



# Solvent extraction studies of class b metal ions with cyclic and acyclic polythio ethers

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# 神戸大学博士論文

Solvent Extraction Studies of Class b Metal

Ions with Cyclic and Acyclic Polythio Ethers

(環状及び非環状ポリチオエーテルによるクラスb  
金属イオンの溶媒抽出に関する研究)

平成 2 年 1 月

茶 山 健 二

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## Chapter 1. Introduction

Organic reagents, selective and specific for metals, are very important in analytical chemistry. Because the determination of a trace impurity in highly pure materials is one of the central problems in analytical chemistry. These reagents will form the basis of selective analytical procedure and make possible the combined separation and enrichment of trace constituents.

Pearson,<sup>1)</sup> introduced the concept of hard and soft Lewis acids and bases, pointed out that hard metal ions give stable complexes with hard ligands and soft metal ions do with soft ligands. In this classification, hard metal ions mean those belonging to class a in Ahrland's classification,<sup>2)</sup> and soft metal ions to class b. According to his concept, ligands containing sulfur atoms are selective reagents for class b metals. In fact, reagents containing sulfur atoms as mercapto groups R-SH, 8-mercaptoquinoline,<sup>3)</sup> dithizone and dialkylaminodithiocarbamic acid<sup>4)</sup> for example, act as selective reagents for class b metals. Nevertheless of poor coordinating ability, thioether groups (R-S-R) are softer Lewis bases than mercapto groups (R-SH), more selective for metals belonging to class b. Moreover, "polythio ethers" will be increasingly able to wrap around the central metal ion. If the polythio



ether itself is so constructed as to form a ring, it will have a cavity within the ligand where the bonded metal ion must fit. This may impose rather strict steric requirements on the metal ion, making macrocyclic polythio ethers much more selective than the corresponding noncyclic one. The resulting complex is highly lipophilic, and with suitable counter anions, is easily extracted into organic solvents. Since Pedersen<sup>5)</sup> reported the first paper on crown ether, the chemistry of macrocyclic compounds has developed extensively. Studies of macrocyclic polythio ether, "thiacrown ethers" have also developed in coordination<sup>6)-28)</sup> and analytical<sup>29)-47)</sup> chemistry for the last decade. However, only a few studies of acyclic polythio ethers have been reported.

In this study, some cyclic and acyclic polythio ethers were synthesized, and tested as selective organic reagents for class b metals. Detailed extraction behavior of class b metals with these reagents and counter anions was examined and compared. Further, for the purpose of the extractive spectrophotometric determination of class b metals, new thiacrown compounds were designed. If a group which can act both as a counter anion to form ion pairs and as a chromophore is introduced into a thiacrown compound, the product should be able to extract class b metals selectively without the need for an auxiliary counter anion, and to give

a compound suitable for determining the metal by spectrophotometry after extraction. Moreover, if the group functions as a univalent counter anion, the reagent should serve as a selective extracting and spectrophotometric reagent for univalent class b metals, and even be specific for a certain metal. In this study, three new chromogenic thiacycrown compounds were synthesized and their properties as extracting and spectrophotometric reagents were examined. Finally in order to make the more sensitive and selective determination of metals, effects of counter anions on extraction of metals were examined by use of a hexathio ether as the ligand. The use of counter anion of which the absorptivity is high, made possible the sensitive determination of copper(II) and silver(I).

This thesis consists of nine chapters.

In Chapter 2, the syntheses of reagents discussed in this work were described. Three new acyclic tetrathio ether and three new chromogenic thiacycrown ethers were synthesized. The other four tetra- and hexa-thio ethers were synthesized.

In Chapter 3, studies on liquid-liquid extraction of various metals with seven cyclic and acyclic tetrathio ethers were described.

In Chapter 4, details of extraction behavior of copper(I) with six cyclic and acyclic tetrathio ethers was discussed. The extraction constants of copper(I) with these

reagents were evaluated.

In Chapter 5, extraction behavior of silver(I) with six cyclic and acyclic tetrathio ethers was discussed. The extraction constants of silver(I) were evaluated. Further, the results of X-ray crystallographic analysis of silver(I) complexes with 1,4,8,11-tetrathiacyclotetradecane and the acyclic counterpart were compared and discussed.

In Chapter 6, extraction behavior of palladium(II) with three benzotetrathio ethers was discussed. Molecular designs for analytical reagents selective for palladium(II) were discussed.

In Chapter 7, extraction mechanism of copper(II) with the cyclic and acyclic tetrathio ethers was studied. Then, thermodynamic parameters of these extraction reactions were evaluated and discussed.

In Chapter 8, properties of three new chromogenic thiacycrown ethers as extracting and spectrophotometric reagents were described.

In Chapter 9, extractive spectrophotometric determination of copper(II) with a hexathiacrown ether and an anion dye were described. Effects of counter anions on the determination of copper(II) were examined.

In Chapter 10, an application of established system from Chapter 9 to the determination of silver(I) in the standard steel sample was described.

## Chapter 2. Syntheses of reagents

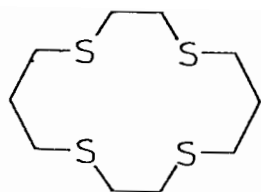
### 2.1 Introduction

Several kinds of thiacycrown ethers have been synthesized by Bush et al.,<sup>6)</sup> Black et al.<sup>7)</sup> and Ochrymowycz.<sup>8)</sup> However, acyclic polythio ethers have not synthesized so many as cyclic ones. Further, little is known about the syntheses of polythio ethers into which a functional group is introduced. In this study, ten kinds of polythio ethers shown in Fig.2-1 were synthesized. In these reagents, TTCT and Bz-TTCP were synthesized by a method similar to that of Bush et al.<sup>6)</sup> shown in Fig.2-2, HTCO was done by a method of Black et al.<sup>7)</sup> shown in Fig.2-3. Three new acyclic tetrathio ethers and three new chromogenic cyclic tetrathio ethers were synthesized by methods described below.

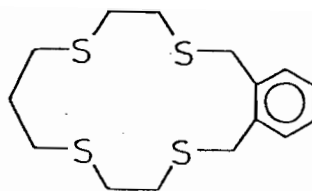
### 2.2 Experimental

#### 2.2.1 Syntheses of cyclic tetra- and hexathio ethers

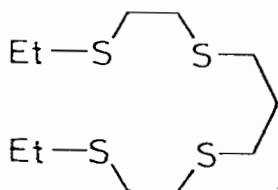
Cyclic tetrathio ethers, 1,4,8,11-tetrathiacyclotetradecane (TTCT) and 13,14-benzo-1,4,8,11-tetrathiacyclopentadec-13-ene (Bz-TTCP) were synthesized by the synthetic routes shown in Fig.2-2. The cyclic hexathio ether 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO) was synthe-



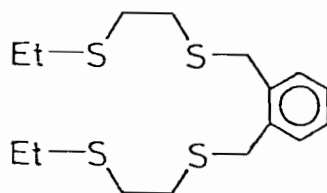
(1) TTCT



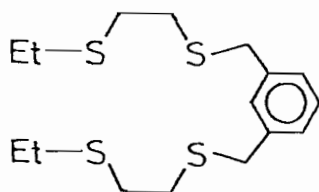
(2) Bz-TTCP



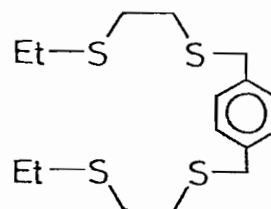
(3) TTAP



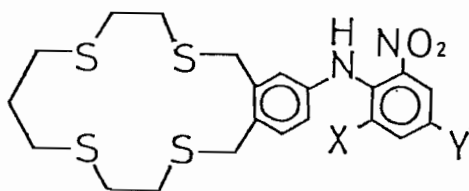
(4) o-xy-(ETET)<sub>2</sub>



(5) m-xy-(ETET)<sub>2</sub>



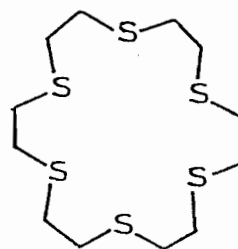
(6) p-xy-(ETET)<sub>2</sub>



(7) X = NO<sub>2</sub> Y = NO<sub>2</sub>

(8) X = CF<sub>3</sub> Y = NO<sub>2</sub>

(9) X = NO<sub>2</sub> Y = CF<sub>3</sub>



(10) HTCO

Fig.2-1. Reagents discussed in this study.

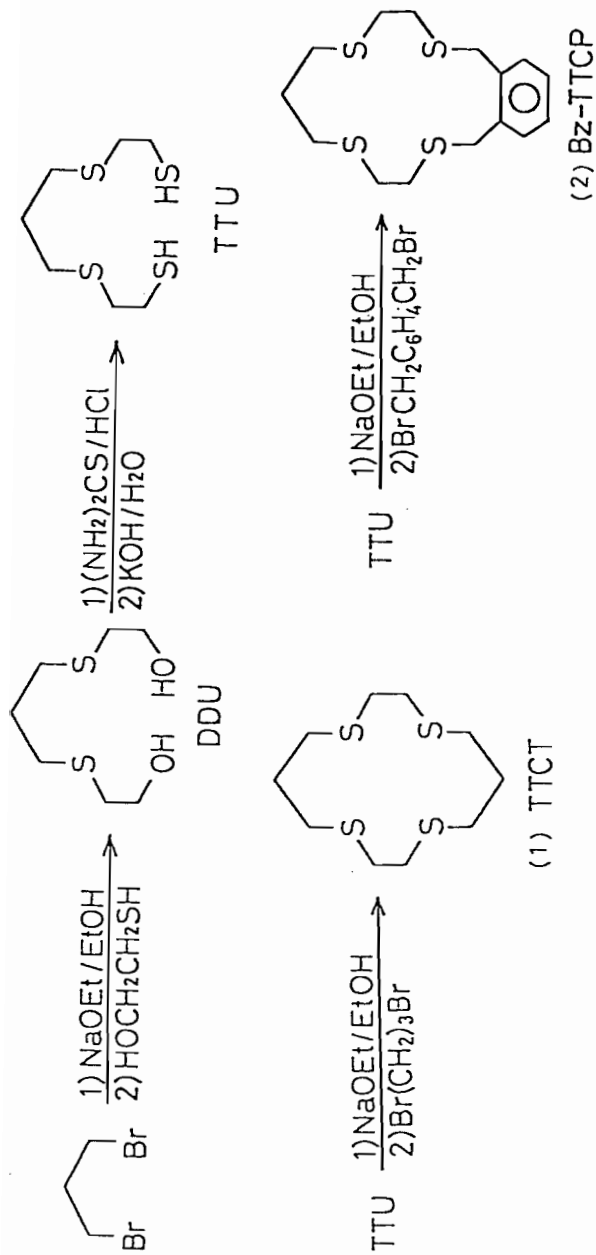


Fig.2-2. Synthetic routes for TTCT and Bz-TTCP.

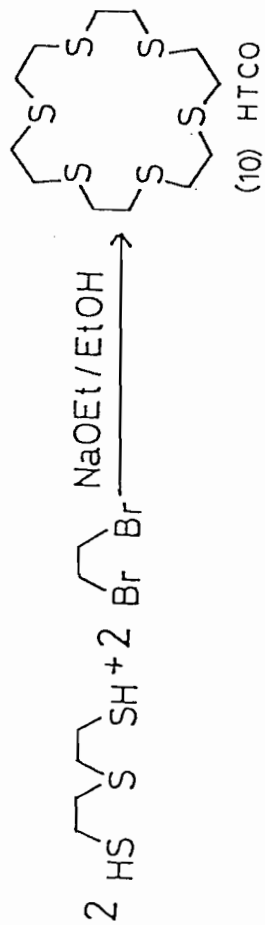


Fig.2-3. Synthetic route for HTCO.

sized by the synthetic route shown in Fig.2-3.<sup>7)</sup> These cyclization reactions were performed by the "high-dilution method". Main products of these reactions were chromatographed on a silica gel column with hexane-ethylacetate mixture. Each of TTCT and Bz-TTCP was recrystallized from ethanol, and HTCO from hexane.

### 2.2.2 Syntheses of acyclic tetrathio ethers

**2-Mercaptodiethylsulfide** In a 500 ml three necked flask, 21.6 g (0.2 mole) of 2-ethylthioethanol, 44.2 ml of conc. hydrochloric acid and 15.25 g (0.2 mole) of thiourea were mixed and refluxed under nitrogen for 10 hours. After cooling, 200 ml of 1M potassium hydroxide solution was added dropwise into the mixture and refluxed for 3 hours. After the mixture was acidified with 6N HCl, the resulting oily substance was extracted into ethyl ether, and then dried over MgSO<sub>4</sub>. The ether solution was filtrated and evaporated in vacuo. Then, the obtained oily residue was distilled in 15 mmHg at 65° C.

**Acyclic tetrathio ethers (3), (4), (5), (6)** Under nitrogen, 1.2 g (0.52 mole) of sodium metal was dissolved in 200 ml of ethanol, and 6.38 g (0.052 mole) of 2-mercaptodiethylsulfide was added dropwise into this solution. Benzene solution (50-100 ml) of 2.94 g (0.026 mole) of 1,3-dichloropropane for TTAP (3), 6.86 g (0.026 mole) of  $\alpha, \alpha'$ -dibromo-o-xylene for

o-xy-(ETET)<sub>2</sub> (4), 6.86 g (0.026 mole) of  $\alpha, \alpha'$ -dibromo-m-xylene for m-xy-(ETET)<sub>2</sub> (5) and 4.55 g (0.026 mole) of  $\alpha, \alpha'$ -dichloro-p-xylene for p-xy-(ETET)<sub>2</sub> (6) was added into above solution. After stirring overnight at room temperature, the mixture was filtrated and evapolated in vacuo. The oily residue dissolved in chloroform was washed with water, dried over MgSO<sub>4</sub>, and then evapolated. For p-xy-(ETET)<sub>2</sub> (6), the white product was twice recrystallized from ethanol. For TTAP (3), o-xy-(ETET)<sub>2</sub> (4) and m-xy-(ETET)<sub>2</sub> (5), the oily residue was chromatographed on a silica gel column with chloroform-ethylacetate as the eluting solvent.

**3,6,10,13-Tetrathiapentadecane; TTAP (3)** Liquid at room temperature (crystallized at < 5° C). A infrared spectrum (KBr) indicated a peak at 703 cm<sup>-1</sup> (C-S-C), but no absorption at 2550 cm<sup>-1</sup> (S-H). <sup>1</sup>H NMR (CDCl<sub>3</sub>) gave  $\delta$ =1.0-1.3 (6H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.8 (2H, m, CH<sub>2</sub>CH<sub>3</sub>CH<sub>2</sub>), 2.3-2.7 (16H, t and s, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>3</sub>). Mass spectrometry (MS)(70eV) gave m/Z 284.

**1,2-Bis-(2,5-dithiaheptyl)-benzene; o-xy-(ETET)<sub>2</sub> (4), 1,3-Bis-(2,5-dithiaheptyl)-benzene; m-xy-(ETET)<sub>2</sub> (5) and 1,4-Bis-(2,5-dithiaheptyl)-benzene; p-xy-(ETET)<sub>2</sub> (6)** m.p.(4): 29.3° C (white needle), (5): liquid at room temperature, (6): 46.5° C (white plate). IR (KBr) 706 cm<sup>-1</sup> (C-S-C), no absorption at 2550 cm<sup>-1</sup> (S-H). <sup>1</sup>H NMR(CDCl<sub>3</sub>) gave  $\delta$ =1.1-1.3 (6H, t, CH<sub>2</sub>CH<sub>3</sub>), 2.3-2.6 (12H, t and s, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>3</sub>), 3.6-3.9



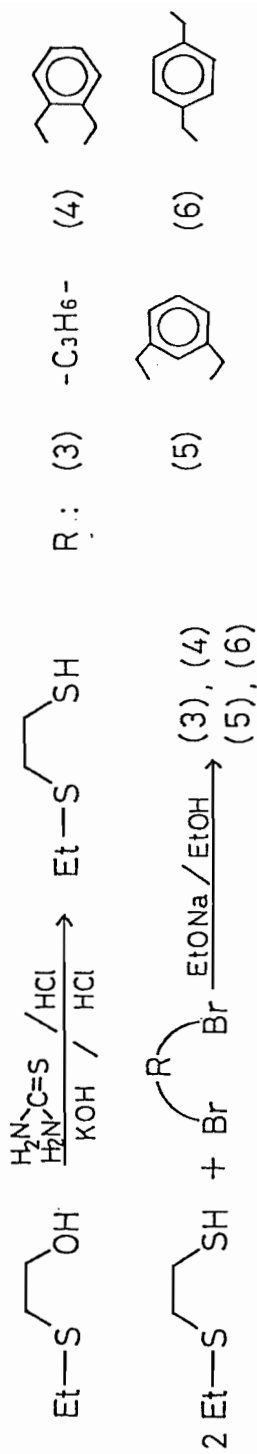


Fig.2-4. Synthetic routes for acyclic tetrathio ethers.

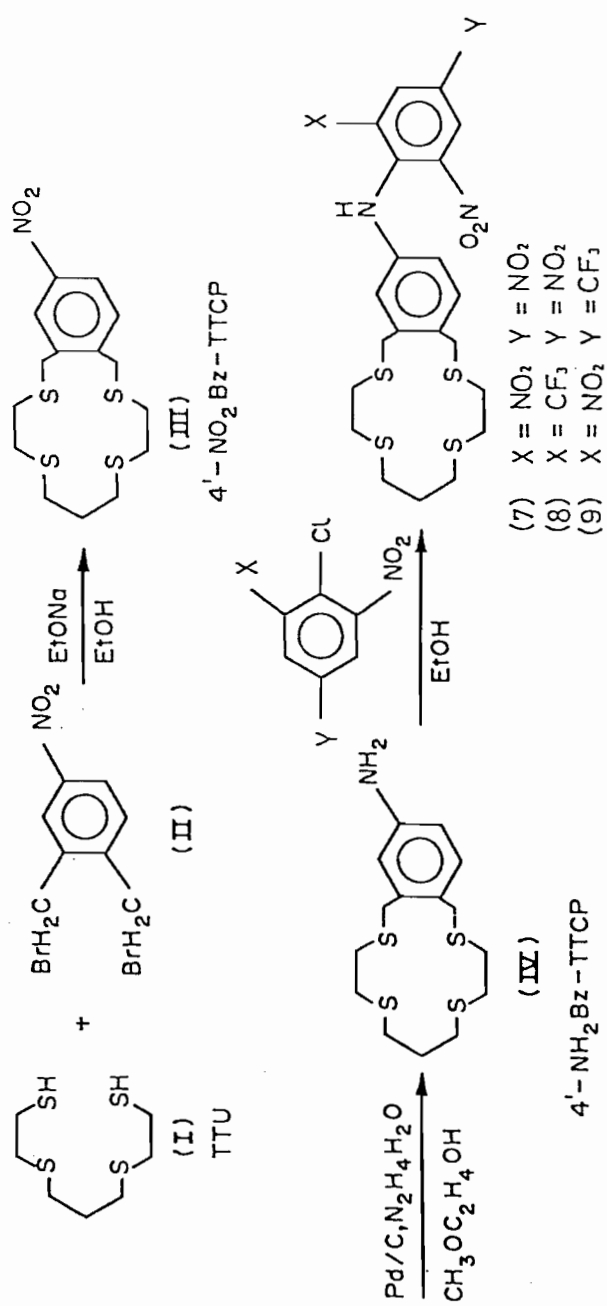


Fig.2-5. Synthetic routes for chromogenic thiacycrown ethers.

(4H, s, CH<sub>2</sub>Ph), 7.06-7.30 (4H, s, aromatic H). MS(70 eV) gave m/Z 346.

### 2.2.3 Syntheses of chromogenic thiacycrown ethers

#### 2.2.3.1 Synthesis of 4'-PicNHBz-TTCP (7)

*4'-Nitrobenzo-1,4,8,11-tetrathiacyclopentadec-13-ene; 4'-NO<sub>2</sub>Bz-TTCP (III)* In 700 ml of absolute ethanol, under nitrogen, 1.02 g (0.044 mole) of sodium metal was dissolved. To this solution 5.02 g (0.022 mole) of 1,4,8,11-tetrathiaundecane (TTU) (I) dissolved in 200 ml of benzene and 6.80 g (0.022 mole) of  $\alpha,\alpha'$ -dibromo-4-nitro-o-xylene(II) dissolved in 200 ml of benzene were simultaneously added dropwise during 5 hr at room temperature. After stirring overnight, the precipitate was filtered off and washed with benzene. The filtrate and washing were combined and evaporated under reduced pressure. The residue was dissolved in chloroform and water, then the organic layer was separated, washed with water and dried. The solvent was removed again under reduced pressure and the residual oil was chromatographed on a silica gel column with benzene-dichloroethane (1:1 v/v) mixture. The first of two major bands was collected and on recrystallization from chloroform-ethanol gave colorless curdy crystals, m.p. 102-3C°, yield 4.97 g (61%). Found: C47.9%, H5.7%, N3.7%; C<sub>15</sub>H<sub>21</sub>NO<sub>2</sub>S<sub>4</sub> requires C47.97%, H5.64%, N3.73%. The infrared spectrum (KBr) had bands at 1510,

1350  $\text{cm}^{-1}$  ( $\text{NO}_2$ ), but no absorption by S-H at 2550  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) gave  $\delta=1.80$  (2H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.50-3.00 (12H, overlapping t and s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2$ ), 4.05 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.30-8.40 (3H, m, aromatic H).

**4'-Aminobenzo-1,4,8,11-tetrathiacyclopentadec-13-ene; 4'- $\text{NH}_2\text{Bz-TTCP}$  (IV)** Into 90 ml of 2-methoxyethanol 1.5 g (4 mmole) of 4'- $\text{NO}_2\text{Bz-TTCP}$  (III) was mixed and the reaction was started by addition of 0.2 g of 10% Pd/C catalyst and 10 ml hydrazine monohydrate. After refluxing for 1 hr the hot reaction mixture was filtered and evaporated under reduced pressure. Recrystallization from ethanol gave colorless needles, m.p. 122-3°C, yield 1.24 g (90%). Found: C51.9%, H6.7%, N:4.2%;  $\text{C}_{15}\text{H}_{23}\text{NS}_4$  requires C52.13%, H6.71%, N4.05%. The infrared spectrum (KBr) had bands at 3430, 3350  $\text{cm}^{-1}$  ( $\text{NH}_2$ ). Mass spectrometry (MS)(70 eV) gave m/z (relative intensity) 345 ( $\text{M}^+$ , 9), 150 (100).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) gave  $\delta=1.90$  (2H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.60-3.00 (12H, t and s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2$ ), 3.65 (2H, br. s,  $\text{NH}_2$ ), 3.90 (4H,  $\text{CH}_2\text{Ph}$ ), 6.40-7.25 (3H, m, aromatic H).

**4'-Picrylamino-1,4,8,11-tetrathiacyclopentadec-13-ene; 4'-PicNHBz-TTCP (7)** 4'- $\text{NH}_2\text{Bz-TTCP}$  (IV) 1.04 g (3 mole) was mixed with 400 ml of absolute ethanol and a solution of 0.74 g (3 mmole) of picryl chloride in 100 ml of absolute ethanol was added dropwise at 40°C. To the solution 0.41 g of sodium carbonate was added. After 15 min the reaction

mixture was poured into chloroform, and the organic layer was separated and washed with water. The organic solvent was then evaporated under reduced pressure and the residual yellow crystals were recrystallized from benzene-ethanol mixture. The product had m.p. 161-2° C, yield 1.3 g (80%). Found: C45.4%, H4.3%, N10.0%;  $C_{21}H_{24}N_4O_6S_4$  requires C45.31%, H4.35%, N10.06%. The infrared spectrum (KBr) had bands at 1530, 1510, 1350  $cm^{-1}$  ( $NO_2$ ). MS (70 eV) gave m/z (relative intensity) 556 ( $M^+$ , 3), 361(89), 167(59), 106(100).  $^1H$  NMR (DMSO- $d_6$ ) gave  $\delta=1.80$  (2H, m,  $CH_2CH_2CH_2$ ), 2.80 (4H, s,  $CH_2CH_2CH_2$ ), 3.30 (8H, s,  $CH_2CH_2$ ), 3.90 (4H, s,  $CH_2Ph$ ), 6.90-7.45 (3H, m, aromatic H), 9.90 (2H, s, aromatic H).

