Ln[Co(CN)_6]\cdot nH_2O$ ($Ln$=La~Lu, $n$=4, 5) have been extensively studied [1–3]. In 1979, Mullica *et al.* [4] reported that $La[Co(CN)_6]\cdot 5H_2O$ is of hexagonal system symmetry, $P6_3/m$. Further, the crystal structures of a series of complexes of $Ln[Co(CN)_6]\cdot nH_2O$ have been determined by single crystal X-ray diffraction analysis [5–7].

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In the previous paper [8], we have reported that the color of the anhydride complex ($La[Co(CN)_6]$) changes from white to pale blue at around 230°C, and on heating the pale blue specimen, the color changes to deep blue at around 290°C. When the pale blue specimen is exposed to the atmosphere for a few hours, it returns reversibly to the original white hydrate, $La[Co(CN)_6]\cdot5H_2O$. On the other hand, when the deep blue specimen is allowed to stand for a few hours, the color changed to pink. These color changes were rationalized in terms of changes to the cobalt coordination sphere and the reduction of Co(III). $Co^{3+}$ ions in $La[Co(CN)_6]\cdot5H_2O$ are located at the center of an $O_h$ coordinational field consisting of six $CN^-$ ions and the $Co^{3+}$ ions in the pale blue specimen are situated in a field of $D_{4h}$. In the $D_{4h}$ field, two bond lengths of Co–CN in the $O_h$ field lengthen along the $z$-axis [8, 9]. Although a distinct mass loss was not observed over the temperature range of 230–300°C on the TG curve, a gaseous product was evolved at around 280°C and the mass spectrum observed at 293°C indicated loss of CN groups [9]. In the deep blue specimen, $Co^{3+}$ is reduced to $Co^{2+}$ which has $T_d$ symmetry as $[Co(CN)_4]^{2-}$ [8]. However, the structure of the pink form has not been elucidated.

In this paper, the structure of the deep blue specimen is reexamined and the structure of the pink specimen is investigated by electronic UV-VIS spectra, powder X-ray diffraction, EXAFS and DV-Xα molecular orbital cluster method [10], and these color changes of the specimens are discussed from the viewpoint of the structural changes around $Co^{2+}$ ions.

The Raman spectrum of the complex of $La[Co(CN)_6]\cdot5H_2O$ was measured at 25, 80 and 230°C to futher rationalize the structural changes of the complexes [11].

## Experimental

$La[Co(CN)_6]\cdot5H_2O$ was synthesized by mixing 0.2 mol $dm^{-3}$ $K_3[Co(CN)_6]$ aqueous solution and 0.2 mol $dm^{-3}$ $LaCl_3\cdot7H_2O$ aqueous solution and heating to around 90°C [8, 9].

The pale blue anhydride was prepared by heating $La[Co(CN)_6]\cdot5H_2O$ to 230°C in a Yamato drying oven DP222 and the deep blue specimen was obtained by heating $La[Co(CN)_6]\cdot5H_2O$ at 290°C. When the deep blue specimen was permitted to stand for a week in air, it changed to the pink specimen. Since both the pale blue and the deep blue specimens were rehydrated easily, EXAFS and UV-VIS spectra were measured using the Nujol mull method [8, 9].

The thermogravimetry (TG) and differential thermal analysis (DTA) curves were simultaneously recorded on a Rigaku Thermoflex TAS200 TG-DTA, at a heating rate of 5°C $min^{-1}$ in air. About 10 mg of sample were weighed into an aluminum crucible and measured using α-alumina as a reference material [1–3, 8, 9].

X-ray powder diffraction (XRD) profiles were obtained using a Rigaku Geigerflex RAD-3R diffractometer equipped with a high temperature sample holder. $MoK_\alpha$ radiation (0.7093 Å) was monochromatized using a graphite monochrometer [1–3, 8, 9].

