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# A THERMAL AND STRUCTURAL STUDY ON LANTHANUM HEXACYANOCOBALTATE(III) PENTAHYDRATE. Part II

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## Abstract

The thermal dehydration of $La[Co(CN)_6]\cdot 5H_2O$ proceeded through at least three stages from the temperature range of 30~230°C, and an abrupt mass loss occurred around 350°C and the perovskite type oxide, $LaCoO_3$ was obtained at 1000°C.

After dehydration, the color of the anhydride changed from white to pale blue around 230°C and furthermore, the color changed to blue around 290°C. These color changes were discussed on the basis of the changes of coordination structures around Co ions.

In $La[Co(CN)_6]\cdot 5H_2O$, $Co^{3+}$ ions lie at the center of the $O_h$ crystal field consisted of six $CN^-$ ions. However, in the pale blue specimen, $Co^{3+}$ ions were situated in the center of $D_{4h}$ crystal field which was distorted the $O_h$ one by lengthening of the trans $CN^-$ ions along *z*-axis. In the blue specimen, $Co^{3+}$ ions were reduced to $Co^{2+}$ ions which were situated in the $T_d$ crystal field formed by four $CN^-$ ions as $[Co(CN)_4]^{2-}$.

**Keywords:** lanthanum hexacyanocobaltate(III), magnetic susceptibility, thermal structural and color change

## Introduction

Thermal properties of the series complexes of $Ln[Co(CN)_6]\cdot 5H_2O$ (*Ln* =La~Lu) have also been studied [1–4]. Masuda *et al.* [2, 3] reported that the dehydration of $Ln[Co(CN)_6]\cdot 5H_2O$ (*Ln*=La~Nd) took place at least three stages, and the dehydration of $Ln[Co(CN)_6]\cdot 4H_2O$ (*Ln*=Sm~Lu) proceeded through at least two stages. The enthalpy changes for these steps were reported.

In the previous paper [4], authors reported that the color of $La[Co(CN)_6]$ changed from white to blue around 290°C, an abrupt mass loss occurred at 350°C and

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$LaCoO_3$ was obtained at 1000°C as the final product of the thermal decomposition of $La[Co(CN)_6]$. The color change was ascribed to the change of coordination geometry around of Co ions from an octahedral structure to a tetrahedral one.

Further examining the color change of the anhydride complex after the dehydration, the color of the complex changed from white to pale blue around 230°C. When the pale blue specimen was permitted to stand in atmosphere, it returned to white, $La[Co(CN)_6]\cdot 5H_2O$. Heating the pale blue specimen, it changed to deep blue before the decomposition around 290°C. Moreover, the deep blue specimen was allowed to stand in air, the color changed to pink. Those color changes have not yet been reported in detail.

In this paper, the relationship between the thermal structural change and the color changes of the complex was investigated by means of the thermal analyses, powder X-ray diffraction analysis, UV-VIS spectra, measuring the magnetic susceptibility, EXAFS and DV-X$\alpha$ cluster method [5]. These color changes were discussed from the viewpoint of the coordination structural changes around Co ion.

## Experimental

$La[Co(CN)_6]\cdot 5H_2O$ was synthesized by mixing 0.2 mol $dm^{-3}$ $K_3[Co(CN)_6]$ aqueous solution and 0.2 mol $dm^{-3}$ $LaCl_3\cdot 7H_2O$ aqueous solution and heating the mixture to ca. 90°C [4].

The pale blue anhydride was prepared by heating $La[Co(CN)_6]\cdot 5H_2O$ to 230°C in a Yamato Vacuum Drying Oven DP222. When the pale blue specimen was allowed to stand in air, the color returned easily to white. The deep blue specimen was obtained by heating $La[Co(CN)_6]\cdot 5H_2O$ at 250°C for 12 h. Since both the pale blue and the deep blue specimens rehydrated easily, the EXAFS and UV-VIS spectra were measured using nujol mull method.

The thermogravimetry (TG) and differential thermal analysis (DTA) curves were simultaneously recorded on a Rigaku Thermoflex TAS200 and $\alpha$-alumina was used as reference [4]. The measurements were performed in an atmosphere of air in the temperature ranges from 20 to 300 and 20 to 1000°C with the heating rates of 5 and 10°C $min^{-1}$, respectively.

X-ray powder diffraction (XRD) profiles were obtained using a Rigaku Geiger-flex RAD-3R diffractometer equipped with a high temperature sample holder. $MoK_\alpha$ radiation ($\lambda$=0.7093 Å) was monochromatized using a graphite monochrometer [4].

