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Liquid-Liquid Extraction of Palladium(II) with Phenylene-incorporated Tetrakis(thioether)s

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Synopsis. Extraction behaviors of palladium(II) with three cyclic and noncyclic phenylene-incorporated tetrakis(thioether)s were examined. Picrate ion as a counter anion and 1,2-dichloroethane as an extraction solvent were used. The extractability of palladium ion with the acyclic tetrakis(thioether) used in this study was higher than that with the corresponded cyclic one.

Poly(thioether)s react selectively with soft metals, because thioether moieties (R-S-R) act as soft Lewis bases. The use of them as extractants makes possible the separation of soft metal ions from other metal ions.[1] Palladium(II) is one of soft metals belonging to class *b*, classified by Ahrland.[2] In our previous work,[3] the extraction of palladium(II) into 1,2-dichloroethane with six kinds of tetrakis(thioether)s was examined. The results suggest that the extractabilities of palladium ion with tetrakis(thioether)s which contain benzene ring are higher than those without a benzene ring, and the extractabilities with acyclic tetrakis(thioether)s are higher than those with cyclic tetrakis(thioether)s. In the present study, extraction behaviors of palladium(II) with three phenylene-incorporated tetrakis(thioether)s were examined. Three ligands used were the cyclic one, 13,14-benzo-1,4,8,11-tetrathiacyclopentadec-13-ene (Bz-TTCP) and two acyclic ones, 1,2-bis(2,5-dithiaheptyl)benzene (*o*-xy-(ETET)$_2$) and 1,4-bis(2,5-dithiaheptyl)benzene (*p*-xy-(ETET)$_2$), which are shown in Fig. 1. Picrate as a counter anion and 1,2-dichloroethane as an extraction solvent were used.

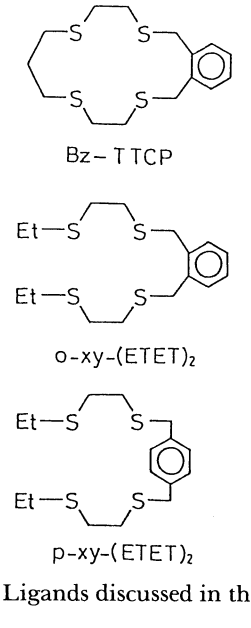

Fig. 1. Ligands discussed in this study.

Experimental

The cyclic tetrakis(thioether), Bz-TTCP was synthesized by a method similar to that described by Rosen and Bush.[4] Two acyclic tetrakis(thioether)s, *o*-xy-(ETET)$_2$ and *p*-xy-(ETET)$_2$ were synthesized by the method described before.[3] Palladium sulfate used was dissolved in sulfuric acid solution to prepare 1×10^{-2} M(=mol dm^{-3}) solution of palladium ion. The extraction solvent, 1,2-dichloroethane was purified by washing three times with 2M potassium hydroxide solution and then three times with water and distilled after drying with calcium chloride. Other reagents used were of guaranteed-reagent grade.

Apparatus. A Taiyo M incubator was used for shaking the solution. A Hitachi Z-8000 atomic absorption spectrophotometer was used for the determination of palladium ion. UV and visible absorption spectra were measured with a Shimadzu UV-240 recording spectrophotometer. The pH of the aqueous phase was measured with a Hitachi-Horiba M-7 pH meter.

Liquid-Liquid Extraction of Palladium. Ten milliliters of the aqueous solution containing 5×10^{-5} M palladium ion, 1×10^{-3} M picrate ion and 1×10^{-2} M acetate buffer, were kept at an ionic strength of 0.1 with sodium sulfate. This solution was kept in a stoppered 50 ml glass cylindrical tube. Ten milliliters of 5×10^{-3} M tetrakis(thioether) solution of 1,2-dichloroethane was added to the aqueous solution. The mixture was shaken for 30 min on 200 strokes/min at 25±0.1 °C, and then centrifuged for 5 min at 2000 rpm. After two phases were separated, the pH of the aqueous phase was measured and the concentration of picrate ion in the aqueous phase was determined spectrophotometrically at 354 nm. The concentrations of the palladium ion in the aqueous and organic phase were determined by the atomic absorption spectrophotometry.

