Synthesis of Centered Icosahedral Europium Cluster Formed by Bis(L-prolinato)nickel(II) Ligands and Isolation of an Electrochemically Reduced Product of Its Cluster

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A centered icosahedral europium(III) cluster formed by bis(L-prolinato)nickel(II) ligands was prepared and an electrochemically reduced product of its cluster was isolated. The crystal of the reduced product was isomorphous to that of the Eu^{III}-cluster and the cluster structure was retained in the reduced product.

Heteronuclear and/or polynuclear complexes are interesting materials due to their structures and properties. Recently the chemistry of the heteropolynuclear complexes with a transition metal or a lanthanide has been of interest because of the magnetic and electronic properties.[1] Various preparation methods have been proposed in order to obtain such polynuclear complexes. As a part of this study, Sakagami and Okamoto reported a chromium(III)-neodymium(III) hetero-nuclear complex prepared by utilizing *unsym-cis*-[Cr(eddp)(ox)]$^-$ as a building block,[2] and nickel(II)-Ln^{III} (Ln = Sm~Lu) prepared by using [Ni(tdo)]$^{2-}$ and [Ni(edo)]$^{2-}$ (H_4tdo = trimethylenebis(oxamide), H_4edo = ethylenebis(oxamide)) were reported by Sanada *et al.*[3]

In our group, an amino acid complex was used as a ligand in order to synthesize a new heteronuclear complex. By such a strategy, a centered icosahedral twelve-coordinate samarium cluster formed by six bis(L-prolinato)nickel(II) ([Ni(pro)$_2$]) ligands, [Sm{Ni(pro)$_2$}$_6$]$^{3+}$, has been obtained.[4] In this work, by using this preparation method, synthesis of a centered icosahedral europium(III) cluster formed by bis(L-prolinato)nickel(II) ligands was attempted: according to a textbook,[5] higher coordination numbers, 10 to 12, are sometimes found for the largest metal ions, but examples of a 12-coordinate complex with lanthanide ions smaller than samarium(III) have not been reported yet. Furthermore, isolation of an electrochemically-reduced product of the Eu^{III}-cluster was tried.

The centered icosahedral twelve-coordinate europium cluster formed by six [Ni(pro)$_2$] was prepared according to the method for the preparation of [Sm{Ni(pro)$_2$}$_6$]$^{3+}$:[4] [Ni(pro)$_2$] (3 mmol) was dissolved in methanol (15 ml) and Eu(ClO$_4$)$_3$ methanol solution (0.2 mol dm^{-3}, 2.5 ml) was added. Purple tetrahedral crystals were obtained from the mixed solution by keeping it for a few days at room temperature. Tetramethylammonium (TMA) salts, TMA[Eu{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$, were prepared by recrystallization of [Eu{Ni(pro)$_2$}$_6$](ClO$_4$)$_3$·nH$_2$O from an acetonitrile solution with TMAClO$_4$.

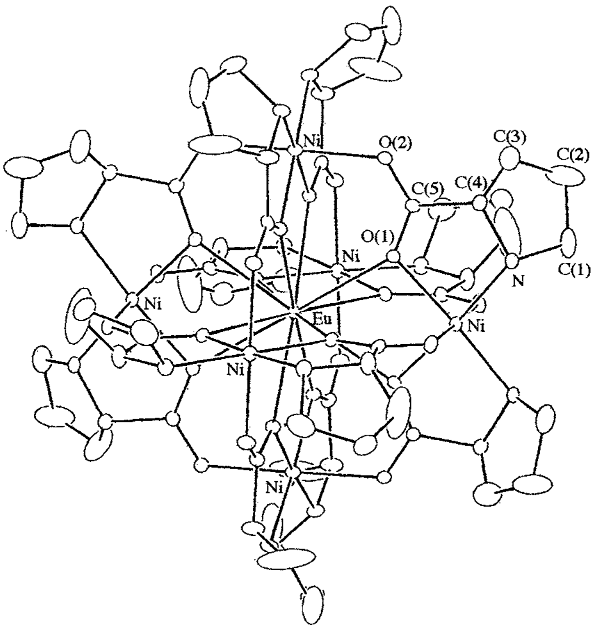

Figure 1. ORTEP drawing of [Eu{Ni(pro)$_2$}$_6$]$^{3+}$. [Eu{Ni(pro)$_2$}$_6$]$^{2+}$ has the same structure.

