Synthesis of Stable Crystals of a Self-Assembled Centered Icosahedral Samarium Cluster Formed by Bis(L-prolinato)nickel(II) Ligands

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A centered icosahedral 12-coordinate samarium cluster formed by six bis(L-prolinato)nickel(II) ($[Ni(pro)_2]$) ligands, $[Sm\{Ni(pro)_2\}_6]^{3+}$, was prepared. The reaction of Sm with $[Ni(pro)_2]$ in a small excess (a 2-fold excess) and also in a large excess (even a 10-fold excess) of the latter produced the cluster. Therefore, this system is a self-assembly. In the cluster, 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 oxygen atoms which link the neighboring nickel atoms. The samarium atom is coordinated by six $[Ni(pro)_2]$ ligands, and the metal is in an icosahedral environment formed by 12 oxygen atoms. The icosahedral geometry is almost ideal. Crystals of $[Sm\{Ni(pro)_2\}_6](ClO_4)_3 \cdot 6MeOH$, which were prepared from a methanol solution, immediately decompose after filtration because of loosely trapped MeOH molecules in the crystal lattice. Therefore, crystals without MeOH molecules, which must be stable, were prepared by recrystallization from acetonitrile with tetramethylammonium perchlorate (TMAP). According to the X-ray crystal analysis, the cluster is $TMA[Sm\{Ni(pro)_2\}_6](ClO_4)_4$, cubic of space group *F*23, with $a = 21.273(9)$ Å, $V = 9626(1)$ Å^3, and $Z = 4$; $R = 0.053$ ($R_w = 0.049$) for 1296 reflections. In addition, several crystals of cluster salts that have different counteranions, i.e., tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), iodide (I^-), and nitrate (NO_3^-), were prepared. The order of increasing ease of crystallization of the cluster salts was $I^- > PF_6^- \sim ClO_4^- > BF_4^- \gg NO_3^-$. The cluster structure is retained in alcohol and acetonitrile solutions; the UV−vis spectra of the solutions are perfectly consistent with the powder diffuse reflection spectrum. Cyclic voltammograms of $[Sm\{Ni(pro)_2\}_6]^{3+}$ in acetonitrile proved that the structure of $[Sm\{Ni(pro)_2\}_6]^{3+}$ is retained in the redox process and that the nickel atoms electrochemically interact with one another. Thermal analysis of the cluster salts with different counteranions was investigated. The results imply that the cluster is very stable until bis(L-prolinato)nickel(II) ligands, which form the cage structure, disintegrate and that the thermal decomposition processes of the cluster salts depend on their counteranions.

Introduction

Heteronuclear and/or polynuclear complexes are interesting materials because of their structures and properties. Various preparation methods have been proposed to obtain such polynuclear complexes. One such method was the preparation of complexes from the interaction of ≥2 mol of *cis*-$[MA_4(OH)_2]^+$ (where A_4 was a single tetradentate amine ligand, two bidentate amines, or four monodentate amines) with metal halides;[1−4] the dihydroxo complexes that were used as ligands were coordinated to the other metals by the hydroxo oxygen atoms. Winpenny and co-workers have reported attempts to link mononuclear and/or small polynuclear compounds into larger units; especially, they have been exploring the coordination of ligands derived from 2-hydroxypyridine (2-pyridone) with first-row transition metals.[5−12]

Recently, the chemistry of heteropolynuclear complexes with transition metals and the lanthanides has been of interest because of their magnetic and electronic properties.[13−20] As a part of this study, Sakagami and Okamoto reported a chromium(III)−

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neodymium(III) heteronuclear complex prepared by utilizing *unsym-cis*-[Cr(eddp)(ox)]$^-$ as a building block,[21] and nickel(II)−Ln(III) (Ln = Sm−Lu) complexes prepared by using [Ni(tdo)]$^{2-}$ and [Ni(edo)]$^{2-}$ (H_4tdo = trimethylenebis(oxamide), H_4edo = ethylenebis(oxamide)) were reported by Sanada et al.[22]

In our group, an amino acid complex was used as a ligand to synthesize a new heteronuclear complex. Amino acids have two or more types of coordination atoms and can act as various kinds of bridging ligands by using a carboxylate.[23−29] Taking advantage of the properties of amino acid ligands, we achieved the synthesis of a heterometal complex with a bridging amino acid. A lanthanide ion, a hard acid, and a bis(amino acidato) complex were chosen for the purpose of preparing the heterometal complex; they were mixed in a nonaqueous solvent having poor coordination ability. By such a strategy, a centered icosahedral 12-coordinate samarium cluster containing six bis(L-prolinato)nickel(II) ([Ni(pro)$_2$]) ligands, [Sm{Ni(pro)$_2$}$_6$]$^{3+}$, was obtained.[30] However, the crystals were not stable in the atmosphere: they immediately decomposed upon filtration. In this work, stable crystals containing [Sm{Ni(pro)$_2$}$_6$]$^{3+}$ were prepared by recrystallization from an acetonitrile solution with tetramethylammonium perchlorate. On recrystallization, it was found that counterions played an important role in obtaining good crystals. Therefore, several crystals of the cluster salts having different counteranions, i.e., tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), iodide (I^-), and nitrate (NO_3^-), were prepared to investigate conditions for preparing stable crystals. Subsequently, the spectroscopic, electrochemical, and thermal properties of the cluster salts were investigated.

