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Effects of Crown-Type Host-Guest Complexation on Electrochemical Profiles of Pb^{2+} Ion

Hiroshi TSUKUBE,* Kentaro TAKAGI, Tatsuo HIGASHIYAMA, Tadashi IWACHIDO, and Naomi HAYAMA
Department of Chemistry, College of Liberal Arts & Science, Okayama University, Okayama 700

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Synopsis. Crown ethers, cryptands, and related synthetic host molecules modified electrochemical profiles of Pb^{2+} ion by host-guest complexations. The reduction potentials of the Pb^{2+} complexes were significantly correlated with their complex stabilities.

Crown ethers, cryptands, and other synthetic host molecules specifically bind guest cations and often modify their physicochemical properties and chemical reactivities. For example, solubility, spectroscopic profile, and catalytic activity of the guest cation were demonstrated to be varied by host-guest complexation.[1]

Here we examined electrochemical properties of a series of Pb^{2+} complexes with tripodes, crown ethers, double armed crowns, and cryptand molecules, and revealed an interesting relationship between thermodynamic stabilities and reduction potentials of Pb^{2+} complexes. Since electrochemical properties of the Pb^{2+} complexes were significantly influenced by the natures and the structures of ligating host molecules, the present study may provide further possibilities in controlling redox chemistry of active guest species at will.

Results and Discussion

We employed a series of tripodes, crown ethers, and cryptands, which had various distributions, numbers, and types of donor groups (Fig. 1).[2,3] Typical cyclic voltammograms for aqueous solutions of Pb^{2+} ion in the presence and absence of double armed crown ether **8** are shown in Fig. 2. When 0.5 equiv of double armed crown ether **8** was added to a solution of Pb^{2+} ion, new reduction peak B appeared at more negative potential than that of initially observed peak A. Then peak A disappeared in the presence of ca. 1.0—2.0 equiv of **8** to Pb^{2+} ion, and only peak B remained in the presence of excess of **8**. Similar successive changes were observed in the other examined systems, and crown-type host-guest complexation may be essentially involved in such a heterogeneous electrochemical reaction.[4] Although free Pb^{2+} ion showed more positive reduction peak potential (−0.51 V) than Cd^{2+} and Zn^{2+} ions (−0.83 and −1.27 V) under the employed conditions (see Experimental), double armed crown ether **8**, and cryptands **10** and **11** modified Pb^{2+} ion less reducible than Cd^{2+} ion.

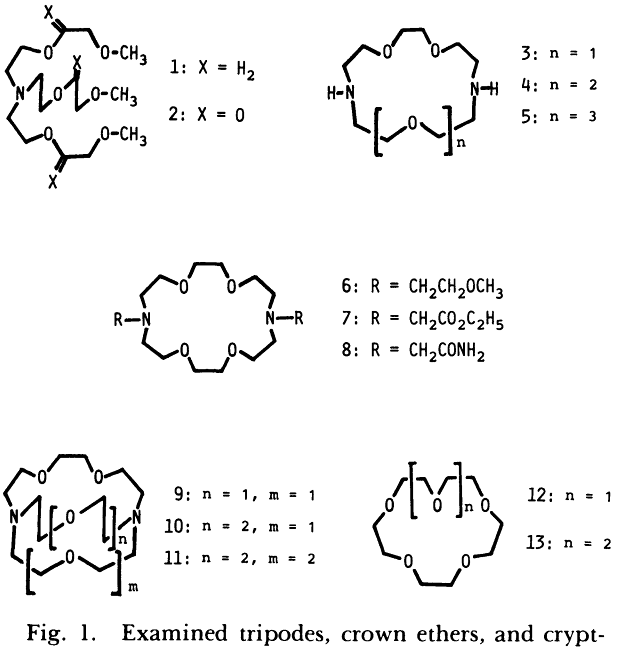

Fig. 1. Examined tripodes, crown ethers, and cryptands.

Figure 3 shows relationship between induced shifts of reduction peak potentials by complexation and stability constants for corresponding Pb^{2+} complexes.[5] It clearly indicates that redox reaction of

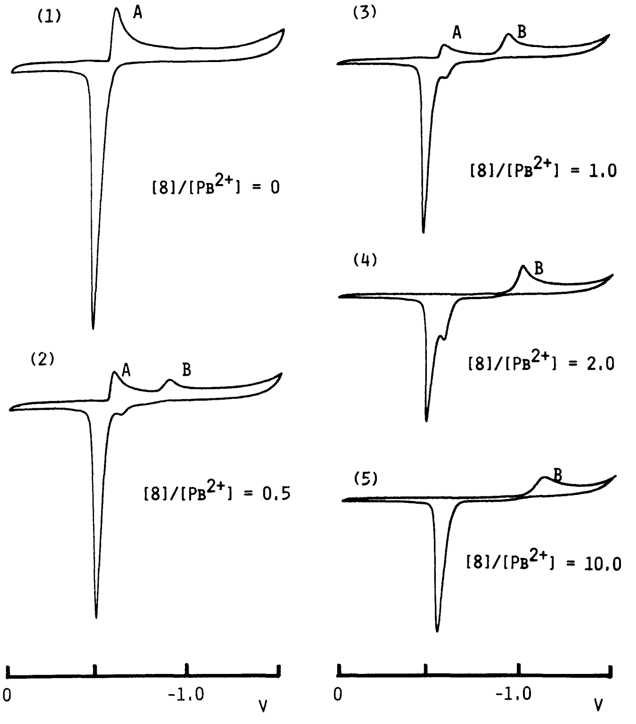

Fig. 2. Cyclic voltammograms for Pb^{2+}/Pb^0 couple in the (1) absence, (2) presence of 0.5 equiv, (3) presence of 1.0 equiv, (4) presence of 2.0 equiv, and (5) presence of 10.0 equiv of double armed crown ether **8**. $Pb(ClO_4)_2$, 6.1×10^{-4} M.

