Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 1033–1041

A THERMAL AND STRUCTURAL STUDY ON LANTHANUM HEXACYANOCOBALTATE(III) PENTAHYDRATE, $La[Co(CN)_6]\cdot 5H_2O$

Y. Masuda[1*], *Y. Seto*[2], *X. Wang*[2], *Y. Yukawa*[1] *and T. Arii*[3]

[1]Department of Environmental Science, Faculty of Science, Niigata University
2-8050 Ikarashi, Niigata 950-2181
[2]Graduate School of Science and Technology, Niigata University
2-8050 Ikarashi, Niigata 950-2181
[3]Thermal Analysis Division, Rigaku Corporation, 3-9-12 Matubara-cho
Akishima, Tokyo 196-8666, Japan

Abstract

Thermal and structural changes of lanthanum hexacyanocobaltate(III) pentahydrate, $La[Co(CN)_6]\cdot 5H_2O$ were investigated by means of thermal analysis, visible electronic spectra, IR, powder X-ray diffraction, EXAFS and TG-MS. The dehydration of $La[Co(CN)_6]\cdot 5H_2O$ proceeded reversibly through three steps and steps corresponded to the losses of H_2O, $3H_2O$ and H_2O, and the enthalpy changes for these steps were 51.3, 211.0 and 38.7 kJ mol^{-1}, respectively.

After the dehydration, the colour of the anhydride changed from white to blue around 290°C and an abrupt mass loss occurred at 350°C. The colour change seems to be attributable to the change of coordination geometry around the Co ions from an octahedral structure to a tetrahedral one. $LnCoO_3$ was obtained as a final product by heating the sample to 1000°C.

Keywords: dehydration, lanthanum hexacyanocobaltate(III), structural change, thermal analysis

Introduction

It has been known that the lanthanide series has a variation in ionic radii by 20% for La^{3+} to Lu^{3+} [1]. The influence of the shrinkage of ionic radii on coordination number and coordination geometry is a unifying concept in the coordination chemistry of the lanthanide ions. It is of interest to study whether the successive structural changes and the change of ionic radii of lanthanide ions have any effect on the thermal behaviour of the coordination compounds.

Lanthanide hexacyanocobaltates(III) have been widely studied and their structures and properties have been investigated for a long time [2–10]. Since there have been many discussions about the hydration number of the complexes, the present authors prepared a series of complexes of lanthanide hexacyanocobaltates(III) *n*-hydrates,

---

[*] Author for correspondence: E-mail: masuda@geb.ge.niigata-u.ac.jp

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$Ln[Co(CN)_6]\cdot nH_2O$, to determine the boundary hydrates between the pentahydrate and tetrahydrate, and to investigate the thermal dehydration processes of the hydrates by means of X-ray analysis, thermal analysis and Raman spectroscopy [11–13]. The result was as follows: the complexes with lanthanides lighter than Nd were the pentahydrate, hexagonal ($P6_3/m$), and the other complexes with lanthanides heavier than Nd were the tetrahydrate, orthorhombic (Cmcm). Nd formed the pentahydrate, however, the crystals were orthorhombic ($C222_1$). Therefore, $Nd[Co(CN)_6]\cdot 5H_2O$ had a boundary structure.

TG-DTA showed that the dehydration of $La[Co(CN)_6]\cdot 5H_2O$ took place in at least three stages. After dehydration, the colour of the complex changed from white to blue around 290°C, and then the anhydride decomposed. In 1968, Gallagher studied the thermal decomposition of $La[Co(CN)_6]\cdot 5H_2O$ to prepare $LaCoO_3$ [14], and recently Sadaoka *et al.* [15] investigated the thermal decompositions of a series complexes of $Ln'_x Ln''_{1-x}[Fe_y Co_{1-y}(CN_6]\cdot nH_2O$ (Ln', Ln''=La–Yb) to obtain homogeneous perovskite type oxides. However, they did not mention the colour change of the specimen.

In the present paper, we study the relationship between the colour change and the initiation of decomposition in view of thermal structural change of the coordination arrangement around the Co ions, by means of thermal analysis, visible electronic spectra, IR, powder X-ray diffraction, EXAFS and TG-MS.

Experimental

Potassium hexacyanocobaltate(III), $K_3[Co(CN)_6]$ was purchased from Sigma-Aldrich Co. and lanthanum chloride *n*-hydrate, $LaCl_3\cdot nH_2O$ (99.9%) from Shin-etu Chemical Co. $K_3[Co(CN)_6]$ was recrystallized from distilled water before use, and $LaCl_3\cdot nH_2O$ was used without any purification. Lanthanum hexacyanocobaltate(III) pentahydrate, $La[Co(CN)_6]\cdot 5H_2O$ was prepared from the reaction of aqueous solutions of $LaCl_3$ and $K_3[Co(CN)_6]$ at room temperature [11–13].

