Stabilization of Tetravalent Cerium upon Coordination of Unsaturated Heteropolytungstate Anions

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Monovacant Keggin derivative anions $X^{n+}W_{11}O_{39}^{(12-n)-}$ (X = P, Si, Ge, B) and a monovacant Dawson derivative anion $P_2W_{17}O_{61}^{10-}$ were adopted as the ligand for cerium(III). The formation of the complexes $[CeL]^{(m-3)-}$ and $[CeL_2]^{(2m-3)-}$ was confirmed by means of absorption spectroscopy, where L^{m-} denotes an unsaturated heteropolytungstate anion of P, Si, or Ge, while clear evidence for the complexation of $BW_{11}O_{39}^{9-}$ was not obtained. Electrochemical behaviors of heteropolytungstocerates(III) were studied by cyclic and differential pulse voltammetry in aqueous solution. The redox potential of the cerium(IV/III) couple was considerably lowered (below +1 V vs Ag/AgCl) upon coordination of heteropolytungstate in aqueous solution at pH 4.5. The magnitude of the potential shift for $[CeL]^{(m-3)-}$ increased in the order $PW_{11}O_{39}^{7-}$, $P_2W_{17}O_{61}^{10-}$, $GeW_{11}O_{39}^{8-}$, and $SiW_{11}O_{39}^{8-}$. A similar trend was observed for $[CeL_2]^{(2m-3)-}$ with larger potential shift than those of $[CeL]^{(m-3)-}$. The shift of the redox potential for cerium(IV/III) is caused primarily by the large negative charge of the unsaturated heteropolytungstate.

Introduction

The tetravalent states of rare earth metals are usually unstable in aqueous solution. For example, it had been said that terbium-(IV) can exist only in the solid phase and not exist in the liquid phase because of the high redox potential of the terbium(IV/III) couple (+3.3 V vs. NHE).[1] Cerium(IV) is relatively stable both in aqueous solutions and solid states. In 1 M perchloric acid, the redox potential of cerium(IV/III) couple is about +1.7 V vs NHE.[2] The redox potential varies in different acid solutions and also depends upon the pH and the concentration of the complexing anions of the acids. The oxidation potential for cerium(III) is, for example, +1.44 V in 1 M sulfuric acid and +1.61 V vs. NHE in 1 M nitric acid.[2] The cerium(IV/III) redox potential is a function of the negative charge of the ligands and the ratio of the stability constants of the cerium(IV) and cerium(III) complexes. The negative charge of the ligand raises the metal orbital by σ-donation and electrostatic effect. Coordination of the negatively charged ligand destabilizes the metal-centered electron and results a cathodic shift of the oxidation potential. The relation between the stability constants and redox potentials was reported for the other rare earth metal ions.[3,4] We attempted to prepare complexes of stabilized tetravalent cerium on the basis of the viewpoint above for the reason that the redox potential for cerium(IV/III) can be lowered to a convenient potential region for conventional voltammetry, since cerium has less positive potential for (IV/III) pairs than other rare earth metals have. Stabilization in this manner can be applied to other rare earth metals.

In previous studies,[5–8] it was confirmed that in the presence of an unsaturated (or lacunary) heteropolytungstate anion, $PW_{11}O_{39}^{7-}$ or $P_2W_{17}O_{61}^{10-}$, terbium(III) is easily oxidized to terbium(IV) in

strong acidic solution by potassium peroxodisulfate. It was considered that tetravalent state of terbium is stabilized by formation of the $[Tb^{IV}L_2]^{(2m-4)-}$ complex. The structures of these $[Tb^{IV}L_2]^{(2m-4)-}$ complexes might be similar to those of $Cs_{12}[U^{IV}-(GeW_{11}O_{39})_2]\cdot13-14H_2O^9$ and $K_{16}[Ce^{IV}(P_2W_{17}O_{61})_2]\cdot50H_2O,^{10}$ in which the central metal ion could accept electrons from the highly negative anions and be shielded from the external environments.

The above two factors must be important for the stabilization of the tetravalent state of rare earth metals. However, studies on the stabilization of the tetravalent state of rare earth metals by an unsaturated heteropolytungstate anion have been limited to qualitative ones by means of UV–vis absorption and ESR spectroscopies.[5–8] On the other hand, the chemistry of heteropolytungstate has not been clarified. When solutions of Keggin or Dawson type heteropolytungstate anions are treated with base, a complex series of hydrolysis reactions occur, leading to a variety of lacunary anions. Such decomposition and isomerization reactions are affected by conditions of pH, temperature, etc.[11] These lacunary polyanions act as ligand for metal ions. In spite of the variety of the complexes with metal ions, their chemistry has not been investigated enough. In many cases, reports have been limited to synthesis, analysis, and a discussion of the ligand field spectrum of the metal ion, and no formation constants have been published. In general, these complexes are stable at pH ca. 4–8. In acidic solutions the complexes lose the metal ions and the lacunary ligands are converted to initial Keggin or Dawson anions.[11] It is reported that the 1:2 complexes for rare earth metal(III) ions with lacunary polyanions derived from Keggin or Dawson type heteropolytungstate anions.[11,12] These 1:2 complexes also react with acid or base, leading to decomposition, hydrolysis, or protonation reactions.[11]

In this study, the potentials and reversibilities for cerium(IV/III) couple were investigated for cerium(III) complexes with a variety of unsaturated heteropolytungstate anions by cyclic and differential pulse voltammetry. Complexation of the heteropolytungstate anions with cerium(III) ion was discussed by use of

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UV–vis absorption spectroscopy. To make clear the influence by dissociation of cerium(III) complex, all measurements were made for the isolated complexes and mixed solutions with various molar ratio of cerium(III) and unsaturated heteropolytungstate anions. The effects of the heteroatom (P, Si, Ge, B) and structure (monovacant Keggin or Dawson derivative) of the unsaturated heteropolytungstate anion on the stabilization of tetravalent state of cerium in aqueous solution were discussed.

Experimental Section

Materials and Preparations. Rare earth metal nitrates and sulfate were prepared from rare earth metal oxides (99.9%) (Shiga Rare Metals & Chemicals Co.).

Heteropolytungstates and their complexes with rare earth metals were obtained by modifications of literature procedures as described below.

