Changing Mixed-valence State of Hexacobalt Cluster by Substituting Central Metal Ion and by Electrochemical Reduction —Different Mixed-valence States of [M{Co(prolinato)$_2$}$_6$]$^{4+}$(M = Ba^{2+} and La^{3+})

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Clusters, Ba{Co(prolinato)$_2$}$_6$ and La{Co(prolinato)$_2$}$_6$, which are bridged by prolinato ligands, were crystallized as [M{Co(prolinato)$_2$}$_6$](ClO$_4$)$_4$. The Ba{Co(pro)$_2$}$_6$ cluster has two Co^{III} and four Co^{II} and the La{Co(pro)$_2$}$_6$ cluster has one Co^{III} and five Co^{II}; i.e., the mixed-valence state of the cobalt cluster is different according to the oxidation number of the central ion. The both mixed-valence clusters change into divalent hexacobalt clusters by electrochemical reduction.

Heteronuclear and/or polynuclear complexes are interesting materials because of their structures and properties. Among them, compounds with two or more centers of mixed valency in a similar or identical setting have become the focus of research, now as in ages past.[1] The mixed-valence species, [(NH$_3$)$_5$Ru-pyz-Ru(NH$_3$)$_5$] (pyz = pyrazine), was originally obtained by Taube et al.[2] One of the intriguing mixed-valence species is a polymeric oxo-centered triruthenium cluster with a general core, Ru$_3$(μ_3-O)(μ-O$_2$CR)$_6$. They exhibit multiple redox behavior with rich mixed-valence chemistry.[3] Compared with abundant examples of ruthenium clusters for investigation of redox properties, much fewer clusters with the other transition metal are known. Recently we have synthesized Ni$_6$-clusters, which were bridged by L-prolinato (pro) or L-azetidine-2-carboxylic acidato (azca) ligands containing a lanthanide ion centered cage of six symmetry equivalent Ni^{II} ions, and have investigated their electrochemical behavior.[4] The nickel atoms in the Ni$_6$-clusters were oxidized by turns and interact with one another. The Ni$_6$-clusters can involve both trivalent and divalent metal centers but the valency of the six Ni does not change: (NMe$_4$)$_n$[Ln{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$ ($n = 1$ for Ln = Sm^{III4a,4c} (**1**) and Eu^{III4b} (**2**), $n = 2$ for Ln = Eu^{II4b} (**3**) and Sr^{II4d} (**4**)). It is interesting to control the metal centers of mixed valency in a cluster with a synthetic method instead of electrochemical procedure. In this work, we have prepared the Co$_6$-clusters instead of Ni$_6$-clusters in anticipation of mixed-valence clusters: preparation of complexes with cobalt(II) salts in air often produces mixed-valence Co^{II}Co^{III} compounds.[5]

[Ba{Co(pro)$_2$}$_6$](ClO$_4$)$_4$, (**5**), and [La{Co(pro)$_2$}$_6$](ClO$_4$)$_4$, (**6**), were synthesized.[6] The constant potential electrolytic reduction of **5** produced (NMe$_4$)$_2$[Ba{Co(pro)$_2$}$_6$](ClO$_4$)$_4$ (**7**).[7] Similarly, the cluster, (NMe$_4$)[La{Co(pro)$_2$}$_6$](ClO$_4$)$_4$ (**8**) was obtained by the electrochemical method. The electrolytic reductions of **5** and **6** completed with almost ideal quantity of electricity: two-electron reduction for **5** and one electron for **6**.

To explore the electrochemical behavior of the cluster ions, we recorded cyclic voltammograms (CV) in acetonitrile medi-

um.[8] Figure 1 shows the CV of **5** at 25 °C. Scanning to the negative from the rest potential showed two reduction peaks corresponding to two electrons. Six pairs of peaks can be observed from ca. −0.6 to 1.3 V vs ferrocinium/ferrocene (Fc$^+$|Fc). The analyses of CV and differential-pulse voltammograms indicated that the first to the sixth oxidation steps were one-electron processes.
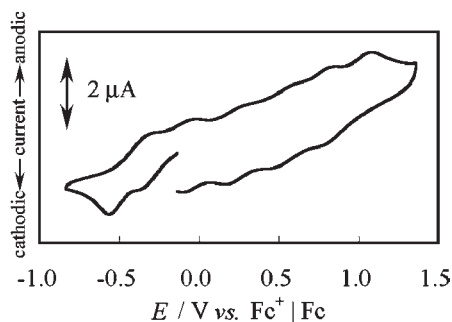

Figure 1. CV of **5** in acetonitrile at 25 °C.

