Preparation and Characterization of Heteronuclear Hexacyano Complexes, $Ln_xSm_{1-x}[Co(CN)_6] \cdot nH_2O$ (Ln = La, Er, and Yb)

Yoshihiko Sadaoka,* Enrico Traversa,† and Masatomi Sakamoto††
Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
†*Department of Chemical Sciences and Technologies, University of Rome "Tor Vergata", Roma 00173, Italy*
††*Department of Material and Bioloical Chemistry, Faculty of Science, Yamagata University, Yamagata 990*

(Received November 22, 1995)

Heteronuclear hexacyano complexes Ln_xSm_{1-x} $[Co(CN)_6] \cdot nH_2O$ (Ln = La, Er and Yb) were synthesized. In the orthorhombic series, the lattice parameters increase linearly with the effective radii of rare earth ions ($r_{eff} = x\, r_{Ln} + (1-x)r_{Sm}$), a parameter which is here introduced.

Recently, there has been considerable interest in rare earth orthoferrites and the analogous cobalt compounds. The catalytic, semiconductive, and/or magnetic behavior of these compounds has been the subject of controversy; these properties have been shown to be markedly dependent upon the method of preparation. These differences can arise from inhomogeneities or variations in stoichiometry of both cations and anions which are the result of the preparative technique employed.[1] Rare-earth chromi-, ferri-, and cobalti-cyanides are very interesting heteronuclear complexes which can be used as precursors for the preparation of perovskite-type oxides, because they possess the desired stoichiometry in a unique compound. These complexes can be prepared from the reactions $LnX_3(aq) + K_3T(CN)_6(aq) \rightarrow LnT(CN)_6 \cdot nH_2O(s) + 3KX(aq)$, (T=Fe, Co, X=Cl, NO_3). The resulting products are stoichiometric within the accuracy of the chemical analysis.[2] Previously, we confirmed that perovskite-type oxides with relatively high specific surface area can be formed even at low temperatures by the thermal decomposition of the heteronuclear complexes isolated in advance.[3-5] This approach has been proved to be successful for the general preparation of rare earth orthoferrites and analogous cobalt compounds. In the present work, we report the synthesis of heteronuclear complexes containing two rare earth elements and cobalt as the transition metal. Some complexes with general composition Ln_xSm_{1-x} $[Co(CN)_6] \cdot nH_2O$ (x=0~1) were prepared and their crystal parameters were determined.

The complexes, $Ln[Co(CN)_6] \cdot nH_2O$, (Ln=La, Pr, Nd, Sm, Eu Gd, Dy, Ho, Er, and Yb), and $Ln'_xSm_{1-x}[Co(CN)_6] \cdot nH_2O$, (Ln'=La, Er, and Yb, x=0~1) were synthesized by mixing the prescribed amounts of Ln(III) and Sm(III) nitrate hydrate aqueous solution(0.05mole/60cm^3) and potassium hexacyano cobaltate(III) aqueous solution (0.05 mole/60cm^3) under stirring. The resulting precipitate after ~1 h was washed with water, ethanol and diethyl ether and dried in air. X-ray diffraction analysis was performed, using a CuKα radiation, to determine the crystal structure of the complexes and their lattice parameters. The number of the crystallization water molecules was determined by thermogravimetry.

The XRD spectra of $Ln[Co(CN)_6] \cdot nH_2O$ showed that two types (A and B) of samples were obtained for Ln=La. The XRD pattern reported in the literature for $La[Co(CN)_6] \cdot 5H_2O$ (JCPDS file No.36-674) is similar to the obtained LaCo-A-complex. The crystal structure of the literature pattern is not defined, but the spectrum is very similar to the pattern of $La[Fe(CN)_6] \cdot 5H_2O$ (JCPDS file No.251198), which has an hexagonal structure. The measured XRD pattern for LaCo-A-complex assigned to the hexagonal phase (a=b=0.54401±0.00005nm, c=1.3101±0.0002nm, α=β=90°, γ=120°). The observed XRD pattern of LaCo-B-complex resembled the JCPDS file No.36-675, which is reported for $La[Fe(CN)_6] \cdot 5H_2O$, with no defined crystal structure. It has been reported by Hulliger et al.[2] that two types of rare earth ferricyanides can be obtained for Ln=La, Ce, Pr and Nd, depending on the number of crystallization water molecules; hexagonal for n=5 and orthorhombic for n=4. The hexagonal and orthorhombic structures have been determined on single crystals[2] and the two structures are closely related, i.e. removal of 1 H_2O per formula unit reduces the hexagonal symmetry to orthorhombic. Therefore, we tried to fit the measured pattern of LaCo-B-complex with an orthorhombic structure, without success. From the thermogravimetric analysis, the number of crystallization water molecules for LaCo-A- and LaCo-B-complexes was determined to be 5 and 4.5 per formula unit, respectively. The XRD spectrum of LaCo-B-complex was analyzed by assuming that it consisted of a mixture of two crystal types, i.e. hexagonal and orthorhombic. The hexagonal components were subtracted from the spectrum of LaCo-B-complex. The remaining peaks assigned to the orthorhombic structure (a=0.7496±0.0005nm, b=1.295±0.001nm, c=1.385±0.001nm, α=β=γ=90°). We assumed thus that the LaCo-B-complex is a mixture of hexagonal and orthorhombic structures, in agreement with a number of crystallization water molecules of 4.5. For the complexes with Pr ~ Yb, only the orthorhombic structure was observed. This was confirmed by thermogravimetry, which allowed us to estimate 4 molecules of crystallization water for all the LnCo-complex, except for LaCo-