$K_7PW_{11}O_{39} \cdot nH_2O$.[13] Dodecatungstophosphoric acid, 20 g, was dissolved in 100 mL of hot water. One gram of solid potassium chloride was added to this solution. Aqueous solution of 1 M potassium hydrogencarbonate was added dropwise under vigorous stirring until pH of the suspension becomes 5. After several minutes, the reaction mixture was filtered with a membrane filter. The filtrate was concentrated and allowed to stand at room temperature. The white crystalline salt that developed was recrystallized from hot water. Anal. Calcd for $K_7PW_{11}O_{39} \cdot 12H_2O$: K, 8.64; P, 0.98; W, 63.85; H, 0.77. Found: K, 8.7; P, 0.96; W, 64.0; H, 0.74.

$K_{8-x}Na_xSiW_{11}O_{39} \cdot nH_2O$.[13,14] Sodium tungstate dihydrate, 90.7 g, was dissolved in 150 mL of water. Sodium metasilicate, 3.05 g, was added to this solution. The mixture was stirred and heated. A 100-mL portion of 4 M hydrochloric acid was added dropwise to the hot solution under vigorous stirring. The solution was boiled for about 1 h and cooled to room temperature. White salt was precipitated upon adding 37.5 g of solid potassium chloride. The salt was recrystallized from hot water. Anal. Calcd for $K_6Na_2SiW_{11}O_{39} \cdot 13H_2O$: K, 7.36; Na, 1.44; Si, 0.88; W, 63.41; H, 0.82. Found: K, 7.4; Na, 1.4; Si, 0.92; W, 63; H, 0.82.

$K_{8-x}Na_xGeW_{11}O_{39} \cdot nH_2O$.[13,14] A 2.092-g portion of germanium dioxide was dissolved in 40 mL of 1 M sodium hydroxide solution. An aqueous solution containing 72.6 g of sodium tungstate dihydrate in 120 mL of water was added to the solution. The mixture was stirred and heated. A 80-mL portion of 4 M hydrochloric acid was added dropwise to the hot solution under vigorous stirring. The solution was boiled for about 1 h and cooled to room temperature. A white salt was precipitated upon addition of 30 g of solid potassium chloride. The salt was recrystallized from hot water. Anal. Calcd for $K_6Na_2GeW_{11}O_{39} \cdot 13H_2O$: K, 7.25; Na, 1.42; Ge, 2.25; W, 62.54; H, 0.81. Found: K, 7.4; Na, 1.4; Ge, 2.0; W, 63; H, 0.82.

$K_{9-(x+y)}Na_xH_yBW_{11}O_{39} \cdot nH_2O$.[11,15] Boric acid, 5 g, was dissolved in a solution of 72.5 g of sodium tungstate dihydrate in 300 mL of water. The pH of solution was adjusted at 6.1 with hydrochloric acid. The solution was boiled for about 1 h. After boiling, 40 g of solid potassium chloride was added to the hot solution. A white cubic salt was crystallized by cooling the solution to room temperature. The salt was recrystallized from hot water. Anal. Calcd for $K_7NaHBW_{11}O_{39} \cdot 13H_2O$: K, 8.58; Na, 0.72; B, 0.34; W, 63.41; H, 0.86. Found: K, 8.1; Na, 0.75; B, 0.32; W, 65; H, 0.83.

$K_{10}P_2W_{17}O_{61} \cdot nH_2O$.[16] Sodium tungstate dihydrate, 100 g, was dissolved in hot water. Phosphoric acid was added to this hot solution in a 1:4 ratio of $Na_2WO_4 \cdot 2H_2O/H_3PO_4$. The mixture was boiled for about 5 h with stirring. A few drops of concentrated nitric acid were added to the hot solution after boiling. The $K_6P_2W_{18}O_{62} \cdot nH_2O$ salt was obtained by adding solid potassium chloride after cooling the solution. The pure salt was obtained by reprecipitation with a concentrated aqueous solution of potassium chloride and recrystallization from water.

$K_{10}P_2W_{17}O_{61} \cdot nH_2O$ was precipitated by adding 10% aqueous solution of potassium hydrogencarbonate dropwise to a saturated aqueous solution with $K_6P_2W_{18}O_{62} \cdot nH_2O$ under vigorous stirring. A white salt was filtrated and recrystallized from hot water. Anal. Calcd for $K_{10}P_2W_{17}O_{61} \cdot 17H_2O$: K, 8.04; P, 1.27; W, 64.30; H, 0.71. Found: K, 8.1; P, 1.27; W, 62.8; H, 0.69.

$K_{11}[RE(PW_{11}O_{39})_2] \cdot nH_2O$ (RE = La, Ce, Gd, Tb).[17] Dodecatungstophosphoric acid, 20 g, was dissolved in hot water. Concentrated rare earth metal(III) nitrate solution was added to the hot solution in a molar proportion $(H_3PW_{12}O_{40}:RE(NO_3)_3)$ of 2:1. Then concentrated potassium acetate solution (20 g of potassium acetate in 20 mL of water; pH was adjusted at 7 with acetic acid or nitric acid) was added dropwise under vigorous stirring. After being allowed to stand for several minutes, the reaction mixture was filtered with a membrane filter. When the filtrate was cooled to 5 °C, the desired salt was precipitated completely. The salt was recrystallized from water at least three times and dried in a desiccator over P_2O_5. Anal. Calcd for $K_{11}[La(PW_{11}O_{39})_2] \cdot 18H_2O$: K, 6.88; W, 64.74; H, 0.58. Found: K, 6.9; W, 66; H, 0.57. Calcd for $K_{11}[Ce(PW_{11}O_{39})_2] \cdot 17H_2O$: K, 6.90; Ce, 2.25; P, 0.99; W, 64.91; H, 0.55. Found: K, 6.8; Ce, 2.00; P, 0.99; W, 63.8; H, 0.56. Calcd for $K_{11}[Gd(PW_{11}O_{39})_2] \cdot 17H_2O$: K, 6.88; Gd, 2.52; W, 64.73; H, 0.55. Found: K, 6.9; Gd, 2.59; W, 67; H, 0.55. Calcd for $K_{11}[Tb(PW_{11}O_{39})_2] \cdot 10H_2O$: K, 7.02; Tb, 2.60; W, 66.05; H, 0.33. Found: K, 6.5; Tb, 2.58; W, 66; H, 0.34.