Experimental Section

Chemicals. In the preparations of the compounds investigated in this work, the following chemicals were used: $SmCl_3 \cdot 6H_2O$ and $Sm(NO_3)_3$ (purchased from Shin-etsu Chemical Co.); $AgClO_4$ (Waco Pure Chemical Ltd.); $NiSO_4 \cdot 6H_2O$ and NaOH (Waco); tetramethylammonium (TMA) salts ((TMA)ClO_4 (Sigma Chemical Co.); (TMA)BF_4 and (TMA)I (Nacalai Tesque Inc.); (TMA)PF_6 (Aldrich Chemical Co.); (TMA)NO_3 was prepared from (TMA)OH and HNO_3); tetrabutylammonium (TBA) salts (TBA)BF_4 and (TBA)I (Nacalai); (TBA)PF_6 (Aldrich).

CAUTION! Perchlorate salts with organic ligands are potentially explosive and *should be handled with the necessary precautions.*

Preparations. Bis(L-prolinato)nickel(II) was prepared according to a modified version of a method in the literature for the preparation of $Cu(pro)_2 \cdot 2H_2O$.[31] The centered icosahedral 12-coordinate samarium cluster formed by six [Ni(pro)$_2$] ligands was prepared by reacting $Sm(ClO_4)_3$ with a 6-fold excess of [Ni(pro)$_2$] in relation to the samarium concentration. [Ni(pro)$_2$] (3 mmol) was dissolved in methanol (15 mL) and a $Sm(ClO_4)_3$−methanol solution (0.2 mol dm^{-3}, 2.5 mL) was added. The addition of $Sm(ClO_4)_3$ changed the color of the solution from blue to purple. Purple tetrahedral crystals of [Sm{Ni(pro)$_2$}$_6$](ClO_4)$_3$·6MeOH were obtained from the mixed solution after allowing it to stand for a few days at room temperature. [Sm{Ni(pro)$_2$}$_6$](NO_3)$_3$·nH_2O was prepared according to the method for the perchlorate salt using $Sm(NO_3)_3$ instead of $Sm(ClO_4)_3$. Salts of the cluster ion with BF_4^-, PF_6^-, and I^-, [Sm{Ni(pro)$_2$}$_6$]X_3·nH_2O (X = BF_4^-, PF_6^-, I^-), were prepared by adding the corresponding tetrabutylammonium salts to acetonitrile or methanol solutions of [Sm{Ni(pro)$_2$}$_6$](NO_3)$_3$·nH_2O. TMA[Sm{Ni(pro)$_2$}$_6$]X'_4 salts (X′ = BF_4^-, PF_6^-, NO_3^-) were prepared by recrystallization of [Sm{Ni(pro)$_2$}$_6$]X'_3·nH_2O (X′ = BF_4^-, PF_6^-, NO_3^-; 0.5 mmol/50 mL) from acetonitrile solutions containing (TMA)X (0.5 mmol). To an acetonitrile solution of [Sm{Ni(pro)$_2$}$_6$](ClO_4)$_3$·6MeOH (0.25 mmol/15 mL) was added an acetonitrile solution of (TMA)ClO_4 (0.5 mmol/10 mL), and TMA[Sm{Ni(pro)$_2$}$_6$](ClO_4)$_4$ was obtained. When an acetonitrile solution of (TMA)I (0.5 mmol/50 mL) was added to an acetonitrile solution of [Sm{Ni(pro)$_2$}$_6$]I_3·nH_2O (0.5 mmol/50 mL), a purple precipitate of TMA[Sm{Ni(pro)$_2$}$_6$]I_4 soon separated out, and the precipitate was recrystallized from acetonitrile. *As a precaution with all perchlorate salts, quantities of the materials were kept to a minimum for safety reasons.* Single crystals of all the cluster salts were prepared by storing the corresponding solutions in a desiccator containing diethyl ether for few days. Purple tetrahedral crystals were obtained.

Measurements. Crystals for X-ray diffraction measurements were mounted on a glass fiber except for the crystal of TMA[Sm{Ni(pro)$_2$}$_6$](NO_3)$_4$, which was mounted in a capillary with the mother solution. Measurements were made on a Rigaku AFC-7R diffractometer using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 65° (for the salts of BF_4^-, PF_6^-, and NO_3^-) and on a Rigaku RAXIS-IV diffractometer (for the I^- salt) with graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation at 23 °C. Ultraviolet−visible (UV−vis) absorption and powder diffuse reflection spectra of the samples were recorded on a Hitachi U-3200 spectrophotometer: a 1 cm quartz cell was used for a solution sample, and a standard Hitachi reflection attachment and magnesium oxide (for the standard and a diluent) were used for a powder sample. Infrared (IR) absorption spectra were obtained by means of a Horiba FT-300 infrared spectrophotometer with the powder diffuse reflection method using silicon as a matrix. Electrochemical measurements were made at +25 and −40 °C with a Huso HECS 312B potentiostat, a Huso HECS 317B coulometer, and a Riken Denshi model F-3DGX-Y recorder. Acetonitrile (HPLC grade) and methanol (HPLC grade) were dried over 3 Å molecular sieves for electrochemical measurements. The solvents containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (Nacalai Tesque. Inc.) were used as base solutions. The test electrode was a glassy carbon disk electrode (3.0 mm diameter); this was used for the cyclic voltammetry. The reference electrode used at both temperatures was Ag/0.01 mol dm^{-3} $AgNO_3$ (acetonitrile). Ferrocene was used as an internal reference. The potentials of the ferrocenium/ferrocene (Fc^+/Fc) couple were 0.31 V (vs Ag/0.01 mol dm^{-3} $AgNO_3$) at 25 °C and 0.24 V at −40 °C in the acetonitrile medium and 0.34 V at 25 °C and 0.27 V (ΔE_p = 140 mV) at −40 °C in the methanol medium. The simultaneous thermogravimetric (TGA) and differential thermal (DTA) analyses were carried out with Rigaku Thermoflex TAS-200 and Shinku-Riko DSC-1500MS instruments[32,33] using samples weighing about 5 mg; the reference was α-alumina, and the heating rate was 20 °C min^{-1} in N_2 atmosphere and in air.