The TG-DTA analysis was performed on a Rigaku Thermoflex TAS-200 at heating rates 2 to 5 K min^{-1} in air. About 10 mg of the sample was weighed in an aluminum crucible and α-alumina was used as a reference material.

The enthalpy change for the dehydration (ΔH) was determined using a Rigaku Thermoflex DSC-TAS 200. The instrument was calibrated with the enthalpy changes of the phase transition of potassium nitrate (400.9 K, ΔH=5.4 kJ mol^{-1}) and the enthalpy changes of melting of gallium, indium, tin, lead and zinc (Ga, 309.94 K, ΔH=5.59 kJ mol^{-1}; In, 430 K, ΔH=3.3 kJ mol^{-1}; Sn, 505 K, ΔH= 7.07 kJ mol^{-1}; Pb, 600.6 K, ΔH=4.77 kJ mol^{-1}; Zn, 692.7 K, ΔH=6.57 kJ mol^{-1}) [16, 17].

The powder X-ray diffraction (XRD) profiles of the samples were obtained with a Rigaku RAD-R diffractometer equipped with a high-temperature sample holder. MoK_α radiation, a nickel filter and a graphite monochromator were used in all measurements. The diffraction data were collected in the 2θ range from 20 to 70° with step-scan width of 0.02° and fixed time (10 s) counting procedure.

Electronic spectra of the visible region were measured with a Hitachi U-3200 spectrophotometer.

X-ray absorption spectra at the Co K-edge (7710 eV) of the complexes were measured with a Rigaku R-EXAFS. For the measurement of X-ray absorption fine-structure spectra (EXAFS), the integration time was set to 150 s in the region of 7510–8710 eV. The data were analyzed using Rigaku EXAFS (REX-2).

IR spectra were measured by means of a diffuse reflectance method, using silicone powder as a diluent with a Horiba FT-300 spectrophotometer.

The mass spectrum of the gases evolved from the sample in a mixed atmosphere (O_2:He=1:4) was monitored simultaneously with a Rigaku Thermo Mass system coupled with a TG-DTA 8120D via the gas interface whose capillary was heated at 250°C. The quadrupole mass spectrometer (Q-MS), Anelva model MQ-200TS with a thoria-coated filament, was used in electron impact mode, operated with an ionization potential of 70 eV and the mass region for the detection was 10–60 amu. The carrier gas including the evolved gases was introduced to the mass detector which was backed up by a turbo molecular pump (63 L s^{-1}) and an oil-rotary pump (90 L min^{-1}). A low background pressure of nitrogen (*m*/*z* 28) and water vapour which remained in the atmosphere was achieved so that carbon monoxide (*m*/*z* 28) and water vapour evolved from the sample were successfully evacuated. In these TG-MS measurements, the TG and DTA curves obtained are simultaneously combined with the mass spectrometer total ion current (TIC), or the mass chromatogram which is obtained by the selected *m*/*z* values, to allow the identification of the evolved gases corresponding to the mass losses. The NIST/EPA/NIH chemical structures database was used to compare the mass spectrum of an unknown compound with a library of reference spectra.

Results and discussion

From the TG curve, the dehydration seems to proceed through three steps. The DTA curve for the dehydration of $La[Co(CN)_6]\cdot 5H_2O$ shows at least four endothermic peaks up to 320°C (Fig. 1). The first one was observed at 72°C with a mass loss corresponding to H_2O in the temperature range from 45 to 100°C (1st step). The second and third peaks were recognized continuously at 145 and 165°C, respectively, accompanying a mass loss of $3H_2O$ (2nd step). The last peak was recognized at 205°C with a mass loss of H_2O (3rd step). The enthalpy changes for the dehydration are shown in Table 1.