$K_{13}[RE(SiW_{11}O_{39})_2] \cdot nH_2O$ (RE = Ce, Tb).[12] Dodecatungstosilicic acid, 20 g, was dissolved in 40 mL of hot water. Concentrated rare earth metal(III) nitrate solution was added to the hot solution in a molar proportion $(H_4SiW_{12}O_{40}:RE(NO_3)_3)$ of 2:1. Concentrated potassium acetate solution (16 g of potassium acetate in 20 mL of water; pH was adjusted at 7 with acetic acid) was added dropwise under vigorous stirring. After several minutes, the solution was filtered with a membrane filter. When the filtrate was cooled to room temperature, an oil separated out at the bottom of the beaker and crystallized in a refrigerator. The crystals were filtered and recrystallized from water three times or more and dried in a desiccator over P_2O_5. Anal. Calcd for $K_{13}[Ce(SiW_{11}O_{39})_2] \cdot 15H_2O$: K, 8.11; Ce, 2.24; Si, 0.90; W, 64.53; H, 0.48. Found: K, 8.1; Ce, 2.16; Si, 0.92; W, 69; H, 0.49. Calcd for $K_{13}[Tb(SiW_{11}O_{39})_2] \cdot 14H_2O$: K, 8.11; Tb, 2.54; Si, 0.90; W, 64.53; H, 0.45. Found: K, 7.8; Tb, 2.57; Si, 0.88; W, 65; H, 0.46.

$K_{13}[Ce(GeW_{11}O_{39})_2] \cdot nH_2O$.[18,19] Sodium tungstate dihydrate, 27.2 g, was dissolved in 100 mL of hot water. A 26.9-g portion of tungsten trioxide was added to the solution and suspended. The suspension was boiled and stirred. After the addition of 1.73 g of germanium dioxide, 2.5 g of sodium carbonate was added little by little to the hot suspension. A clear solution was obtained after 3 h. Concentrated hydrochloric acid, 30 mL was added dropwise under vigorous stirring. White precipitates were developed upon cooling in a cold water bath and filtered off. By addition of 100 mL of ether to the filtrate, dodecatungstogermanic acid was separated in the lowest, thick, and yellowish layer of the three layers. The acid $H_4GeW_{12}O_{40} \cdot 13H_2O$ was obtained by evaporation to dryness of the ether extract and dried in vacuo.

Concentrated cerium(III) nitrate solution (2.6 g of $Ce(NO_3)_3 \cdot 6H_2O$ in a small amount of water) was added to the hot solution of 37.896 g (0.012 mol) of $H_4GeW_{12}O_{40} \cdot 13H_2O$. Potassium acetate, 40 g, in 40 mL of water (pH was adjusted at 7 with acetic acid) was added dropwise under vigorous stirring. After several minutes, the solution was filtered with a membrane filter. When the filtrate was cooled to room temperature, an oily substance formed at the bottom of the beaker and was crystallized in a refrigerator. The crystals were filtered and recrystallized from water more than two times and dried over P_2O_5 in a desiccator. Anal. Calcd for $K_{13}[Ce(GeW_{11}O_{39})_2] \cdot 21H_2O$: K, 7.86; Ce, 2.17; Ge, 2.25; W, 62.57; H, 0.66. Found: K, 7.7; Ce, 2.04; Ge, 2.3; W, 65; H, 0.66.

$K_{15}[Ce(BW_{11}O_{39})_2] \cdot nH_2O$.[17] Sodium tungstate dihydrate, 36.3 g, was dissolved in 150 mL of water, and the pH was adjusted at 6.3 with acetic acid. A 2.5-g portion of boric acid was added, and the mixture was heated to 80 °C. Concentrated cerium(III) nitrate solution (2.17 g of $Ce(NO_3)_3 \cdot 6H_2O$ in a small amount of water) was added dropwise under vigorous stirring, followed by an addition of 20 g of potassium chloride. After filtration of the white precipitates formed, the filtrate was concentrated to 70 mL at 80 °C and cooled to room temperature. Brown crystals were obtained by allowing the solution to stand for about 1 week. The brown crystals obtained were recrystallized from water and dried in a desiccator over P_2O_5. Anal. Calcd for $K_{15}[Ce(BW_{11}O_{39})_2] \cdot 20H_2O$: K, 9.16; Ce, 2.19; W, 63.19; H, 0.63. Found: K, 9.0; Ce, 2.54; W, 68; H, 0.63.

$K_{17}[Ce(P_2W_{17}O_{61})_2] \cdot nH_2O$.[20] Aqueous solution containing 2.17 g of $Ce(NO_3)_3 \cdot 6H_2O$ was added to a hot solution of 47.8 g of K_6P_2-

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$W_{18}O_{62} \cdot 10H_2O$. Concentrated potassium acetate solution (40 g of potassium acetate in 50 mL of water; pH was adjusted at 7 with acetic acid) was added slowly under vigorous stirring. When the solution was cooled to 5 °C, a dark brown salt was precipitated completely. The salt was recrystallized from water three times or more and dried over P_2O_5 in a desiccator. Anal. Calcd for $K_{17}[Ce(P_2W_{17}O_{61})_2] \cdot 31H_2O$: K, 6.86; Ce, 1.45; P, 1.28; W, 64.51; H, 0.65. Found: K, 6.7; Ce, 1.30; P, 1.18; W, 62.5; H, 0.64.

Chemical Analyses. Determination of each element was interfered with by the presence of the other components in these compounds, and the analytical method and pretreatment must be carefully considered for each heteropolytungstate or cerium(III) complex. For example, tungsten in potassium tungstophosphate or the complex with cerium(III) was determined by EDTA back-titration[21] and tungsten in the other compounds in which the heteroatom was silicon, germanium, or boron was determined by atomic absorption spectrometry. The significant figures and the errors depend on the analytical procedure for each heteropolytungstate compound. The preferred analytical procedures have been recently improved.

The content of potassium or sodium was determined by atomic absorption spectrometry. Silicon, germanium, and boron were determined by atomic absorption spectrometry after the alkaline decomposition of the salts. Silicon in $K_{13}[Tb(SiW_{11}O_{39})_2]$ was determined by atomic absorption spectrometry without alkaline decomposition of the complex. Phosphorus was determined by EDTA back-titration.[21] Hydrogen was determined at the Elemental Analysis Service Center, Kyushu University. The content of cerium was determined by absorption spectrophotometry with arsenazo I after the alkaline decomposition of the complex and the separation of cerium hydroxide. The content of gadolinium or terbium was determined volumetrically (back-titration of excess EDTA with manganese(II) sulfate[12]).