#### 2.2.3.2 Syntheses of two other chromogenic thiacyclopentadec-13-ene

Compounds, (8): 13,14-[4-[(2,4-dinitro-6-trifluoromethylphenyl)amino]benzo]-1,4,8,11-tetrathiacyclopentadec-13-ene, symbolized as 6TF and (9): 13,14-[4-[(2,6-dinitro-4-trifluoromethylphenyl)amino]benzo]-1,4,8,11-tetrathiacyclopentadec-13-ene, symbolized as 4TF were synthesized by the method similar to that of compound (7). 4'- $NH_2Bz$ -TTCP was reacted with the corresponding trifluoride, 2-chloro-3,5-dinitrobenzylidynetrifluoride for (8) and 4-chloro-3,5-dinitrobenzylidinetrifluoride for (9) in ethanol. The products were recrystallized from chloroform-ethanol.

**6TF (8)** m.p.188° C. IR (KBr): 1530,1510,1350  $cm^{-1}$  ( $NO_2$ ). 3330  $cm^{-1}$  (NH). NMR (DMSO- $d_6$ ):  $\delta=1.80$  (2H, m,  $CH_2CH_2CH_2$ ),

2.0-2.3 (12H, overlapping t and s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>), 3.85 (4H, s, CH<sub>2</sub>Ph), 6.6-7.3(3H, m, aromatic H), 8.4-8.7(2H, q, aromatic H).

*4TF (9)* m.p.205° C. IR(KBr): 1530, 1510, 1350 cm<sup>-1</sup>(NO<sub>2</sub>). 3350 cm<sup>-1</sup>(NH). NMR (DMSO-d<sub>6</sub>): δ=1.80 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.4-2.9 (12H, overlapping t and s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>), 3.85 (4H, s, CH<sub>2</sub>Ph), 6.7-7.2 (3H, m, aromatic H), 8.4 (2H, s, aromatic H).

## 2.3 Results and discussion

### 2.3.1 Syntheses of acyclic tetrathio ethers

Acyclic tetrathio ether (3) was synthesized in two steps as shown in Fig.2-3. This method is different from that including methylation of 1,4,8,11-tetrathiaundecane by Rosen and Bush.<sup>6)</sup> In the present study, 2-ethylthioethanol was transformed into 2-mercaptodiethylsulfide, and TTAP was successfully synthesized by the reaction of 1,3-dichloropropane and the thiol. Xylene dihalides provided the three isomers of tetrathio ethers (4),(5) and (6) which have a benzene ring in their structure. It will be possible to introduce the anionic chromogenic group into these ligands by the method similar to the syntheses of the compounds (7)-(9). The syntheses of macrocyclic polythio ethers needs long time and much solvent for "the high-

dilution method", nevertheless, their yields are low. While that of acyclic polythio ethers may be synthesized without long time and large amount of solvent.

### 2.3.2 Syntheses of chromogenic thiacycrown ethers

The reagent, 4'-PicNHBz-TTCP, was synthesized in three steps as shown in Fig.2-4. 13,14-Benzo-1,4,8,11-tetrathia-cyclopentadec-13-ene (Bz-TTCP) could not be used as the starting material, because the nitration of Bz-TTCP with nitric acid to obtain 4'-NO<sub>2</sub>Bz-TTCP (III), oxidizes the thioether group in the Bz-TTCP, although Bz-15-crown-5 is easily nitrated. Therefore, TTU (I) and  $\alpha, \alpha'$ -dibromo-4-nitro-*o*-xylene (II) synthesized by the method of Kleinschmidt et al.,<sup>46)</sup> were used as starting materials. The cyclization reaction of the dithiol (I) and the dibromide (II) was performed by the high-dilution method, with sodium ethoxide in absolute ethanol. The cyclic polythio ether, 4'-NO<sub>2</sub>Bz-TTCP (III) was separated by silica gel column chromatography, with benzene-dichloroethane. The reduction of the nitro group of (III) to the amino group of 4'-NH<sub>2</sub>Bz-TTCP (IV) was successfully performed by use of Pd/C as a catalyst and hydrazine monohydrate as reducing agent, without inhibition of the catalysis by sulfur atoms. The final product, 4'-PicNHBz-TTCP (7), was obtained by the reaction of (IV) and picryl chloride. Two other chromogenic

compounds (8) and (9) were synthesized by the similar method.

## Chapter 3.

### Liquid-liquid extraction of metals with cyclic and acyclic tetrathio ethers

#### 3.1 Introduction

Sevdic et al. showed the extractability of thiacycrown compounds for silver(I) and mercury(II), at first.<sup>29)</sup> K.Saito et al. examined the liquid-liquid extraction of various metals with a typical thiacycrown ether, TTCT.<sup>33)</sup> It becomes clear that class b metals are extracted with TTCT selectively. In this study, in order to evaluate the selectivity and the extractability of two cyclic and four acyclic tetrathio ethers, liquid-liquid extraction of thirteen kinds of metals with these reagents were examined. Picrate ion was used as counter anion. Further, the liquid-liquid extraction of metals with the chromogenic thiacycrown ether (7) was examined without the use of counter anion.

#### 3.2 Experimental

##### 3.2.1 Apparatus

Extraction was done in a Taiyo M incubator at  $25 \pm 0.1^\circ \text{C}$ . A Seiko SAS-725 atomic absorption spectrophotometer was used to determine the concentration of metals except for



mercury(II). For mercury(II), a Hiranuma mercury(II) meter HG-1 flameless atomic absorption spectrophotometer was used. Ultraviolet and visible absorption spectra were measured with a Shimadzu self-recording spectrophotometer UV-240. The pH of an aqueous phase was measured with a Hitachi-Horiba M-7II pH meter.

### 3.2.2 Reagents

Tetrathio ethers (1)-(7) were synthesized and purified by the methods described in Chapter 2. The metal sulfates (guaranteed-reagent grade) were used to prepare  $1 \times 10^{-2}$  M solutions of metal ions, which were standardized by compleximetric titrations. 1,2-Dichloroethane was shaken three times with 2 M potassium hydroxide and distilled water, dried with calcium chloride, and distilled. Other reagents were of guaranteed-reagents grade.

### 3.2.3 Liquid-liquid extraction of metals

An aliquot (10 ml) of the aqueous solution containing the metal ion ( $5 \times 10^{-5}$  M), picrate ion ( $1 \times 10^{-3}$  M) and acetate buffer ( $1 \times 10^{-2}$  M) was taken in a 50 ml glass cylindrical tube with a glass stopper. The ionic strength was kept at 0.1 with sodium sulfate. After the addition of 10 ml of a tetrathio ether solution of 1,2-dichloroethane ( $5 \times 10^{-3}$  M), the mixture was shaken for 30 min at 200 strokes/min at

25±0.1°C. After the mixture was centrifuged at 2000 r.p.m. for 5 min, the pH of the aqueous phase was measured and the metal concentration was measured by atomic absorption spectrometry using the resonance line for each metal. The metal concentration in organic phases was determined as follows: 5 ml of the 1,2-dichloroethane phase was allowed to evaporate, the residue was decomposed and dissolved in concentrated nitric acid and diluted to 10 ml with water, and the concentration of metal ion in this solution was determined by atomic absorption spectrometry. For the copper(I) extraction, the aqueous solution containing copper(II) ion ( $5 \times 10^{-5}$  M), picrate ion, acetate buffer ( $1 \times 10^{-2}$  M) and hydroxylammonium sulfate (0.033 M) was used. After the extraction, the concentration of picrate ion in the aqueous phase was determined spectrophotometrically at 354 nm.

#### 3.2.4 Liquid-liquid extraction of metals with the chromogenic thiocrown ether (7)

An aliquot (10 ml) of aqueous solution containing the metal ion ( $5 \times 10^{-5}$  M) and sodium hydroxide-borax buffer solution ( $1 \times 10^{-5}$  M) was taken in a stoppered 50 ml glass cylindrical tube. The ionic strength was kept at 0.1 with sodium sulfate. To obtain a copper(I) solution, enough hydroxylammonium sulfate was added to copper(II) solution to

tetrathio ether. These results suggest that these polythio ethers bond selectively with only class b metals because of the soft character of thioether groups. The percent extraction (%E) of the benzothiacrown ether, Bz-TTCP, is higher than that of TTCT for each of all metals. This fact may be explained by the higher lipophilicity of Bz-TTCP, than TTCT. In the same reason, %E of o-xy-(ETET)<sub>2</sub> is higher than TTAP. The %E of metals is as follows: univalent class b metals, Cu(I) and Ag(I), are extracted more than 99% with each ligand. In the case of Pd(II), the extractability of cyclic tetrathio ether, TTCT, is inferior to that of the corresponding acyclic tetrathio ether, TTAP. And also extractability of acyclic o-xy-(ETET)<sub>2</sub> is superior to that of cyclic Bz-TTCP. It is interesting that the %E value of m-xy-(ETET)<sub>2</sub> and p-xy-(ETET)<sub>2</sub> for Pd(II) is higher than that of o-xy-(ETET)<sub>2</sub>. Probably, two thioether chains of o-xy-(ETET)<sub>2</sub> are restricted to locate the optimum position as a quadridentate ligand. In excess of the ligand concentration, palladium(II) complexes of m- and p-xy-(ETET)<sub>2</sub> will form the stable 1:2 (Pd(II):ligand) complexes in 1,2-dichloroethane. D.B.Rorabacher et al.<sup>14)</sup> indicated the lack of "macrocyclic effect" for the mercury(II) complex by comparing the formation constant of Hg(II)-16-membered cyclic tetrathio ether complex with that of its acyclic counterpart complex. However, as revealed by the data in Table 3-1, Hg(II) is

give a 0.1 M solution. After the addition of 10 ml of  $2.5 \times 10^{-3}$  M 4'-PicNHBz-TTCP (7) 1,2-dichloroethane solution, the mixture was shaken for 30 min at 200 strokes/min at  $25 \pm 0.1^\circ \text{C}$ . The mixture was then centrifuged for 5 min, the pH of aqueous phase was measured and the absorbance of the organic phase was measured at 510 nm against a reagent blank. When the degree of extraction was very high, as in the case of silver(I) and copper(I), the metal concentration in the aqueous phase was measured by atomic absorption spectrometry.

### 3.3 Results and discussion

#### 3.3.1 Liquid-liquid extraction of various metals with six tetrathio ethers

The following metal ions were examined; Na(I) and Mg(II) as class a metals, Mn(II), Co(II), Ni(II) Zn(II), Cu(II) and Tl(I) as class ab metals and Cd(II), Cu(I), Ag(I), Pd(II) and Hg(II) as class b metals. The results are shown in Table 1 along with those for extraction with TTCT.<sup>33)</sup> Class b metals such as Cu(I), Ag(I), Pd(II) and Hg(II) were extracted well with each tetrathio ether, but Cd(II) belonging to the class b metal was hardly extracted at all. Other metals that belongs to class a or class ab metals except for Cu(II), were not extracted at all with each

Table 3-1. Extraction percent of various metals with tetrathio  
ethers into 1,2-dichloroethane.

Metal	Class <sup>a</sup>	TTCT <sup>b</sup>	Bz-TTCP	TTAP	o-xy-(ETET) <sub>2</sub>	m-xy-(ETET) <sub>2</sub>	p-xy-(ETET) <sub>2</sub>
Na(I)	a	0	0	0	0	0	0
Mg(II)	a	0	0	0	0	0	0
Mn(II)	ab	0.8	0	0	0	0	0
Co(II)	ab	0.8	0	0	0	0	0
Ni(II)	ab	0.7	0	0	0	0	0
Cu(II)	ab	5.9	8.0	5.9	11.9	9.9	1.6
Zn(II)	ab	0.5	0	0	0	0	0
Tl(I)	ab	0.8	0	0	0	0	0
Cd(II)	b	0.8	0	0	0	0	0
Cu(I)	b	99.4	99.6	99.6	99.6	99.6	99.6
Ag(I)	b	99.9	99.8	99.8	99.8	99.8	99.8
Pd(II)	b	14.3	57.3	30.1	66.7	97.8	97.9
Hg(II)	b	89.5	97.7	79.2	94.3	94.8	90.7

a. Classified by Ahrland et al.      b. Ref. 33).

more extracted with the cyclic tetrathio ethers, TTCT and Bz-TTCP than with the acyclic counterparts TTAP and o-xy-(ETET)<sub>2</sub>. It is considered that the extraction equilibria include several important equilibria other than complex formation equilibria under the condition of an excess of the ligand concentration. Copper(II) which belongs to class ab metals is extracted with tetrathio ethers at 1.6-11.9 %E. The %E values of Bz-TTCP (2), o-xy-(ETET)<sub>2</sub> (4) and m-xy-(ETET)<sub>2</sub> (5) in which have benzene ring are higher than that of TTCT. The cavity of TTCT provides an optimum fit for planar coordination around copper(II).<sup>21)</sup> p-Xy-(ETET)<sub>2</sub> is not suitable for the copper(II), because its structure seems to be not able to act as the quadridentate ligand. However, copper(II) is extracted more than 99.9 %E by using tetraphenylborate ion instead of picrate ion with each ligand.

### 3.3.2 Liquid-liquid extraction of various metals with

#### 4'-PicNHBz-TTCP (7)

Liquid-liquid extraction of metal ions with one of three chromogenic thiacycrown ethers(7), was tested without the counter anion. The following ions were examined: Na(I) and Mg(II) (class a), Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) (class ab), and Cu(I), Ag(I), Hg(II) and Pd(II) (class b). The results are shown in Table 3-2 along with

Table 3-2. Degree of extraction of various metals with 4'-PicNHBz-TTCP into 1,2-dichloroethane.

Metal	Class <sup>a</sup>	$\alpha$ Value <sup>b</sup>	4'-PicNHBz-TTCP		TTCT <sup>c</sup>	
			pH	%E	pH	%E
Na(I)	a	0	10.3	0	5.4	0
Mg(II)	a	0	10.3	0	5.4	0
Mn(II)	ab	0	10.3	0	5.4	0.8
Co(II)	ab	1.39	10.3	0	5.8	0.8
Ni(II)	ab	1.41	10.3	0	5.4	0.7
Zn(II)	ab	1.25	10.3	0	5.4	0.5
Cu(II)	ab	1.64	10.3	0	5.4	5.9
Cd(II)	b	1.66	10.3	0	5.4	0.8
Cu(I)	b	3.92	7.4	99.5	5.4	99.4
			3.6	15.4		
Ag(I)	b	3.60	8.3	99.8	5.4	99.9
			3.5	8.0		
Pd(II)	b	5.33	10.3	0	5.4	14.3
Hg(II)	b	5.83	10.3	0	5.1	89.5

a. Classified by Ahrland.

b. Ref 2).

c. Ref 33).

those for extraction with TTCT. Na(I) and Mg(II) were not extracted at all, with either reagent. Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) were not extracted with 4'-PicNHBz-TTCP (7) but slightly extracted with TTCT. Only Ag(I) and Cu(I) were well extracted with (7) (%E>99). Bivalent class b ions such as Hg(II), Cd(II) and Pd(II) were not extracted at all, although they are well extracted with TTCT. 4'-PicNHBz-TTCP (7), (8) or (9) which have only one dissociable proton, will form intramolecular ion-pair metal complexes only with univalent class b metals.



## Chapter 4.

### Liquid-liquid extraction of Copper(I)

#### 4.1 Introduction

As mentioned in Chapter 3, copper(I) is extracted with cyclic and acyclic tetrathio ethers as well as silver(I), more than 99%. However in this case, the ligand concentration is large amount excess over the copper(I) concentration. Study of the extraction equilibria will suggest the extractability of each ligand and the composition of extracted species. In this chapter, detailed extraction behavior of copper(I) with six neutral tetrathio ethers was examined. Further, the composition and the extraction constant of each ligand was evaluated.

#### 4.2 Experimental

##### 4.2.1 Liquid-liquid extraction of copper(I)

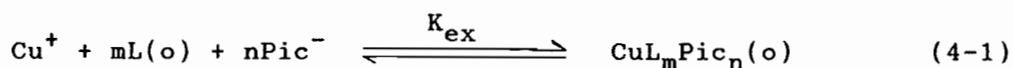
To obtain a copper(I) solution, enough hydroxylammonium sulfate was added to  $5 \times 10^{-5}$  M copper(II) sulfate solution to give a 0.033 M. The aliquot (10 ml) of solution containing the acetate buffer solution and picrate ion was shaken with 10 ml of a tetrathio ether solution of 1,2-dichloroethane. After the mixture was centrifuged, the pH of the aqueous

phase was measured and the copper concentration was measured by atomic absorption spectrometry.

### 4.3 Results and discussion

#### 4.3.1 Extraction equilibria of copper(I)

Extraction behavior of copper(I) with ligands from the aqueous solution containing picrate ion into 1,2-dichloroethane was examined. Extraction was performed at pH>4 owing to the decrease of the reducing power of hydroxylammonium sulfate at pH<4.<sup>33)</sup> The extraction equilibria of copper(I) are shown in Fig.4-1. The extraction constant and the distribution ratio are defined as follows:



$$K_{\text{ex}} = [\text{CuL}_m\text{Pic}_n]_{\text{o}} / ([\text{Cu}^+][\text{L}]_{\text{o}}^m[\text{Pic}^-]^n)$$

$$D = [\text{CuL}_m\text{Pic}_n]_{\text{o}} / ([\text{CuL}_m\text{Pic}_n] + [\text{CuL}_m^+] + [\text{Cu}^+]) \quad (4-2)$$

where "L" and "Pic" indicate ligand and picrate ion, respectively. And the subscript "o" and (o) mean the species in organic phase. From Eqn.(4-1), (4-2) and the approximation<sup>35)</sup>, the following logarithmic expression is obtained.

$$\log D = \log K_{\text{ex}} + m\log[\text{L}]_{\text{o}} + n\log[\text{Pic}^-] \quad (4-3)$$

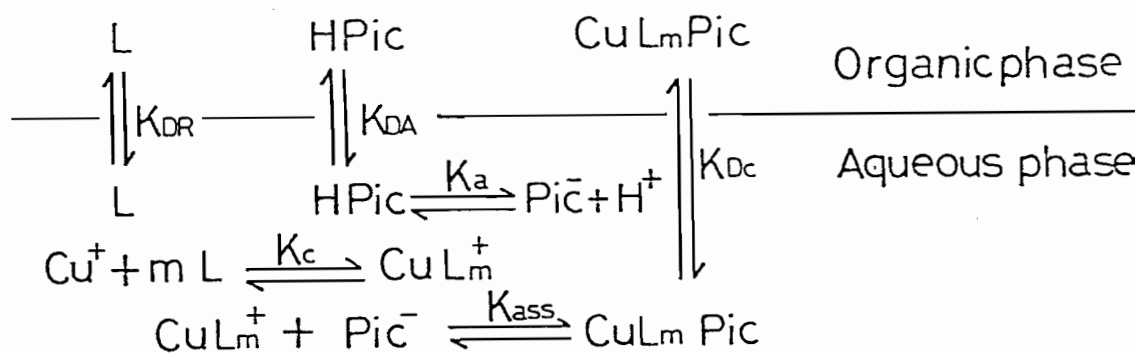


Fig.4-1. Equilibria in the liquid-liquid distribution for copper(I)-tetrathio ether-Pic system.

#### 4.3.2 Extraction behavior of copper(I) with six tetrathio ethers

The relationship between the logarithm of distribution ratio ( $\log D$ ) and the logarithm of picrate ion concentration in the aqueous phase at pH 4.3 is shown in Fig.4-2. Straight lines with the slope of +1 for each ligand, were obtained, therefore,  $n=1$ . The structure of tetrathio ethers are reflected in the extractability of copper(I). The extractability of the benzotetrathio ethers such as Bz-TTCP and o-xy-(ETET)<sub>2</sub> is superior to nonbenzotetrathio ethers such as TTCT and TTAP. It is thought that the lipophilic ligands such as benzotetrathio ethers form the metal complexes which is easily soluble in 1,2-dichloroethane. Nevertheless, the extractability of benzotetrathio ethers, m-xy-(ETET)<sub>2</sub> and p-xy-(ETET)<sub>2</sub>, are inferior to nonbenzotetrathio ethers, because their structures will be unsuitable for the complex formation. Study of the solid-state structure and the thermodynamic stability for copper(I) with TTCT and TTAP<sup>21)</sup> suggested that the stability constant for the copper(I) complex formed with TTAP was larger than the corresponding value for copper(I)-TTCT complex. As shown in Fig.4-2, complexing ability of TTAP seems to be superior to that of TTCT and similarly o-xy-(ETET)<sub>2</sub> to Bz-TTCP. Acyclic tetrathio ether is so flexible that copper(I) which favors the tetrahedral arrangement,

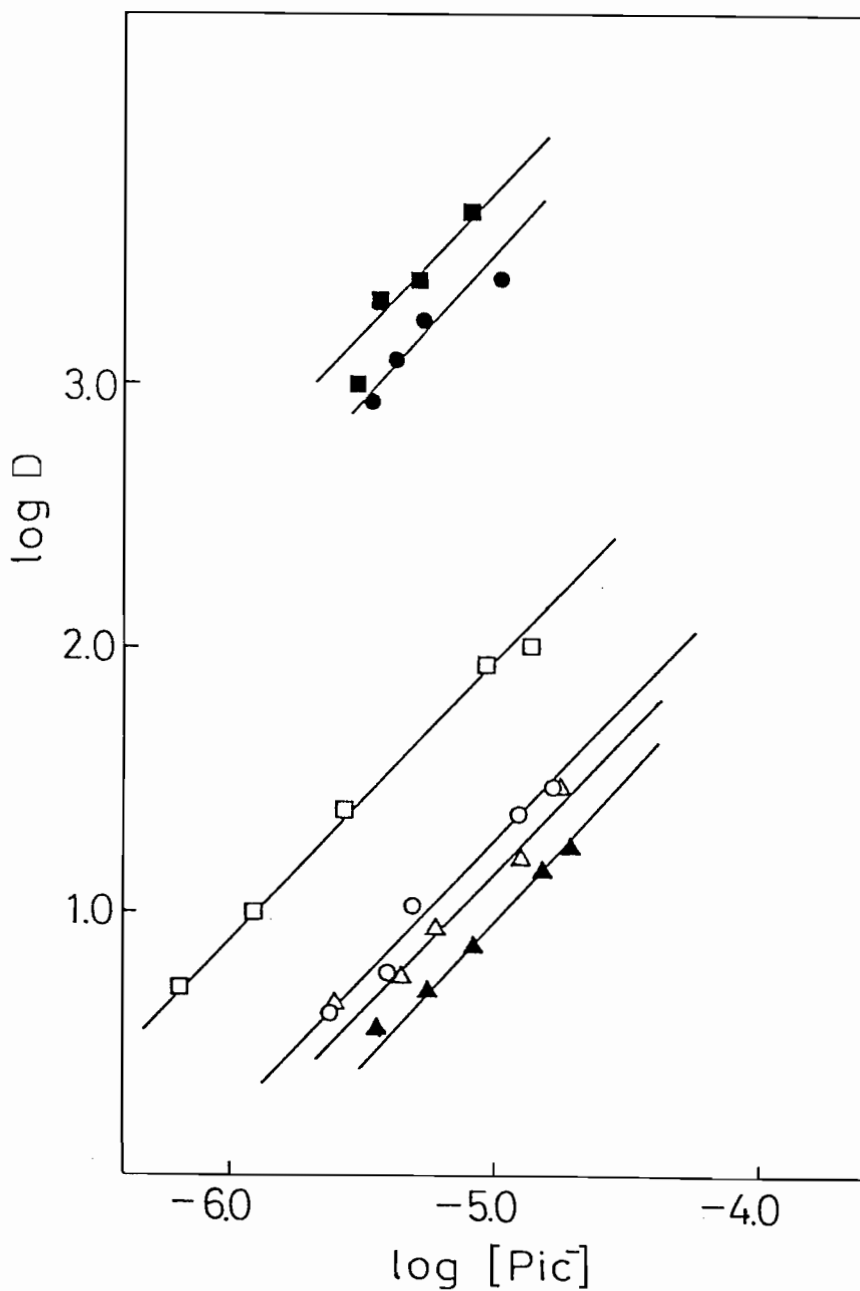


Fig.4-2. Plots of  $\log D$  vs.  $\log[\text{Pic}^-]$  at pH 4.3.  
 Initial concentration:  $5 \times 10^{-4} \text{M}$  copper(I),  
 $1 \times 10^{-3} \text{M}$  ligand.  $\circ$  : TTCT,  $\bullet$  : Bz-TTCP,  
 $\square$  : TTAP,  $\blacksquare$  : o-xy-(ETET) $_2$ ,  $\triangle$  : m-xy-(ETET) $_2$ ,  
 $\blacktriangle$  : p-xy-(ETET) $_2$ .

seems to be encircled by them, whereas cyclic tetrathio ethers is unfavorable to accommodate to the copper(I) owing to the ligand strain.