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Table 1. Crystal Data for TMA[Sm{Ni(pro)$_2$}$_6$](A)$_4$ (A = ClO_4^-, BF_4^-, PF_6^-, I^-, NO_3^-)

	counteranion (A)				
	ClO_4^-	BF_4^-	PF_6^-	NO_3^-	I^-
fw	2344.03	2293.44	256.09	2194.25	2453.85
cryst syst	cubic	cubic	cubic	cubic	cubic
space group	*F*23	*F*23	*F*23	*F*23	*F*23
a, Å	21.278(3)	21.201(2)	21.610(1)	21.389(3)	21.037(3)
V, Å^3	9633(3)	9528(3)	10091(2)	9785(2)	9310(1)
Z	4	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.616	1.599	1.663	1.489	1.750
μ (Mo Kα), cm^{-1}	19.48	18.70	18.46	18.05	32.06
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
no. of observs	1014	832	1206	869	665
no. of variables	99	105	105	87	96
R_{ino}	0.031	0.035	0.029	0.037	
R^a	0.035	0.037	0.042	0.036	0.099
R_w^{a}	0.052	0.052	0.063	0.052	0.130
GOF^b	1.205	1.025	1.126	1.088	1.509

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_W = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 1/\sigma(|F_o|)^2$. [b] GOF = $\{[\sum w(|F_o| - |F_c|)^2]/(N_{reflcns} - N_{params})\}^{1/2}$.

Results and Discussion

The cluster [Sm{Ni(pro)$_2$}$_6$]$^{3+}$ forms a crystal with very high symmetry (cubic, space group *F*23). Four ClO_4^- ion sites must exist in the unit cell, and each ClO_4^- ion lies on the 3-fold axis. However, this is contradictory to the result of the gravimetric analysis of ClO_4^- using tetraphenylarsonium chloride: found, 12.33%; calculated for [Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_3$·6MeOH, 12.63%. Therefore, the occupancy of ClO_4^- was fixed at 0.75 when the structure was refined.[30] The methanol molecules are considered to be loosely trapped in the lattice because of the extremely large thermal parameters of all the solvent molecules. This is the cause of the crystals immediately decomposing after filtering. Therefore, preparations of crystals without MeOH molecules, which must be stable, were attempted. According to crystallography, four ClO_4^- ions, which lie on the 3-fold axis, are required to construct the stable single crystals. Thus, a fourth ClO_4^- ion was added to [Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_3$ with a suitable cation by recrystallization from acetonitrile. As the suitable cation, the tetramethylammonium ion was chosen because it has the same symmetry as ClO_4^- when methyl groups are regarded as spheres. The stable crystals were obtained as TMA[Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$, which has no solvent molecules. The counterions likely play an important role in preparing single crystals. To confirm this prediction, BF_4^-, PF_6^-, NO_3^-, and I^- were used for preparing crystals of salts with the cluster instead of ClO_4^-. The cluster salts with BF_4^- and PF_6^- were obtained as stable single crystals: in the crystals of the BF_4^- salt, the fluorine atoms are disordered because the anion is smaller than ClO_4^-, though it has the same symmetry as ClO_4^-. The salt containing NO_3^- did not form stable crystals. The order of increasing ease of crystallization of the cluster salts was determined by crystallizing the salts from solutions containing a different pair of anions (ClO_4^-, BF_4^-, PF_6^-, NO_3^-, and I^-) and the cluster ion: the anion in a crystallized salt was confirmed by its IR spectrum. The order was $I^- > PF_6^- \sim ClO_4^- > BF_4^- \gg NO_3^-$. The diffraction data for the crystal of the NO_3^- salt were collected using a crystal shielded in a capillary with the mother liquid, since the NO_3^- salt immediately decomposes upon filtering. When the tetraethylammonium or tetrabutylammonium ion was used instead of TMA$^+$, no single crystal was obtained. The results suggest that crystallization of the cluster salts requires a counteranion and a cation that have symmetries higher than tetrahedral. To construct crystals with the space group *F*23, suitable counterions have to occupy *T* symmetry sites; i.e., when the cluster ion acquires suitable cations and anions, it can crystallize. Crystals containing I^- (the ion has a spherical symmetry, which is higher than *T*) are stable in the atmosphere but are unstable toward X-radiation. Therefore, the X-ray diffraction data for the iodide salt were measured by the Rigaku RAXIS-IV diffractometer with imaging plates.