Measurements. Measurements were made for the isolated complexes and the mixed solutions with various molar ratios of cerium(III) and unsaturated heteropolytungstate anions.
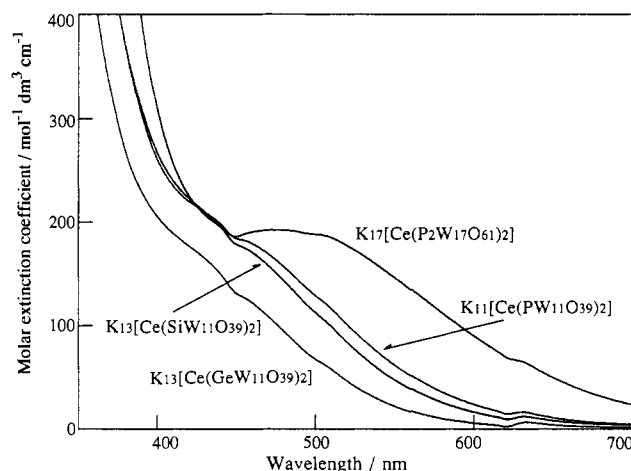
Cyclic voltammograms and differential pulse voltammograms were obtained on a HECS 312B dc pulse polarograph from Fuso Electrochemical System attached to a HECS 321B potential sweep unit of the same manufacture. A glassy-carbon disk (3.2 mm o.d.) electrode was employed as the working electrode. The electrode was polished with 0.05 μm alumina, underwent ultrasonic washing for 5 min, and was washed with water and acetone prior to every measurement. A platinum wire was used as the counter electrode. The reference electrode was a silver/ silver chloride (Ag/AgCl) electrode (BAS Inc. + 0.199 V vs NHE). The measurements were carried out at 25 °C in water (pH 4.5) containing 0.1 M sodium sulfate as the supporting electrolyte. The pH of the solution was adjusted at 4.5 with sulfuric acid or sodium hydroxide solution. The concentration of cerium(III) or cerium(III) complex was 1 mM.

Since heteropolytungstate anions and their complexes have a large negative charge, these strongly adsorbed to the electrode surface in the positive range for cyclic voltammetry and the data; in particular, the peak to peak separations (reversibility) are affected. Reproducibility is highly dependent on the polishing procedure for electrode surface. Cyclic voltammograms of these compounds were measured many times and the peak potentials were estimated on their averages.

UV–vis absorption spectra were recorded on a Jasco Ubest-50 UV/vis spectrophotometer for aqueous solutions. The concentration of cerium(III) or cerium(III) complex was 2 mM. The pH of the solution was not adjusted.

Results and Discussion

UV–Vis Absorption Spectra. UV–vis absorption spectra for various potassium bis(heteropolytungsto)cerates(III) in aqueous solutions are shown in Figure 1. In all spectra, a cerium(III) to ligand CT band was found. In the cases of the cerium(III) complexes with monovacant Keggin derivative anions [Ce-$(X^{n+}W_{11}O_{39})_2]^{(21-2n)-}$, the CT band shifted to shorter wavelength by changing the heteroatom successively from P to Si and Ge. The obvious CT band was not observed in the spectrum for the solution of $K_{15}[Ce(BW_{11}O_{39})_2]$. The cerium(III) complex with Dawson derivative anion, $[Ce(P_2W_{17}O_{61})_2]^{17-}$, showed a distinct CT band at longer wavelength than that for the the corresponding

Figure 1. Absorption spectra for 2 mM aqueous solutions of $K_{11}[Ce(PW_{11}O_{39})_2]$, $K_{17}[Ce(P_2W_{17}O_{61})_2]$, $K_{13}[Ce(GeW_{11}O_{39})_2]$, and $K_{13}[Ce(SiW_{11}O_{39})_2]$.

Keggin derivative while the latter gave an overlapping of the CT band with a tail of an intense absorption band.

The absorption spectra were obtained for aqueous solutions of cerium(III) containing an unsaturated heteropolytungstate anion in various concentrations. The mixed solution at a ratio of 1:2 or 1:3 for $PW_{11}O_{39}^{7-}$, $SiW_{11}O_{39}^{8-}$, $GeW_{11}O_{39}^{8-}$, or $P_2W_{17}O_{61}^{10-}$ showed a similar absorption spectrum to that for the corresponding complex, $[CeL_2]^{(2m-3)-}$, suggesting strongly that the complex $[CeL_2]^{(2m-3)-}$ was formed in the solution. But the mixed solution at ratio of 1:0.5 or 1:1 showed a smaller absorption band than that for $[CeL_2]^{(2m-3)-}$. These observations showed that the complexation between heteropolytungstate anion and cerium(III) took place stepwise. Peacock and Weakley also reported that $[CeL]^{(m-3)-}$ is formed before the formation of $[CeL_2]^{(2m-3)-}$.[12] This consecutive complex formation could be confirmed by cyclic voltammetry as described below. The mixed solution could not be prepared for $BW_{11}O_{39}^{9-}$, because of precipitation.