X-ray absorption spectra at Co K-edges (7710 eV) [8, 9] and La $L_{III}$-edges (5489 eV) were measured with a Rigaku laboratory EXAFS spectrometer, R-EXAFS. The data were analyzed using a Rigaku EXAFS data analysis system, REX-2000.

The UV-VIS spectra of samples were obtained with a Hitachi U-3210 spectrophotometer [8, 9]. The spectra were measured in the range from 200 to 800 nm with a step scan width of 0.2 nm by means of the Nujol mull method and the diffuse reflectance method.

In order to discuss the electronic spectra, the energy-level diagrams obtained by the splitting of d orbitals of cobalt ion were calculated using the DV-Xα molecular orbital cluster method [8–10].

The Raman spectra were measured by a Jobin Yvon U-1000 spectrometer equipped with a handmade heating block, and the exciting line (514.5 nm, 100 mW) was provided by a NEC GLG 3200 $Ar^+$ ion laser [11]. The temperature of the heating block was raised up to a given temperature and maintained at the temperature by use of an Ohokura EC5600 controller.

## Results and discussion

Figure 1 shows the TG-DTA curves of $La[Co(CN)_6]\cdot5H_2O$. The dehydration of this complex proceeds via three steps corresponding to the loss of $H_2O$, $3H_2O$ and $H_2O$. During dehydration, the color of the anhydride changes from white to pale blue at around 230°C. Heating the pale blue specimen, the color changes to deep blue at around 290°C [8, 9]. When the pale blue and the deep blue complexes are permitted to stand for a few hours, the former returns to the original pentahydrate $La[Co(CN)_6]\cdot5H_2O$, however, the latter changes to the pink specimen [8].

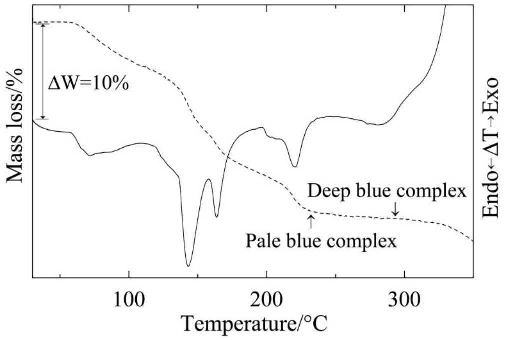

**Fig. 1** TG-DTA curves for $La[Co(CN)_6]\cdot5H_2O$ (heating rate 5°C $min^{-1}$ in air); - - - - TG; —— DTA

In previous papers, these color changes were discussed on the basis of the coordination geometries around Co ions from visible electronic spectra, powder X-ray diffraction, EXAFS, measuring magnetic susceptibility and DV-Xα cluster method [8–10]. The results were summarized schematically in the Fig. 2.

The deep blue specimen has an absorption band at 581 nm with shoulders at around 560 and 590 nm. As described previously, these shoulders are due to the pale blue specimen contaminated [8], and the deep blue color is assigned to the electronic

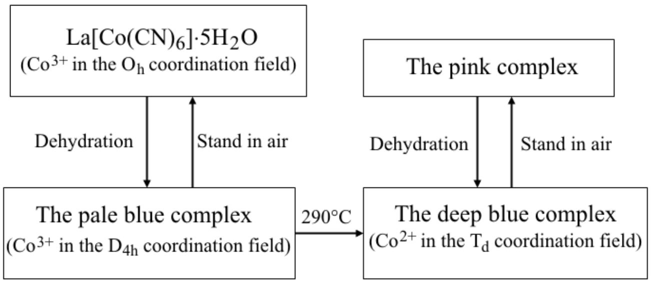

**Fig. 2** Thermal and structural change of $La[Co(CN)_6]\cdot 5H_2O$

transition among the splitting d orbitals of $Co^{2+}$ ions in the $T_d$ crystal field of $[Co(CN)_4]^{2-}$ ions. However, the calculated wavelengths (610.4–621.2 nm) was not consistent satisfactory with the observed one, 581 nm [8].