Table 1 ΔH for the dehydration of $La[Co(CN)_6]\cdot 5H_2O$

Step	T^*/°C	ΔH/kJ mol^{-1}
1st	74	51.3
2nd	145, 161	211.0
3rd	205	38.7

T^* means the peak temperature of the DSC curve

Figure 2 shows the powder X-ray diffraction (XRD) profiles. The agreement between the profile of the anhydrous complex after standing in a humid atmosphere for a week and that of $La[Co(CN)_6]\cdot 5H_2O$, showed the gradual transformation of

$La[Co(CN)_6]$ into $La[Co(CN)_6]\cdot 5H_2O$ on standing. Therefore, the dehydration was reversible

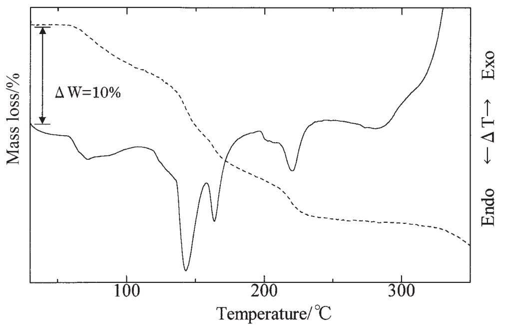

Fig. 1 TG-DTA curves for the thermal dehydration of $La[Co(CN)_6]\cdot 5H_2O$ (heating rate: 5°C min^{-1}); dotted line – TG; solid line – DTA

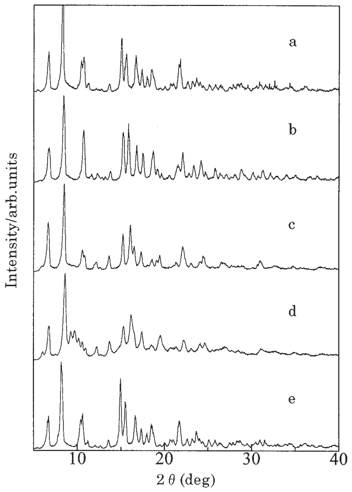

Fig. 2 XRD profiles. a – $La[Co(CN)_6]\cdot 5H_2O$; b – $La[Co(CN)_6]\cdot 4H_2O$; c – $La[Co(CN)_6]\cdot H_2O$; d – $La[Co(CN)_6]$; e – $La[Co(CN)_6]$; after standing in a humid air for a week

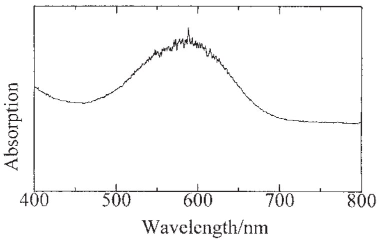

Fig. 3 Absorption spectra of the blue sample measured using a Nujol mull in the visible region (cell thickness 2 mm)

$$\mathrm{La[Co(CN_6]{\cdot}5H_2O \leftrightarrow La[Co(CN_6]{+}5H_2O}$$

After the dehydration, the colour of the anhydride changed from white to blue around 290°C and the decomposition was initiated around 320°C,. Although no visible absorption band has been observed for $\mathrm{La[Co(CN)_6]{\cdot}5H_2O}$ [18], the electronic spectra of the blue specimen, measured using a Nujol mull (Fig. 3), showed a band at 580 nm.

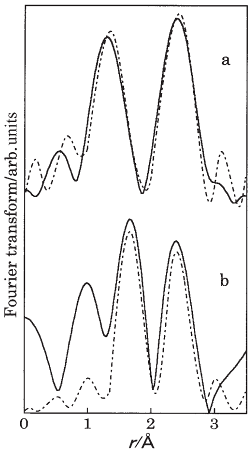

Fig. 4 Fourier transforms of (a) – k^3-EXAFS of $\mathrm{La[Co(CN)_6]{\cdot}5H_2O}$ and the blue complex (b); solid line – observed values; dotted line – calculated values

It is known that the complexes with lanthanides lighter than Nd form hexagonal pentahydrate crystals (space group P63/m), and the complexes with lanthanides heavier than Nd form orthorhombic tetrahydrates (space group Cmcm) [11, 12]. The crystal structure of $\mathrm{La[Co(CN)_6]{\cdot}5H_2O}$ was characterized as follows. La; nine-coordinated in the form of the $\mathrm{LaN_6(H_2O)_3}$. Co; six-coordinated in the form of an octahedral $\mathrm{CoC_6}$ group. CN linkages between $\mathrm{LaN_6(H_2O)_3}$ and $\mathrm{CoC_6}$ groups build an infinite polymeric array, two uncoordinated water molecules occupy zeolitic holes in the structure on a 6-hold rotatory inversion axis above and below the La atom [5, 11].