In order to determine the composition of copper(I)-tetrathio ether complexes, the molar ratio method of copper(I) to the ligand was examined. The results are shown in Fig.4-3. The breaks appear clearly at the point of  $[L]_o/[Cu^+]_i=1.0$ , that is,  $m=1$  in the case of TTCT, TTAP, Bz-TTCP and o-xy-(ETET)<sub>2</sub>. On this point, copper(I) was extracted more than 99%, though the %E value with TTCT is 96%. Therefore these ligands might form the stable 1:1 copper(I) complex by taking the tetrahedral configuration. On the other hand, the curve of m-xy-(ETET)<sub>2</sub> goes along with the same line when the ratio of  $[L]_o/[Cu^+]_i$  is below 0.5 indicates the formation of the 1:1 (Cu(I):L) complex but the plots begin to deviate from the straight line and at the ratio of  $[L]_o/[Cu^+]_i=2.0$ , the %E value is close to 100. Further, the curve of p-xy-(ETET)<sub>2</sub> deviates obviously from the line indicating the formation of the 1:1 complex, may indicate the formation of the mixture of 1:1 and 1:2 complex.

#### 4.3.3 Compositions and extraction constants

From the extraction data shown in Figs.4-2 and 4-3 and Eqn.(4-3), the composition and the extraction constant  $K_{ex}$

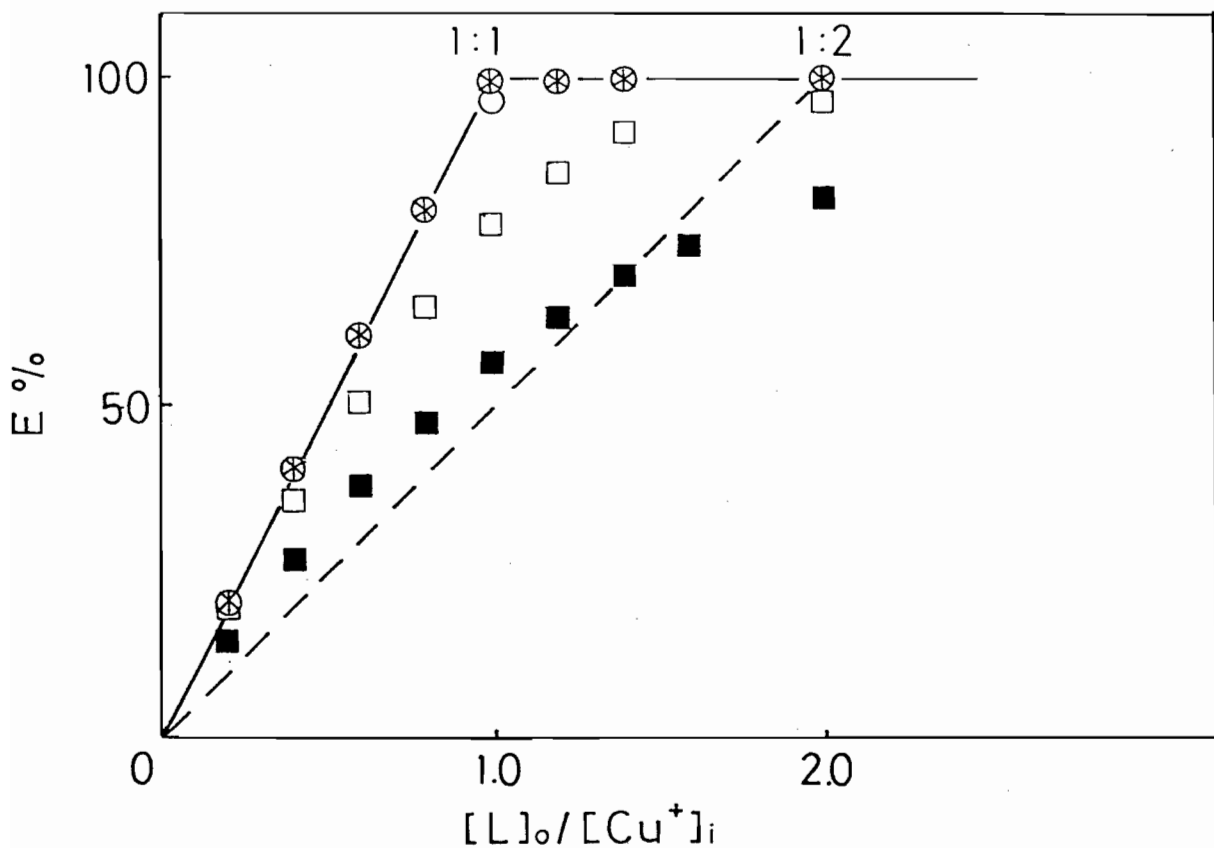


Fig.4-3. Molar ratio methods at pH 5.5.  
 Initial concentration:  $5 \times 10^{-5} \text{M}$  copper(I). ○ : TTCT,  
 ⊗ : Bz-TTCP, ⊙ : TTAP, ⊖ : o-xy-(ETET)<sub>2</sub>,  
 □ : m-xy-(ETET)<sub>2</sub>, ■ : p-xy-(ETET)<sub>2</sub>.

of extracted copper(I)-tetrathio ether complexes are obtained, and listed in Table 4-1. The order of  $K_{ex}$  is as follows;  $o\text{-xy}-(\text{ETET})_2 > \text{Bz-TTCP} > \text{TTAP} > \text{TTCT} > m\text{-xy}-(\text{ETET})_2 > p\text{-xy}-(\text{ETET})_2$ . For the extraction of class b metals with polythio ethers, the lipophilicity of the complex and the ligand structure suitable for the coordination may be important.

Table 4-1. Composition and extraction constant of Copper(I)-tetrathio ether complexes.

Ligand	Cu(I):L:Pic <sup>-</sup>	logK <sub>ex</sub>
TTCT	1:1:1	9.3
Bz-TTCP	1:1:1	11.5
TTAP	1:1:1	10.0
$o\text{-xy}-(\text{ETET})_2$	1:1:1	11.7
$m\text{-xy}-(\text{ETET})_2$	1:1:1	9.2
$p\text{-xy}-(\text{ETET})_2$	1:1:1 1:2:1	—



## Chapter 5.

### Liquid-liquid extraction of silver(I) with cyclic and acyclic tetrathio ethers

#### 5.1 Introduction

Silver(I) ion belonging to class b metal is extracted perfectly with a tetrathio ether and appropriate counter anion, when the ligand concentration is excess over the silver(I) concentration. In the previous study,<sup>47)</sup> the structure of the dimeric complex of Bz-TTCP has been clarified. On the other hand, studies of extraction equilibria have shown the composition of extracted species with TTCT of which the ratio is 1:2:1 (Ag(I):TTCT:Pic).<sup>35)</sup> However, the molecular structure of Ag(I)-TTCT-picrate complex has not been reported yet. Even the extraction study of silver(I) with acyclic tetrathio ethers corresponding to cyclic ones has not been studied. In this chapter, extraction behavior of silver(I) with cyclic and acyclic tetrathio ethers was examined. Further, the molecular structures of extracted Ag(I)-TTCT-picrate complex and Ag(I)-TTAP-picrate complex were clarified by X-ray crystallographic analysis.

## 5.2 Experimental

### 5.2.1 Liquid-liquid extraction of silver(I)

Extraction was done by the method described in Chapter 3. The silver(I) concentrations of two phases were measured by atomic absorption spectrometry.

### 5.2.2 Crystal formation of the two silver(I)-tetrathioether complexes

A hundred ml of the aqueous solution at pH 4.7 containing silver(I) nitrate ( $5 \times 10^{-4}$  M), picric acid ( $2.5 \times 10^{-3}$  M) and acetate buffer solution (0.1 M), and 100 ml of 1,2-dichloroethane solution containing TTCT or TTAP ( $1 \times 10^{-3}$  M) were prepared. Both solutions were mixed and shaken for 30 min at 25°C. After centrifugation followed by the phase separation, hexane was added into the organic phase. The coarse crystals which formed were filtered after two days. For the Ag(I)-TTCT complex, acetone was added to dissolve them. The resulting solution was allowed to stand for two days; yellow single crystals suitable for X-ray crystallographic analysis were obtained. For the Ag(I)-TTAP complex ethylacetate was added to dissolve them. Hexane was added into the solution and filtered. The resulting solution was allowed to stand for two or three days; yellow single crystals suitable for X-ray crystallographic analysis were

obtained.

### 5.2.3 X-ray analysis

Accurate lattice constants and intensities were measured on a Rigaku AFC-5 diffractometer with  $\text{MoK}\alpha$  radiation monochromatized by a graphite crystal. The crystal data of Ag(I)-TTCT-Pic are:  $[\text{Ag}(\text{C}_{10}\text{H}_{20}\text{S}_4)]^+[\text{C}_6\text{H}_2\text{O}(\text{NO}_2)_3]^-$ , F.W.=604.5, triclinic, space group  $\text{P}\bar{1}$ ,  $a=14.305$ ,  $b=16.878$ ,  $c=9.346 \text{ \AA}$ ,  $\alpha=90.54$ ,  $\beta=99.88$ ,  $\gamma=94.06^\circ$ ,  $V=2216.95 \text{ \AA}^3$ ,  $Z=4$ ,  $D_m(\text{flotation})=1.807$ ,  $D_x=1.810 \text{ g/cm}^3$ ,  $\text{MoK}\alpha=0.71073$ ,

$\mu$  (absorption coefficient)= $12.97 \text{ cm}^{-1}$ , crystal dimension:  $0.3 \times 0.1 \times 0.1 \text{ mm}^3$ . The crystal data of Ag(I)-TTAP-Pic complex are:  $[\text{Ag}(\text{C}_{11}\text{H}_{22}\text{S}_4)]^+[\text{C}_6\text{H}_2\text{O}(\text{NO}_2)_3]^-$ , F.W.=620.5, triclinic, space group  $\text{P}\bar{1}$ ,  $a=12.805$ ,  $b=17.782$ ,  $c=12.180 \text{ \AA}$ ,  $\alpha=98.77$ ,  $\beta=91.05$ ,  $\gamma=116.06^\circ$ ,  $V=2451.17 \text{ \AA}^3$ ,  $Z=4$ ,  $D_m(\text{flotation})=1.675$ ,  $D_x=1.681 \text{ g/cm}^3$ ,  $\text{MoK}\alpha=0.71073$ ,  $\mu$  (absorption coefficient)= $11.82 \text{ cm}^{-1}$ , crystal dimension:  $0.3 \times 0.3 \times 0.1 \text{ mm}^3$ .

The intensity data were collected by the  $2\theta$ - $\omega$  scan technique with a scan rate of  $6 \text{ min}^{-1}$ . A total of 8624 reflections with  $2\theta < 50^\circ$  for Ag(I)-TTCT-Pic, and 8105 reflections with  $2\theta < 48^\circ$  for Ag(I)-TTAP-Pic were collected. The intensity data were corrected for the Lorentz and polarization effects, but not for absorption. Independent reflections with  $|F_o| > 3\sigma(F_o)$  ( $2\theta < 50.0^\circ$ ) were considered as "observed" and 4453 reflection for Ag(I)-TTCT-Pic and 4091

reflection ( $2\theta < 46.0^\circ$ ) for Ag(I)-TTAP-Pic were used for the structure analysis. The structure was solved by direct methods, and refined by the block-diagonal least-squares method. In the least-squares refinement, the weighting scheme,  $w = [1 + 0.1185(|F_o| - F_m)]^{-1}$  ( $|F_o| > F_m$ ) was employed. The final discrepancy factors were  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.083$  and  $R_2 = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2} = 0.087$  for TTCT and  $R_1 = 0.120$ ,  $R_2 = 0.132$  for TTAP. The atomic scattering factors and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.<sup>48)</sup> All the calculations were carried out on the ACOS 1000 computer at the Information Processing Center of Kobe University by the use of programs of The Universal Crystallographic Computing System-Osaka (1979).

### 5.3. Results and Discussion

#### 5.3.1 Extraction equilibria of silver(I)

As mentioned in Chapter 3, silver(I) or copper(I) was extracted into 1,2-dichloroethane more than 99%, when the concentrations of tetrathio ether and picrate ion were 100 and 10 times excess of metal concentration ( $5 \times 10^{-5}$  M), respectively. The extraction equilibria of silver(I) ion are shown in Fig.5-1, where L indicates the tetrathio ether used. The extraction constant  $K_{ex}$  and the distribution ratio

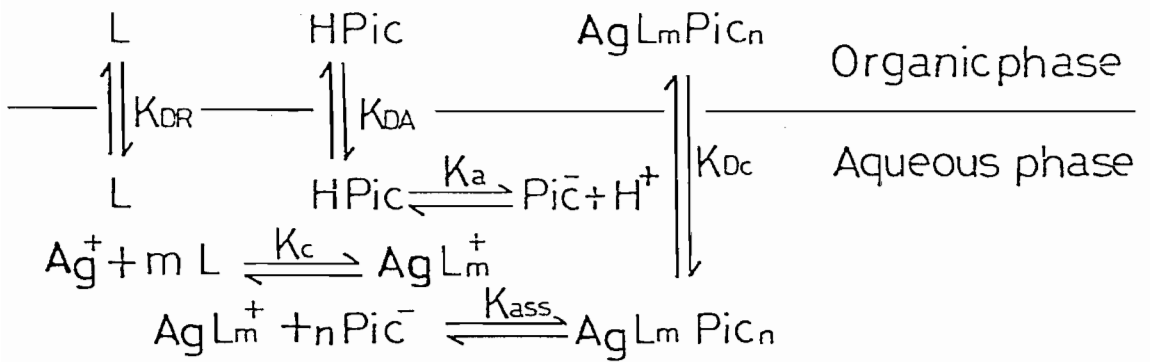
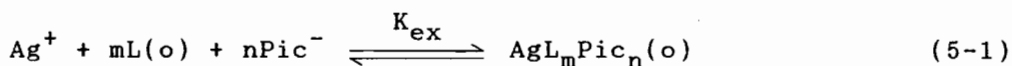


Fig.5-1. Equilibria in the liquid-liquid distribution for silver(I)-tetrathio ether-Pic system.

D are defined as follows:



$$K_{\text{ex}} = [\text{AgL}_m\text{Pic}_n]_{\text{o}} / [\text{Ag}^+][\text{L}]_{\text{o}}^m[\text{Pic}^-]^n \quad (5-2)$$

$$D = [\text{AgL}_m\text{Pic}_n]_{\text{o}} / ([\text{AgL}_m\text{Pic}_n] + [\text{AgL}_m^+] + [\text{Ag}^+]) \quad (5-3)$$

From Eqns.(5-1), (5-2), (5-3) and the suitable approximation, the following logarithmic expression is obtained.

$$\log D = \log K_{\text{ex}} + m \log [\text{L}]_{\text{o}} + n \log [\text{Pic}^-] \quad (5-4)$$

### 5.3.2 Extraction behavior of silver(I) with six tetrathio ethers

The relationships between the logarithmic distribution ratio ( $\log D$ ) and the logarithm of picrate ion concentration in the aqueous phase at pH4.5 are shown in Fig.5-2. Straight lines with the slope of +1 for each ligand were obtained. Therefore "n" in Eqn.(5-3) is regarded as  $n=1$ . Figure 5-2 suggests the order of extractability of ligands. The order is as follows: o-xy-(ETET)<sub>2</sub> > Bz-TTCP > m-xy-(ETET)<sub>2</sub> > TTAP > p-xy-(ETET)<sub>2</sub> > TTCT.

The extractability of the benzo-tetrathio ether such as o-xy-(ETET)<sub>2</sub> or Bz-TTCP is superior to that of the nonbenzo-tetrathio ether such as TTAP or TTCT, respectively. The high extractability of benzo-ligand is due to the high lipophilicity of the silver(I)-benzo-tetrathio ether complex. Noncyclic tetrathio ethers such as o-xy-(ETET)<sub>2</sub> and

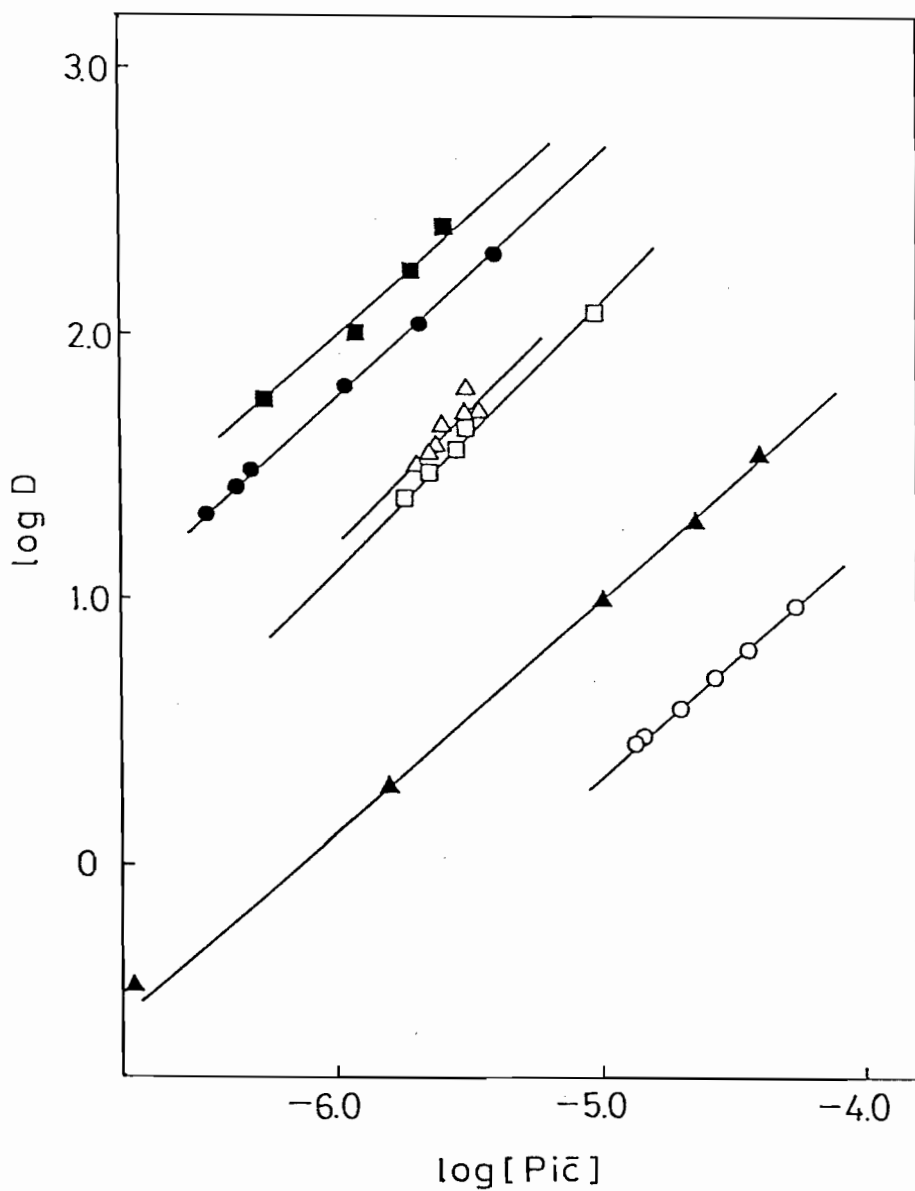


Fig.5-2. Plots of  $\log D$  vs.  $\log[\text{Pic}^-]$  at pH 4.5.  
 Initial concentration:  $5 \times 10^{-5} \text{M}$  silver(I),  
 $5 \times 10^{-4} \text{M}$  ligand.                       $\circ$ : TTCT,  
 $\bullet$ : Bz-TTCP,  $\square$ : TTAP,  $\blacksquare$ : o-xy-(ETET) $_2$ ,  
 $\triangle$ : m-xy-(ETET) $_2$ ,  $\blacktriangle$ : p-xy-(ETET) $_2$ .

TTAP show higher extractabilities than corresponding cyclic tetrathio ethers, Bz-TTCP and TTCT. These results are similar with the case of extraction behavior of copper(I). In the case of copper(I) as shown in Chapter 4, the order of extractability of these ligands is as follows: o-xy-(ETET)<sub>2</sub> > Bz-TTCP > TTAP > TTCT > m-xy-(ETET)<sub>2</sub> > p-xy-(ETET)<sub>2</sub>. Although the extractability of m-xy-(ETET)<sub>2</sub> for silver(I) is higher than TTAP. Even that of p-xy-(ETET)<sub>2</sub> is higher than that of TTCT. As copper(I) prefers the tetrahedral configuration in general, m-xy-(ETET)<sub>2</sub> or p-xy-(ETET)<sub>2</sub> is unlikely to accommodate the copper(I) because of the structure of these ligands. It is interesting, m-xy-(ETET)<sub>2</sub> and p-xy-(ETET)<sub>2</sub> show such high extractabilities of silver(I), will be discussed later. The relationships between the extractabilities of silver(I) and the mole ratio of the initial concentration of four acyclic ligands to that of silver(I) are shown in Fig.5-3a. For cyclic ligands TTCT and Bz-TTCP, the results which have been reported previously,<sup>47)</sup> are shown in Fig.5-3b. At the point of the mole ratio [Ligand]/[Ag(I)]=1.0, the extractabilities of silver(I)(%E) with cyclic Bz-TTCP, acyclic o-xy-(ETET)<sub>2</sub> and TTAP are more than 99%. These results suggest that the molar ratio of extracted species is 1:1(Ag(I):ligand), therefore m=1 in Eqn.(5-1). However it is uncertain whether monomeric or dimeric complex is extracted.



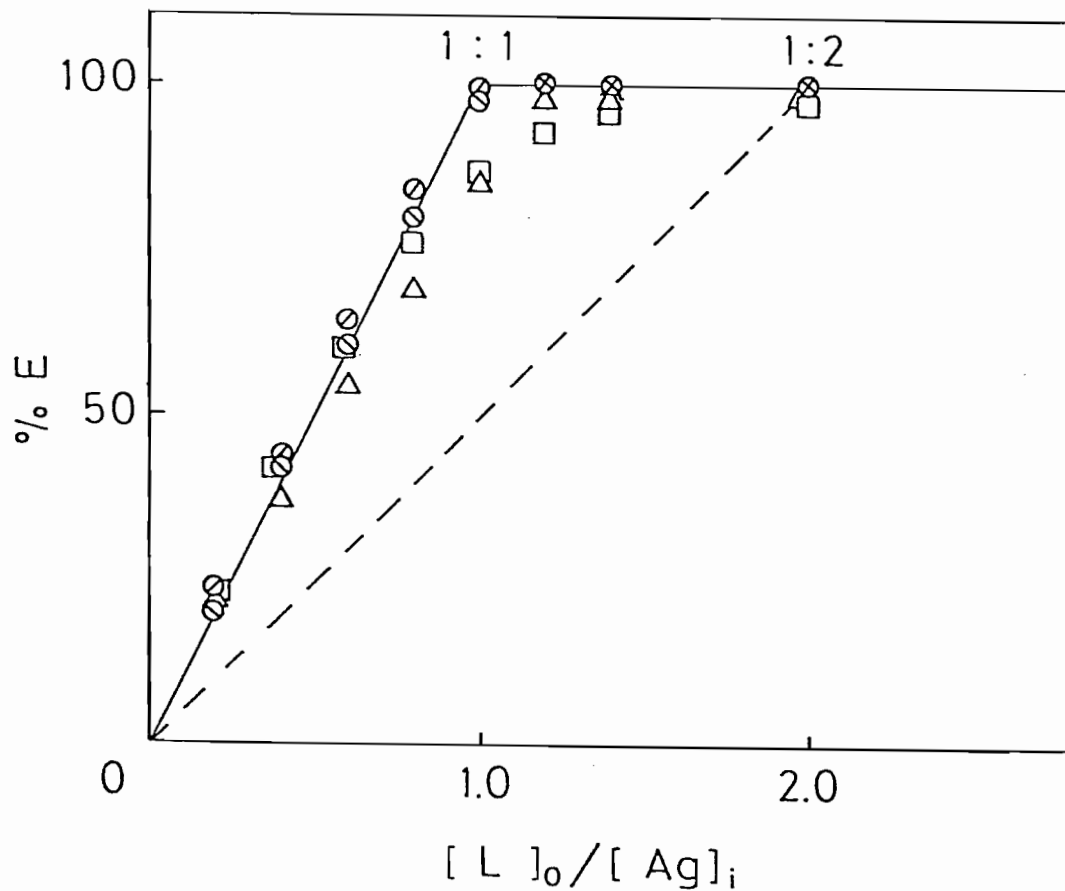


Fig.5-3a. Molar ratio methods at pH 4.5. Initial concentration:  $5 \times 10^{-5} \text{M}$  silver(I),  $1 \times 10^{-3} \text{M}$  picrate ion.  $\odot$ : TTAP,  $\ominus$ : o-xy-(ETET)<sub>2</sub>,  $\triangle$ : m-xy-(ETET)<sub>2</sub>,  $\square$ : p-xy-(ETET)<sub>2</sub>.