So, in this study, the structure of $[Co(CN)_4]^{2-}$ was reexamined using EXAFS, and the bond length of Co–C was revised from 1.65 to 1.67 Å (Table 1). On the basis of this structure, the wavelength, 578 nm calculated by use of the DV-Xα method was in fairly good agreement with observational one, 581 nm.

When the deep blue specimen permitted to stand for a few hours, it changed to pink. The UV-VIS spectra of the pink specimen showed three absorption bands at 258, 308 and 521 nm. The bands at 258 and 315 nm are assigned to $^1A_{1g}\rightarrow{}^1T_{2g}$ and $^1A_{1g}\rightarrow{}^1T_{1g}$ for $Co^{3+}$ ion of $La[Co(CN)_6]\cdot 5H_2O$ [12, 13]. It has been known that $Co^{2+}$ forms a pink complex ion, $[Co(H_2O)_6]^{2+}$ in solution and the complex ion has an absorption band at 510 nm [14]. It is worth noting that the band at 521 nm for the pink specimen is consistent approximately with the band at 510 nm of $[Co(H_2O)_6]^{2+}$. The XRD profile of the pink specimen was similar to that of $La[Co(CN)_6]\cdot 5H_2O$ (Fig. 3).

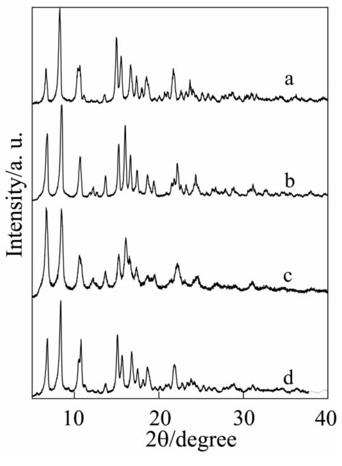

**Fig. 3** XRD profiles of a – $La[Co(CN)_6]\cdot 5H_2O$, b – the pale blue specimen, c – the deep blue specimen and d – the pink specimen

These results indicate that the pink specimen consists of two components of which major component is original white La[Co(CN)$_6$]·5H$_2$O formed by the rehydration of La[Co(CN)$_6$] and minor is the pink species. In order to elucidate the pink species, EXAFS oscillation for the pink specimen was measured at Co K-edges and its Fourier transition was shown in Fig. 4. The pink species was estimated to [Co(CN)$_4$(H$_2$O)$_2$]$^{2-}$ from the curve fitting (Table 1).

**Table 1** Coordination number (*CN*), bond length (*r*), Debye–Waller factor (σ) and R-factor (*R*) obtained from curve-fitting results for Fourier-filtered $k^3\chi(k)$ of Co K-sample

| | Atom | *CN* | *r*/Å | σ/Å | *R*/% |
|---|---|---|---|---|---|
| La[Co(CN)$_6$]·5H$_2$O$^{\alpha}$ | C | 6 | 1.887 | | |
| | N | 6 | 3.043 | | |
| Deep blue specimen[b] | C | 4 | 1.65 | 0.01 | |
| | N | 4 | 2.65 | 0.01 | |
| | C | 4 | 1.86 | 0.01[d] | |
| | C | 2 | 2.41 | 0.05[d] | |
| | N | 4 | 2.87 | 0.01[d] | |
| | N | 2 | 3.37 | 0.01[d] | |
| Deep blue specimen[c] | C | 4 | 1.67 | 0.06 | |
| | N | 4 | 2.65 | 0.01 | |
| | C | 4 | 1.86 | 0.01[d] | |
| | C | 2 | 2.41 | 0.05[d] | |
| | N | 4 | 2.87 | 0.01[d] | |
| | N | 2 | 3.37 | 0.01[d] | 3.83 |
| Pink specimen | C | 4 | 1.89 | 0.01 | |
| | N | 4 | 2.9 | 0.01 | |
| | O | 2 | 1.85 | 0.01 | |
| | C | 6 | 1.89 | 0.05[e] | |
| | N | 6 | 3.06 | 0.01[e] | 5.89 |