Electrochemical Properties. Cerium(III) sulfate in aqueous solution at pH 4.5 showed no redox waves in the potential range from −1 to +1 V vs Ag/AgCl under voltammetric conditions. The heteropolytungstate anions except $P_2W_{17}O_{61}^{10-}$ in aqueous solution at pH 4.5 gave no redox waves in the positive potential range under the conditions for cyclic and differential pulse voltammetry, while showing several redox waves around 0 V or in the negative potential range. The cyclic voltammogram for $PW_{11}O_{39}^{7-}$ anion in aqueous solution is shown as an example at the top of Figure 2. For $P_2W_{17}O_{61}^{10-}$, small broad redox peaks were also observed near at +0.05 V in addition to those in the negative potential range. These waves are due to the redox processes of the heteropolytungstate anions. The cyclic voltammograms for $K_{11}[La(PW_{11}O_{39})_2]$ and $K_{11}[Ce(PW_{11}O_{39})_2]$ in aqueous solution are shown in Figure 2. Figure 3 shows cyclic voltammograms for mixed aqueous solutions of various molar ratios of cerium(III) to $PW_{11}O_{39}^{7-}$. The waves attributable to the redox processes of $PW_{11}O_{39}^{7-}$ in the negative potential range were shifted to lower potential by complexation between the rare earth metal(III) (La or Ce) and $PW_{11}O_{39}^{7-}$. But no wave in the positive potential range was observed in the cyclic voltammogram for $K_{11}[La(PW_{11}O_{39})_2]$. $K_{11}[Gd(PW_{11}O_{39})_2]$ and $K_{11}[Tb(PW_{11}O_{39})_2]$ also showed no redox waves in this region. Redox wave(s) in the positive region is, therefore, assigned to redox process(es) of complexed cerium ion. Similar behaviors were observed in the cases of $SiW_{11}O_{39}^{8-}$, $GeW_{11}O_{39}^{8-}$, or $P_2W_{17}O_{61}^{10-}$. In all measurements potential sweep were carried out for negative and positive ranges, but the negative parts are omitted for clarity in Figures 4–7.
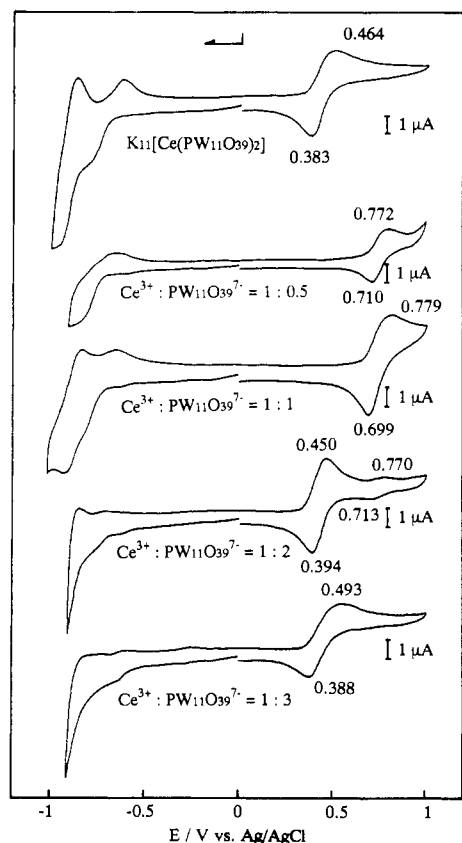
The cyclic voltammograms for the aqueous solutions of various potassium bis(heteropolytungsto)cerates(III), $K_{11}[Ce(PW_{11}O_{39})_2]$,

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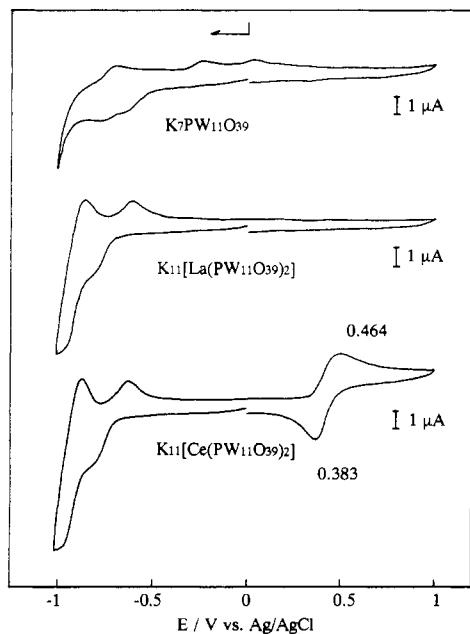
Figure 2. Cyclic voltammograms for $K_7PW_{11}O_{39}$ and $K_{11}[RE(PW_{11}O_{39})_2]$ in aqueous solution at pH 4.5 Concentration of the tungstate or rare earth metal(III) complex is 1 mM. Concentration of supporting electrolyte, Na_2SO_4, was adjusted to 0.1 M. Potential sweep rate was 10 mV s^{-1}.

Figure 3. Cyclic voltammograms for 1 mM $K_{11}[Ce(PW_{11}O_{39})_2]$ and 0.5 mM $Ce_2(SO_4)_3$ with various molar ratio of $PW_{11}O_{39}{}^{7-}$ anion in 0.1 M Na_2SO_4 aqueous solutions at pH 4.5. Potential sweep rate was 10 mV s^{-1}.

$K_{17}[Ce(P_2W_{17}O_{61})_2]$, $K_{13}[Ce(GeW_{11}O_{39})_2]$, and $K_{13}[Ce(Si-W_{11}O_{39})_2]$ are shown in Figure 4. The cyclic voltammograms for the mixed aqueous solutions of the molar ratios of cerium(III) to unsaturated heteropolytungstate anions 1:1 and 1:2 are shown in Figures 5 and 6, respectively. The reversibility of the electrode reaction was examined from the separation of the redox peaks,
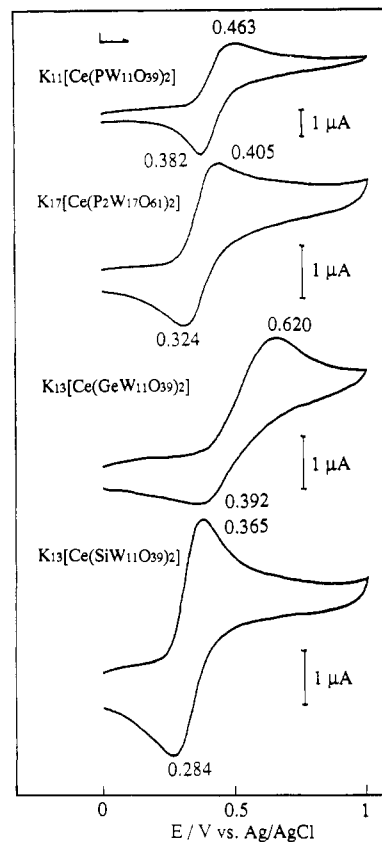
Figure 4. Cyclic voltammograms for 1 mM $K_{11}[Ce(PW_{11}O_{39})_2]$, K_{17}-$[Ce(P_2W_{17}O_{61})_2]$, $K_{13}[Ce(GeW_{11}O_{39})_2]$, and $K_{13}[Ce(SiW_{11}O_{39})_2]$ in 0.1 M Na_2SO_4 aqueous solutions at pH 4.5. Potential sweep rate was 10 mV s^{-1}.

$\Delta E_p = E_{pa} - E_{pc}$, and the ratio of peak currents, I_{pa}/I_{pc}, in the cyclic voltammogram, where E_p and I_p stand for peak potential and peak current, respectively. The half-peak width of the wave in the differential pulse voltammogram was also adopted to examine the reversibility. The voltammetric results are summarized in Tables 1 and 2. Potentials were reproducible on repeated runs.