X-ray absorption spectra at CoK-edges (7710 eV) of the samples were measured with a Rigaku Laboratory EXAFS spectrometer, R-EXAFS [4].

The magnetic susceptibility of the samples was measured with a Shimadzu magnetic balance. The data were collected in the temperature ranges from 20 to 150°C with step-scan width of 1°C, fixed time (60 s) counting procedure, and the strength of a magnetic field was $6.5\cdot 10^3$ Gauss.

The UV-VIS spectra of samples were obtained with a Hitachi U-3210 spectrophotometer. The spectra were measured in the wavelength ranges from 250 to 800 nm with step-scan width of 0.2 nm by use of nujol mull and diffuse reflectance methods.

In order to discuss the electronic spectra, the energy-level diagrams obtained by the splitting of d orbitals of cobalt ion were calculated using DV-X$\alpha$ calculating program, SCAT [5].

## Results and discussion

It was shown that the dehydration of $La[Co(CN)_6]\cdot 5H_2O$ took place through three steps and these steps were reversible. After dehydration, the color of the anhydride changed from white to pale blue around 230°C [4]. When the pale blue specimen was heated to 290°C (Fig. 1), the color changed to deep blue. Moreover, permitting to stand the deep blue specimen in air for a few hours, it changed to pink. These color changes were correlated with the coordination structural changes around Co ion.

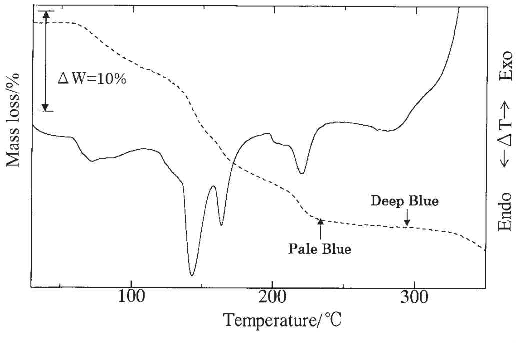

**Fig. 1** TG-DTA curves for $La[Co(CN)_6]\cdot 5H_2O$ (heating rate 5°C $min^{-1}$ in air); dotted line – TG, solid line – DTA

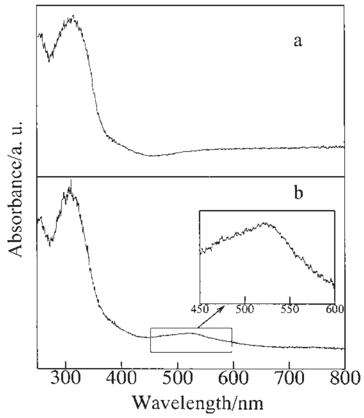

**Fig. 2** UV-visible spectra of $La[Co(CN)_6]\cdot 5H_2O$ (a) and the pink specimen (b) measured by powder diffuse reflectance method

In the crystal of $La[Co(CN)_6]\cdot 5H_2O$, $Co^{3+}$ ions located at the center of the $O_h$ crystal field consisting of six $CN^-$ ions [6]. The EXAFS data for $La[Co(CN)_6]\cdot 5H_2O$ showed that the bond distances of Co–C (1.89 Å) and Co–N (2.90 Å) and the coordination number around $Co^{3+}$ ions (N=6) were consistent with those expected from the result of single crystal data (Table 1). The UV-VIS powder diffuse reflectance spectrum of $La[Co(CN)_6]\cdot5H_2O$ (Fig. 2) showed two absorption bands at 261 and 315 nm assigned to $^1A_{1g}\rightarrow{}^1T_{2g}$ and $^1A_{1g}\rightarrow{}^1T_{1g}$ for $Co^{3+}$, respectively [7, 8].

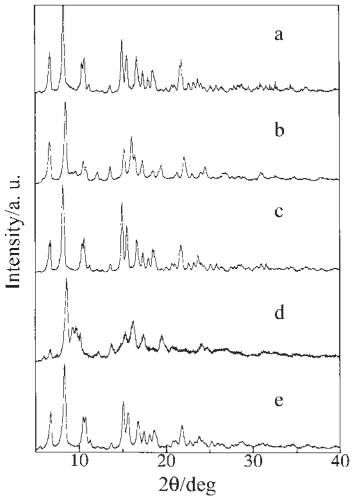

**Fig. 3** XRD profiles of $La[Co(CN)_6]\cdot5H_2O$ (a), the pale blue specimen (b), the rehydrated product of the pale blue specimen (c), the deep blue specimen (d) and the pink specimen (e)