[a] single crystal data [4]

[b] old structure model analyzed by Rigaku EXAFS data analysis system, REX2

[c] new structure model analyzed by Rigaku EXAFS data analysis system, REX-2000

[d] due to the pale blue specimen

[e] due to La[Co(CN)$_6$]·5H$_2$O

The complex ion, [Co(CN)$_4$(H$_2$O)$_2$]$^{2-}$ has two isomeric forms, i.e., *cis* and *trans*. To determine which form is the pink species, the wavelengths of UV-VIS absorption bands for both the forms were calculated by means of the DV-Xα molecular orbital method. The wavelength for the trans form, 523 nm was in better agreement with the observed one, 521 nm than that for the cis form, 591 nm. From this result, the pink species was estimated to *trans*-[Co(CN)$_4$(H$_2$O)$_2$]$^{2-}$.

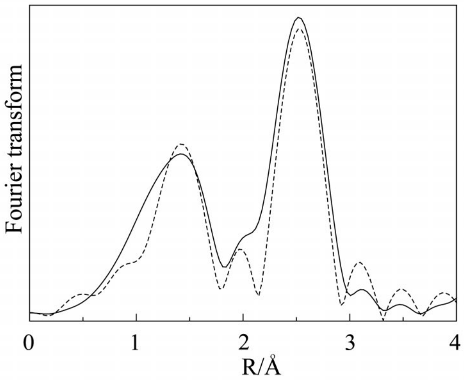

**Fig. 4** Fourier transforms of EXAFS oscillation at K-edges of Co for the pink specimen; —— observed values; - - - - calculated values

The Raman spectra measured at 25, 80 and 230°C (Fig. 5). The spectrum measured at 25 for $La[Co(CN)_6]\cdot 5H_2O$ displayed two bands at 2157 and 2176 $cm^{-1}$ associated with the vibration modes of C–N [14]. The band at 2157 $cm^{-1}$ split into two bands at 2150 and 2156 $cm^{-1}$ at 80°C for $La[Co(CN)_6]\cdot 4H_2O$.

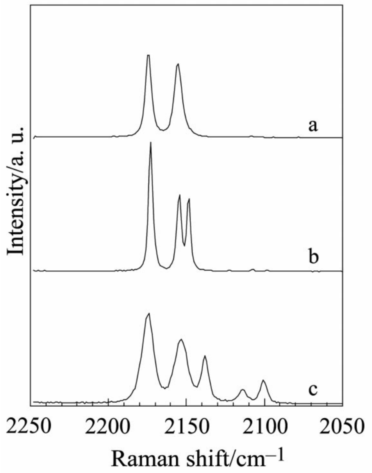

**Fig. 5** Raman spectra of $La[Co(CN)_6]\cdot 5H_2O$ measured at a – room temperature, b – 80°C and c – 230°C

The factor group of Bravais unit cell of $La[Co(CN)_6]\cdot 5H_2O$ is $C_{6h}$, and both the site symmetries for La and Co are $C_{3h}$. The active modes of La and Co atoms are associated with $E_{2g}$, $E_{1u}$, $B_g$ and $A_u$. Among these modes, only $E_{2g}$ is Raman-active. On the other hand, the factor group of $La[Co(CN)_6]\cdot 4H_2O$ is $D_{2h}$ and the site symmetries for La and Co are $C_{2v}$ and $C_{2h}$, respectively. La is associated with $A_g$, $B_{2u}$, $B_{3g}$, $B_{1u}$, $B_{1g}$ and $B_{3u}$ modes, and Co with $A_u$, $2B_{1u}$ and $2B_{3u}$ modes. Among these modes, $A_g$, $B_{1g}$ and $B_{3g}$ are Raman-active. Therefore, $La[Co(CN)_6]\cdot 4H_2O$ has more active Raman modes than La[Co(CN)$_6$]·5H$_2$O, and the vibrational modes of bridging –C≡N– between La and Co must be split [11, 15].