The crystal data for the cluster salts are shown in Table 1. All crystals of the cluster salts are the same space group, *F*23. The cluster ion is located on the face center: the site has *T* symmetry. Every counteranion occupies the same C_3 symmetry site (the coordinate is (*x*, *x*, *x*) when the center of the cluster ion is set on (0, 0, 0)) in each crystal. All the cations, except for those in the NO_3^- salt, are located in the same *T* symmetry site ($^1/_4$, $^1/_4$, $^1/_4$) in the cluster salt crystals, as shown in Figure 1. In the NO_3^- salt, the cation is positioned at a different *T* symmetry site ($^1/_2$, $^1/_2$, $^1/_2$). The center-to-center distances between the cluster ion and anions or cations and between the anions and cations are listed in Table 2. The normalized cluster−anion (C−A) distances based on the lattice constants for ClO_4^-, BF_4^-, PF_6^-, and I^- salts are almost the same (the average value is 0.414). The cation (TMA$^+$)−anion (T−A) distances (average = 0.215) are as well, and the cluster−cation (C−T) separations all have the same value, 0.433. On the other hand, in the NO_3^- salt, the C−A distance is 0.421, that of T−A is 0.188, and the C−T separation is 0.5: the differences between values for the nitrate anion and the averages for the other anions, Δ(C−A), Δ(T−A), and Δ(C−T), are 0.007, −0.027, and 0.067, respectively. These differences are responsible for the lower symmetry of NO_3^- compared to that of the other anions. The crystal symmetry of the cluster salts, *F*23, is determined by the symmetry of the cluster ion. To construct the space group, the counterions require suitable symmetries. The anions ClO_4^-, BF_4^-, PF_6^-, and I^- have sufficiently high symmetries to satisfy this requirement: the symmetry of ClO_4^- and BF_4^- is T_d, that of PF_6^- is O_h, and I^- has a spherical symmetry. Thus, these anions can fulfill the requirements of both the cluster ion and the cation. Therefore, the cluster ion, anion, and cation can be arranged on the appropriate sites. Since the nitrate ion does not have such a high symmetry, however, the anion (symmetry D_{3h}) cannot be directed toward the cation and thus cannot force the cation to locate on a suitable site when the anions are positioned around the cluster ion. Consequently, the cation is shifted to a site that is closer to the anion. Therefore, the crystal packing of the NO_3^- salt is considered to be unstable.

The cluster ion, [Sm{Ni(pro)$_2$}$_6$]$^{3+}$, has the same structure both in [Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_3$·6MeOH[30] and in every TMA-

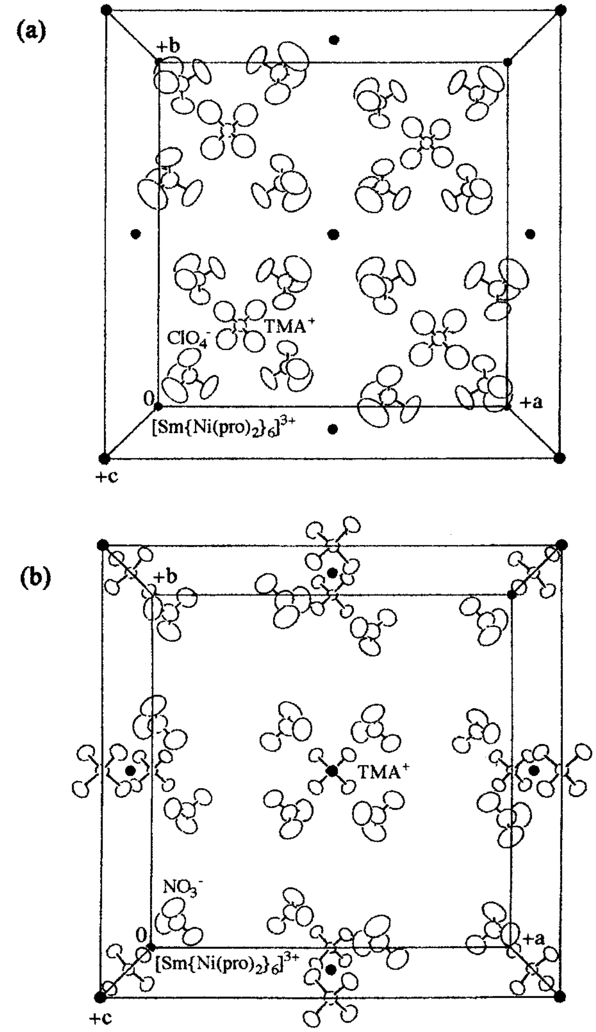

Figure 1. Crystal packing of TMA[Sm{Ni(pro)$_2$}$_6$](A)$_4$ (A = ClO_4^-, BF_4^-, PF_6^-, I^-, and NO_3^-): (a) TMA[Sm{Ni(pro)$_2$}$_6$](ClO_4)$_4$; (b) TMA-[Sm{Ni(pro)$_2$}$_6$](NO_3)$_4$. The centroid of the cluster ion, [Sm{Ni-(pro)$_2$}$_6$]$^{3+}$, is represented by ●. Counteranions BF_4^-, PF_6^-, and I^- are located in the same sites as ClO_4^- in (a).