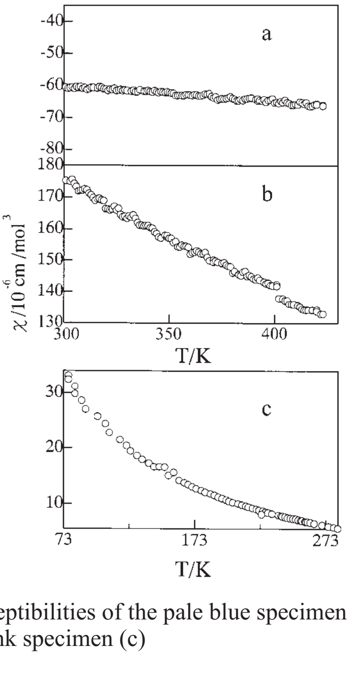

**Fig. 4** The magnetic susceptibilities of the pale blue specimen (a), the deep blue specimen (b) and the pink specimen (c)

The XRD profile of the pale blue specimen was different from that of $La[Co(CN)_6]\cdot 5H_2O$. This specimen was permitted to stand in atmosphere for a few minutes, the color returned easily to white. The XRD profile of the white specimen was in agreement with that of $La[Co(CN)_6]\cdot 5H_2O$ (Fig. 3). These results indicated that the dehydration of $La[Co(CN)_6]\cdot 5H_2O$ was reversible.

**Table 1** Curve-fitting results for Fourier-filtered $k^3$ $\chi(k)$ CoK-edge EXAFS

| Sample | Atom | CN[a] | $r$/Å[b] | δ /Å[c] | $R$/%[a] |
|---|---|---|---|---|---|
| $La[Co(CN)_6]\cdot 5H_2O$[e] | C | 6 | 1.887 | | |
| | N | 6 | 3.043 | | |
| $La[Co(CN)_6]\cdot 5H_2O$ | C | 6 | 1.89 | 0.06 | |
| | N | 6 | 2.90 | 0.01 | 9.13 |
| Pale blue specimen | C | 4 | 1.86 | 0.01 | |
| | C | 2 | 2.41 | 0.05 | |
| | N | 4 | 2.87 | 0.01 | |
| | N | 2 | 3.37 | 0.01 | 8.29 |
| Deep blue specimen | C | 4 | 1.65 | 0.01 | |
| | N | 4 | 2.65 | 0.01 | |
| | C | 4 | 1.84 | 0.01[f] | |
| | C | 2 | 2.39 | 0.05[f] | |
| | N | 4 | 2.78 | 0.01[f] | |
| | N | 2 | 3.36 | 0.01[f] | |

[a]coordination number; [b]bond distance; [c]Debye–Waller factor; [d]$R$-factor; [e]single crystal data [2]; [f]due to the pale blue specimen

Since pale blue specimen showed diamagnetic susceptibility (Fig. 4), the electronic configuration of cobalt ion was considered to be $Co^{3+}$ ($d^6$). Figure 5 showed the Fourier transform of EXAFS oscillation for the pale blue specimen. The curve fitting data such as the bond distances of Co–C and Co–N and the coordination number around $Co^{3+}$ ions were tabulated in Table 1. These results showed that $Co^{3+}$ ion in the pale blue specimen was located at the center of the $D_{4h}$ field which was distorted the $O_h$ field by lengthening of two trans $CN^-$ ions along the $z$-axis. The UV-VIS spectrum of the pale blue specimen measured by nujol mull method, had a strong absorption bands around 300 and a weak band at 595 nm which had a shoulder around 560 nm (Fig. 6). The strong band at 300 nm was seemed to be attributable to the scattering by

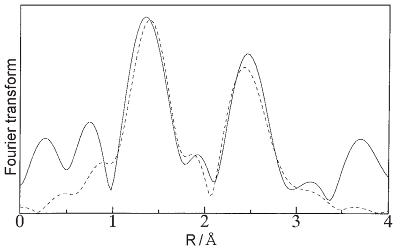

**Fig. 5** Fourier transforms of EXAFS oscillation for the pale blue specimen; solid line – observed values, dotted line – calculated values

the solid sample dispersed in nujol. The weak bands were in agreement approximately with the calculated wavelength (568.9~610.2 nm) by the DV-Xα for the energy level splitting of d orbitals of $Co^{3+}$ ions in the $D_{4h}$ crystal field.