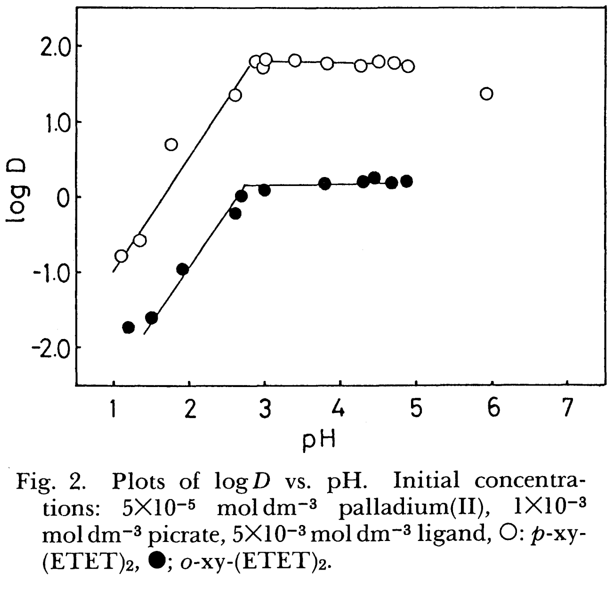

Fig. 2. Plots of log*D* vs. pH. Initial concentrations: 5×10^{-5} mol dm^{-3} palladium(II), 1×10^{-3} mol dm^{-3} picrate, 5×10^{-3} mol dm^{-3} ligand, ○: *p*-xy-(ETET)$_2$, ●; *o*-xy-(ETET)$_2$.

Results and Discussion

Extraction behaviors of palladium(II) with two acyclic tetrakis(thioether)s were examined in the pH range from 1 to 6. Plots of the logarithmic distribution ratio of palladium(II) against the pH of aqueous phase are shown in Fig. 2. Each extractability is kept constant at the $\log D$ value of 1.8 for *p*-xy-(ETET)$_2$ and 0.3 for *o*-xy-(ETET)$_2$ respectively, in the pH range from 2.8 to 5.0. The decrease in $\log D$ values below pH 2.8 is due to the decrease of picrate ion by changing to picric acid. It is interesting that the extractability of palladium(II) with *p*-xy-(ETET)$_2$ is higher than that with *o*-xy-(ETET)$_2$. For *o*-xy-(ETET)$_2$ was designed to be a quadridentate ligand, whereas *p*-xy-(ETET)$_2$ may be not able to act as a quadridentate ligand but as a bidentate ligand. Then, the composition of the extracted species with *p*-xy-(ETET)$_2$ is different from that with *o*-xy-(ETET)$_2$, is considered. In the case of *p*-xy-(ETET)$_2$, the organophilic species such as $PdL_2(pic)_2$ may be extracted. The extraction constant K_{ex} and the distribution ratio D are defined as follows without considering the hydrolysis of palladium(II):

$$Pd^{2+} + mL_{(o)} + nPic^- \overset{K_{ex}}{\rightleftarrows} PdL_mPic_{n(o)} \quad (1)$$

$$K_{ex} = [PdL_mPic_n]_o/[Pd^{2+}][L]_o{}^m[Pic^-]^n \quad (2)$$

where the subscript "o" indicates the organic phase. From equation (1), (2) and the suitable approximation, the following logarithmic expression is obtained.

$$\log D = \log K_{ex} + m \log[L]_o + n \log[Pic^-] \quad (3)$$

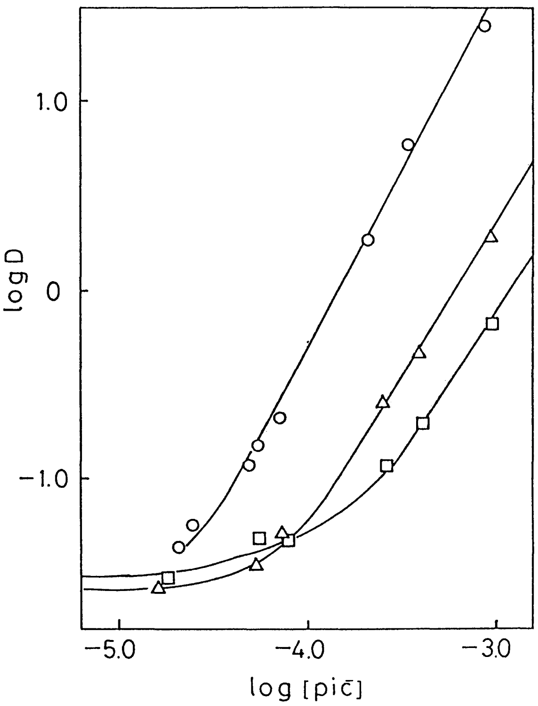

Fig. 3. Plots of $\log D$ vs. $\log[Pic^-]_w$ at pH 2.9. Initial concentrations: 5×10^{-5} mol dm^{-3} palladium(II), 5×10^{-3} mol dm^{-3} ligand, ○: *p*-xy-(ETET)$_2$, △: *o*-xy-(ETET)$_2$, □: Bz-TTCP.