Figure 1 shows the structure of the Eu^{III}-cluster ion.[6a] The cluster ion, [Eu{Ni(pro)$_2$}$_6$]$^{3+}$, has the same structure as [Sm{Ni(pro)$_2$}$_6$]$^{3+}$ has.[4] Each nickel atom is surrounded by six atoms: two amino nitrogens, two carboxylate oxygens, which form chelate rings with the nitrogen atoms, and two carboxylate oxygens, which link the neighboring nickel atoms. The europium atom is coordinated to twelve oxygen atoms; six [Ni(pro)$_2$] units are coordinated by means of the two carboxylate oxygen atoms forming chelate rings. Consequently, in the cluster ion, the europium atom is coordinated by six [Ni(pro)$_2$] ligands and the metal is in icosahedral geometry. To our knowledge, [Eu{Ni(pro)$_2$}$_6$]$^{3+}$ is the example of the twelve-coordinate complex with the smallest central ion.

The structure is retained in the alcohol and acetonitrile solutions; uv-vis spectra in the solutions are perfectly consistent with the powder diffuse reflection spectrum. A cyclic voltammogram of TMA[Eu{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$ in acetonitrile medium at 25 °C was measured.[7] It exhibited one pair of peaks on the negative side and four complicated peaks on the positive side. The results agree with those of TMA[Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$.[4] The one pair of peaks at -0.72 V ($(E_{pa}+E_{pc})/2$, $\Delta E_p=$ 80 mV) vs. Fc$^+$/Fc corresponds to a Nernstian one-electron-reduction step without subsequent reactions; the peak potentials and the peak-current ratio (approximately unity) were independent of the sweep rate (50~200 mV s^{-1}). This indicates that the structure of the cluster ion is retained when the Eu^{III} ion is reduced. To confirm the fact, isolation of an electrochemical-reduced product of Eu^{III}-cluster was tried.[8] To the solution of the reduced product, a mixed solution of ether and acetonitrile and ether were added in order to make a concentration gradient. Reddish purple tetrahedral crystals were obtained from the

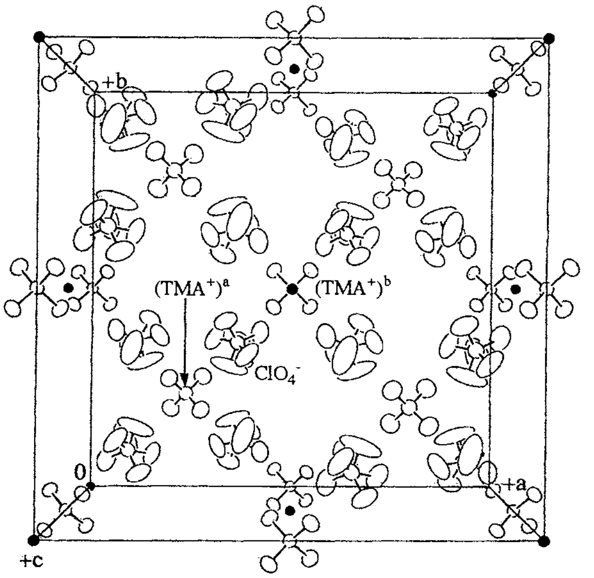

Figure 2. Crystal packing of $TMA_2[Eu\{Ni(pro)_2\}_6](ClO_4)_4$. $[Eu\{Ni(pro)_2\}_6]^{2+}$ is represented by ●. [a]site of (1/4, 1/4, 1/4). [b]site of (1/2, 1/2, 1/2). In the crystal of $TMA[Eu\{Ni(pro)_2\}_6](ClO_4)_4$, $[Eu\{Ni(pro)_2\}_6]^{3+}$ is located at the position of ● and the TMA is in the site of (1/4, 1/4, 1/4). Oxygen atoms of ClO_4^- are disordered in the crystal of $TMA_2[Eu\{Ni(pro)_2\}_6](ClO_4)_4$, in contrast with that of $TMA[Eu\{Ni(pro)_2\}_6](ClO_4)_4$.

Table 1. Selected interatomic distances (Å) and bond angles / degree for Eu^{III}- and Eu^{II}-cluster

	Eu^{III}-cluster	Eu^{II}-cluster
Eu-O(1)	2.683(2)	2.756(3)
O(1)-O(1)*(ave.)	2.822(8)	2.898(10)
Ni-O(1)	2.038(3)	2.025(3)
Ni-O(2)	2.052(3)	2.083(4)
Ni-N(1)	2.058(4)	2.089(5)
Eu-Ni	3.6962(6)	3.6940(7)
Ni-Ni	5.2273(8)	5.224(1)
O(1)-Eu-O(1)* (ave.)	63.4(2)	63.4(2)
O(1)-Ni-O(1)*	90.4(1)	94.5(2)
O(1)-Ni-N(1)	84.7(1)	82.6(2)
O(2)-Ni-O(2)*	178.8(2)	179.0(2)
N(1)-Ni-N(1)	100.5(2)	100.5(3)