The XRD profile of the deep blue specimen was different from that of the pale blue specimen (Fig. 2). Around 230 to 300°C there was almost no mass change from the TG trace (Fig. 1) but however, a gaseous product was recognized around 280°C from the total ion current, and their mass spectra measured at 293°C showed the evolution of C, N, $N_2$, CO, NO and $CO_2$ which was attributable to the cleavage of $CN^-$ group [4]. The deep blue specimen shows paramagnetic susceptibility, therefore $Co^{3+}$ ion seemed to be reduced by $CN^-$ in the decomposition around 290°C, and the electronic configuration of cobalt ion was considered to be $Co^{2+}$ ($d^7$) ion. Gallagher also reported similar phenome-

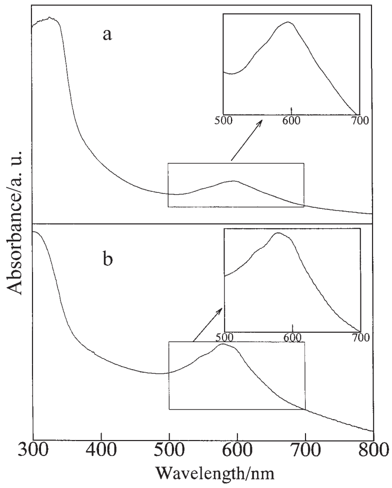

**Fig. 6** UV-visible spectra of the pale blue (a) and the deep blue (b) specimens measured by nujol mull method

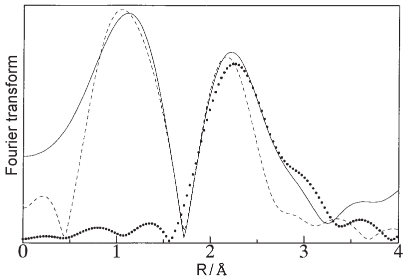

**Fig. 7** Fourier transforms of EXAFS oscillation for the deep blue specimen (a) solid line: observed value, (b) broken line: calculated from the mixture of pale blue specimen C; 1.84 Å (4), N; 2.78 Å (4) and deep blue specimen C; 1.65 Å (4), N; 2.65 Å (4), and (c) dotted line; calculated for the mixture of pale blue specimen C; 2.39 Å (2), N; 2.78 Å (4), N; 3.36 Å (4) and deep blue specimen N; 2.65 Å (4). The numbers in parentheses mean the coordination number

non that $Fe^{3+}$ ion was reduced to $Fe^{2+}$ ion during the decomposition of $Eu[Fe(CN)_6]^{3-}$ around 370°C [9]. EXAFS analysis of the deep blue specimen indicated the existence of a $[Co(CN)_4]^{2-}$ group in the structure (Fig. 7, Table 1), and the $Co^{2+}$ ion was located at the center of the $T_d$ crystal field consisting of four $CN^-$ ions. These findings supported the above structural change from octahedral to tetragonal one was occurred at the temperature ranges around Co ions.

The deep blue specimen had two absorption bands around 300 and at 581 nm having shoulders around 560 and 590 nm (Fig. 6). As described previously, the band at 300 nm seemed to be attributable to the scattering by the solid sample dispersed in nujol. The shoulders observed around 560 and 590 nm were due to the pale blue specimen contaminated. The band of 581 nm was consistent approximately with the calculated wavelength (610.4~621.2 nm) from the energy levels splitting of *d* orbitals of $Co^{2+}$ ions in the $T_d$ crystal field. These results indicated that the deep blue color may be caused by the ions of $[Co(CN)_4]^{2-}$ ($T_d$) contained in the pale blue specimen.

When the deep blue specimen was 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 (Fig. 2). The bands of 258 and 315 nm were ascribable to $La[Co(CN)_6]\cdot 5H_2O$ [7, 8], and the band of 521 nm seemed to cause pink color. It is known that $Co^{2+}$ ion forms pink complex $[Co(H_2O)_6]^{2+}$ in aqueous solution and the complex ion has an absorption band at 510 nm [10], which is consistent approximately with the observed band at 521 nm. The pink complex showed paramagnetic susceptibility (Fig. 3).

The XRD profile of the pink specimen was very similar to that of $La[Co(CN)_6]\cdot 5H_2O$ (Fig. 2). Although the structure of the pink species is not elucidated at present, from above results it seems to be a complex ion, $[Co(CN)_4(H_2O)_2]^{2-}$. The pink specimen seems to be a mixture of which the main component of $La[Co(CN)_6]\cdot 5H_2O$ is contaminated by small amount of $[Co(CN)_4(H_2O)_2]^{2-}$, which gives the pink color.

After dehydration, an abrupt mass loss accompanied with an exotherm at 350°C and perovskite type, $LaCoO_3$ was obtained at 1000°C as a final product [4]. The observed mass loss 44.1% at 1000°C was in agreement with the calculated one 44.6% expected from the formation of $LaCoO_3$.

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