[Sm{Ni(pro)$_2$}$_6$](A)$_4$ complex (A = ClO_4^-, BF_4^-, PF_6^-, NO_3^-, I^-). The interatomic distances and bond angles for the cluster in TMA[Sm{Ni(pro)$_2$}$_6$](ClO_4)$_4$, as a representative of the cluster salts, are listed in Table 3. ORTEP plots of the cluster ion and of the environment around the Sm and Ni atoms in the cluster ion are shown in Figures 2 and 3, respectively. 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 samarium atom is coordinated to 12 oxygen atoms; six [Ni(pro)$_2$] units are coordinated by the two carboxylate oxygen atoms forming chelate rings. Consequently, in the cluster ion, the samarium atom is coordinated by six [Ni(pro)$_2$] ligands and the metal is in an icosahedral environment. There are several reports regarding 12-coordinate complexes.[34−38] In these compounds, the small bite of bidentate ligands such as NO_3^- and 1,8-naphthyridine makes the 12-coordination possible. The icosahedral coordination geometry is rather distorted because of the extreme shortness of the O−N−O or N−C−N bite and the particular mode of bidentate bonding. A centered icosahedral gold cluster compound has also been reported:[39] [Au_{13}(PMe_2Ph)$_{10}$$C_{12}$]($PF_6$)$_3$, in which 12 of the gold atoms define an icosahedral structure and the 13th lies at the centroid of the polyhedron. The gold−gold distances on the periphery of the polyhedron lie in the range 2.852(3)−2.949(3) Å, and the lengths of the bonds connecting the central gold atom to the peripheral gold atoms are in the range 2.716(2)−2.789(2) Å. The icosahedron of the gold cluster is also distorted. In [Sm-{Ni(pro)$_2$}$_6$]$^{3+}$, however, the samarium atom, which is coordinated by the rather large bidentate ligands, [Ni(pro)$_2$], is 12-coordinate and the icosahedral geometry is almost ideal. All the Sm−O bond lengths are 2.691(3) Å, the average of the nearest neighboring O−O lenths is 2.83 Å (the ratio (O−O)/(Sm−O) = 1.05), and the angles between two adjacent metal−ligand bonds are 62.8(3)−65.1(1)° (average = 63.4°); the ideal angle between two adjacent metal (M)−ligand (L) bonds is 63.43°, and the ratio (L−L)/(M−L) = 1.0515.[40] The lanthanide ions reported to form 12-coordinate compounds are La^{3+},[34] Ce^{3+},[35] Ce^{4+},[36] Pr^{3+},[37] and Nd^{3+}.[38] It is very difficult to prepare the 12-coordinate complex of samarium even if the NO_3^- ligand is used. As a high coordination number complex, an eleven-coordinate Sm complex, [Sm(NO_3)$_5$$H_2O$]$^{2-}$, was reported.[41] Recently a “12-coordinate Sm complex” with tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate (L), [Sm(L)$_2$](BPh_4), was reported.[42] However, half of the 12 Sm−N bond lengths in the complex are extremely long: the average of the longer lengths is 2.95 Å and that of the remaining bonds is 2.66 Å. Therefore, the cluster ion that is reported in this work is very novel in that it has so much symmetry. The samarium−oxygen bond lengths in the present cluster ion, 2.691(3) Å, are a little longer than those in 11- and 10-coordinate samarium complexes.[43,44] This distance can be compared with those of Sm^{2+} complexes:[45] Sm−O = 2.493(4)−2.668(4) Å in [Sm(NO_3)$_5$$H_2O$]$^{2-}$,[43] 2.36-(1)−2.64(1) Å in [Sm(ClO_4)$_3$(dbc-6)] (dbc-6 = diisopropyl *N,N*-diethylcarbamylmethylenephosphonate),[44] and 2.676(4)−2.720-(4) Å in [SmI_2{O(CH_2CH_2OMe)$_2$}$_2$].[45] The elongation of the Sm−O bonds in [Sm{Ni(pro)$_2$}$_6$]$^{3+}$ may arise from restrictions due to the six-[Ni(pro)$_2$] cage structure and the 12-coordination.

The icosahedral cluster structure is very stable in crystals and in solutions. It was confirmed that the cluster ion is retained in the salts with different anions and is retained even during decay of the crystals, according to the diffraction data of slightly decayed crystals of [Sm{Ni(pro)$_2$}$_6$](ClO_4)$_3$·6MeOH. Moreover, the structure is also retained in the alcohol and acetonitrile solutions; UV−vis spectra of the solutions are perfectly consistent with the powder diffuse reflection spectrum: the reflection bands are similar to those of [Ni(pro)$_2$(H_2O)$_2$] but clearly blue-shifted, and thus the bands are probably attributable to a typical octahedral nickel(II) chromophore. In the solutions,

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Table 2. Center-to-Center Distances between $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$ and A ($=\mathrm{ClO_4^-}$, $\mathrm{BF_4^-}$, $\mathrm{PF_6^-}$, $\mathrm{I^-}$, $\mathrm{NO_3^-}$) or TMA, with the Lattice Constants for the Crystals of the Salts

	counteranion (A)				
	$\mathrm{NO_3^-}$	$\mathrm{ClO_4^-}$	$\mathrm{BF_4^-}$	$\mathrm{PF_6^-}$	$\mathrm{I^-}$
a, Å	21.389(3)	21.278(3)	21.201(2)	21.610(1)	21.037(3)
$[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$−TMA, Å	10.695	9.214	9.180	9.357	9.109
normalized value based on *a* (C−T)[a]	0.5	0.433	0.433	0.433	0.433
$[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$−A, Å	8.995	8.814	8.783	8.964	8.703
normalized value based on *a* (C−A)[b]	0.421	0.414	0.414	0.415	0.414
TMA−A, Å	4.016	4.566	4.553	4.709	4.445
normalized value based on *a* (T−A)[c]	0.188	0.215	0.215	0.218	0.211

[a] Label of the normalized center-to-center distance between $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$ and $\mathrm{TMA^+}$. [b] Label of the normalized center-to-center distance between $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$ and the anion. [c] Label of the normalized center-to-center distance between $\mathrm{TMA^+}$ and the anion.