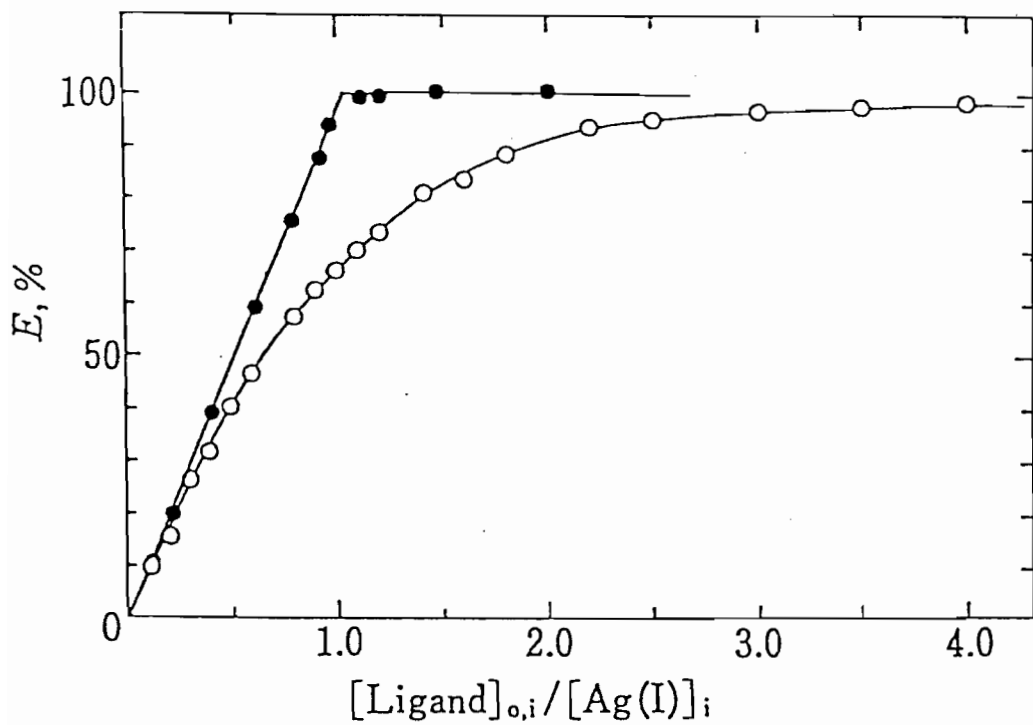


Fig.5-3b. Molar ratio methods at pH 4.0. Initial concentration:  $5 \times 10^{-5}$  M silver(I),  $5 \times 10^{-3}$  M picrate.  
 ○ : TTCT, ● : Bz-TTCP.

Extraction curves of m-xy-(ETET)<sub>2</sub> and p-xy-(ETET)<sub>2</sub> go along with that indicates the molar ratio of Ag(I):ligand=1:1. Only the curve of TTCT deviates from the line of the 1:1 complex. In the previous paper,<sup>35)</sup> the composition of the extracted species, [Ag(ttct)<sub>2</sub>]Pic, was obtained for the large excess of TTCT by the displacement method of the extraction equilibria. Although, a distinct break point is not found at the ratio of 1:2 in Fig.5-3b. The formation of both 1:1 and 1:2 complexes is expected. From the extraction data shown in Figs.5-2, 5-3a, 5-3b and Eqn.(5-3), the compositions and the extraction constants  $K_{ex}$  of extracted silver(I)-tetrathio ether complexes are evaluated without considering the formation of dimer complexes. These are listed in Table 5-1.

### 5.3.3 Results of X-ray analysis

*Structure of Ag(I)-TTCT-Pic complex* As mentioned in the case of Ag(I)-Bz-TTCP-Pic complex previously,<sup>47)</sup> there were no direct interactions between the Ag(I)-TTCT complex cation and picrate ion. The ORTEP drawing of one of silver(I)-TTCT complex cation is shown in Fig.5-4, where bonds between silver(I) and sulfur atoms are drawn with heavy lines. The interatomic distances between silver(I) and each sulfur atom, and their angles are listed in Table 5-2. The silver(I)-TTCT complex cation exists as its dimer, that is,

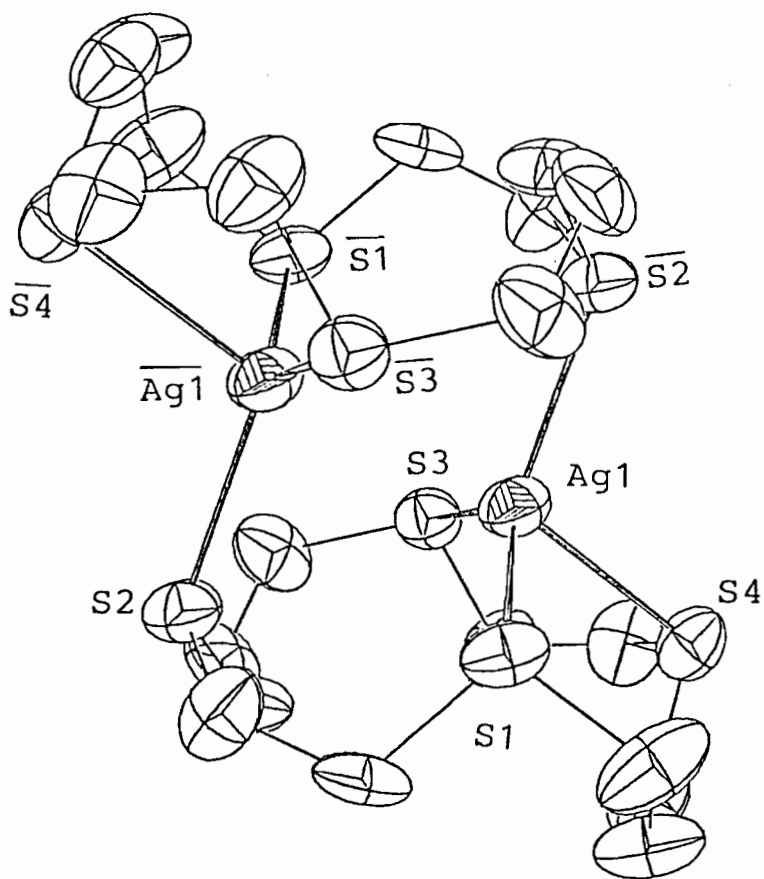


Fig.5-4. ORTEP drawing of the dimeric complex cation,  $[\text{Ag}_2-(\text{ttct})_2]^{2+}$ , with some atom-numbering.

Table 5-1. Composition and extraction constant of silver(I)-tetrathio ether complexes.

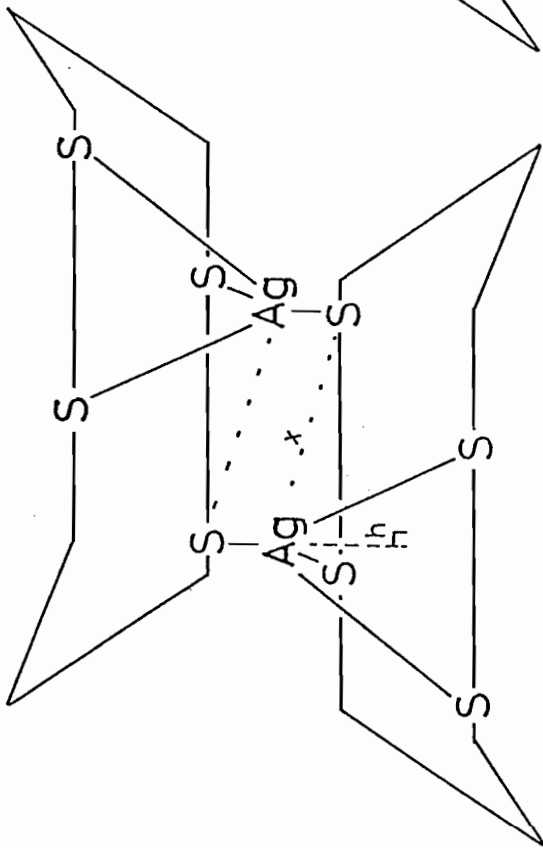
Ligand	Ag(I):L:Pic	log K <sub>ex</sub>
o-xy-(ETET) <sub>2</sub>	1:1:1	11.2
Bz-TTCP	1:1:1	11.0
m-xy-(ETET) <sub>2</sub>	1:1:1	10.5
TTAP	1:1:1	10.4
p-xy-(ETET) <sub>2</sub>	1:1:1	9.3
TTCT	1:1:1 1:2:1	-

Table 5-2. Some data of interatomic distances (Å) and angles (°) for the dimer of the silver(I)-TTCT complex cation.

Ag1 - S1	2.550 Å	S1 - Ag1 - S2̄	115.4°
Ag1 - S2	2.551 Å	S1 - Ag1 - S3	135.0°
Ag1 - S3	2.599 Å	S1 - Ag1 - S4	93.3°
Ag1 - S4	2.675 Å	S2̄ - Ag1 - S3	108.3°
		S2̄ - Ag1 - S4	109.2°
		S3 - Ag1 - S4	81.4°

$[\text{Ag}_2(\text{ttct})_2]^{2+}$  in the solid state. The dimeric complex cation has a symmetry center on the center of the square plane formed with Ag1,  $\text{S}\bar{2}$ ,  $\text{Ag}\bar{1}$  and S2 atoms. The coordination number of the silver(I) is 4 and the silver(I) is coordinated as the distorted tetrahedral with four sulfur atoms, S1, S3 and S4 of one TTCT molecule and  $\text{S}\bar{2}$  of another TTCT molecule. The dimeric structure resembles the structure of Ag(I)-Bz-TTCP complex cation, although the coordination number of the silver(I) is 5. The structures of Ag(I)-TTCT and Ag(I)-Bz-TTCP dimeric complex cations are shown schematically in Fig.5-5. In the case of Bz-TTCP, one of the sulfur atoms coordinates to two silver(I) ions by using two lone paired electron. One of their bond lengths is the shortest one (2.55 Å), and another is the longest one (2.93 Å). On the other hand in the case of TTCT, corresponding bond lengths are 2.55 and 3.69 Å. The latter is too long to regard as the bond. The largest bond angle of the Ag(I)-Bz-TTCP complex between silver(I) and sulfur atoms, 145.5° is closest to that of linear configuration (180°). The angle consists of the two shortest bonds (2.55 and 2.56 Å). However, the angle of Ag(I)-TTCT complex, consists of two short bonds (2.55 Å) is 115.4°, not the largest one. The other angles close to that of tetrahedral angle.

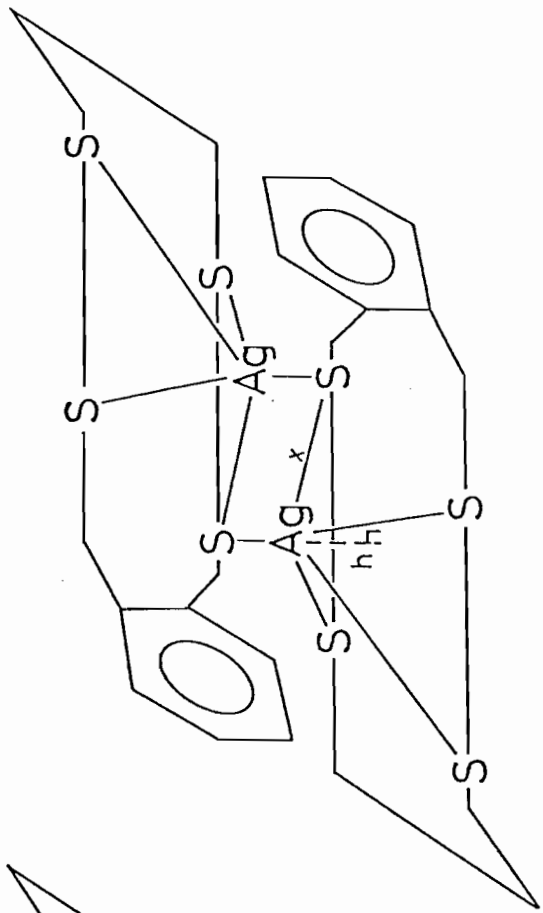
In the Ag(I)-TTCT complex cation, silver(I) comes up



Ag-TTCT complex

$h = 1.14 \text{ \AA}$

$x = 3.69 \text{ \AA}$



Ag-Bz-TTCP complex

$h = 0.94 \text{ \AA}$

$x = 2.93 \text{ \AA}$

Fig.5-5. Structures of dimeric complex cations,  $[\text{Ag}_2(\text{ttct})_2]^{2+}$  and  $[\text{Ag}_2(\text{bz-ttcp})_2]^{2+}$ , drawn schematically.

1.14 Å from the least square plane formed by four sulfur atoms. Whereas in the case of the Bz-TTCP which has slightly larger cavity than that of TTCT, silver(I) comes up 0.94 Å from the 4S plane. It is considered that the larger cavity of Bz-TTCP makes the coordination number of silver(I) five and the cavity of TTCT makes that four.

*Structure of Ag(I)-TTAP-Pic complex* There are also no direct interactions between the Ag(I)-TTAP complex cation and picrate anion. The ORTEP drawing of the silver(I)-TTAP complex cation is shown in Fig.5-6. The interatomic distances between silver(I) and each sulfur atom and their angles are listed in Table 5-3. The silver(I)-TTAP complex cation also exists as its dimer,  $[\text{Ag}_2(\text{ttap})_2]^{2+}$  in the solid state. Although there is no symmetry center in the cation itself. Two silver(I) ions are sandwiched with two molecule of TTAP which exist parallel with each other. For example, the silver(I), Ag1 is coordinated as the distorted tetrahedral with four sulfur atoms, S11 and S12 of one TTAP molecule and S21 and S22 of another molecule. The average bond length between two silver(I) ions and eight sulfur atoms, 2.57 Å, is shorter than that of Ag(I)-TTCT complex cation, 2.59 Å. The bond length 2.49 Å is the shortest of those of three complex cations discussed. As shown in Table 3, some of angles are close to 180°, that is, the linear configuration which silver(I) prefers.



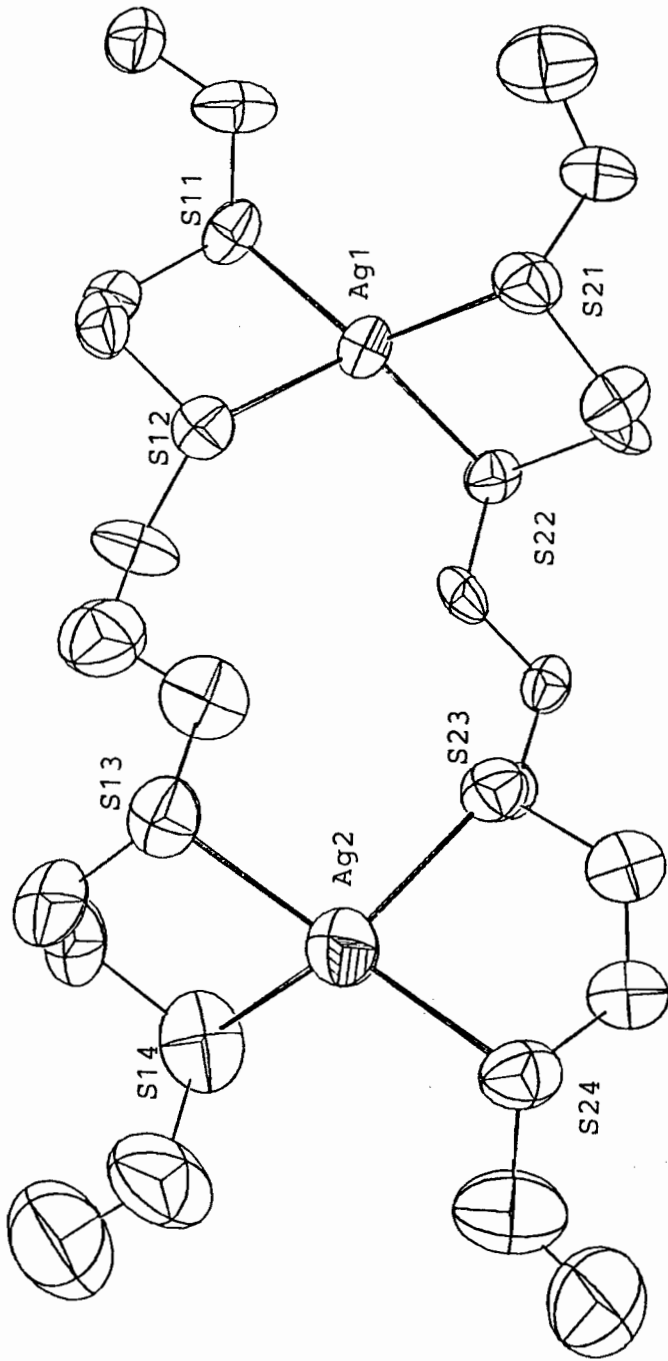


Fig.5-6. ORTEP drawing of the dimeric complex cation,  $[Ag_2-(ttap_2)]^{2+}$ , with some atom-numbering.

Table 5-3. Some data of interatomic distances (Å) and angles (°) for the dimer of the silver(I)-TTAP complex cation.

Ag1 - S11	2.489 Å	S11 - Ag1 - S12	86.9°
Ag1 - S12	2.624 Å	S11 - Ag1 - S21	124.7°
Ag1 - S21	2.578 Å	S11 - Ag1 - S22	132.2°
Ag1 - S22	2.563 Å	S12 - Ag1 - S21	110.4°
		S12 - Ag1 - S22	116.9°
		S21 - Ag1 - S22	87.1°
Ag2 - S13	2.623 Å	S13 - Ag2 - S14	86.9°
Ag2 - S14	2.524 Å	S13 - Ag2 - S23	100.9°
Ag2 - S23	2.601 Å	S13 - Ag2 - S24	143.1°
Ag2 - S24	2.527 Å	S14 - Ag2 - S23	130.8°
		S14 - Ag2 - S24	116.7°
		S23 - Ag2 - S24	85.0°

#### 5.3.4 Molecular structure and extraction behavior

It becomes clear that the structures of Ag(I)-TTCT and Ag(I)-TTAP complex cations in solid state are dimers. If extracted species of silver(I)-tetrathio ether complex is assumed to be the dimer, extraction behavior is explained reasonably. In these dimeric cations, ethylene or propylene chains wrap around the silver(I) ion bonded with sulfur atoms. Such lipophilic cations with appropriate counter anions will be easily dissolved in organic solvents immiscible with water, and extracted into those such as 1,2-dichloroethane or chloroform. In the case of Bz-TTCP, a distinct break point at  $[bz-ttcp]_{o,i}/[Ag(I)]=1$  in Fig.5-3b suggests that the stable dimeric complex ( $[Ag_2(bz-ttcp)_2]Pic^-_2$ ) is extracted. As shown in Fig.5-5, the contribution of benzene rings of Bz-TTCP which not only increase the lipophilicity of the complex but shield two silver(I) ions effectively, may stabilize the complex. On the other hand, in the case of TTCT, a distinct break point can not be found. It is considered that the dimer of Ag(I)-TTCT complex is not so stable as that of Ag(I)-Bz-TTCP. As previously reported,<sup>35)</sup> 1:2 complex in which a silver(I) ion is sandwiched with two TTCT molecules may become to be extracted as increasing the ligand concentration. It has been expected that a silver(I) ion is encircled with one molecule of acyclic TTAP, as shown in Fig.5-7a. However, the

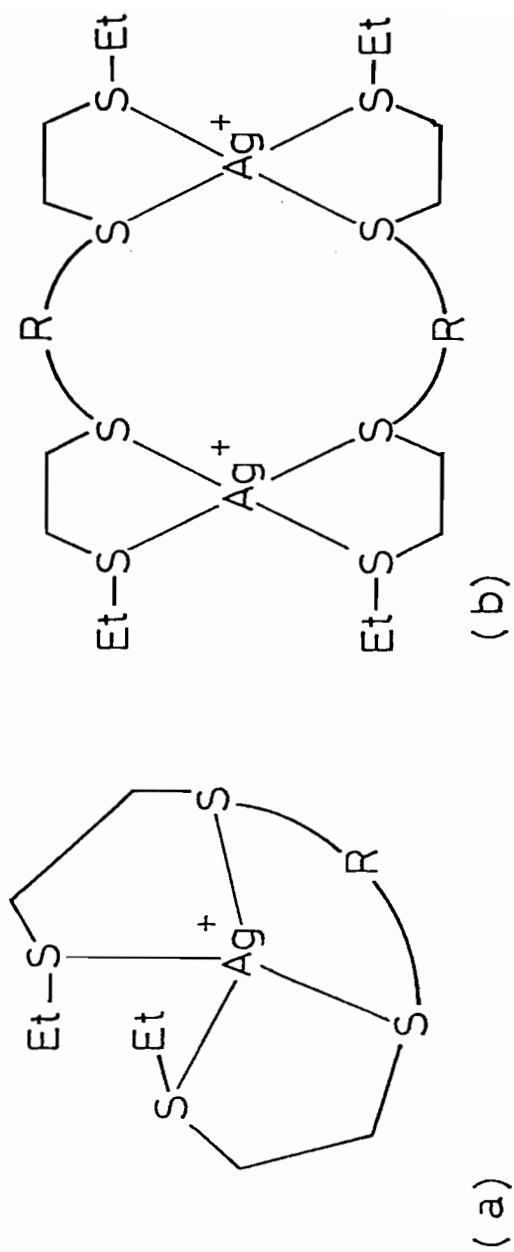


Fig.5-7. Schematic representation of possible configurations of silver(I)·TTAP complex.

structure in solid state shown in Fig.5-7b is more stable than that of Ag(I)-TTCT dimeric complex. Complexation shown in Fig.5-7a seems to have more entropic disadvantage than dimeric complexes. Nevertheless m-xy-(ETET)<sub>2</sub> or p-xy-(ETET)<sub>2</sub> is not able to act as a quadridentate ligand but as a bidentate one, the order of extractability of them are high when compared with the case of copper(I) extraction. Such high extractabilities can be explained reasonably, if extracted species exist as their dimers in 1,2-dichloroethane.

## Chapter 6.

### Liquid-liquid extraction of palladium(II) with three benzotetrathio ethers

#### 6.1 Introduction

Palladium(II) is one of soft metals belonging to class b, classified by Ahrlund.<sup>2)</sup> In Chapter 3, the extraction of palladium(II) with six kinds of tetrathio ethers was examined. The results suggest that the extractabilities of tetrathio ethers which contain benzene ring are higher than those of nonbenzotetrathio ethers, and those of noncyclic tetrathio ethers are higher than those of cyclic tetrathio ethers. It is interesting to examine the extraction behavior of palladium(II) with these ligands in detail. The results will give us a guide to synthesize new reagents selective for palladium(II). In this chapter, extraction behavior of palladium(II) with three benzotetrathio ethers were examined. Three ligands used were the cyclic one, Bz-TTCP (2) and two acyclic ones, o-xy-(ETET)<sub>2</sub> (4) and p-xy-(ETET)<sub>2</sub> (6). Picrate as counter anion and 1,2-dichloroethane as extraction solvent were used.