Cerium(III)–PW$_{11}$O$_{39}$$^{7-}$ System. The cyclic voltammogram for $K_{11}[Ce(PW_{11}O_{39})_2]$ in aqueous solution (Figures 2–4) indicated one redox wave near at $E_{1/2}$ ($=(E_{pc} + E_{pa})/2$) = +0.42 V vs. Ag/AgCl with peak separation (ΔE_p) of about 80 mV. These waves are attributable to a reaction described as follows:

$$[Ce^{III}(PW_{11}O_{39})_2]^{11-} \rightleftharpoons [Ce^{IV}(PW_{11}O_{39})_2]^{10-} + e^-$$
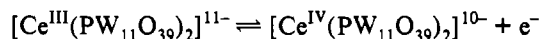
It is confirmed that the redox potential of cerium(IV/III) couple drops by about 1 V by complexation of cerium(III) and $PW_{11}O_{39}{}^{7-}$. The solution of $K_{11}[Ce(PW_{11}O_{39})_2]$ at pH 4.5 were stable for at least 47 days as judged by cyclic voltammetry.

Figure 3 shows cyclic voltammograms for mixed aqueous solutions of various molar ratios of cerium(III) to $PW_{11}O_{39}{}^{7-}$. At the ratios 1:0.5 and 1:1, a single redox wave was observed approximately at $E_{1/2}$ = +0.74 V with ΔE_p = 60–80 mV. At ratios of 1:2 and 1:3, a large redox wave and a very small one were found nearly at $E_{1/2}$ = +0.42 and +0.74 V, respectively. Even in the cyclic voltammograms for the 1:2 mixed solutions prepared under the different conditions of pH, solution age, and temperature, the additional small waves were also observed near at $E_{1/2}$ = +0.74 V.

From the above observations, it is suggested that in the presence of $PW_{11}O_{39}{}^{7-}$, cerium(III) reacts with $PW_{11}O_{39}{}^{7-}$ to give $[CePW_{11}O_{39}]^{4-}$ and $[Ce(PW_{11}O_{39})_2]^{11-}$ complexes and accordingly shows redox waves at $E_{1/2}$ = +0.74 and +0.42 V, respectively. This presumption is in accord with that considered from UV–vis absorption study.
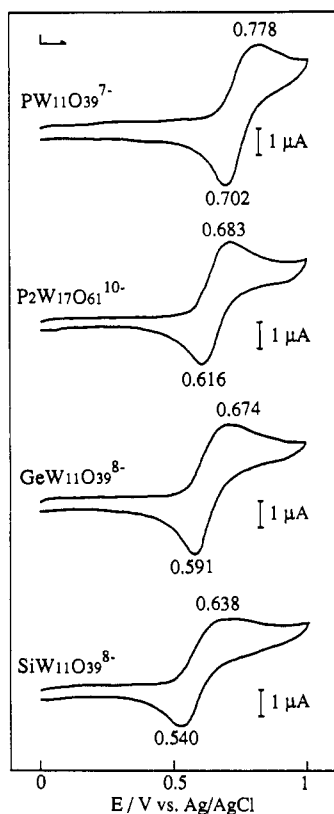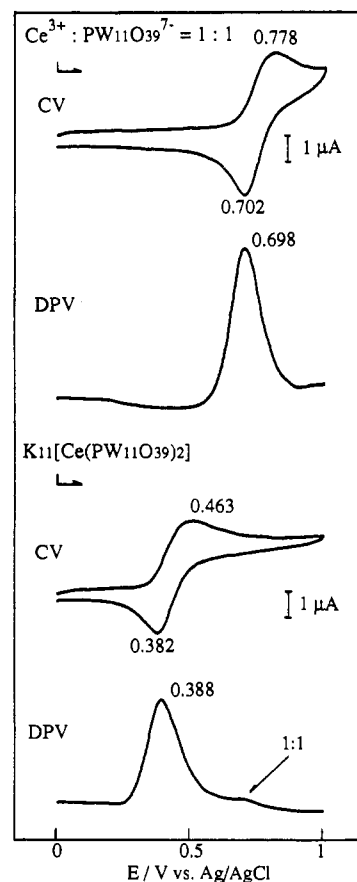
Figure 5. Cyclic voltammograms for 0.5 mM $Ce_2(SO_4)_3$ in the presence of 1 mM $PW_{11}O_{39}^{7-}$, $P_2W_{17}O_{61}^{10-}$, $GeW_{11}O_{39}^{8-}$, and $SiW_{11}O_{39}^{8-}$ anions in 0.1 M Na_2SO_4 aqueous solutions at pH 4.5. Potential sweep rate was 10 mV s^{-1}.
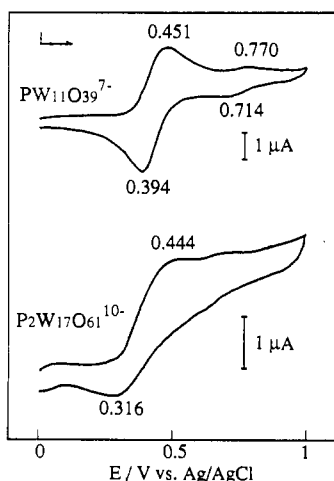
Figure 6. Cyclic voltammograms of 0.5 mM $Ce_2(SO_4)_3$ in the presence of 2 mM $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$ anions in 0.1 M Na_2SO_4 aqueous solutions at pH 4.5. Potential sweep rate was 10 mV s^{-1}.

Figure 7 shows the differential pulse voltammograms for K_{11}-$[Ce(PW_{11}O_{39})_2]$ in aqueous solution at pH 4.5 for 5 h after preparation. The peak at E_p = +0.39 V could be assigned to the $[Ce(PW_{11}O_{39})_2]^{11-}$ complex. A small peak appeared nearly at E_p = +0.7 V. It is likely to be due to the $[CePW_{11}O_{39}]^{4-}$ complex from the above discussion and the differential pulse voltammogram for the 1:1 mixed solution shown in Figure 7. It is explained that the $[Ce(PW_{11}O_{39})_2]^{11-}$ complex is fairly stable in aqueous solution at pH 4.5, but a small part of the $[Ce(PW_{11}O_{39})_2]^{11-}$ complex dissociates to give the $[CePW_{11}O_{39}]^{4-}$ complex.