Table 3. Selected Bond Distances (Å) and Angles (deg) in $\mathrm{TMA[Sm\{Ni(pro)_2\}_6](ClO_4)_4}$[a]

Sm−O(1)	2.687(3)	Sm···Ni	3.6996(7)
		Ni···Ni	5.2320(9)
O(1)−O(1)$^{\mathrm{I}}$	2.891(6)		
O(1)−O(1)$^{\mathrm{II}}$	2.820(9)	O(1)−C(5)	1.263(5)
O(1)−O(1)$^{\mathrm{III}}$	2.798(9)	O(2)−C(5)	1.252(5)
O(1)−O(1) (av)	2.825(8)	N(1)−C(1)	1.486(7)
		N(1)−C(4)	1.507(10)
Ni−O(1)	2.037(3)	C(1)−C(2)	1.48(2)
Ni−O(2)	2.048(3)	C(1)−C(5)	1.505(7)
Ni−N(1)	2.064(4)	C(2)−C(3)	1.45(2)
		C(3)−C(4)	1.45(2)
O(1)−Sm−O(1)$^{\mathrm{I}}$	65.1(1)	Sm−O(1)−Ni	102.2(1)
O(1)−Sm−O(1)$^{\mathrm{II}}$	63.3(2)	Sm−O(1)−C(5)	143.9(3)
O(1)−Sm−O(1)$^{\mathrm{III}}$	62.8(2)	Ni−O(1)−C(5)	113.9(2)
O(1)−Sm−O(1) (av)	63.4(2)	Ni$^{\mathrm{I}}$−O(2)−C(5)	123.3(3)
		Ni−N(1)−C(1)	106.8(3)
O(1)−Ni−O(1)$^{\mathrm{I}}$	90.4(1)	Ni−N(1)−C(4)	116.9(5)
O(1)−Ni−O(2)$^{\mathrm{II}}$	90.0(3)	C(1)−N(1)−C(4)	105.7(8)
O(1)−Ni−O(2)$^{\mathrm{III}}$	89.0(2)	N(1)−C(1)−C(2)	105.5(9)
O(1)−Ni−N(1)	84.8(1)	N(1)−C(1)−C(5)	115.3(4)
O(1)−Ni−N(1)$^{\mathrm{I}}$	173.2(2)	C(2)−C(1)−C(5)	114(1)
O(2)$^{\mathrm{II}}$−Ni−O(2)III	178.6(2)	C(1)−C(2)−C(3)	109.1(9)
O(2)$^{\mathrm{II}}$−Ni−N(1)	86.1(2)	C(2)−C(3)−C(4)	104.1(9)
O(2)$^{\mathrm{II}}$−Ni−N(1)I	94.8(3)	N(1)−C(4)−C(3)	108.5(9)
N(1)−Ni−N(1)$^{\mathrm{I}}$	100.4(2)	O(1)−C(5)−O(2)	125.9(4)
		O(1)−C(5)−C(1)	119.0(4)
		O(2)−C(5)−C(1)	115.0(4)

[a] Key to symmetry operations: (I) *x*, −*y*, −*z*; (II) *y*, *z*, *x*; (III) *y*, −*z*, −*x*.

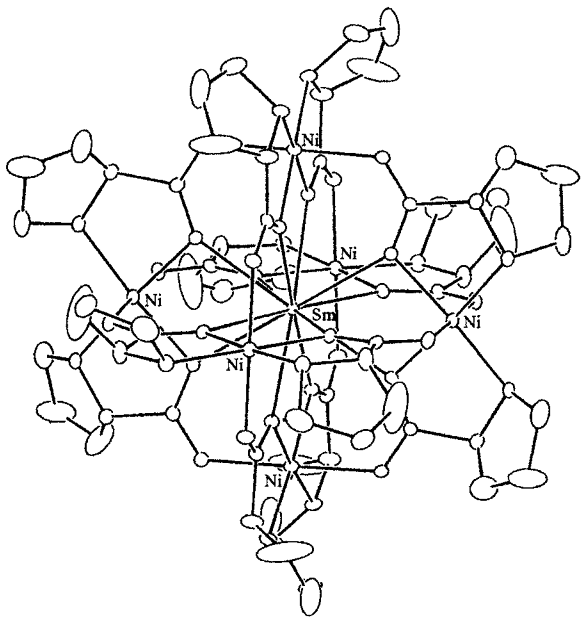

Figure 2. ORTEP plot of the structure of $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$.