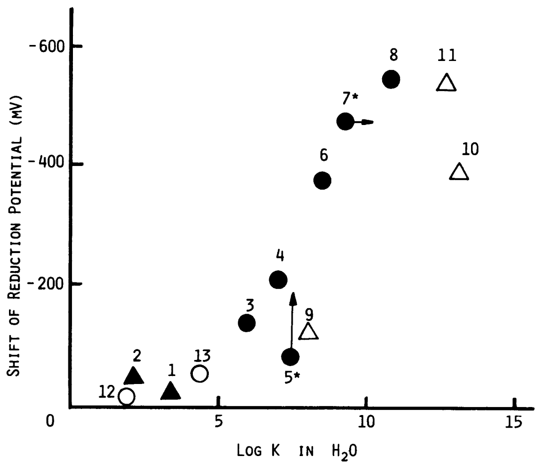

Fig. 3. Relationship between induced shift in reduction potential of Pb^{2+} complex and its stability constant in H_2O.

▲ tripodes **1** and **2**, ● aza-crown ethers **3—8**, △ crystands **9—11**, ○ oxa-crown ethers **12** and **13**.

*Log *K* for aza-crown ether **7** was obtained as higher than 8.7.

Since aza-crown ether **5** and/or its Pb^{2+} complex were suspended under the employed electrochemical conditions. The shift value indicated was estimated as smaller.

Pb^{2+} complex largely depended on the nature and the structure of the ligating molecule. The relationship is almost sigmoidal and provides some indication of the structures of the Pb^{2+} complexes with the various ligands. Interestingly, double armed crown ethers **6—8** and cryptands **10—11** showed greater induced shifts in the reduction potentials than tripodes and simple crown ethers. Since ^{13}C NMR studies have strongly suggested that these host molecules could completely wrap around the electroactive Pb^{2+} ion and effectively shield it from the surroundings,[6] they markedly inhibited electron transfer reaction and offered much negative reduction potentials. These observations offer an interesting method for correlating the stability constants and electrode potentials for the Pb^{2+} ion, and further possibilities that electrochemistry of other kinds of guest species may be controlled by appropriate choice of crown ethers and/or related host molecules.

Experimental

1. **Host Molecules.** Host molecules **2**, **6**, **7**, and **8** were prepared by the literature methods,[2,3] and showed satisfactory mass, ^1H NMR, and IR spectroscopic data as well as physical properties.

Other employed host molecules and reagents were commercially available and used as received.

2. **Cyclic Voltammetry Experiments.** Electrochemical measurements were conducted under an Ar in a buffered aqueous solution (0.1 M CH_3CO_2H/0.1 M CH_3CO_2Na, 1 M=1 mol dm^{-3}, pH=6.22). A standard H-cell, glassy carbon (working electrode), and a platinum wire (counter-electrode) were used. All the cyclic voltammograms were recorded at room temperature after several scans (scan rate; 20 mV s^{-1}), and reduction peak potentials were obtained vs. Ag/AgCl electrode.

3. **Determination of Stability Constant for Pb^{2+} Complex.** Stability constants of host molecules **1**, **2**, **5**, and **7** for Pb^{2+} ion were determined potentiometrically at 17 °C by a modification of the Frensdorff method:[7] log *K*=3.6 for **1**; 2.1 for **2**; 7.4 for **5**; and >8.7 for **7**. Pb^{2+} ion specific electrode (Denki Kagaku Keiki, Model 7180) was used to ascertain stability constants, and the reference electrode was Ag/AgCl (Orion, Model 90-01). The activities of Pb^{2+} ion were measured in an aqueous solution of $Pb(ClO_4)_2$ both in the absence and presence of each host molecule: $Pb(ClO_4)_2$, 1.0×10^{-3} M; host, 3.0×10^{-3} M. The stability constants for other host molecules were found in the literature:[5] Log *K*=5.85 for **3**; 6.90 for **4**; 8.39 for **6**; 10.70 for **8**; 7.93 for **9**; 13.12 for **10**; 12.72 for **11**; 1.85 for **12**; and 4.27 for **13**.

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4) Although a detailed mechanism is not clear, the following electrochemical and complexation processes may be possible:

$$\begin{aligned} &Pb^{2+} + 2e^- \rightleftharpoons \underline{Pb^0} \\ &Pb^{2+} + \text{Host} \rightleftharpoons (Pb^{2+}\cdot\text{Host}) \\ &(Pb^{2+}\cdot\text{Host}) + 2e^- \rightleftharpoons \underline{(Pb^0\cdot\text{Host})} \\ &\underline{(Pb^0\cdot\text{Host})} \rightleftharpoons \underline{Pb^0} + \text{Host} \end{aligned}$$

The species underlined are deposited on electrode surface. It is noted that Pb^0 is much weakly bound to the each host.

5) Stability constants of **3**, **4**, **6**, **8**, **9**, **10**, **11**, **12**, and **13**: See R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev.*, **85**, 271 (1985).

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