Cerium(III)–SiW_{11}O_{39}^{8-} System. The complex $K_{13}[Ce-(SiW_{11}O_{39})_2]$ in aqueous solution showed a pair of redox waves like that for $K_{11}[Ce(PW_{11}O_{39})_2]$ (Figure 4). The half-wave potential, $E_{1/2}$, was at +0.32 V with ΔE_p of 80 mV. The waves are attributed to the cerium(IV/III) redox processes of the

Figure 7. Cyclic voltammograms and differential pulse voltammograms for 0.5 mM $Ce_2(SO_4)_3$ in the presence of 1 mM $PW_{11}O_{39}^{7-}$ anion and 1 mM $K_{11}[Ce(PW_{11}O_{39})_2]$ in 0.1 M Na_2SO_4 aqueous sotluions at pH 4.5. Potential sweep rate was 10 mV s^{-1}. Pulse amplitude was 50 mV. Electrolysis time by pulse was 100 ms. Sampling time was 20 ms. Pulse repetition time was 0.2 s.

Table 1. Cyclic Voltammetric Results of Potassium Bis(heteropolytungsto)cerates(III) in Aqueous Solution at 25 °C

salt	E_{pc}/V^a	E_{pa}/V^a	$E_{1/2}{}^b$/V^a	$\Delta E_p{}^c$/mV
$K_{11}[Ce(PW_{11}O_{39})_2]$	0.383	0.464	0.424	81
$K_{17}[Ce(P_2W_{17}O_{61})_2]$	0.324	0.405	0.365	81
$K_{13}[Ce(GeW_{11}O_{39})_2]^d$	(0.392)	(0.620)		
$K_{13}[Ce(SiW_{11}O_{39})_2]$	0.283	0.363	0.323	80

^{a} Potential (vs Ag/AgCl) measured in 0.1 M Na_2SO_4 at pH 4.5. ^{b} (E_{pc} + E_{pa})/2. ^{c} E_{pa} – E_{pc}. ^{d} Unstable at pH 4.5.

Table 2. Cyclic Voltammetric Results of $Ce_2(SO_4)_3$ in the presence of Unsaturated Heteropolytungstate Anions in Aqueous Solution at 25 °C

anion	complex	E_{pc}/V^a	E_{pa}/V^a	$E_{1/2}{}^b$/V^a	$\Delta E_p{}^c$/mV
$PW_{11}O_{39}^{7-}$	1:1	0.701	0.779	0.740	78
	1:2	0.394	0.451	0.423	57
$P_2W_{17}O_{61}^{10-}$	1:1	0.617	0.685	0.651	68
	1:2	0.316^d	0.444^d		
$GeW_{11}O_{39}^{8-}$	1:1	0.592	0.671	0.632	79
	1:2	n.d.^{e}	n.d.^{e}		
$SiW_{11}O_{39}^{8-}$	1:1	0.541	0.638	0.590	97
	1:2	n.d.^{e}	n.d.^{e}		

^{a} Potential (vs Ag/AgCl) measured in 0.1 M Na_2SO_4 at pH 4.5. ^{b} (E_{pc} + E_{pa})/2. ^{c} E_{pa} – E_{pc}. ^{d} Broad peak affected by 1:1 complex. ^{e} Peak was not detected.

$[Ce(SiW_{11}O_{39})_2]^{13-}$ complex, because corresponding waves were not observed in case of $SiW_{11}O_{39}^{8-}$ or $K_{13}[Tb(SiW_{11}O_{39})_2]$.

Redox behaviors of the mixed solutions of cerium(III) and $SiW_{11}O_{39}^{8-}$ at lower concentration of the latter were similar to the case of cerium(III) and $PW_{11}O_{39}^{7-}$ except for the half-wave potentials (Figure 5). The half-wave potential of the former case

was +0.59 V and was 0.27 V higher than that of $K_{13}[Ce(SiW_{11}O_{39})_2]$. But at ratios of 1:2 and 1:4, no wave was not observed clearly. The $[Ce(SiW_{11}O_{39})_2]^{13-}$ complex is probably hydrolyzed in this system. In fact, the aqueous solution for $K_{13}[Ce(SiW_{11}O_{39})_2]$ showed an obvious redox wave at +0.32 V immediately after preparation, while the redox wave broadened over 2 h.

The differential pulse voltammograms for the aqueous solution of $K_{13}[Ce(SiW_{11}O_{39})_2]$ and the 1:1 mixed solution showed that the reversibility for the cerium(IV/III) wave of the $[CeSiW_{11}O_{39}]^{5-}$ complex is lower than that of the $[CePW_{11}O_{39}]^{4+}$ complex. It is attributed to the hydrolysis of the $[CeSiW_{11}O_{39}[^{5-}$ complex as well as $[Ce(SiW_{11}O_{39})_2]^{13-}$.

Cerium(III)–$GeW_{11}O_{39}{}^{8-}$ System. In the case of the aqueous solution of $K_{13}[Ce(GeW_{11}O_{39})_2]$, a considerably broad voltammogram was obtained (Figure 4). The mixed solutions of cerium-(III) ion and $GeW_{11}O_{39}{}^{8-}$ showed redox behaviors similar to those of $SiW_{11}O_{39}{}^{8-}$. At the ratios 1:0.5 and 1:1 (Figure 5), one redox wave was observed near $E_{1/2}$ = +0.63 V, and at the ratios 1:2 and 1:4, only broad voltammograms were obtained. It is reckoned that in the case of $GeW_{11}O_{39}{}^{8-}$, the $[Ce(GeW_{11}O_{39})_2]^{13-}$ complex is also unstable in aqueous solution at pH 4.5, similar to the case of $K_{13}[Ce(SiW_{11}O_{39})_2]$. The reversibility for the cerium(IV/III) wave of the $[CeGeW_{11}O_{39}]^{5-}$ complex was very close to that of the $[CePW_{11}O_{39}]^{4+}$ complex judged from each half-peak width.