## 6.2 Experimental

### 6.2.1 Reagents

Palladium sulfate used was dissolved in sulfuric acid solution to prepare  $1 \times 10^{-2}$  M solution of palladium(II) ion.

### 6.2.2 Liquid-liquid extraction of palladium(II)

A 10 ml of the aqueous solution containing  $5 \times 10^{-5}$  M palladium(II) ion,  $1 \times 10^{-3}$  M picrate ion and  $1 \times 10^{-2}$  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. A 10 ml of  $5 \times 10^{-3}$  M 1,2-dichloroethane solution of tetrathio ether was added to the aqueous solution. The mixture was shaken for 30 min on 200 strokes/min at  $25 \pm 0.1^\circ\text{C}$ , and then centrifuged for 5 min at 2000 r.p.m. 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(II) ion in the aqueous and organic phase were determined by atomic absorption spectrometry.

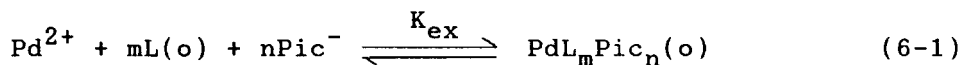
## 6.3 Results and discussion

### 6.3.1 Effect of pH on extraction of palladium(II) with tetrathio ethers

Extraction behavior of palladium(II) with two acyclic tetrathio ethers was 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.6-1. Each extractability is kept constant at the logD value of 1.8 for p-xy-(ETET)<sub>2</sub> and 0.3 for o-xy-(ETET)<sub>2</sub> respectively, in the pH range from 2.8 to 5.0. The decrease of logD values below pH 2.8 is due to the decrease of picrate ion changed to picric acid. It is interesting that the extractability of palladium(II) with p-xy-(ETET)<sub>2</sub> is higher than that with o-xy-(ETET)<sub>2</sub>. For o-xy-(ETET)<sub>2</sub> is designed to be a quadridentate ligand, whereas p-xy-(ETET)<sub>2</sub> may be not able to act as a quadridentate ligand but as a bidentate ligand.

### 6.3.2 Extraction equilibria of palladium(II)

The extraction equilibria of palladium(II) are shown in Fig.6-2 without considering the hydrolysis of palladium(II). The extraction constant  $K_{ex}$  and the distribution ratio  $D$  are defined as follows:



$$K_{ex} = [\text{PdL}_m\text{Pic}_n]_o / [\text{Pd}^{2+}][L]_o^m [\text{Pic}^-]^n \quad (6-2)$$



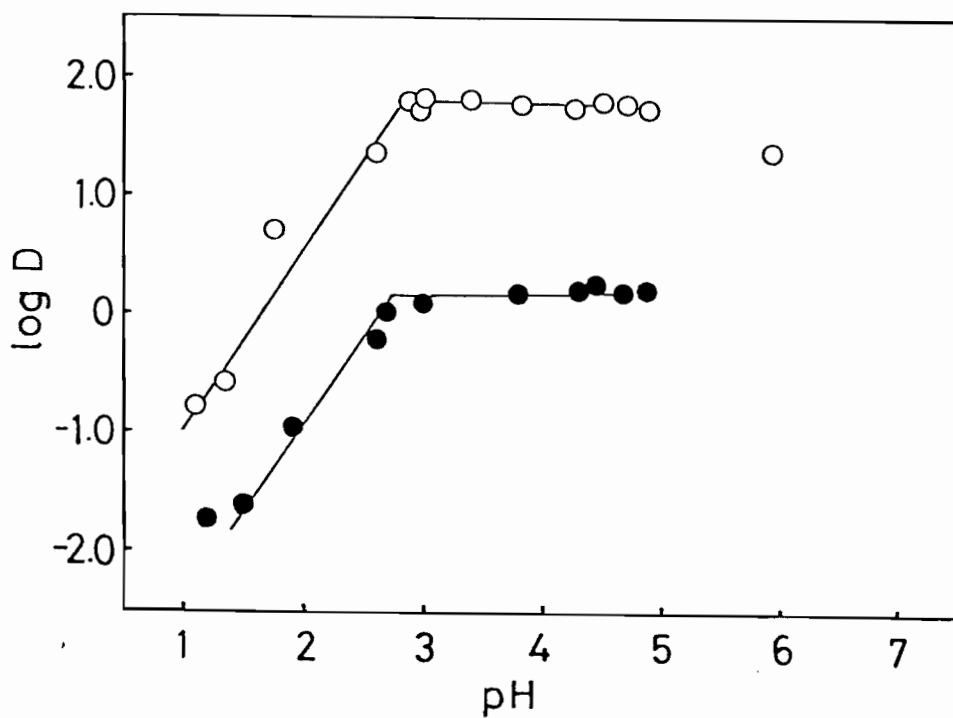


Fig.6-1. Plots of logD vs. pH. Initial concentration:  $5 \times 10^{-5} \text{M}$  palladium(II),  $1 \times 10^{-3} \text{M}$  picrate,  $5 \times 10^{-3} \text{M}$  ligand. ● : o-xy-(ETET)<sub>2</sub>, ○ : p-xy-(ETET)<sub>2</sub>.

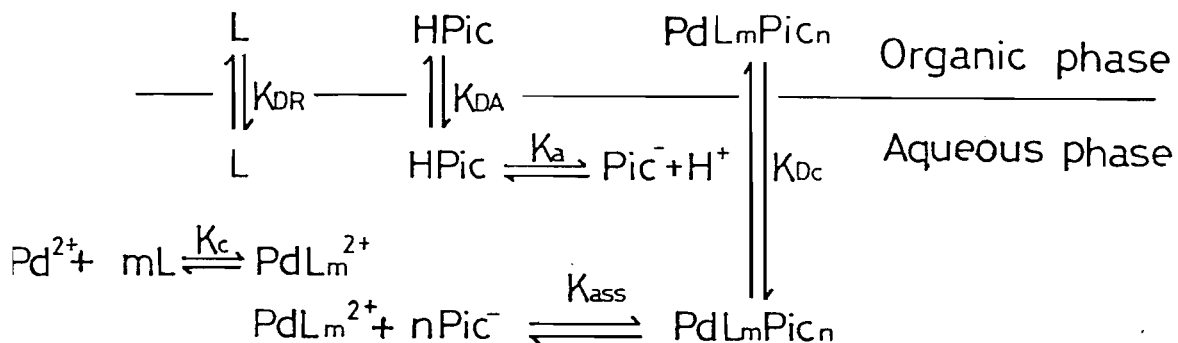


Fig.6-2. Equilibria in the liquid-liquid distribution for palladium(II)-benzotetrathio ether-Pic system.

From Eqns.(6-1), (6-2) and the suitable approximation, the following logarithmic expression is obtained.

$$\log D = \log K_{ex} + m \log [L]_o + n \log [\text{Pic}^-] \quad (6-3)$$

### 6.3.3 Extraction behavior of palladium(II) with three benzo-tetrathio ethers

**Slope analysis** The relationships between the logarithm of distribution ratio ( $\log D$ ) and the logarithm of picrate ion concentration in the aqueous phase at pH 2.9 are shown in Fig.6-3. The straight line with the slope of +2 for p-xy-(ETET)<sub>2</sub> was obtained: therefore,  $n=2$ . In the case of o-xy-(ETET)<sub>2</sub> and Bz-TTCP, those with the slope near +2 were obtained in the region of  $\log[\text{pic}^-] > -4.0$ . The slope of two lines come near zero at the concentration of picrate ion below  $1 \times 10^{-4}$  M. In this region, counter anions other than picrate ion form the ion pair and are extracted with the complex cation, is considered. As the formation of hydroxo complex of palladium(II) can not be ignored completely at pH 2.9, the extracted species containing hydroxide ion may be formed. The order of the extractability is as follows: p-xy-(ETET)<sub>2</sub> > o-xy-(ETET)<sub>2</sub> > Bz-TTCP. The extractability of acyclic tetrathio ether o-xy-(ETET)<sub>2</sub> is higher than that of the corresponding cyclic tetrathio ether, Bz-TTCP. In general, the extractability of metals such as silver(I), copper(I) and (II) with flexible acyclic tetrathio ether is

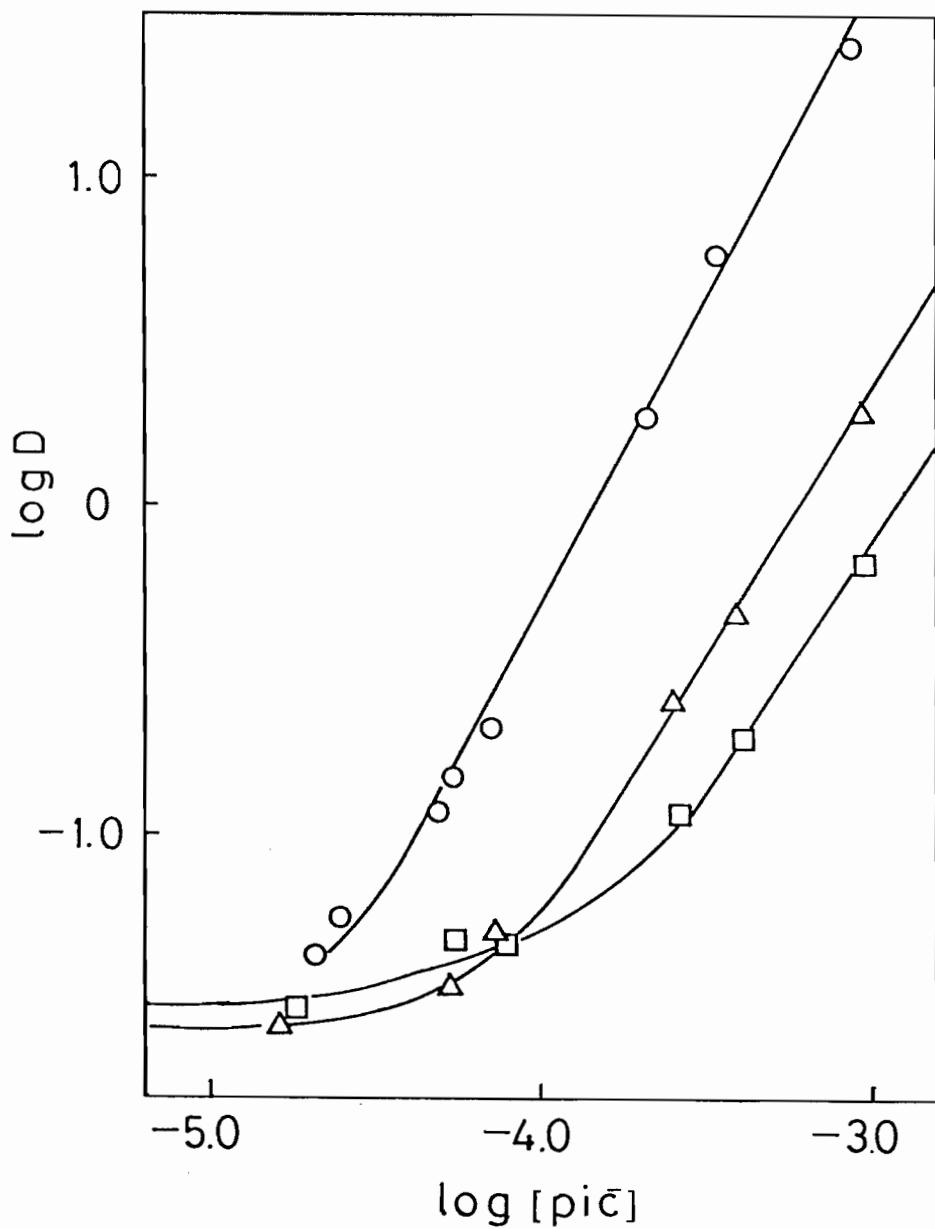


Fig.6-3. Plots of  $\log D$  vs.  $\log[\text{Pic}^-]$  at pH 2.9. Initial concentration:  $5 \times 10^{-5} \text{M}$  palladium(II).  
 ○ : p-xy-(ETET)<sub>2</sub>, △ : o-xy-(ETET)<sub>2</sub>, □ : Bz-TTCP.

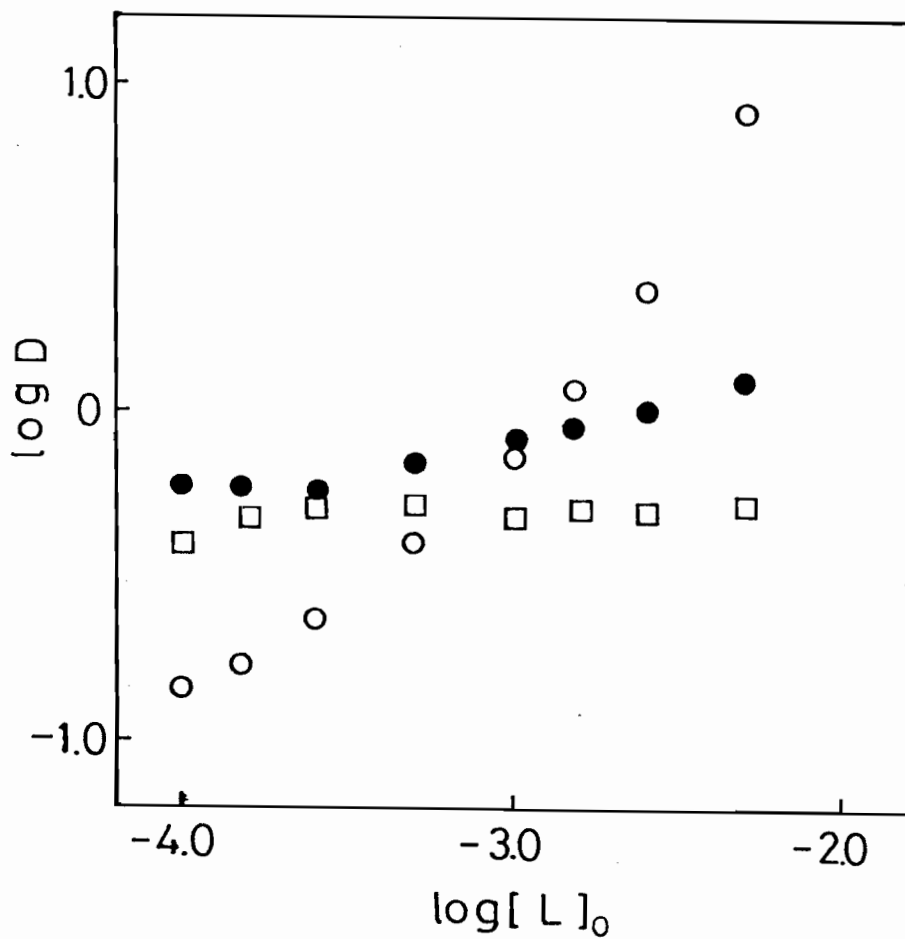


Fig.6-4. Plots of  $\log D$  vs.  $\log[L]_0$  at pH 2.9. Initial concentration:  $5 \times 10^{-5} \text{M}$  palladium(II),  $1 \times 10^{-3} \text{M}$  picrate.  $\circ$ : p-xy-(ETET)<sub>2</sub>,  $\bullet$ : o-xy-(ETET)<sub>2</sub>,  $\square$ : Bz-TTCP.

superior to that with the cyclic counterpart. Relationships between the logarithmic distribution ratio of palladium(II) and the logarithm of ligand concentration in 1,2-dichloroethane are shown in Fig.6-4. The distribution ratio of palladium(II) with Bz-TTCP is independent of the concentration of Bz-TTCP. It is thought that the solubility of the ion pair compound,  $[\text{Pd}(\text{bz-ttcp})_m]\text{Pic}_2$  in 1,2-dichloroethane limits the distribution of palladium(II). In the case o-xy-(ETET)<sub>2</sub>, the logD value slightly increases as increasing the concentration of the ligand. However, the slope of the line is less than +1.0. When the concentration of p-xy-(ETET)<sub>2</sub> is lower than  $1 \times 10^{-3}$  M, the extractability of palladium(II) with p-xy-(ETET)<sub>2</sub> is lower than that with o-xy-(ETET)<sub>2</sub> or Bz-TTCP. As increasing the concentration of p-xy-(ETET)<sub>2</sub>, the logD value increases, and becomes to be higher than that with two other ligands at  $\log[L]_0 > -3.0$ . The slope of the line near +2.0 suggests the formation of the complex  $[\text{PdL}_2]^{2+}(\text{Pic}^-)_2$ , when the ligand concentration is more than  $1 \times 10^{-3}$  M. As palladium(II) favors the square planar arrangement, each two sulfurs of two molecules of p-xy-(ETET)<sub>2</sub> coordinate to the palladium(II) ion, is considered.

**Molar ratio methods**            Molar ratio methods were used in order to examine the extraction behavior of palladium(II) under the condition of relatively low concentration of the

ligand to palladium(II) ion ( $5 \times 10^{-5}$  M). The results are shown in Figs.6-5a and 6-5b. As shown in Fig.6-5a, the break point appears clearly at  $[L]_o/[Pd(II)]_i=1.0$  that is  $m=1$  in Eqn.(6-3) in the o-xy-(ETET)<sub>2</sub>. 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 Figs.6-4 and 6-5a show that the logD value is kept constant at -0.3 when the concentration of Bz-TTCP is more than twice time of that of palladium(II). From the result of X-ray crystallographic analysis, palladium(II) was just fitted into the cavity of the 1,4,8,11-tetrathiacyclo-tetradecane (TTCT) derivative which has 14 membered ring. As Bz-TTCP, 15 membered ring has a slightly 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)<sub>2</sub> of low concentration relative to the palladium(II), the yellow precipitate formed between the two phases. Figure 6-5b shows the plot of the palladium(II) concentration in the aqueous or the organic phase vs. the ratio of  $[p\text{-xy}-(\text{ETET})_2]_{o,i}$  to  $[Pd(II)]_i$ . Nevertheless the concentration of palladium(II) in organic phase is kept constant at  $1 \times 10^{-5}$  M, that in aqueous phase decrease, up to the point of  $[L]_o/[Pd(II)]_i=1.0$ . The result suggests that the Pd(II)-p-

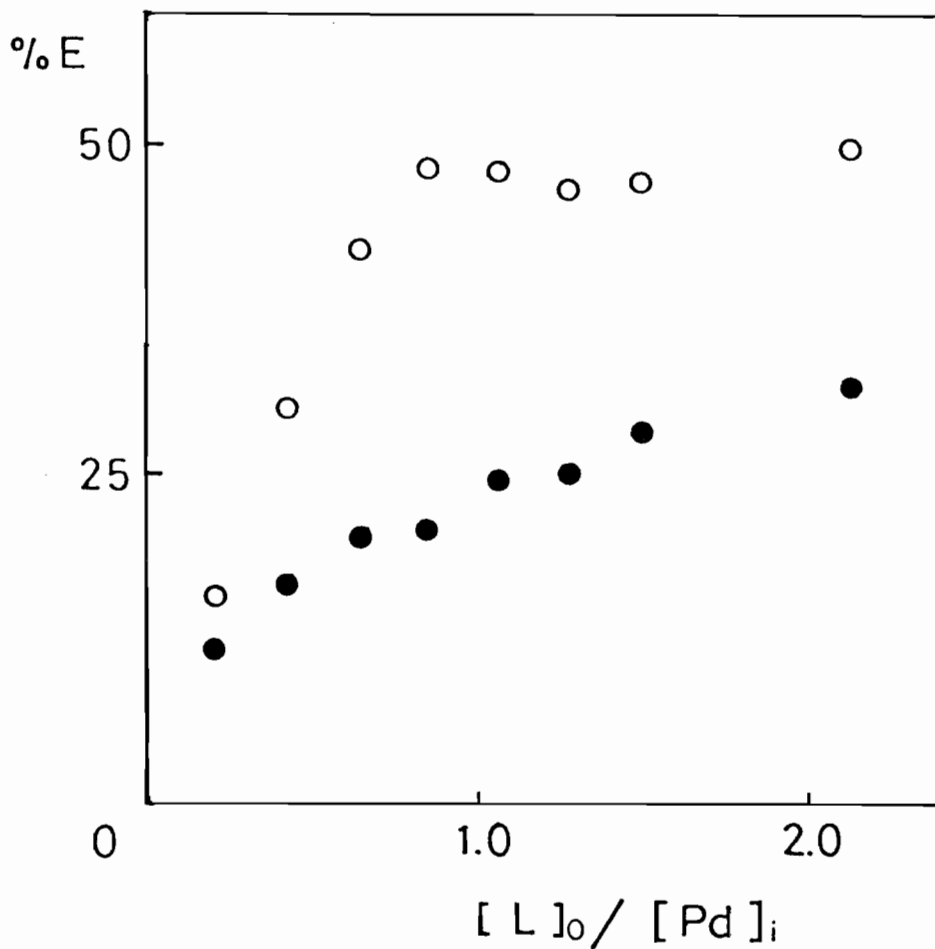


Fig.6-5a. Molar ratio methods at pH 2.9. Initial concentration:  $5 \times 10^{-5} \text{M}$  palladium(II),  $1 \times 10^{-3} \text{M}$  picrate.  
 ○ : o-xy-(ETET)<sub>2</sub>, ● : Bz-TTCP.



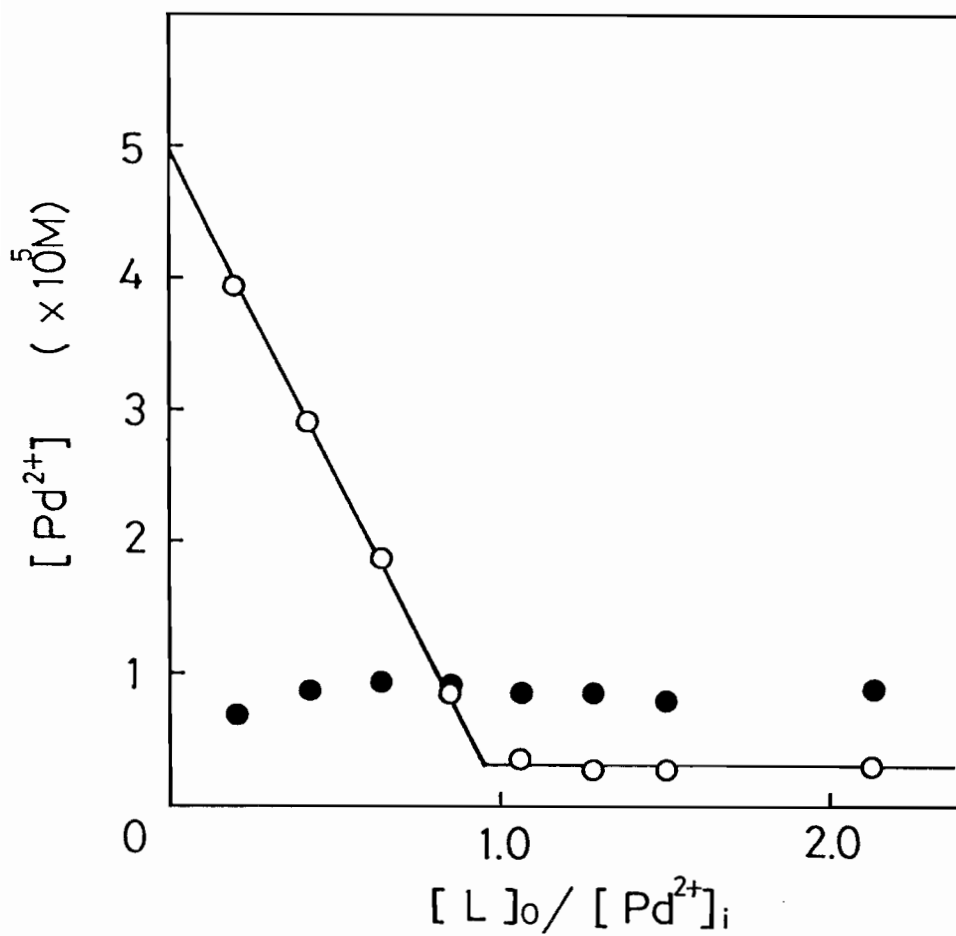
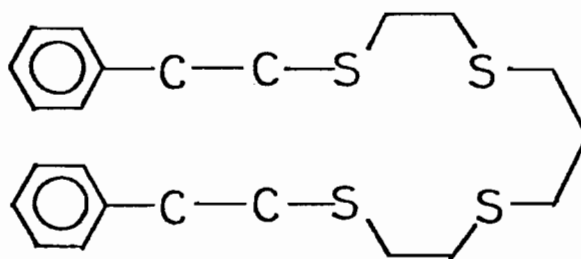


Fig.6-5b. Molar ratio methods for p-xy-(ETET)<sub>2</sub> at pH 2.9.  
 Initial concentration:  $5 \times 10^{-5} \text{M}$  palladium(II),  
 $1 \times 10^{-3} \text{M}$  picrate.  
 ○: palladium(II) in aqueous phase,  
 ●: palladium(II) in organic phase.