Figure 4 shows the Fourier transforms of oscillations for $\mathrm{La[Co(CN)_6]{\cdot}5H_2O}$ and the blue specimen. The EXAFS data were transformed from k space to r space, where k is the wavenumber of a photoelectron. An inverse Fourier transform was performed in the range of r from 1.2 to 3.1 Å, and gave $k^3\chi(k)$. The data were analyzed by a curve-fitting procedure to obtain the coordination number (CN), bond distance r and Debye–Waller factor (σ). The degree of fitting was estimated by the R factor described as following:

$$R=\left\{\sum\frac{(k^3\chi_{\mathrm{obsd}}-k^3\chi_{\mathrm{calcd}})^2}{(k^3\chi_{\mathrm{obsd}})^2}\right\}^{1/2}.$$

Table 2 Curve-fitting results for Fourier-filtered $k^3\chi(k)$ Co K-edge EXAFS

Sample	Atom	CN[a]	r/Å	σ/Å[b]	R/%[c]
$La[Co(CN)_6]\cdot5H_2O$	C	6	1.89		
Single crystal data[d]	N	6	3.01		
$La[Co(CN)_6]\cdot5H_2O$	C	6	1.89	0.06	
EXAPFS data	N	6	2.85	0.01	9.13
$La[Co(CN)_6]$[e]	C	4	1.97	0.01	
(blue sample)	N	4	2.84	0.01	8.14

[a]Coordination number, [b]Debye–Waller factor, [c]*R*-Factor, [d]data obtained by single crystal X-ray method [5], [e]sample heated to 280°C

The curve-fitting results are tabulated in Table 2. The bond distances of Co–C and Co–N and the coordination number around Co^{3+} ions for $La[Co(CN)_6]\cdot5H_2O$ were consistent with those expected from the results of single crystal data [5]. On the other hand, the result of EXAFS of the blue specimen shows the existence of a $Co(III)(CN)_4$ group in the structure, which indicates the possibilities of a tetrahedral or a square-planar structure for the $Co(III)(CN)_4$ group. It is also not possible to rule out the existence of $Co(II)(CN)_4$, because the colour of the blue specimen changed to pink on standing the specimen for a few hours in contact with air, and its aqueous solution had an absorption band at 510 nm assigned to octahedral coordinated Co^{2+} ions. Gallagher also reported that the reduction of iron(III), during the decomposition of hexacyanoferrate(III) to $Fe(II)(CN)_2$, was accomplished around 370°C [19]. Because the energy splits of the *d* orbitals in a tetrahedral field are generally smaller than those of an octahedral one, the observed band at 580 nm seems to be attributable to a *d–d* transition of Co^{2+} in the tetrahedral ligand field consisting of CN^- ions.

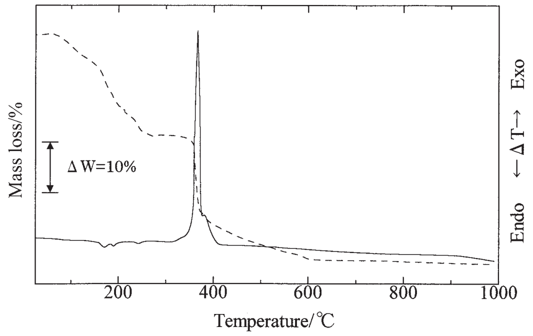

Fig. 5 TG-DTA curves of $La[Co(CN)_6]\cdot5H_2O$ (heating rate: 5°C min^{-1}); dotted line – TG; solid line – DTA

Although a distinct mass loss was scarcely observed around 230 to 300°C from the TG trace (Fig. 5), a gaseous product was recognized around 280°C from the total ion current, and the mass spectrum measured at 293°C showed the evolution of C, N, N_2, CO, NO and CO_2 which is attributed to the cleavage of the CN group (Fig. 6).

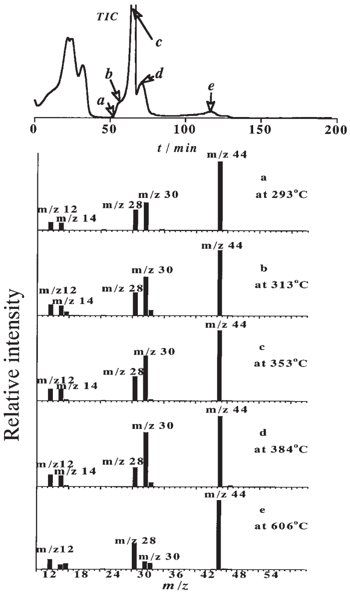

Fig. 6 Total ion currents (TIC) and mass chromatograms obtained at a – 293; b – 313; c – 353; d – 384 and e – 606°C

This fact supports the suggestion that the above structural change around the Co ions from octahedral to tetragonal starts in this temperature range.