Cerium(III)–$BW_{11}O_{39}{}^{9-}$ System. In case of $BW_{11}O_{39}{}^{9-}$, experimental evidence for the formation of stable complexes, $[CeBW_{11}O_{39}]^{6-}$ and $[Ce(BW_{11}O_{39})_2]^{15-}$, was not obtained as mentioned earlier. In spite of the fact that the isolated salt had a composition of $K_{15}[Ce(BW_{11}O_{39})_2]$, the aqueous solution of it at pH 4.5 changed from yellowish brown to pale yellow. This color change is due probably to some decomposition of the complex such as hydrolysis. The voltammogram was, therefore, measured for the sample solution without the adjustment of pH (6.2). A large redox wave and a small one were found nearly at $E_{1/2}$ = +0.21 V with ΔE_p = 140 mV and at $E_{1/2}$ = +0.68 V with ΔE_p = 110 mV, respectively. Most likely, the waves at +0.68 V is attributable to 1:1 complex and the waves at +0.21 V to 1:2 complex. But it is considered that the $BW_{11}O_{39}{}^{9-}$ ion is of fairly distorted structure[11] and is transformed or decomposed depending on pH and several complexes between cerium(III) and $BW_{11}O_{39}{}^{9-}$ were formed even under certain condition. Additional evidences is needed to ascertain the assignments of the two redox waves.

Cerium(III)–$P_2W_{17}O_{61}{}^{10-}$ System. In the cyclic voltammogram for $K_{17}[Ce(P_2W_{17}O_{61})_2]$ in aqueous solution, a redox wave with ΔE_p = 81 mV was observed near at $E_{1/2}$ = +0.36 V for the redox couple of cerium(IV/III) for the $[Ce(P_2W_{17}O_{61})_2]^{17-}$ complex (Figure 4).

The voltammetric measurements were carried out also for mixed solutions of cerium(III) and $P_2W_{17}O_{61}{}^{10-}$ in the range of the molar ratio from 1:0.5 to 1:4. The redox behaviors for the mixed solutions of the Dawson derivative anion were very similar to those of the Keggin derivative anion, $PW_{11}O_{39}{}^{7-}$, except for the redox potential. The mixed solutions containing $P_2W_{17}O_{61}{}^{10-}$ in amounts less than or equal to the cerium(III) content had the redox potential at +0.65 V with peak separation of 68 mV attributable to $[CeP_2W_{17}O_{61}]^{7-}$ (Figure 5). The redox peak around +0.38 V was obtained for the solution containing $P_2W_{17}O_{61}{}^{10-}$ in amounts two times or more greater than the cerium(III) content. Cerium-

(III) and $P_2W_{17}O_{61}{}^{10-}$ in a 1:2 ratio showed weak redox waves at +0.65 V accompanying the main waves (Figure 6). The wave at +0.65 V is attributable to $[CeP_2W_{17}O_{61}]^{7-}$ while the wave at +0.38 V is attributable to $[Ce(P_2W_{17}O_{61})_2]^{17-}$. The solution of $K_{17}[Ce(P_2W_{17}O_{61})_2]$ at pH 4.5 appears to be comparatively stable in aqueous solution like the case of $K_{11}[Ce(PW_{11}O_{39})_2]$, while $K_{13}[Ce(SiW_{11}O_{39})_2]$ or $K_{13}[Ce(GeW_{11}O_{39})_2]$ is hydrolyzed easily.

The reversibility was considered to be higher for the cerium-(IV/III) wave of the $[CeP_2W_{17}O_{61}]^{7-}$ complex than that of $[CePW_{11}O_{39}]^{4+}$ complex from the half-peak width of the wave in a differential pulse voltammogram.

Stabilization of the Tetravalent State of Cerium in the Presence of Unsaturated Heteropolytungstate Anions. Unsaturated heteropolytungstate anions of P, Si, and Ge reacted with cerium-(III) to give complexes $[CeL]^{(m-3)-}$ and $[CeL_2]^{(2m-3)-}$ and their redox potentials for cerium(IV/III) were considerably lowered. The redox potentials of the complexes $[CeL]^{(m-3)-}$ fell in the sequence $PW_{11}O_{39}{}^{7-} < P_2W_{17}O_{61}{}^{10-} < GeW_{11}O_{39}{}^{8-} < SiW_{11}O_{39}{}^{8-}$, a similar trend was obtained for $[CeL_2]^{(2m-3)-}$, and the redox potentials were lower than those of the corresponding $[CeL]^{(m-3)-}$ complexes. This sequence orders the magnitude of the stabilization of tetravalent state of cerium.

As discussed above, the redox potential of the complexes of Keggin derivative anions is affected by the heteroatom of the anions. Two factors are presumed to be significant, i.e., valence and size. The heteroatom of low valency forms a heteropolytungstate anion of large negative charge. The large negative charge destabilizes the metal-centered orbital as mentioned earlier. The size of the heteroatom affects the bite angle of the unsaturated part of the anion. The heteropolytungstate anion with large bite angle forms a stable complex with a trivalent cerium ion rather than with a tetravalent one. The heteropolytungstate anion with a heteroatom of small and low valency is, therefore, preferable for stabilizing the tetravalent state of cerium. The negative charge of the Dawson derivative anion is larger than that of the Keggin derivative anion of the same heteroatom. From the above discussion, it is quite reasonable that the former affords a more stable tetravalent cerium complex than the latter does.

The detailed structural informations are not available for the complexes $[CeL]^{(m-3)-}$ and $[CeL_2]^{(2m-3)-}$ with unsaturated heteropolytungstate anions used in this study. However, the $PW_{11}O_{39}{}^{7-}$, $GeW_{11}O_{39}{}^{8-}$, or $SiW_{11}O_{39}{}^{8-}$ anion has a monovacant Keggin structure and $P_2W_{17}O_{61}{}^{10-}$ has a monovacant Dawson structure, undoubtedly. The unsaturated heteropolytungstate anion acts as a tetradentate ligand in the complexes $[CeL_2]^{(2m-3)-}$, and cerium(III) or cerium(IV) is presumably sandwiched in two anions and is observed in 8-fold coordination by an approximately square antiprism of oxygen atoms.[10]

The stabilization of the tetravalent state of cerium upon coordination of the heteropolytungstate anions is attributed to their large negative charge, as mentioned above. The tetravalent state of cerium, therefore, is more stable in $[CeL_2]^{(2m-3)-}$ than in $[CeL]^{(m-3)-}$.

Further studies are continuing on the pH dependence of redox potential for cerium(IV/III) and the determination of formation constant for each CeL or CeL_2 complex to elucidate the electrochemical behavior of a rare earth metal(III) complex with an unsaturated heteropolytungstate anion.