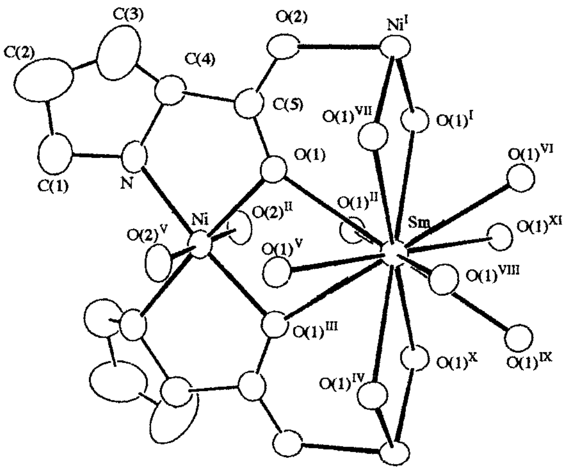

Figure 3. ORTEP plot of the environment around the Sm and Ni atoms in $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$ showing 50% thermal ellipsoids and the atom-numbering scheme. Key to operations: (I) *z*, *x*, *y*; (II) *y*, *z*, *x*; (III) *x*, −*y*, −*z*; (IV) *z*, −*x*, −*y*; (V) *y*, −*z*, −*x*; (VI) −*x*, *y*, −*z*; (VII) −*z*, *x*, −*y*; (VIII) −*y*, *z*, −*x*; (IX) −*x*, −*y*, *z*; (X) −*z*, −*x*, *y*; (XI) −*y*, −*z*, *x*.

the cluster ion is stable regardless of counterions. The cluster ion has an Sm:$[\mathrm{Ni(pro)_2}]$ molar ratio of 1:6. However, the reaction of Sm with $[\mathrm{Ni(pro)_2}]$ in a small excess (2-fold excess) and also in a large excess (even a 10-fold excess) of the latter produced the cluster $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$: both reactions gave the same crystals, and their IR spectra agreed quite well with that of the cluster $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$. These results indicate that this system is a self-assembly of the centered icosahedral samarium cluster formed by bis(L-prolinato)nickel(II) ligands. The self-assembly of the icosahedral cluster is caused by an almost ideal arrangement of the coordination sphere around each nickel atom (octahedral), which makes the icosahedral cavity suitable for the lanthanide ion.

To investigate the thermal stability of the cluster structure, thermal analysis was carried out. The TG−DTA curves of salts of $[\mathrm{Sm\{Ni(pro)_2\}_6}]^{3+}$ with $\mathrm{BF_4^-}$, $\mathrm{PF_6^-}$, and $\mathrm{I^-}$ are shown in Figure 4. Those of $[\mathrm{Ni(pro)_2}]\cdot 2\mathrm{H_2O}$ are also given to facilitate comparison with the cluster. Decomposition of all the cluster salts occurs at about 360 °C. The decomposition temperature corresponds to that of $[\mathrm{Ni(pro)_2}]\cdot 2\mathrm{H_2O}$. Such a result suggests that the cluster is very stable until the $[\mathrm{Ni(pro)_2}]$ units, which form the cage structure, are decomposed. From the TG−DTA curves, it can be seen that the thermal decomposition processes of the cluster salts depend on their counteranions: profiles of the TG−DTA curves of the salts with $\mathrm{BF_4^-}$, $\mathrm{PF_6^-}$, and $\mathrm{I^-}$ are different from one another. The thermal decomposition processes

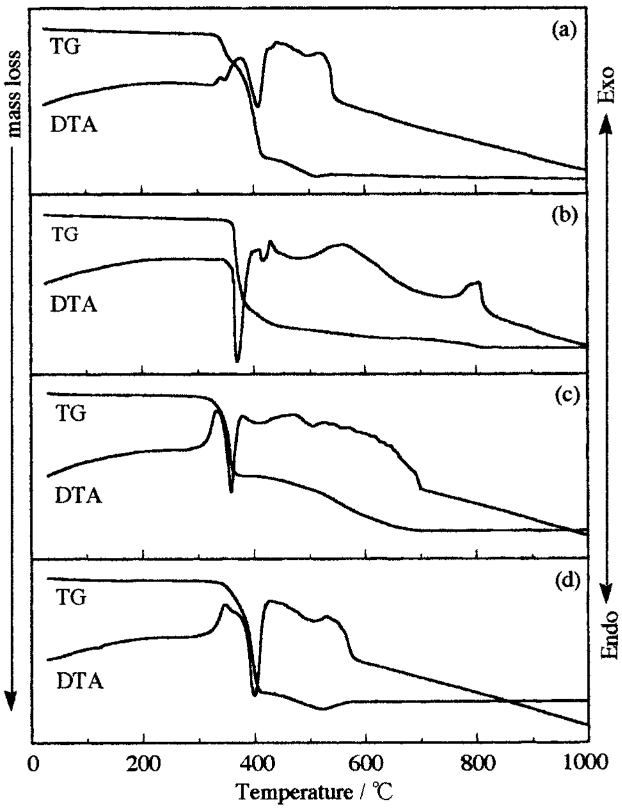

Figure 4. Thermogravimetric and differential thermal analysis curves: (a−c) TMA[Sm{Ni(pro)$_2$}$_6$](A)$_4$ (A = (a) BF_4^-, (b) PF_6^-, (c) I^-); (d) [Ni(pro)$_2$].