Both clusters **5** and **6** form crystals[9] with cubic and space group $F23$ as well as those of (NMe$_4$)[Ln{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$ (**1** and **2**). The formulae of both clusters **5** and **6** are [M{Co(pro)$_2$}$_6$](ClO$_4$)$_4$ (M = Ba (**5**) and La (**6**)) according to elemental analyses.[9] In the nickel clusters, counterions, one cation and one anion, are added to the stoichiometric species: the four counter anions are on the coordinate (x, x, x), and the counter cation is on the site (1/4, 1/4, 1/4) when the center of the cluster ion is set on (0, 0, 0).[4c] On the other hand, in both crystals of **5** and **6** the cluster ion is on (0, 0, 0) and three of four ClO$_4$$^-$ are on (x, x, x) with the occupancy 3/4, and the other one is on (−1/4, −1/4, −1/4). It implies that the M{Co(pro)$_2$}$_6$ core has a total of 4+ charges; i.e., in the cluster **5** the six Co ions have a total of 14+ charges and 13+ in the cluster **6**. Therefore, the cluster **5** has two Co^{III} and four Co^{II} and the cluster **6** has one Co^{III} and five Co^{II}. It is novel thing that the mixed-valence state of the cobalt cluster is different according to the oxidation number of the central ion. The crystal structure of cluster **8** is the same as those of the nickel clusters with **1** and **2**.[4] The cluster **7** has the same crystal packing as that of **3**[4b] and **4**.[4d]

Figure 2 shows the structure of cluster **5**, which is essentially the same as that of the centered Sm or Eu cluster bridged by L-prolinato ligands:[4] the {Co(pro)$_2$} entity has a cis arrangement of the pro ligands and six {Co(pro)$_2$} entities are coordinated to the Ba through two carboxylate groups providing an icosahedral geometry about the metal. Six {Co(pro)$_2$} molecules associate
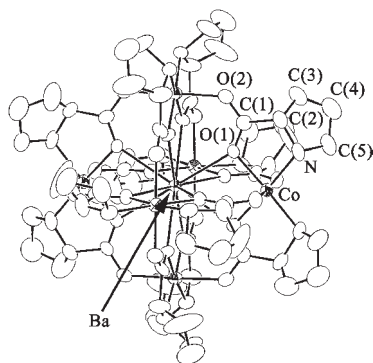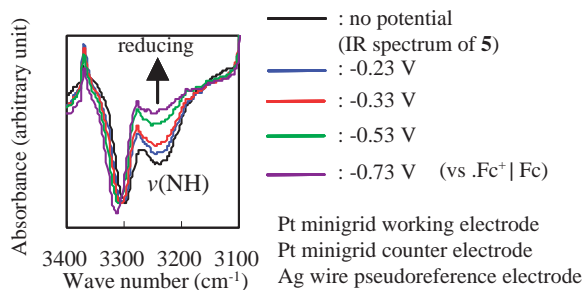
Figure 2. Structure of **5**. Selected bond distances (Å): Ba–O(1) = 2.807(4), Co–O(1) = 2.022(5), Co–O(2) = 2.063(6), Co–N = 2.085(8), O(1)–C(1) = 1.255(9), O(2)–C(1) = 1.269(10), Ba⋯Co = 3.737 (1).

by the coordination of the outer carboxylate oxygen to the axial site of Co of the adjacent molecule, forming a cavity encapsulating the Ba atom. The six cobalt ions are equivalent crystallographically: the clusters arrange randomly different direction in the lattice since the cluster has so high symmetry that is regarded as nearly spherical in the crystal lattice, and thus the bond lengths around the cobalt centers must be detected as the average.

In contrast with X-ray analysis, the results of infrared spectra support the mixed valence state of cluster **5**. The peaks assigned to N–H and COO antisymmetric stretching vibrations split to two and three, respectively: ν(NH); 3313 and 3247 cm^{-1}, ν(COO); 1631, 1614 and 1592 cm^{-1}. On the other hand, those of the corresponding N–H vibration of cluster **7**, in which all of the six cobalt ions are divalent, do not split and those of COO split to two. These imply that there are different types of vibration of N–H and COO antisymmetric stretching modes in the cluster **5**: because of the existence of divalent and trivalent cobalt ions, there are two types of N–H stretching, one is assigned to N–H linked with Co^{II} and the other is with Co^{III}, and similar with ν(COO).