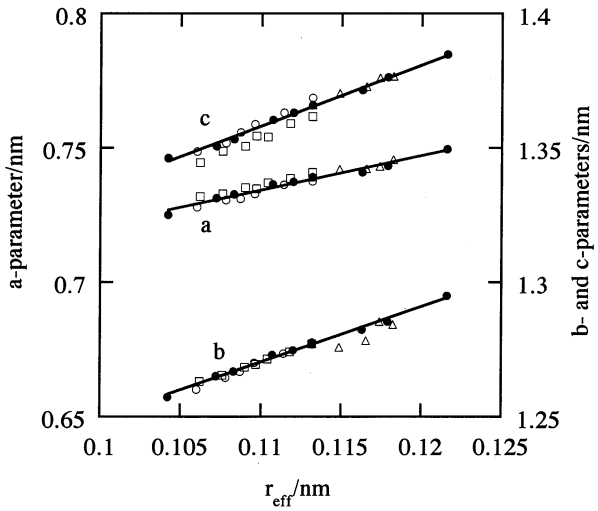

Figure 1. Correlation between lattice parameters and r_{eff} of complexes. (●) LnCo-complexes, (△) $La_xSm_{1-x}Co$-complexes, (□) $Er_xSm_{1-x}Co$-complexes, (○) $Yb_xSm_{1-x}Co$-complexes.

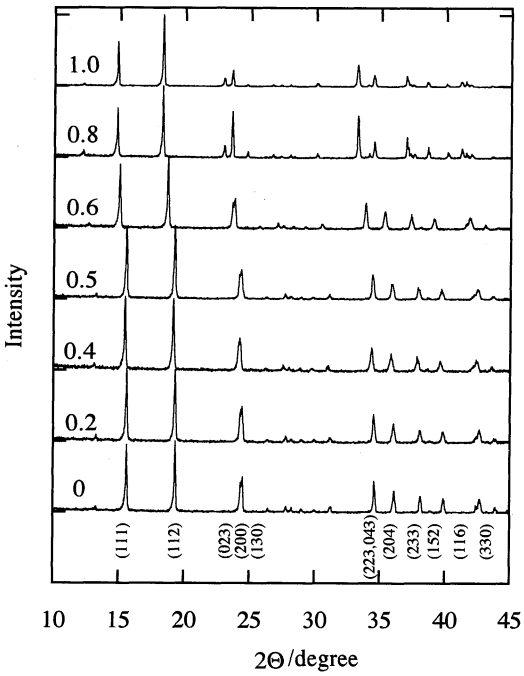

Figure 2. XRD results of $La_xSm_{1-x}Co$-complexes. x value is shown in the figure.

complex.

Figure 1 shows the correlation between the lattice parameters of $Ln[Co(CN)_6] \cdot nH_2O$ and the radii (r_s) of Ln ions.[6,7] The crystal structure and the lattice parameters of the complexes were determined by assuming an orthorhombic structure. As shown in Figure 1, a linear relationship between the lattice parameters and r_s is observed, confirming the results obtained by Hulliger et al. for LnFe- and LnCr-complexes.[2] We reported in Figure1 also the lattice parameters of orthorhombic LaCo-complex, as determined from the spectrum of the LaCo-B-complex. The results obtained are in fair agreement with the linear relationship shown in Figure1.