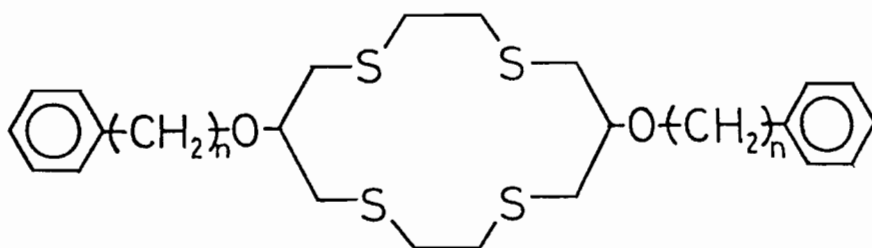
xy-(ETET)<sub>2</sub> complex formed is stable but little soluble in 1,2-dichloroethane. Although p-xy-(ETET)<sub>2</sub> has four sulfur atoms, it can not act as a quadridentate ligand but as a bidentate one. The complex is supposed to be like as [Pd(II)L(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>(Pic<sup>-</sup>)<sub>2</sub> or [Pd(II)L(OH)(OH<sub>2</sub>)]<sup>+</sup>Pic<sup>-</sup>. As increasing the concentration of p-xy-(ETET)<sub>2</sub>, the 1:2 (Pd(II):L) complex easily soluble in the organic phase will become to be predominant, and extracted into 1,2-dichloroethane.

#### 6.4 Molecular design of the reagents selective for Palladium(II)

It becomes clear that the extractability of an acyclic tetrathio ether is higher than cyclic one. One of the acyclic tetrathio ethers p-xy-(ETET)<sub>2</sub> shows the powerful extractability when the ligand concentration is in excess of the metal concentration. The highly lipophilic complex, [Pd(II)L<sub>2</sub>]<sup>2+</sup>(Pic<sup>-</sup>)<sub>2</sub> formed is extracted into 1,2-dichloroethane phase. These results suggest that an acyclic and highly lipophilic quadridentate ligand will extract palladium(II) effectively. From this point of view, a new acyclic tetrathio ether which has two phenyl groups as terminal groups, shown in Fig.6-6a, was synthesized. This reagent showed the higher extractability than the reagents



(a)



(b)

Fig.6-6. Structures of new tetrathio ethers selective for palladium(II).

used in this work. Two phenyl groups may not only increase the lipophilicity of the complex, but cap the axial site of Pd-4S plane in the complex cation. However it is uncertain of the role of such phenyl groups. As palladium(II) was just fitted into the cavity of the TTCT derivative, the double-armed thiocrown ether shown in Fig.6-6b may be a selective extractant rather than powerful for palladium(II).

## Chapter 7.

### Liquid-liquid extraction of copper(II) with cyclic and acyclic tetrathio ethers

#### 7.1 Introduction

The stability constants of Cu(II)-tetrathio ether complexes in aqueous solution were determined by Rorabacher and his coworkers.<sup>15)</sup> According to their studies, TTCT gives a just fit cavity for copper(II) ion, and its stability constant is a hundred fold larger than that of acyclic counterpart, TTAP. It is interesting to examine and compare the extraction behavior of Cu(II) ion by cyclic and acyclic tetrathio ethers. In this chapter, the cyclic tetrathio ether (TTCT) and the acyclic one (TTAP) were used. As the counter anion to form the ion pair, hexanitrodiphenylamine ion (HNDPA) was used. The compositions of extracted complexes were determined and thermodynamic parameters which consist the extraction constants were evaluated.

#### 7.2 Experimental

##### 7.2.1 Reagents

Copper sulfate and hexanitrodiphenylamine sodium salt used were guaranteed reagent grade. 1,2-Dichloroethane was

purified by the method described in Section 3.2.2.

### 7.2.2 Liquid-liquid extraction of copper(II)

A 10 ml of the aqueous solution containing  $5 \times 10^{-5}$  M copper(II) ion, hexanitrodiphenylamine ion ( $1 \times 10^{-6}$  M- $5 \times 10^{-3}$  M) and  $1 \times 10^{-2}$  M acetate buffer or borax-boric acid buffer, were kept at an ion strength of 0.1 with sodium sulfate. The mixture of this solution and 10ml of the tetrathio ether ( $5 \times 10^{-4}$  M- $5 \times 10^{-3}$  M) 1,2-dichloroethane solution in a stoppered 50ml glass cylindrical tube was shaken for 30 min on 200 strokes/min at a constant temperature. The mixture was then centrifuged for 5 min at 2000 r.p.m., the pH of the aqueous phase was measured and the concentrations of HNDPA in the aqueous phase was determined spectrophotometrically at 425 nm. The concentration of copper(II) ion in the aqueous phase and organic phase were determined by atomic absorption spectrometry.

### 7.2.3 Distribution of HNDPA

A 10 ml of aqueous solution containing  $5 \times 10^{-5}$  M HNDPA,  $1 \times 10^{-2}$  M acetate buffer and sodium sulfate to keep the ion strength of 0.1 were shaken with 1,2-dichloroethane by the way same as the copper(II) extraction. After two phases were separated, the concentration of HNDPA in the aqueous phase

was measured spectrophotometrically at 425 nm and that in the organic phase at 378 nm.

#### 7.2.4 Distribution of ligands

A 10 ml of the aqueous solution of which the ion strength was kept at 0.1 and 10 ml of the 1,2-dichloroethane solution of  $5 \times 10^{-3}$  M ligand (TTCT or TTAP) were shaken in the way same as the copper(II) extraction. Then, a 5 ml of aqueous solution containing the acetate buffer, silver(I) sulfate ( $2 \times 10^{-3}$  M), and picrate ion ( $2 \times 10^{-3}$  M) were added to 5 ml of the aqueous phase, and was shaken with 10 ml of 1,2-dichloroethane. The concentration of the silver(I) in the dichloroethane was determined by atomic absorption spectrometry. Thus, the concentration of the ligand distributed to the aqueous solution was determined.

#### 7.2.5 Solubility of ligands in water

One milimole of the ligand was suspended in 200 ml of water in a flask. After stirring over 24 hr and standing, a portion of the water was taken into 50 ml of cylindrical tube, centrifuged for 30 min at 2000 r.p.m. and filtrated. Then, the acetate buffer, silver(I) sulfate and picrate ion solutions were added to the sample, the mixture was shaken with 1,2-dichloroethane in the way same as above description (in Section 7.2.4). The concentration of the silver(I) in

the dichloroethane was determined by atomic absorption spectrometry. Thus the concentration of the tetrathio ether soluble in water was measured.

### 7.3 Results and discussion

#### 7.3.1 pH-Dependence on the distributions

*Distribution of copper(II)* Distribution of copper(II)-tetrathio ether complex was examined on condition that the concentrations of the tetrathio ether (TTCT or TTAP) and HNDPA were 100 and 10 times excess of that of Cu(II) ion, respectively. Plots of the logarithmic distribution ratio of copper(II) with TTCT and TTAP against the pH of the aqueous phase are shown in Fig.7-1a. As increasing the pH in aqueous phase, the logarithmic distribution ratio of copper(II) increased. Two straight lines were obtained with slopes close to +2.0 in the region of pH>6.0.

*Distribution of HNDPA* The pH dependence of the  $\log D_{\text{Cu(II)}}$  is due to the distribution of the counter anion HNDPA (HA). Figure 7-1b shows the plot of the logarithmic distribution ratio of HNDPA between aqueous phase and 1,2-dichloroethane phase against the pH of the aqueous phase. The acid dissociation constant  $K_a$  and the distribution constant  $K_{DA}$  of the monobasic acid HNDPA are expressed as follows:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (7-1)$$



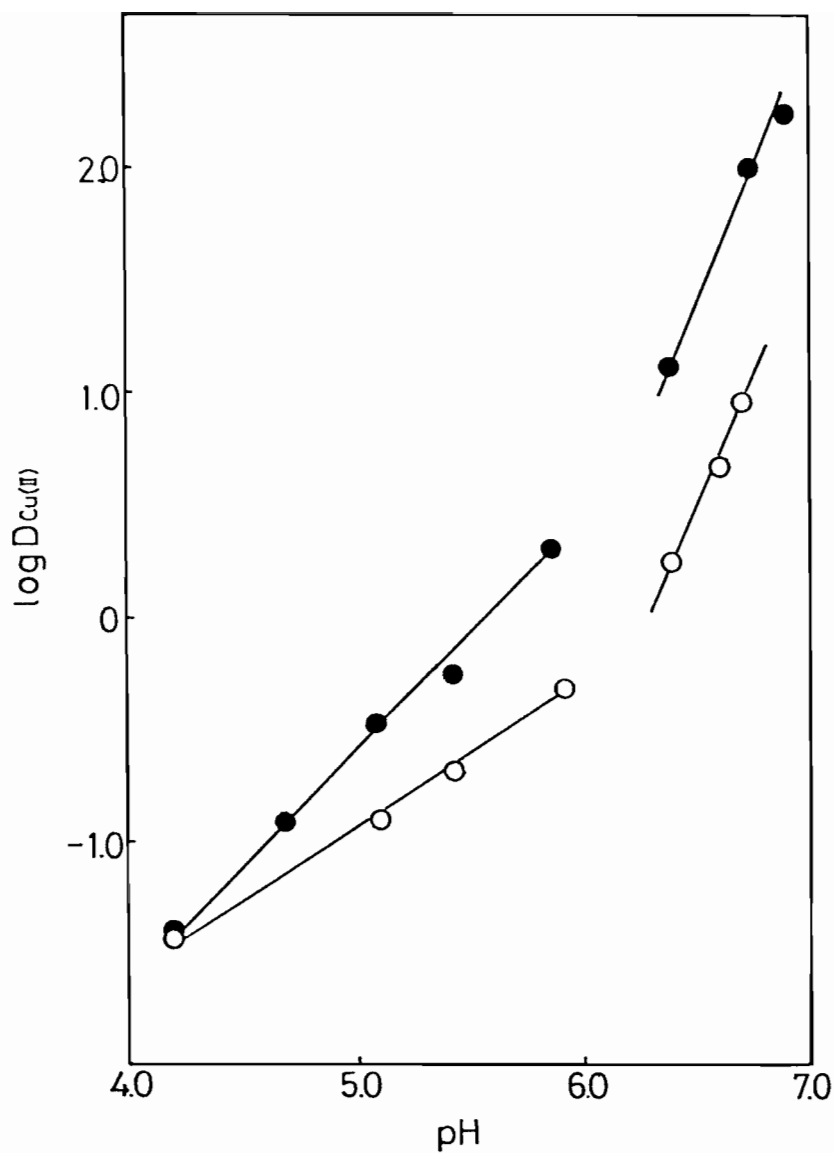


Fig.7-1a. Plots of distribution ratio of copper(II) vs. pH. Initial concentration:  $5 \times 10^{-5} \text{M}$  copper(II),  $5 \times 10^{-4} \text{M}$  HNDPA.  
 ○ :  $5 \times 10^{-3} \text{M}$  TTCT, ● :  $5 \times 10^{-3} \text{M}$  TTAP.

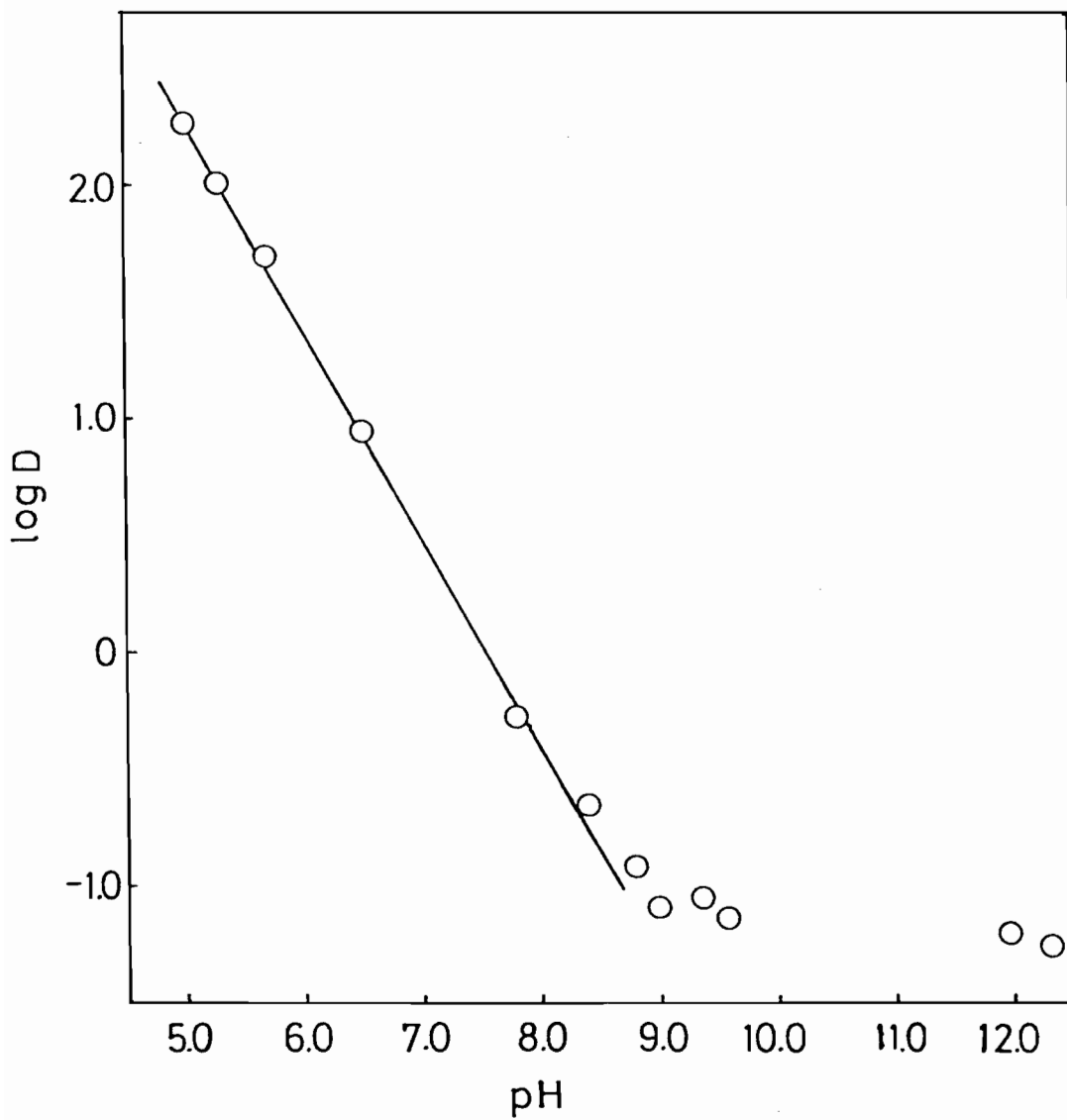


Fig.7-1b. Plots of distribution ratio of HNDPA vs. pH.  
Initial concentration:  $5 \times 10^{-5} \text{M}$  HNDPA.

$$K_{DA} = [HA]_o/[HA] \quad (7-2)$$

For the concentration of the acid form [HA] in aqueous phase is negligible, the logarithmic distribution ratio of HNDPA is then, expressed as follows:

$$\log D = \log K_{DA}/K_a - \text{pH} \quad (7-3)$$

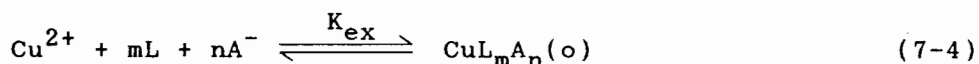
The straight line was obtained with slopes close to -1.0 below pH 9. Therefore, the plot in Fig.7-1b will suggest the concentration of the counter anion, HNDPA ( $A^-$ ), to form the ion pair with copper(II)-tetrathio ether complex cation, in Fig.7-1a.

*Relationship between distributions of copper(II) and HNDPA*

As increasing the pH, the concentration of HNDPA ( $A^-$ ) in aqueous phase increased. Then, the ion pair of copper(II)-tetrathio ether complex cation and HNDPA anion, which tends to distribute to organic phase, increased. At pH 6.0, the concentration of the anion is in excess of copper(II) ion. The distribution ratio of copper(II)-TTCT-HNDPA complex was lower than that of copper(II)-TTAP-HNDPA complex. Against the expectation from the stability constants of those Cu(II)-complexes in aqueous solution,<sup>15)</sup> the copper(II) extractability of acyclic tetrathio ether (TTAP) was superior to that of cyclic tetrathio ether (TTCT). This may be of interest and will be discussed later.

### 7.3.2 Extraction equilibria of copper(II)

If the species extracted into 1,2-dichloroethane is represented by  $\text{CuL}_m\text{A}_n$ , the extraction equilibrium and the extraction constant  $K_{\text{ex}}$  are given by Eqns.(7-4) and (7-5), respectively,



$$K_{\text{ex}} = [\text{CuL}_m\text{A}_n]_{\text{o}} / [\text{Cu}^{2+}][\text{L}]_{\text{o}}^m[\text{A}^-]^n \quad (7-5)$$

and the logarithmic distribution ratio of copper(II),  $\log D_{\text{Cu}}$  is represented by the Eqn.(7-6).

$$\log D_{\text{Cu}} = \log K_{\text{ex}} + m \log [\text{L}]_{\text{o}} + n \log [\text{A}^-] \quad (7-6)$$

### 7.3.3 Extraction behavior of copper(II)

#### 7.3.3.1 Slope analysis

*Variation of ligand concentrations*      The distribution of copper(II)-tetrathio ether complexes at pH 6.7 was examined at various concentration of tetrathio ethers under constant concentration of HNDPA. The relationships between  $\log D_{\text{Cu(II)}}$  and  $\log [\text{L}]_{\text{o}}$  are shown in Fig.7-2a. Two straight lines were obtained with slopes close to +1.0, indicating  $m=1$  in Eqn.(7-6). The result suggests that the ratio of the extracted species was  $\text{Cu:L}=1:1$ . According to the crystallographic studies of solid state  $\text{Cu(II)}$ -tetrathio ether-perchlorate complexes by Rorabacher et al.,<sup>21)</sup> copper(II) ion is fitted into the cavity of TTCT and the two

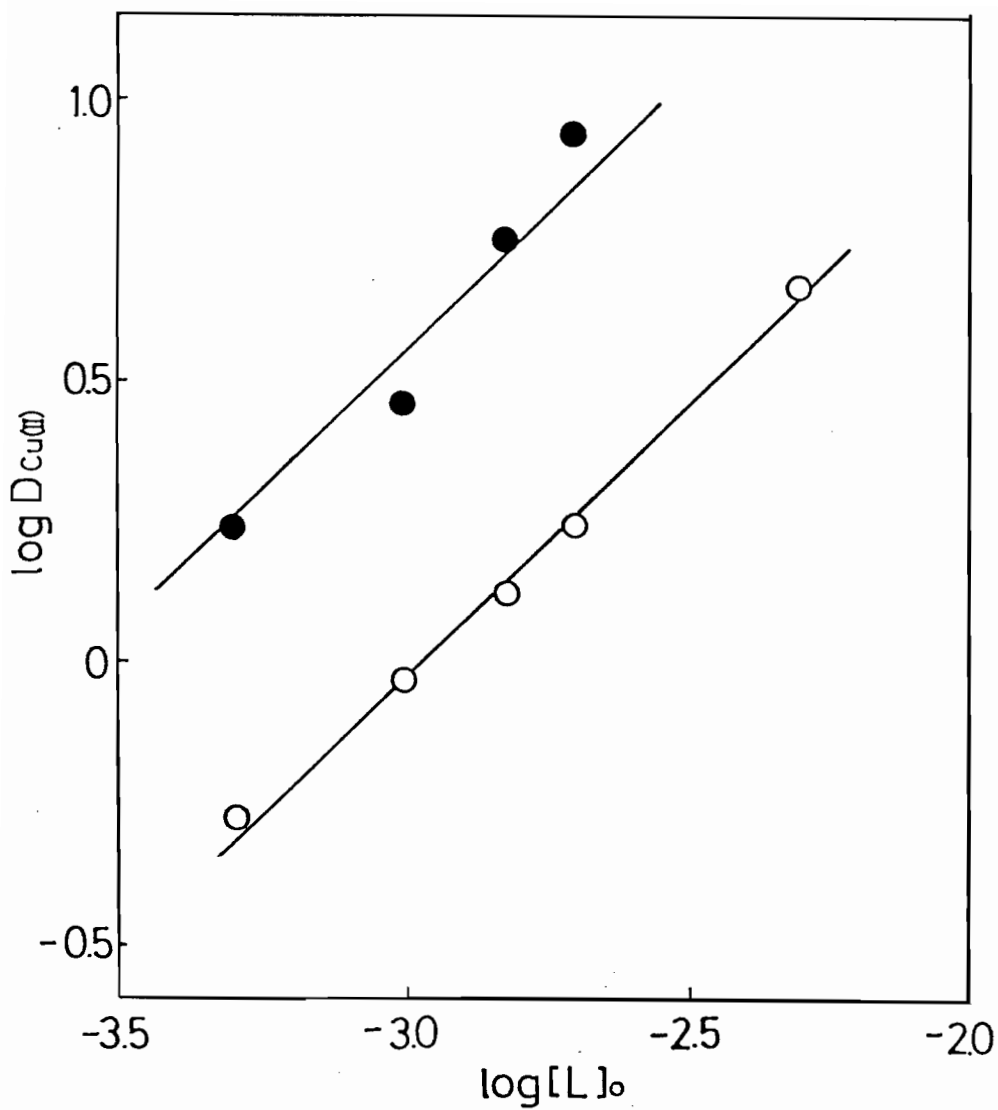


Fig.7-2a. Plots of  $\log D$  vs.  $\log[L]_0$  at pH 6.7. Initial concentration:  $5 \times 10^{-5} \text{M}$  copper(II),  $5 \times 10^{-4} \text{M}$  HNDPA. ○ : TTCT, ● : TTAP.

axial sites of  $\text{CuS}_4$  plane are occupied by two perchlorate ions ( $[\text{Cu}(\text{TTCT})(\text{OClO}_3)_2]$ ); copper(II) ion is encircled by TTAP, and the axial sites of  $\text{CuS}_4$  plane are occupied by a water oxygen and a loosely bonding perchlorate ion ( $[\text{Cu}(\text{TTAP})(\text{OH}_2)(\text{OClO}_3)](\text{ClO}_4)$ ). As expected from the crystallographic data mentioned above, the structures of these Cu(II)-tetrathio ether (1:1) complex cations in 1,2-dichloroethane may be that copper(II) ion exists in the center of 4S plane of cyclic TTCT or pseudocyclic TTAP.

*Variation of HNDPA concentration*      The plots of the logarithmic distribution ratio of copper(II) vs. the logarithmic concentration of HNDPA in the aqueous phase after the extraction are shown in Fig.7-2b. As increasing the concentration of  $\text{HNDPA}(\text{A}^-)$  ion,  $\log D$  values increased. The straight lines with the slope of +1.0 obtained at  $\log[\text{HNDPA}]_a > -4.5$ , indicate  $n=1$  in Eqn.(7-6), 1:1 ratio of copper(II) to  $\text{HNDPA}(\text{A}^-)$  ion. It is interesting because that copper(II)-tetrathio ether complex extracted into 1,2-dichloroethane is forming ion pair with two monoanions such as HNDPA ion, 1:2 ( $\text{Cu}(\text{II}):\text{A}^-$ ) complex, has been expected. Whereas at the logarithmic concentration of HNDPA less than -4.5, the species of 1:1 ( $\text{Cu}(\text{II}):\text{A}^-$ ) complex is not predominant, and the mixture of two or three species exist in 1,2-dichloroethane, are expected.