An abrupt mass loss accompanying an exotherm at 350°C and a gradual decrease were observed up to 600°C, followed by a plateau. The IR spectra of the samples heated to 385, 595, 750 and 1000°C were examined (Fig. 7). The band observed around 2100 cm^{-1} is due to CN ions, and the bands around 1600 cm^{-1} are assigned to carbonate and nitrate ions. These bands gradually disappeared with increasing tem-

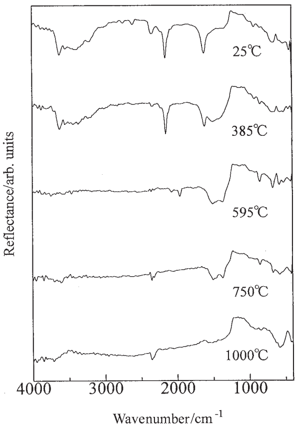

Fig. 7 IR spectra of $La[Co(CN)_6]\cdot 5H_2O$ heated in air

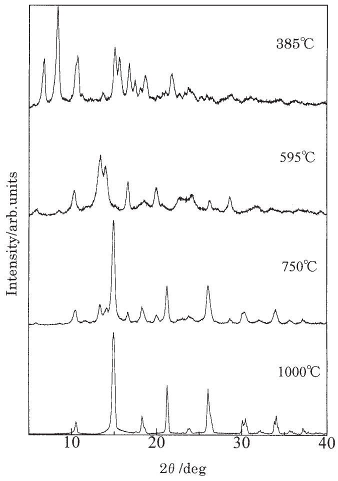

Fig. 8 XRD profiles of $La[Co(CN)_6]\cdot 5H_2O$ heated in air

perature and the bands at around 600 cm^{-1} due to the oxides appeared for the sample heated to 1000°C.

The XRD profiles of the samples heated to 385, 595, 750 and 1000°C are shown in Fig. 8. The phase obtained at 595°C seems to be a mixture of La_2O_3 and Co_2O_4 from their X-ray diffraction profiles (JCPDS files No. 5-0603 and No. 9-418). The profile of the final product obtained at 1000°C was compatible with that of $LnCoO_3$ (JCPDS file No. 25-1060). The MS spectra observed at 313, 353, 384 and 606°C showed the continuous dissociation of the CN group (Fig. 6).

* * *

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas 'New Development of Rare Earth Complexes' Nos 08220224, 07230230 and 06241228 from the Ministry of Education Science Sports and Culture.

References

1 D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 76 (1954) 5237.
2 C. James and P. S. Willard, J. Am. Chem. Soc., 38 (1916) 1497.
3 W. Prandtl and S. Z. Mohr, Z. Anorg. Allg. Chem., 236 (1938) 243.
4 F. Hulliger, M. Landolt and H. Vestch, J. Solid State Chem., 18 (1976) 307.
5 D. F. Mullica, W. O. Milligan and W. T. Kouba, J. Inorg. Nucl. Chem., 41 (1979) 967.
6 D. F. Mullica, H. O. Perkins and E. L. Sappenfield, J. Solid State Chem., 74 (1988) 419.
7 W. Petter, V. Gramlich and F. Hulliger, J. Solid State Chem., 82 (1989) 161.
8 D. F. Mullica and E. L. Sappenfield, J. Solid State Chem., 82 (1989) 168.
9 V. Gramlich, W. Petter and F. Hulliger, Acta Crystallogr., Sect.C, 46 (1990) 724.
10 H. Yokobayashi, Netusokutei, 18 (1991) 157.
11 Y. Yukawa, S. Igarashi, T. Kawaura and H. Miyamoto, Inorg. Chem., 35 (1996) 7399.

12 Y. Masuda, K. Nagaoka, H. Ogawa, O. Nakazato, Y. Yukawa and H. Miyamoto, J. Alloys Compds., 235 (1996) 23.
13 Y. Masuda, K. Kikuchi, Y. Yukawa and H. Miyamoto, J. Alloys Compds., 260 (1997) 70.
14 P. K. Gallagher, Mat. Res. Bull., 3 (1968) 225.
15 Y. Sadaoka, New Development of Studies on Rare Earth Complexes (Report of a priority Area Program supported by The Ministry of Education, Science Sports and Culture, Japan), 1997, p. 785.
16 Kagaku Binran Kisohen (Handbook of Chemistry), Vol. II, The Chemical Society of Japan, Maruzen, Tokyo, 3rd Ed., 1984, p. 267.
17 Y. Yukawa, S. Shirotiri, K. Minagawa and Y. Masuda, J. Alloys Compds., 266 (1997) 123.
18 J. Fujita and Y. Shimura, Bull. Chem. Soc. Jpn., 36 (1963) 1281.
19 P. K. Gallagher and B. Prescott, Inorg. Chem., 9 (1970) 2510.