The relationship between the logarithm of distribution ratio ($\log D$) and the logarithm of picrate ion concentration in the aqueous phase at pH 2.9 is shown in Fig. 3. The straight line with the slope of +2 for *p*-xy-(ETET)$_2$ was obtained: therefore, $n=2$. In the case of *o*-xy-(ETET)$_2$ and Bz-TTCP, those with the slope of +2 were obtained in the region of $\log[Pic^-] > -4.0$. At the concentration of picrate ion below 1×10^{-4} M, the slope of two lines approaches to zero. In this region, counter anions other than picrate ion may form an ion-pair, and be extracted with the complex cation. In as much as the concentration of picrate ion is low, the formation of hydroxo complex of palladium can not be ignored completely at pH 2.9. In such a case, the formation of extracted species containing hydroxide ion is expected. The order of the extractability is as follows: *p*-xy-(ETET)$_2$ > *o*-xy-(ETET)$_2$ > Bz-TTCP. The extractability of acyclic tetrakis(thioether) *o*-xy-(ETET)$_2$ is higher than that of the corresponding cyclic tetrakis(thioether), Bz-TTCP. In general, the extractability of metals such as silver(I) copper(I) and (II) with a flexible acyclic tetrakis(thioether) is superior to that with the cyclic counterpart. Relationship between the logarithmic distribution ratio of palladium(II) and the logarithm of ligand concentration in 1,2-dichloroethane is shown in Fig. 4. The distribution ratio of palladium(II) with Bz-TTCP is independent of the concentration of Bz-TTCP in the organic phase. It is thought that the solubility of the ion pair compound, $[Pd(bz\text{-}ttcp)_m]Pic_2$ in 1,2-dichloroethane limits the distribution of palladium(II). In the case of *o*-xy-(ETET)$_2$, the $\log D$ value increases slightly as the concentration of the ligand increases. However, the slope of the line is less than +1.0. When the concentration of *p*-xy-(ETET)$_2$ is lower than 1×10^{-3} M, the extractability of palladium(II) with *p*-xy-(ETET)$_2$ is lower than that with *o*-xy-(ETET)$_2$ or Bz-TTCP. Along with the increase in the concentration of *p*-xy-

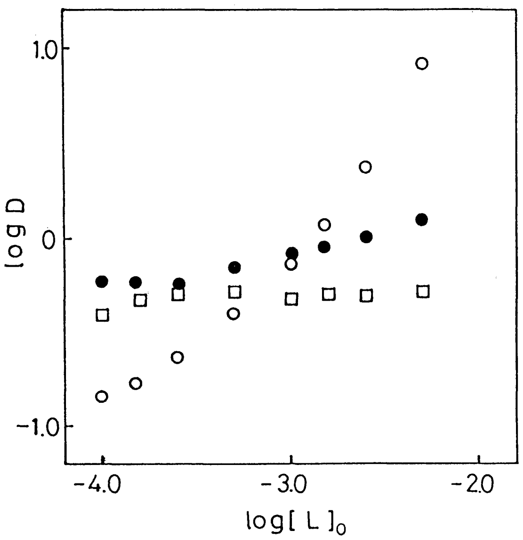

Fig. 4. Plots of $\log D$ vs. $\log[L]_o$ at pH 2.9. Initial concentrations: 5×10^{-5} mol dm^{-3} palladium(II), 1×10^{-3} mol dm^{-3} picrate, ○: *p*-xy-(ETET)$_2$, ●: *o*-xy-(ETET)$_2$, □: Bz-TTCP.