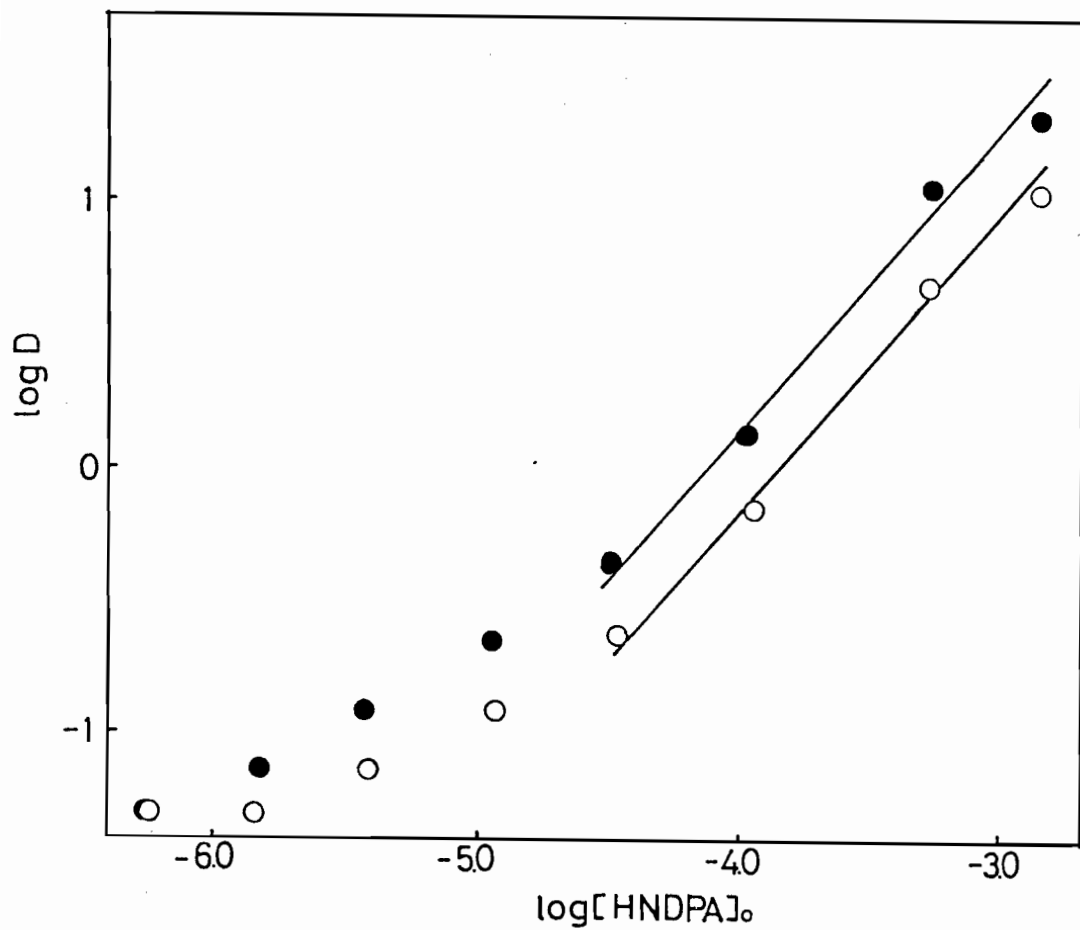


Fig.7-2b. Plots of  $\log D$  vs.  $\log[\text{HNDPA}]_0$ . Initial concentration:  $5 \times 10^{-5} \text{M}$  copper(II),  $5 \times 10^{-4} \text{M}$  ligand.  
 ○ : TTCT, ● : TTAP.

### 7.3.3.2 Composition of extracted species

Absorption spectra of Cu(I)- and Cu(II)-TTAP complexes in 1,2-dichloroethane against reagent blank are shown in Fig.7-3. For the copper(I) solution, hydroxylammonium sulfate as reducing agent was added to aqueous phase containing copper(II) sulfate. Shapes of absorption spectra of extracts are similar to that of anion form HNDPA(A<sup>-</sup>) in aqueous solution. It has been clarified that composition of extracted Cu(I) complex in 1,2-dichloroethane is Cu(I):TTAP:A<sup>-</sup>=1:1:1 at Chapter 4. The molar absorptivity of copper(II) complex at 430 nm is nearly equal to that of copper(I) complex. These results confirm that the molar ratio of the copper(II) complex is Cu(II):HNDPA=1:1. It is expected that another anion (X<sup>-</sup>), to form the ion pair with the copper(II) complex cation ([Cu(II)L](A<sup>-</sup>)<sup>+</sup>) such as sulfate, acetate or hydroxide anion in aqueous phase, is extracted. As previously reported, sulfate ion is not extracted at all with the metal-tetrathio ether complex cation.<sup>33)</sup> In this study, the increase of concentration of acetate ion did not affect the extraction of copper(II), was examined. Therefore, it is clear that hydroxide ion neutralizes the charge of monovalent copper(II)-tetrathio ether complex, and the composition of extracted species is [CuL(OH<sup>-</sup>)]<sup>+</sup>A<sup>-</sup>.



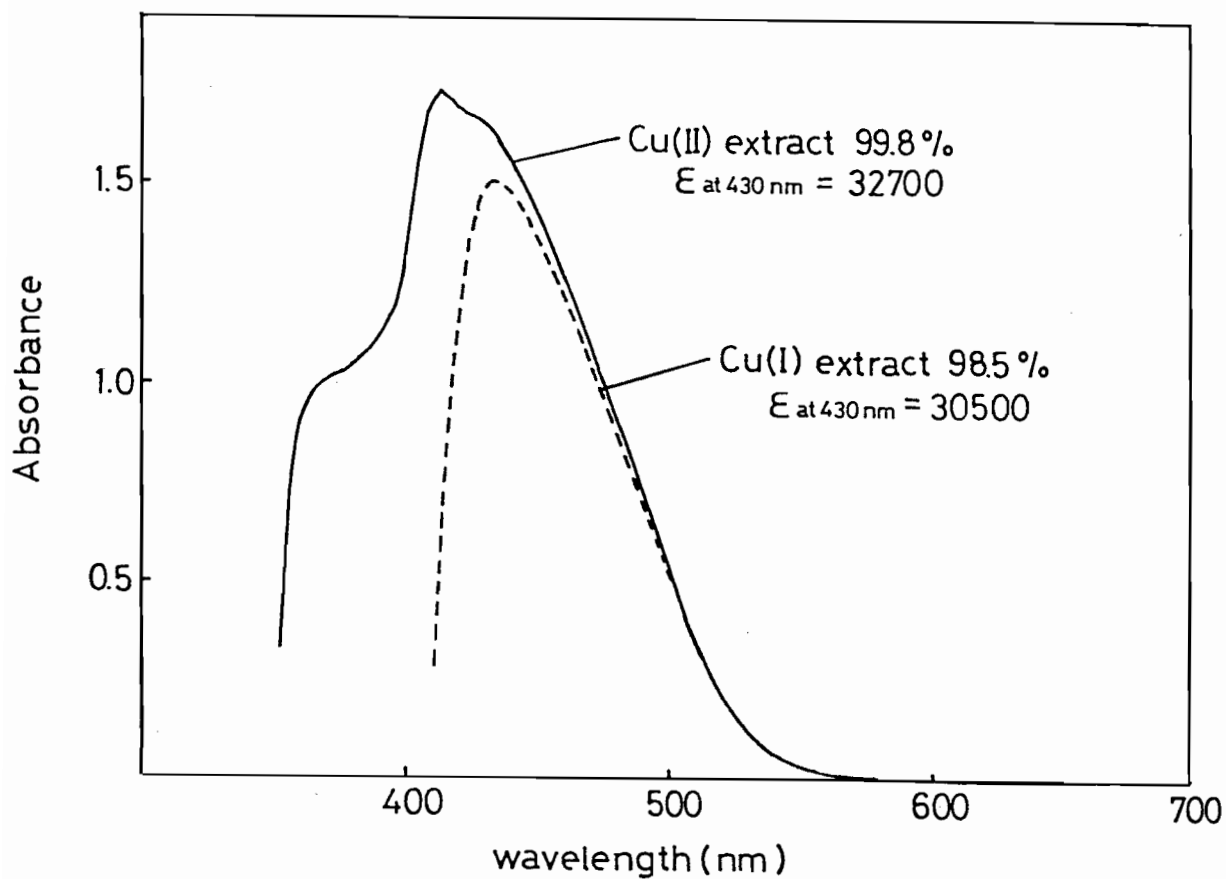
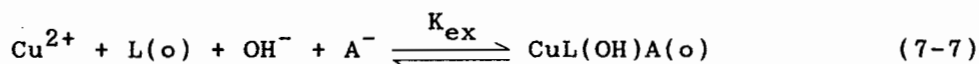


Fig.7-3. Absorption spectra of Cu(II) and (I) extracts in 1,2-dichloroethane. Initial concentration:  $5 \times 10^{-5} \text{M}$  copper(II),  $5 \times 10^{-4} \text{M}$  HNDPA,  $5 \times 10^{-4} \text{M}$  TTAP.

### 7.3.3.3 Proposed extraction mechanism

The recommended extraction mechanism is proposed in Fig.7-4. Copper(II)-tetrathio ether complex is thought to have two water molecules in aqueous solution. When one of them is replaced to HNDPA anion ( $A^-$ ), the species ( $[Cu(II)L(OH_2)](A^-)^+$ ) become more hydrophobic. At  $pH > 6.0$ , a proton of the coordinated water dissociates easily, and then  $[Cu(II)L(OH)]^+(A^-)$  is extracted into 1,2-dichloroethane. The extraction scheme is shown in Scheme 7-1. The extraction constant  $K_{ex}$  is expressed as follows:



$$K_{ex} = [CuL(OH)A]_o / [Cu^{2+}][L]_o [OH^-][A^-] \quad (7-8)$$

The logarithmic extraction constant values at 25°C are 14.65 for TTCT and 14.88 for TTAP, respectively.

### 7.3.4 Evaluation of thermodynamic parameters

**Variation of extraction temperature** The relationship between the logarithmic distribution ratio of copper(II) or HNDPA and temperature are shown in Fig.7-5a or 7-5b. These plots show linear relationship. The logarithmic distribution ratio of HNDPA decreased as increasing the temperature as shown in Fig.7-5b. This means that the concentration of HNDPA ion in aqueous phase increases when temperature becomes to high. Nevertheless, the logarithmic distribution ratio of copper(II) decreased as increasing the temperature

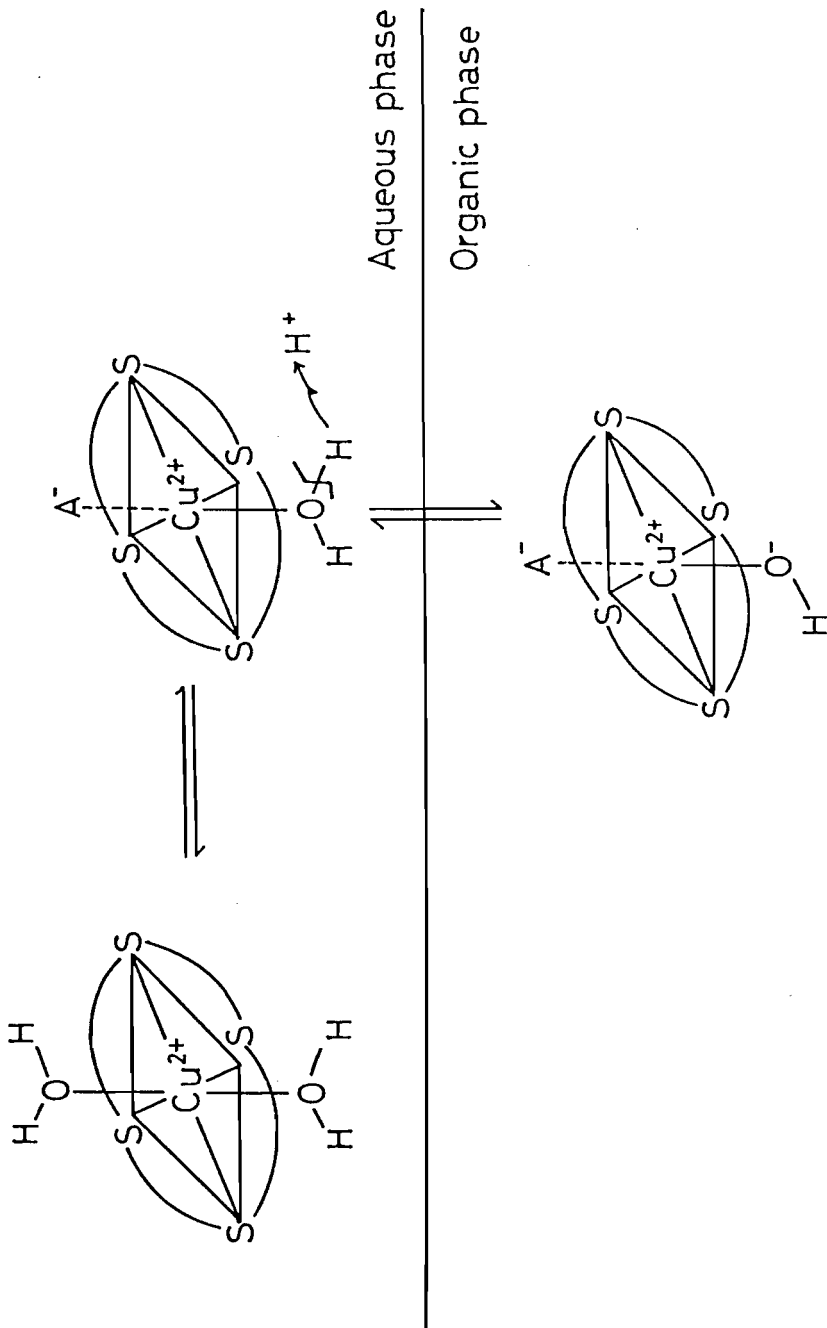
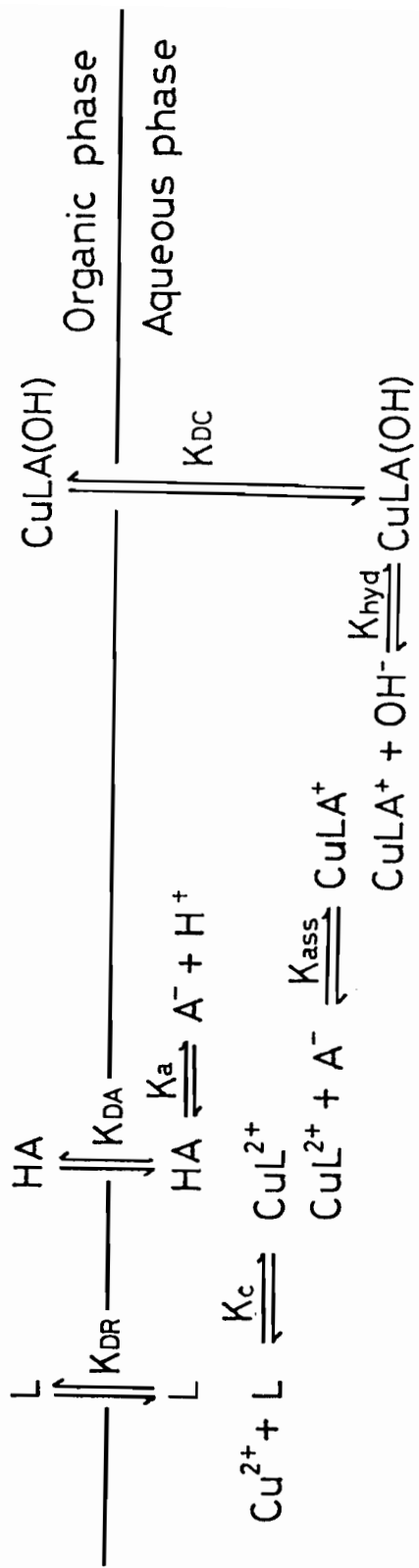


Fig.7-4. Proposed extraction mechanism.



Scheme 7-1. Equilibria in the liquid-liquid distribution for copper(II)-tetrathio ether-HNDPA system.

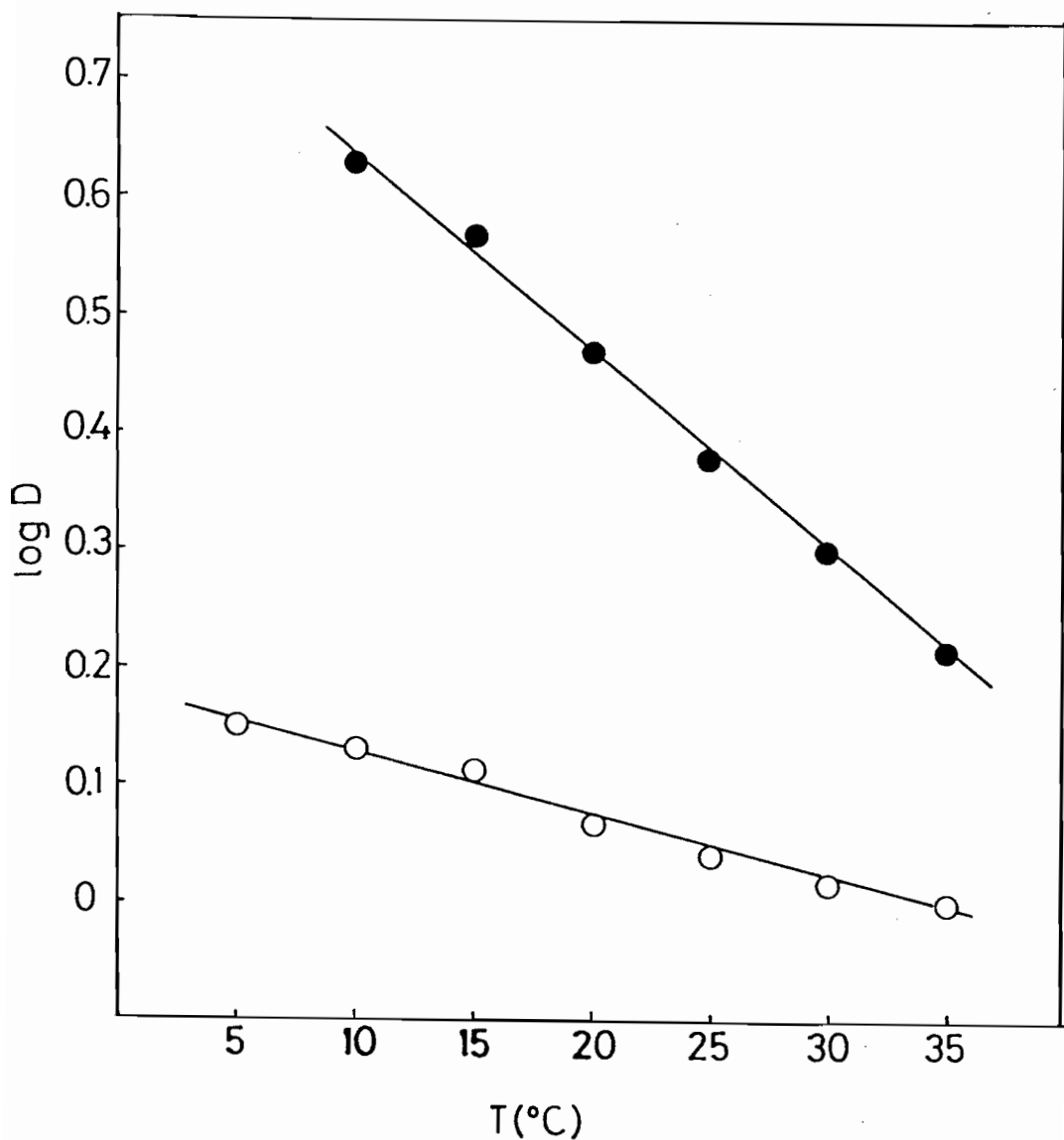


Fig.7-5a. Plots of  $\log D_{\text{Cu(II)}}$  vs. temperature at pH6.8.  
 Initial concentration:  $5 \times 10^{-5} \text{M}$  copper(II),  
 $5 \times 10^{-4} \text{M}$  HNDPA,  $5 \times 10^{-4} \text{M}$  ligands. ○ : TTCT, ● : TTAP.

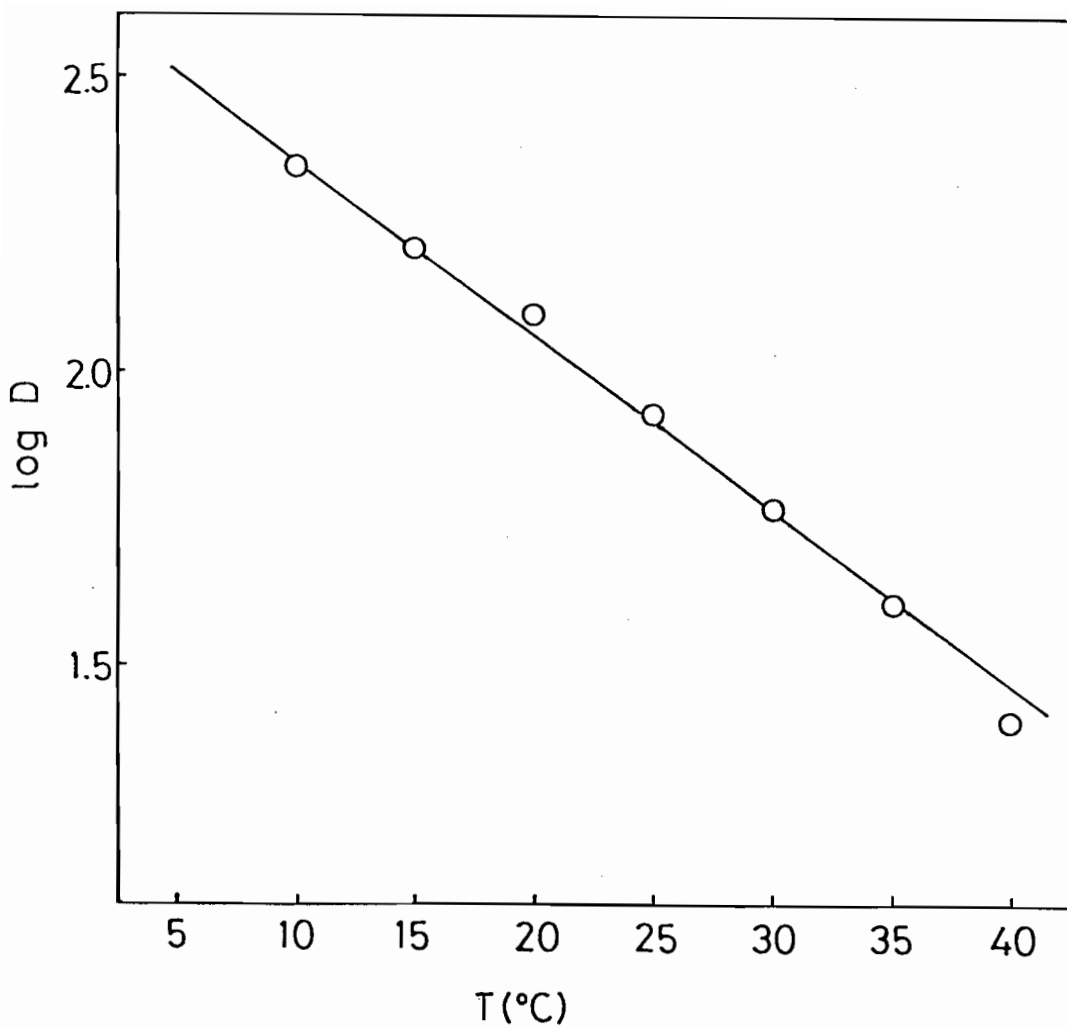


Fig.7-5b. Plots of  $\log D_{HA}$  vs. temperature at pH5.4.  
Initial concentration:  $5 \times 10^{-5} M$  HNDPA.

as shown in Fig.7-5a. The distribution behavior of ion pair of copper(II)-tetrathio ether complex with HNDPA is similar to that of HNDPA itself.