Figure 2 shows the XRD spectra of $La_xSm_{1-x}Co$-complexes. The spectrum of the LaCo-complex is assigned to the hexagonal structure. The XRD profile of $La_{0.2}Sm_{0.8}Co$-complex was more difficult to understand. The pattern is mostly of the hexagonal crystal system, but probably another crystalline phase (orthorhombic) is present. For x=0.4~1, the XRD spectra were different from LaCo-complex; we checked the orthorhombic symmetry and the adherence to the pure orthorhombic structure was confirmed for all these complexes. For the $La_xSm_{1-x}Co$-complexes, the molecules of crystallization water were evaluated to be 5 for x=0, 4.5 for x=0.2, and 4 for x=0.4~1, in agreement with XRD results. In the orthorhombic series, the diffraction peaks of the complexes appeared at lower angles with increasing the La content.

Figure 3 shows the XRD profiles of $Yb_xSm_{1-x}Co$-complexes. For the complexes with Sm and Yb, the number of crystallization water molecules was estimated to be 4 and the crystal form is orthorhombic for all the examined complexes (x=0~1). Similar results were obtained for $Er_xSm_{1-x}Co$-complexes. It was confirmed that the diffraction peaks of the complexes appeared at higher degree values with increasing the Sm content.

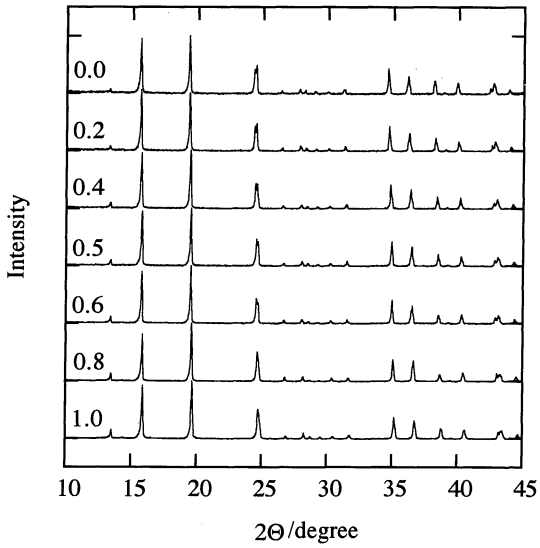

Figure 3. XRD results of $Yb_xSm_{1-x}Co$-complexes. x-value is shown in the figure.

The FWHM (full width at half maximum) of some main XRD peaks were examined for all the complexes. They were hardly influenced by the Ln/Sm ratios. These observations suggested us that the $Ln_xSm_{1-x}Co$-complex are not mixtures of powders of each LnCo- and SmCo-complexes.

For the orthorhombic systems, we introduced the parameter of the effective radius of Ln ions present in the complexes, defined as $r_{eff} = x\, r_{Ln} + (1-x)r_{Sm}$. In Figure 1, the lattice parameters as evaluated from XRD results are reported as a function of the r_{eff}. The linear relationship observed for the LnCo-complexes is confirmed. It is concluded that the lattice parameters of the complexes with orthorhombic structure are controlled only by the size of rare earth ions present in the molecule. The effective radii of Ln ions is a powerful parameter for the understanding of the role played by rare earths elements.

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 07230267 from The Ministry of Education, Science and Culture.

References and Notes

1 P.K.Gallagher, *Mater. Res. Bull.*, **3**, 225 (1968).
2 F.Hulliger, M.Landolt, and H.Vetsch, *J. Solid State Chem.*, **18**, 283 (1976).
3 Y.Sadaoka, K.Watanabe, Y.Sakai, and M.Sakamoto, *J. Ceram. Soc. Jpn.*, **103**, 519 (1995).
4 Y.Sadaoka, K.Watanabe, Y.Sakai, and M.Sakamoto, *J. Alloys Compounds*, **224**, 194 (1995).
5 E.Traversa, P.Nunziante, M.Sakamoto, K.Watanabe, Y. Sadaoka, and Y.Sakai, *Chem. Lett.*, **1995**,189.
6 R.D.Shannon and C.T.Prewitt, *Acta Crystallogr.*, **B25**, 925 (1969); **B26**, 1046 (1970).
7 To estimate the lattice parameters, 7 or more peaks were used. For SmCo-complex, orthorhombic, a=0.7388±0.0003 (nm), b =1.2779±0.0005(nm), c=1.3660±0.0004 (nm), α=β=γ=90°.