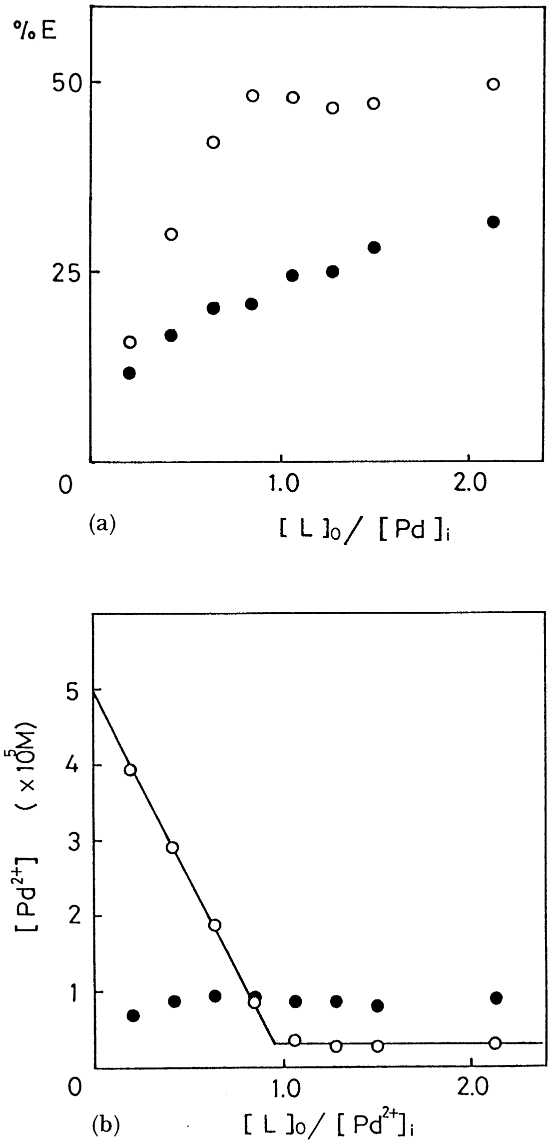

Fig. 5. Molar ratio methods at pH 2.9. Initial concentrations: 5×10^{-5} mol dm^{-3} palladium(II), 1×10^{-3} mol dm^{-3} picrate, (a) ○: *o*-xy-(ETET)$_2$, ●: Bz-TTCP. (b) for *p*-xy-(ETET)$_2$. ○: palladium ion in aqueous phase, ●: palladium ion in organic phase.

(ETET)$_2$, the log*D* value increases, and becomes to be higher than that of two other ligands at log[L]$_o$>−3.0. The slope of the line near +2.0 suggests the formation of the complex [PdL$_2$]$^{2+}$(Pic$^-$)$_2$, when the ligand concentration is more than 1×10^{-3} M. As palladium(II) favors the square planar arrangement, each two sulfurs of two molecules of *p*-xy-(ETET)$_2$ is considered to coordinate to the palladium ion. Molar ratio method was used in order to examine the extraction behavior of palladium(II) under the condition of relatively low concentration of the ligand to palladium ion (5×10^{-5} M). The results are shown in Fig. 5a and 5b, where the subscript "i" denotes the initial concentration. As shown in Fig. 5a, the break point appears clearly at [L]$_o$/[Pd]$_i$=1.0 that is *m*=1 in equation(3) in the *o*-xy-(ETET)$_2$. This means the formation of 1 : 1 (Pd(II) : L) complex in 1,2-dichloroethane. However in the case of Bz-TTCP, a distinct break point is not found. The results of Fig. 4 and 5a shows that the log*D* value was kept constant at −0.3 when the concentration of Bz-TTCP is more than twice of that of palladium(II). From the result of X-ray crystallographic analysis,[5] palladium(II) was just fitted into the cavity of the 1,4,8,11-tetrathiacyclotetradecane (TTCT) derivative which has 14-membered ring. As Bz-TTCP, 15-membered ring has a slight larger cavity than TTCT, the formation of 1 : 1 (Pd(II) : L) complex has been expected. However the solubility of the Pd(II)-Bz-TTCP-picrate complex in 1,2-dichloroethane seems to be low. When palladium(II) was extracted with *p*-xy-(ETET)$_2$ of low concentration relative to the palladium concentration, the yellow precipitate formed between the two phases. Figure 5b shows the plot of the palladium concentration in the aqueous or organic phase vs. the ratio of [*p*-xy-(ETET)$_2$]$_{o,i}$ to [Pd^{2+}]$_i$. Although the concentration of palladium(II) in the organic phase is kept constant (1×10^{-5} M), that in aqueous phase decrease in the range of [L]$_o$/[Pd^{2+}]$_i$=0~1.0. The result suggests that the Pd(II)-*p*-xy-(ETET)$_2$ complex is stable but slightly soluble in 1,2-dichloroethane. Nevertheless *p*-xy-(ETET)$_2$ has four sulfur atoms, it can not act as a quadridentate ligand but as a bidentate one. The complex is supposed to be as [Pd(II)L(OH$_2$)]$^{2+}$(Pic$^-$)$_2$. As the concentration of *p*-xy-(ETET)$_2$ increases, the organophilic 1 : 2 (Pd(II) : L) complex will become to be predominant, and extracted into 1,2-dichloroethane.

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