mixed solution by keeping it for a few days at room temperature. The crystals were stable and X-ray crystal analysis was carried out using a suitable one.[6b] The crystal of the reduced cluster is the same space group, *F*23: the structure of Eu^{II}-cluster ion is the same as that of Eu^{III}-one and the cluster is located on the face center site which has T symmetry. The counter anion, ClO_4^-, and one of the two cations, TMA^+, occupy the same sites as those of the corresponding counter ions of Eu^{III}-cluster: ClO_4^- is located in the C_3 symmetry site and TMA^+ is in the T symmetry site (1/4, 1/4, 1/4). The other cation is in a different T symmetry site (1/2, 1/2, 1/2), as shown in Figure 2. It is very novel that crystals of salts, which have different numbers of counter ions, are isomorphous. Both Eu^{III}- and Eu^{II}-cluster ions are positioned on the same sites in each crystal and we can easily arrange the cluster ions from the crystal shapes. This characteristic is very useful for investigation of properties of the clusters, for example, comparison between theoretical calculations and experimental magnetic properties such as magnetic resonance (ESR) and ultrasonic experiments and so on.

The selected interatomic distances and bond angles for the Eu^{III}- and Eu^{II}-cluster are listed in Table 1. Distances of Eu-O and Ni-O(2) in Eu^{II}-cluster are longer than those in Eu^{III}-cluster. The results are reasonable because the ionic radius of Eu^{II} is larger than that of Eu^{III}. On the other hand, the distance of Eu···Ni scarcely changes between Eu^{III}- and Eu^{II}-clusters. This implies that the cluster structure is rather flexible. The deviation caused by a change of ionic radius of the central ion is distributed to the six $[Ni(pro)_2]$ units, so that the influence of the deviation does not converge to some point. Therefore, the cavity size of the cluster structure is kept constant even if the ionic radius and/or charge of the central ion are changed.

The clusters are to be expected for a model of template assembly of metal aggregates and for new materials for functional compounds.

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6 Crystal and analytical data for a) $TMA[Eu\{Ni(pro)_2\}_6](ClO_4)_4$, $EuN_{i6}C_{64}H_{108}N_{13}O_{40}C_l4$: F.W.=2345.59: Cubic, *F*23 (# 196), *Z*=4, *a*=21.266(2) Å, D_{calcd}=1.620 g cm^{-3}, $\mu(MoK_\alpha)$=19.90 cm^{-1}, Final *R*=0.035 for 1070 observed reflections (I>3 $\sigma(I)$). Anal. Found: Eu, 6.34(4); Ni, 14.75(3)%. Calcl for $EuN_{i6}C_{64}H_{108}N_{13}O_{40}C_{l4}$: Eu, 6.48; Ni, 15.01%. b) $(TMA)_2[Eu\{Ni\text{-}(pro)_2\}_6](ClO_4)_4$, $EuNi_6C_{68}H_{120}N_{14}O_{40}Cl_4$, F.W.=2419.74: Cubic, *F*23 (# 196), *Z*=4, *a*=21.557(4) Å, D_{calcd}=1.604 g cm^{-3}, $\mu(MoK_\alpha)$=19.14 cm^{-1}, Final *R*=0.043 for 1070 observed reflections (I>3 $\sigma(I)$). Anal. Found: Eu, 6.24(4); Ni, 14.44(4)%. Calcl for $EuNi_6C_{68}H_{120}N_{14}O_{40}Cl_4$: Eu, 6.28; Ni, 14.55%. Measurements for diffraction data were carried out on a Rigaku AFC7R diffractometer. The structures were solved by a heavy atom method and refined by a full-matrix least-square treatment.

7 Acetonitrile solution of $TMA[Eu\{Ni(pro)_2\}_6](ClO_4)_4$ (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/ saturated KCl. Ferrocene was used as an internal reference (ferrocenium/ ferrocene couple was 0.47 V vs. Ag/AgCl/ saturated KCl).

8 Equimolecular amounts (0.15 mmol) of $TMA[Eu\{Ni(pro)_2\}_6](ClO_4)_4$ and $TMAClO_4$ are dissolved in 50 ml of acetonitrile with $TBAClO_4$ (supporting electrolyte: 0.02 mol dm^{-3}). Using this solution, electrolysis of $TMA[Eu\{Ni(pro)_2\}_6](ClO_4)_4$ at a constant potential (-0.86 V: vs. Fc^+/Fc) was performed with a platinum gauze electrode for 6 h.