To confirm this, electrospectrometrical measurement was performed. As shown in Figure 3, one of two N–H stretching peaks became small with reducing and went to the spectrum of cluster **7**: the results indicate that peak at 3247 cm^{-1} is assigned to ν(NH) for N–H linked with Co^{III} and the other at 3313 cm^{-1} is for Co^{II}.

The mixed-valence state of the cluster with MCo$_6$(pro)$_{12}$ is able to be controled by displacing the central metal ion with different oxidation number. Moreover, the mixed-valence clusters can be reduced to the isovalent MCo$^{II}_6$(pro)$_{12}$ clusters by constant-potential electrolysis. Further work in this area will be pursued because not only the electrochemical properties but also the magnetic and optical properties of the clusters should be interesting.

References and Notes

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6   To a mixed solvent of methanol/acetonitrile (20/70 mL) Ba(ClO$_4$)$_2$ (2 mmol), AgClO$_4$ (2 mmol), Hpro (24 mmol), and Co(ClO$_4$)$_2$·6H$_2$O (6 mmol) were added. The reddish violet mixed solution was concentrated by heating until the solution suspended. After cooling the mixture of dark brown and gray precipitates was filtered. The mixture was dissolved in acetonitrile (100 mL). After filtration the solution was concentrated and then dark brown powder was obtained in a yield of 29%. Although the crude crystals were obtained without AgClO$_4$, the yield was extremely small. Recrystallization from acetonitrile with diethyl ether gave dark brown tetrahedral crystals. The cluster with La (**6**) was also obtained by the above mentioned method using La(ClO$_4$)$_3$.

7   0.1 mmol of **5** and 0.4 mmol of (NMe$_4$)ClO$_4$ were dissolved in 25 mL of acetonitrile solution of tetrabutyl ammonium perchlorate (0.02 mol dm^{-3}). Using this solution, electrolysis of **5** at a constant potential (−0.80 V: vs Fc$^+$|Fc) was performed with a carbon electrode.

8   Acetonitrile solution of **5** (1 mmol dm^{-3}) containing 0.1 mol dm^{-3} tetrabuthylammonium perchlorate was used. The test electrode was a glassy carbon disk electrode (3.0 mm diameter) and the reference electrode was Ag/AgCl. Fc was used as an internal reference.

9   All the clusters **5–8** crystallize as Cubic, $F23$ (# 196), $Z = 4$. Crystal and analytical data for **5**: BaCo$_6$Cl$_4$O$_{40}$N$_{12}$C$_{60}$H$_{96}$, fw = 2258.22, $a = 21.3922(5)$ Å, $D_{calcd} = 1.532$ g cm^{-3}, μ(Mo $K\alpha$) = 15.81 cm^{-1}, $R = 0.047$ ($R_w = 0.068$) for 789 observed reflections, Anal. Found: C, 31.58; H, 4.29; N, 7.66%. Calcd: C, 31.91; H, 4.28; N, 7.44%. For **6**: LaCo$_6$Cl$_4$O$_{40}$N$_{12}$C$_{60}$H$_{96}$, fw = 2259.79, $a = 21.3387(5)$ Å, $D_{calcd} = 1.545$ g cm^{-3}, μ(Mo $K\alpha$) = 16.23 cm^{-1}, $R = 0.049$ ($R_w = 0.071$) for 968 observed reflections, Anal. Found: C, 31.24; H, 4.28; N, 7.76%. Calcd: C, 31.89; H, 4.28; N, 7.43%. Crystal data for **7**: BaCo$_6$Cl$_4$O$_{40}$N$_{14}$C$_{68}$H$_{120}$, fw = 2406.51, $a = 21.6417(4)$ Å, $D_{calcd} = 1.577$ g cm^{-3}, μ(Mo $K\alpha$) = 15.33 cm^{-1}, $R = 0.049$ ($R_w = 0.064$) for 916 observed reflections. For **8**: LaCo$_6$Cl$_4$O$_{40}$N$_{13}$C$_{64}$H$_{108}$, fw = 2333.94, $a = 21.338(1)$ Å, $D_{calcd} = 1.596$ g cm^{-3}, μ(Mo $K\alpha$) = 16.26 cm^{-1}, $R = 0.043$ ($R_w = 0.057$) for 714 observed reflections. The elemental analysis was performed at Instrumental Analysis Center of Josai University. X-ray diffractions were measured on a Rigaku RAXIS-IV Imaging Plate diffractometer with graphite monochromated Mo $K\alpha$ radiation. The crystallographic data in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 258967–258970.

Figure 3. IR spectroscopic changes from electrospectroscopic measurement of **5** in 0.2 M (n-C$_4$H$_9$)$_4$NBF$_4$–CD$_3$CN.