in N_2 atmosphere and in air are essentially the same, except for the direction of the DTA peak at about 360 °C (in N_2 atmosphere, the peak is endothermic, and in air, it is exothermic). Ash obtained at the final stage of the process in air is likely to contain an oxidation compound from the counteranion. In the cluster salt with BF_4^-, the ash consists of oxides of Sm, Ni, and B, while the ash from the salt having PF_6^- contains phosphonates as well as oxides of Sm, Ni, and P: the IR spectrum of the residue of the PF_6^- salt indicates the existence of the phosphonates with oxides of P. On the other hand, the salt with I^- gave ash composed only of oxides of Sm and Ni. This may imply that the cluster salt becomes a material for formation of a lanthanide oxide if suitable counterions can be chosen for thermal decompositions: formation of lanthanide oxides by means of thermal decomposition of heteronuclear complexes at low temperatures has recently been widely investigated.[46]

To explore the electrochemical behavior of the cluster ion, a cyclic voltammogram of TMA[Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$ in acetonitrile medium at 25 °C was recorded. It exhibited one pair of peaks on the negative side and four complicated peaks on the positive side, as shown in Figure 5a. The one pair of peaks at −2.02 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}). The first oxidation step at 0.71 V ($\Delta E_p = 90$ mV) among the four or more oxidation steps was a Nernstian one-electron process with slow irreversible subsequent homogeneous reactions. The cyclic voltammogram at −40 °C (Figure 5b) showed the same reduction wave at −2.04 V as that observed at 25 °C and three pairs of peaks and three ambiguous peaks on the positive side. The analysis of the cyclic and normal-pulse voltammograms indicated that the first to the third oxidation steps at 0.65, 0.85, and 1.03 V vs Fc$^+$/Fc were Nernstian one-electron processes with slow irreversible subsequent reactions. The fourth to the sixth oxidation steps appear to be one-electron processes with fast irreversible subsequent reactions. The reduction step is assigned to the Sm^{III}/Sm^{II} reduction couple, and the six oxidation steps can be assigned to the six Ni^{III}/Ni^{II} oxidation couples on the basis of voltammetry studies of [Ni(pro)$_2$]: the cyclic voltammogram of [Ni(pro)$_2$] showed the oxidation step with fast irreversible subsequent reactions at 0.77 V vs Fc$^+$/Fc. The six oxidation steps were irreversible at 25 °C. This is attributable to the subsequent irreversible reactions, since a pair of anodic and cathodic peaks corresponding to this step (at 0.69 V) were observed at −40 °C. The six discrete oxidation steps in the icosahedral cluster suggest that the nickel atoms interact with one another, and the observation of a pair of anodic and cathodic peaks based on the first Ni^{III}/Ni^{II} couple in the cluster even at 25 °C suggests that the [Ni(pro)$_2$] unit structure in the cluster is more stable than that in the corresponding mononuclear complex.

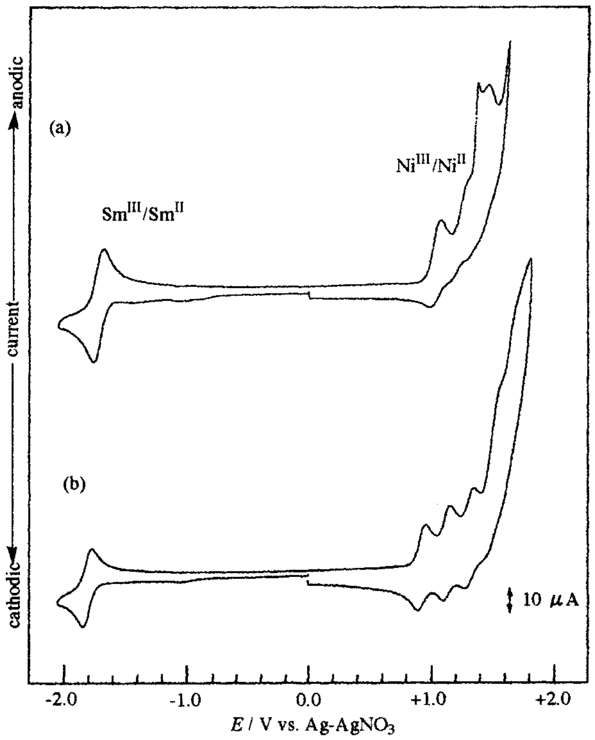

Figure 5. Cyclic voltammograms of TMA[Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_4$ at (a) 25 °C and (b) −40 °C.

Further work in this area will be pursued because not only the electrochemical properties but also the magnetic and optical properties of the cluster should be interesting.

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Supporting Information Available: Details of the X-ray diffraction analyses, including text and tables giving experimental details and tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for [Sm{Ni(pro)$_2$}$_6$](ClO$_4$)$_3$·6MeOH and TMA[Sm{Ni(pro)$_2$}$_6$]-

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$(A)_4$ ($A = ClO_4^-$, BF_4^-, PF_6^-, NO_3^-, I^-), a crystal packing diagram for $[Sm\{Ni(pro)_2\}_6](ClO_4)_3$, UV−vis absorption spectra of $[Sm\{Ni(pro)_2\}_6]^{3+}$ in methanol solution and in acetonitrile solution, and powder diffuse reflection spectra of $[Sm\{Ni(pro)_2\}_6](ClO_4)_3\cdot 6MeOH$, TMA$[Sm\{Ni(pro)_2\}_6](ClO_4)_4$, and $[Ni(pro)_2(H_2O)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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