The Raman spectra at 230°C for the pale blue specimen showed the three new bands at 2103, 2116 and 2141 cm$^{-1}$. The bands at 2103 and 2116 cm$^{-1}$ are corresponded to the stretching vibration of C≡N bonding to Co$^{2+}$ ion [16]. The band at 2141 cm$^{-1}$ is assigned to the stretching vibration of the inverted cyanide C≡N bonding to Co$^{2+}$ ion as follows: –Co–N≡C–La [17].

Figure 6 shows EXAFS spectra of L$_{III}$-edges of La, and the structural data for the pale blue specimen are shown in Table 2. Among the six La–NC bonds, only two bond lengths lengthened. As mentioned previously, the two bond lengths among the six Co–CN bonds also lengthened along *z*-axis in the pale blue specimen [8, 9]. Considering these lengthening interatomic distances of Co–CN and La–NC bonds, the inversion of CN should be easily predictable in the pale blue specimen.

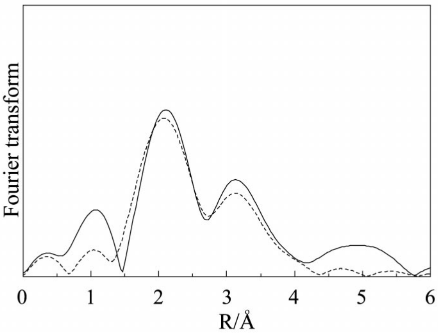

**Fig. 6** Fourier transforms of EXAFS oscillation at L$_{III}$-edges of La for the pale blue specimen; —— observed values; - - - - calculated values

**Table 2** Coordination number (*CN*), bond length (*r*), Debye–Waller factor (σ) and R-factor (*R*) obtained from curve-fitting results for Fourier-filtered $k^3\chi(k)$ of La L$_{III}$-sample

| | Atom | *CN* | *r*/Å | σ/Å | *R*/% |
|---|---|---|---|---|---|
| La[Co(CN)$_6$]·5H$_2$O[a] | O | 3 | 2.602 | | |
| | N | 6 | 2.618 | | |
| | C | 6 | 3.747 | | |
| Pale blue specimen | N | 4 | 2.56 | 0.09 | |
| | C | 4 | 3.69 | 0.03 | |
| | N | 2 | 2.98 | 0.06 | |
| | C | 2 | 4.11 | 0.01 | 0.20 |

[a] single crystal data [4]

Table 3 showed the ratios of peak area of 2141 cm$^{-1}$ to that of 2156 cm$^{-1}$ measured at 225 and 230°C at regular time intervals. The inversion of CN was assumed to proceed as a first order reaction and using these ratios, the rate constants for the inversion at 225 and 230°C were estimated to $4.6\cdot10^{-3}$ and $5.4\cdot10^{-3}$ $min^{-1}$, respectively. The apparent activation energy, 67 kJ $mol^{-1}$ was obtained from these data for the inversion of CN.

**Table 3** Ratios of peak area of 2140 $cm^{-1}$ to that of 2156 $cm^{-1}$

| Temperature/°C | Reaction time/min | Ratio |
|---|---|---|
| 225 | 10 | 0.15 |
| | 20 | 0.17 |
| | 30 | 0.26 |
| 230 | 0 | 0.33 |
| | 10 | 0.45 |
| | 20 | 0.49 |

In 1975, Cosmano and House [17] reported that the inversion of $C\equiv N^-$ of $KCr[Fe(CN)_6]$ occurred at 100°C and the activation energy was 101 kJ $mol^{-1}$. The value obtained in the present study is somewhat smaller than their value.

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