*Thermodynamic parameters* The extraction constants of copper(II) at 10°, 15°, 20°, 25°, 30° and 35°C±0.2°C were evaluated, and thermodynamic parameters were calculated by following equation:

$$\Delta G = -RT \ln K_{ex} = \Delta H - T \Delta S \quad (7-9)$$

where  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  designate the free energy change, the enthalpy change and entropy change of extraction of copper(II), respectively. Thermodynamic quantities at 25°C for the extraction and those for the complex formation in aqueous solution reported by Rorabacher et al.,<sup>15)</sup> are listed in Table 7-1. In aqueous solution, the formation constant  $K_c$  of copper(II) complex with TTCT is 100 fold larger than that with TTAP. Rorabacher suggested that the macrocyclic effect is wholly attributable to the more favorable entropy associated with the less flexible cyclic ligand. On the other hand, the logarithmic extraction constant for acyclic TTAP is slightly larger than that for cyclic TTCT. The large  $T \Delta S$  values contribute to the large extraction constants. The  $-\Delta H$  value for TTCT, 2.20 is smaller than that for TTAP, 6.67 on the extraction, although in aqueous solution that for TTCT is 4.22 > 3.72 for TTAP. The thermodynamic data of complex formation in aqueous solution

Table 7-1. Thermodynamic parameters for extraction and complex formation at 25° C.

Ligand		- Δ G	- Δ H	T Δ S(Kcal mol <sup>-1</sup> )
TTCT	logK <sub>ex</sub> =14.65	19.97	2.20	17.79
	logK <sub>c</sub> = 4.34*	5.92*	4.22*	1.70*
TTAP	logK <sub>ex</sub> =14.86	20.28	6.77	13.52
	logK <sub>c</sub> = 2.18*	2.97*	3.72*	-0.75*

\* : Ref.15.

Table 7-2. Solubilities of ligands in water and distribution constants between 1,2-dichloroethane.

Ligand	logK <sub>DR</sub>	Solubility (mol l <sup>-1</sup> )
TTCT	> 3.1	0.77x10 <sup>-5</sup>
TTAP	> 3.1	1.18x10 <sup>-5</sup>



are not reflected in those of extraction. As shown in Scheme 7-1 the extraction constant involves five constants and the relationship is expressed as follows:

$$K_{\text{ex}} = K_{\text{DC}} K_{\text{hyd}} K_{\text{ass}} K_{\text{C}}/K_{\text{DR}} \quad (7-10)$$

Four constants, other than the complex formation constant, are so complicated, the evaluation of these constants are difficult. One of difficulties is due to the character of the tetrathio ethers or their complexes, which are insoluble in water.

*Solubility of ligands* Solubility of these ligands in water and the distribution constant between 1,2-dichloroethane and water,  $K_{\text{DR}}$  were examined. The results are shown in Table 7-2. Although the solubility of TTAP are higher than that of TTCT, both of them are the same order ( $10^{-5}$  M). The logarithmic distribution ratio of ligands  $K_{\text{DR}}$  are so high ( $\log K_{\text{D}} > 3.1$ , at least), both of ligands distributed into water are undetectable. It is expected, the complex formation reaction may not occur in aqueous phase, but on interface between two phases. If the mechanism of complex formation in aqueous solution is different from that on the interface, thermodynamic quantities of complex formation on interface is advantageous to the flexible ligand TTAP, must be considered.

## Chapter 8.

### Liquid-liquid extraction of silver(I) and copper(I) with chromogenic thiacrown ethers

#### 8.1 Introduction

Recently, new chromogenic crown ethers into which picrylamine<sup>49,50</sup>) or one of its derivatives<sup>51,52</sup>) is introduced have been synthesized, and their use for extraction and spectrophotometric determination of alkali metals has been reported. In Chapter 3, degree of extraction of various metals with 4'-PicNHBz-TTCP (7) is described. It is clear that compound (7) acts as selective extractant for silver(I) and copper(I). These metals are extracted without counter anion, when the pH of aqueous phase is in the appropriate region. In this chapter, properties of (7) as extractive and spectrophotometric reagent were examined. Furthermore, two chromogenic thiacrown ethers, 6TF (8) and 4TF (9) were also examined.

#### 8.2 Experimental

##### 8.2.1 Determination of acid dissociation constants

In an 800 ml water-jacketed vessel controlled at 25°C, 600 ml of  $5 \times 10^{-5}$  M (7), (8) or (9) solution in 50% dioxane-

water mixture were adjusted to pH 3.0 with sulfuric acid. The absorption spectrum was measured in the range 210-700 nm, with a small portion of the solution in a 1 cm quartz cell. The solution was returned to the 800 ml vessel and the pH was raised a little by addition of sodium hydroxide solution of suitable concentration (1-10 M, according to the pH required). The spectrum was again recorded. By repetition of this procedure, the absorption spectra of the reagent over a wide range of pH values were measured. The volume change on addition of the hydroxide solution could be neglected. The acid dissociation constants of these reagents,  $K_a$ , were calculated from  $pK_a = pH - \log[L^-]/[HL] = pH - \log(\epsilon - \epsilon_{L^-})/(\epsilon_{HL} - \epsilon)$  where  $\epsilon_{HL}$  and  $\epsilon_{L^-}$  are the molar absorptivities of pure HL and  $L^-$  solution at a selected wavelength and  $\epsilon$  is the apparent molar absorptivity calculated from the absorbance of the mixed solution at various pH values. When  $\epsilon$  is equal to  $(\epsilon_{HL} + \epsilon_{L^-})/2$ , the pH value is equal to  $pK_a$ . The values of  $\epsilon$  were plotted against pH and the values of  $pK_a$  deduced.

### 8.2.2 Liquid-liquid extraction of silver(I) and copper(I)

Liquid-liquid extraction of silver(I) and copper(I) with (7), (8) or (9) were done by the method described in Section 3.2.2. In order to examine the effects of foreign ions on extraction of silver(I), stock solutions of 0.1 M

Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Fe(III) were prepared. Aqueous solution containing the silver(I) ion ( $5 \times 10^{-5}$  M), diverse ion to be tested ( $1 \times 10^{-2}$  M), buffer solution ( $1 \times 10^{-2}$  M) and 0.1 M tartrate as masking agent was shaken with 1,2-dichloroethane solution of reagent (7) or (8) ( $2.5 \times 10^{-3}$  M or  $1.25 \times 10^{-3}$  M). After two phases were separated, the absorbance of the organic phase was measured at appropriate wave lengths.

### 8.3 Results and discussion

#### 8.3.1 Absorption spectra

*Absorption spectra of 4'-PicNHBz-TTCP (7)* The ultraviolet and visible absorption spectra of  $5 \times 10^{-5}$  M (7) in 50% v/v dioxane-water mixture in the pH range 4.0-11.0 are shown in Fig.8-1. In acidic media (pH 4.3), absorption maxima appear at 253 and 380 nm. The absorption maximum at 380 nm decreases with increase in pH, and a new absorption maximum appears at 445 nm. In alkaline media (pH > 11.0), absorption maxima exist at 253 and 445 nm. The absorption maximum at 253 nm exists in both acidic and alkaline media, although it becomes less intense in alkaline media. Three isobestic points are found, at 264, 308 and 400 nm. These changes in the electronic absorption spectra on change of pH indicate the existence of the acidic form,  $HL^-$  and basic form,  $L^-$ ,

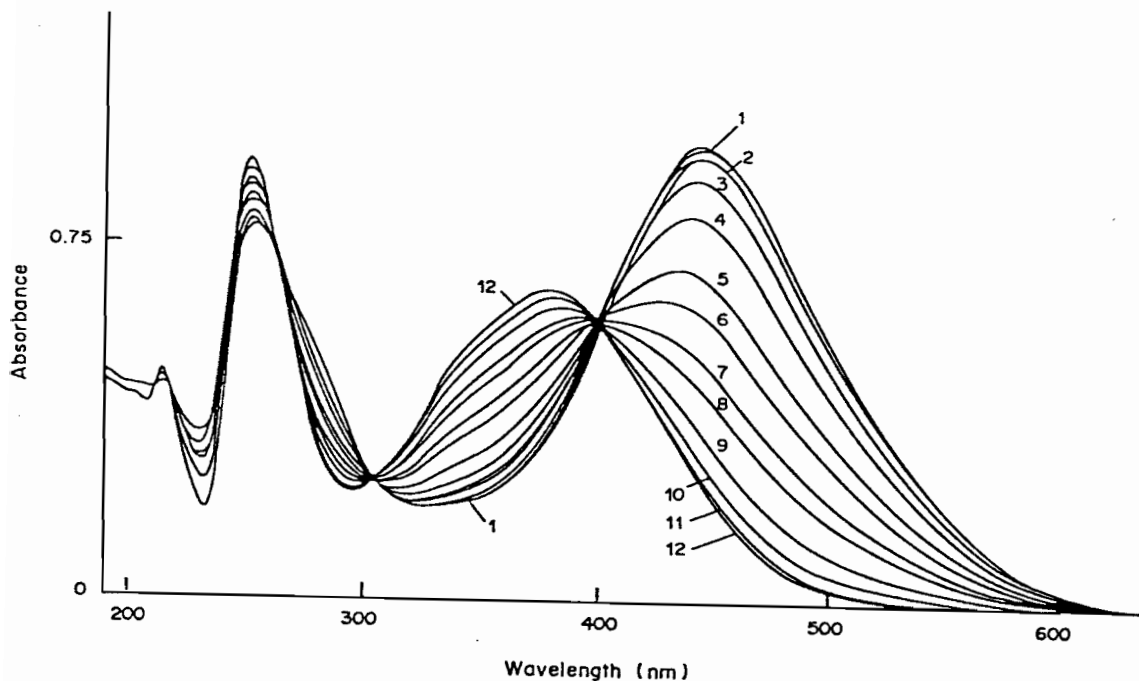


Fig.8-1. Absorption spectra of 4'-PicNHBz-TTCP (7) in 50% v/v dioxane-water mixture. Concentration of (7):  $5 \times 10^{-5} \text{M}$ , pH: 1 - 11.0, 10.72; 2 - 10.33, 10.10, 9.86; 3 - 9.64; 4 - 9.46; 5 - 9.20; 6 - 8.96; 7 - 8.72; 8 - 8.50; 9 - 8.27; 10 - 8.01; 11 - 7.42; 12 - 5.50, 4.75, 4.35, 4.30.

due to the acid dissociation equilibrium of the amino group in (7).

*Absorption spectra of 6TF (8) and 4TF (9)* In the compounds (8) or (9), one of nitro groups was so replaced with trifluoromethyl group as to change the character of chromogenic groups. Figure 8-2 shows the absorption spectra of (8) in the dioxane-water mixture in the pH range 3.05-13.10. Figure 8-3 also shows that of (9) in the pH range of 12.30- >14. Wavelengths (nm) at absorption maxima for HL and L<sup>-</sup> species of compounds (7), (8) and (9) are shown in Table 8-1 with their pK<sub>a</sub> values. In the case of (8), absorption maxima ( $\lambda_{\max}$ ) for acid form appear in the lower wavelength than (7), whereas the  $\lambda_{\max}$  for basic form appear in higher wavelength. In the case of 4TF(9), the wavelength of  $\lambda_{\max}$  for acid form, 410 nm and  $\lambda_{\max}$  for basic form, 555 nm are higher than those of (7) and (8). The difference between  $\lambda_{\max}$  for acid form and  $\lambda_{\max}$  for basic form,  $\Delta\lambda_{\max}$  of (7), (8) and (9) are 65, 90 and 145 nm, respectively. As increasing the  $\Delta\lambda_{\max}$  value, the overlap between absorption spectra of acid form and basic form decreases. Therefore, the spectral overlap of (9) is the smallest of three reagents. The small spectral overlap will be advantageous for the determination of metals, because the spectral overlap between reagent blank (acid form) and the metal complex (basic form) decreases the sensitivity of the

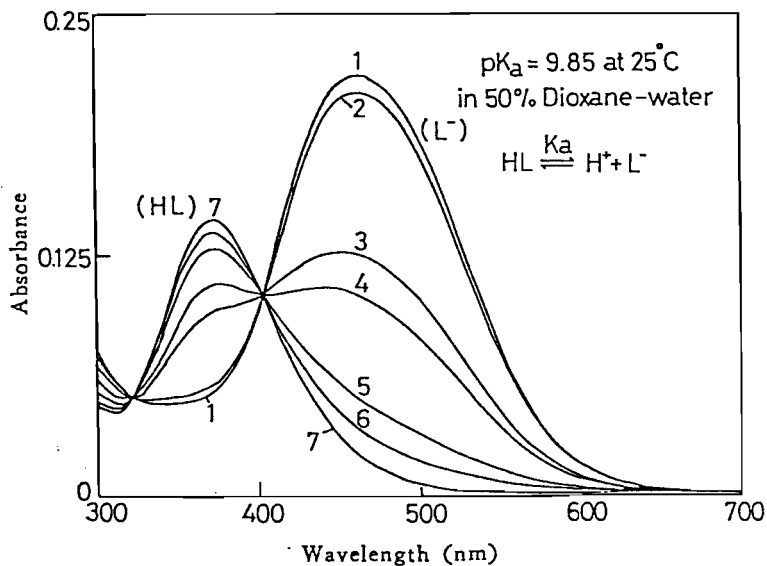


Fig.8-2. Absorption spectra of 6TF (8) in 50% v/v dioxane-water mixture. Initial Concentration of (8):  $5 \times 10^{-5} \text{M}$  (a fraction of (8) was deposited). pH: 1 - 13.10; 2 - 11.22; 3 - 9.90; 4 - 9.65; 5 - 9.20; 6 - 8.78; 7 - 3.05.

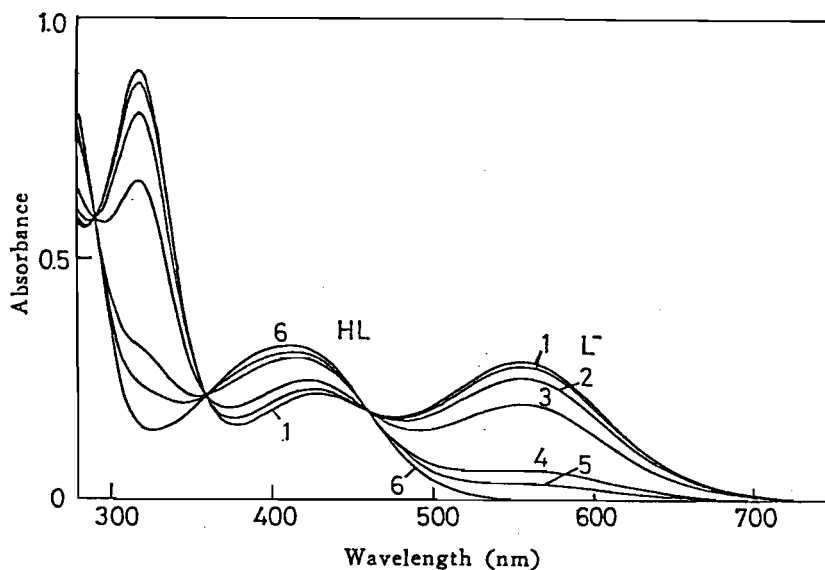


Fig.8-3. Absorption spectra of 4TF (9) in 50% v/v dioxane-water mixture. Concentration of (9):  $5 \times 10^{-5} \text{M}$ . pH: 1 -  $>14$ ; 2 - 13.89; 3 - 13.48; 4 - 12.65; 5 - 12.50; 6 - 12.30.

determination.

### 8.3.2 Acid dissociation constants

*Acid dissociation constants of (7), (8) and (9)* It was necessary to evaluate the dissociation constants of (7), (8) and (9) in order to select the optimum pH for extraction of univalent class b metals. These acid dissociation constants were determined spectrophotometrically, in 50% v/v dioxane-water mixture. The results are shown in Table 8-1. In general, the proton of a secondary amine is difficult to dissociate. The inductive effect of the nitro groups on the picrylamino group results in a  $pK_a$  value of 9.74 for (7). The  $pK_a$  value of 6TF (8) in which a nitro group of 6-position on the picrylamino group is replaced with a trifluoromethyl group, is 9.85, which is nearly same as that of (7). However, that of 4TF (9) can not be evaluated, because the absorption spectra of HL species did not decrease completely, even at pH 13.5. The result suggests that the  $pK_a$  value of 4TF is higher than 13.

*Effect of silver(I) on  $pK_a$  of (7)* In order to determine the effect of complexation on the apparent (conditional) dissociation constant,  $pK_a$  values of (7) were determined in the presence of various concentration of silver(I) ion. The results are shown in Table 8-2. The  $pK_a$  value is decreased in the presence of silver(I), reaching a practically



Table 8-1. Absorption maxima (nm) for HL and  $L^-$  species of compounds (7), (8) and (9), and their  $pK_a$  in 50% v/v dioxane-water mixture.

Compound	Absorption maxima (nm)		
	HL	$L^-$	$pK_a$
(7)	380	445	9.74
(8)	374	464	9.85
(9)	410	555	>13

Table 8-2. Acid dissociation constants of 4'-PicNHBz-TTCP(HL) in 50% v/v dioxane-water mixture.

[HL] M	[Silver] M	Mole ratio HL:Ag	$pK_a$
$5 \times 10^{-5}$	0	1:0	9.70
$5 \times 10^{-5}$	$1.66 \times 10^{-5}$	3:1	9.20
$5 \times 10^{-5}$	$3.33 \times 10^{-5}$	3:2	8.76
$5 \times 10^{-5}$	$5.00 \times 10^{-5}$	1:1	8.57
$5 \times 10^{-5}$	$1.00 \times 10^{-4}$	1:2	8.55
$5 \times 10^{-5}$	$2.00 \times 10^{-4}$	1:4	8.5

constant value of 8.5 when the  $[Ag^+]/[HL]$  ratio is  $>1.0$ . From the result, it becomes clear that the complexation of silver(I) with the 4'-PicNHBz-TTCP makes the proton of picrylamino group easily dissociable. Therefore, extraction of silver(I) with (7) at lower pH than the  $pK_a$  value is expected.

### 8.3.3 Extraction behavior of silver(I) and copper(I) with (7)

**Absorption spectra of extracted species** The absorption spectra of the reagent and its silver(I) and copper(I) complexes with (7) in 1,2-dichloroethane medium are shown in Fig.8-4. The absorption band of HL has its maximum at 380 nm ( $\epsilon_{HL}=1.40 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) and is almost the same as that in 50% dioxane-water medium. The absorption maxima of the extracted silver(I) and copper(I) species are at 450 nm ( $\epsilon_{M^+L^-}=2.30 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). The absorption spectra of the two complexes are identical and very similar to the spectra of the anion of the reagent,  $L^-$ , in 50% dioxane-water mixture. These facts seem to indicate that the deprotonated amino group in the reagent does not bond with silver(I) or copper(I), but provides internal charge-compensation to form an intramolecular ion-pair in which the silver(I) or copper(I) is coordinated with sulfur atoms of the macrocyclic polythio ether.

**Extraction equilibria** If a univalent class b metal ion

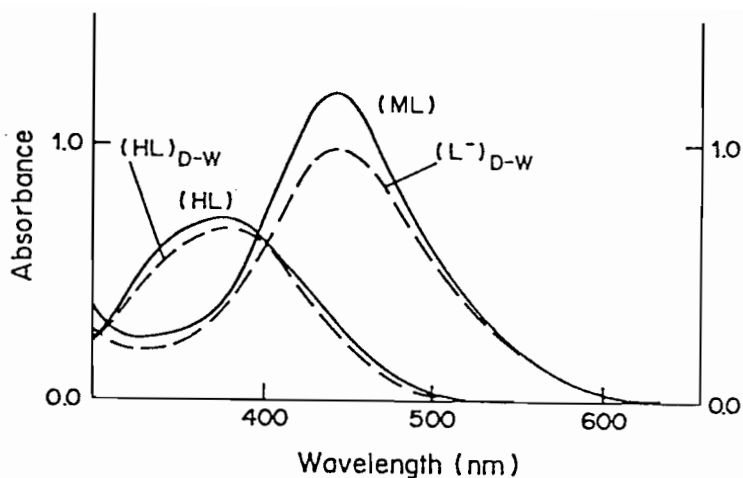


Fig.8-4. Absorption spectra of 4'-PicNHBz-TTCP (7) and its silver(I) and copper(I) complexes in 1,2-dichloroethane. Concentration of (7):  $5 \times 10^{-5} \text{M}$ . Dashed lines: HL and  $\text{L}^-$  species in 50% v/v dioxane-water mixture.

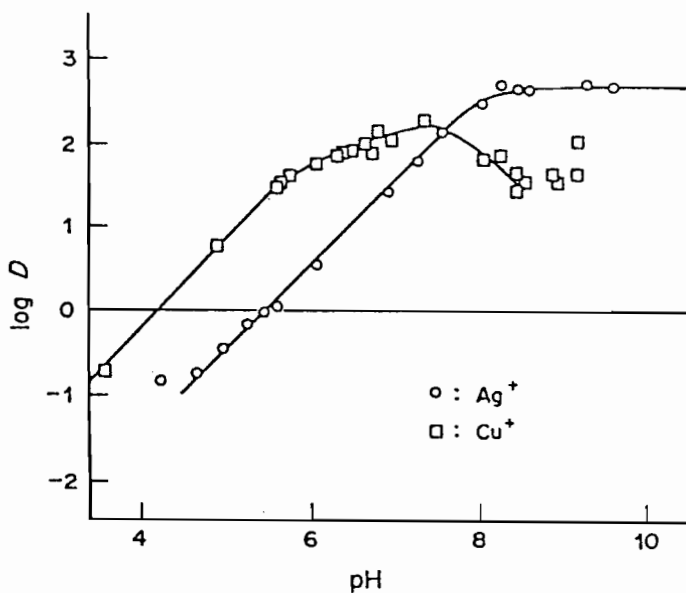
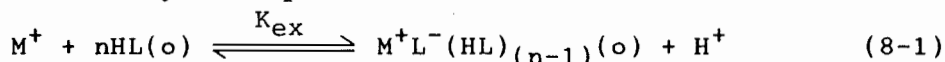


Fig.8-5. Plots of  $\log D$  vs. pH. Initial concentration of silver(I) and copper(I):  $5 \times 10^{-5} \text{M}$ , (7) in 1,2-dichloroethane:  $2.5 \times 10^{-3} \text{M}$ .

$M^+$  reacts with HL, the extraction equilibrium is generally represented by the equation:



The extraction constant is given by:

$$K_{ex} = \frac{[M^+L^-(HL)_{(n-1)}]_o [H^+]}{[M^+][HL]_o^n} \quad (8-2)$$

The distribution constants for the complex and reagent are  $K_{Dc} = [M^+L^-]_o / [M^+L^-]$  and  $K_{DR} = [H^+L^-]_o / [HL]$  respectively, and the formation constant for the complex and the adduct constant are  $K_f = [M^+L^-] / [M^+][L^-]$  and  $K_{add} = [M^+L^-(HL)_{n-1}] / [M^+L^-]_o [HL]_o^{n-1}$ , respectively. The extraction constant can be written as

$$K_{ex} = K_a K_f K_{add} K_{Dc} / K_{DR} \quad (8-3)$$

The distribution ratio of the metal ion is given by:

$$D = \frac{[M^+L^-(HL)_{(n-1)}]_o}{[M^+] + [M^+L^-] + [MHL^+]} \quad (8-4)$$

As the aqueous phase is completely colorless, the concentrations of the metal complexes  $M^+L^-$  and  $MHL^+$  in the aqueous phase must be negligibly small, and the relationship between the distribution ratio, D, and the extraction constant,  $K_{ex}$ , therefore gives the logarithmic expression:

$$\log D = \log K_{ex} + n \log [HL]_o + pH \quad (8-5)$$

*Extraction behavior of silver(I) and copper(I)* Plots of the logarithmic distribution ratio for silver(I) and copper(I) vs. the pH of the aqueous phase are shown in

Fig.8-5. A linear section with a slope of +1 was obtained for both silver(I) and copper(I), as expected from Eqn.(8-5). For extraction of silver(I), logD becomes constant at  $\text{pH} > 8$ , but logD for copper(I) becomes maximal at  $\text{pH} 7.5$  then decreases at higher  $\text{pH}$ . Such decreases in logD on the alkaline side may be attributed to the formation of hydroxo-complexes of copper(I). As seen in Fig.8-5, copper(I) is extracted at lower  $\text{pH}$  than silver(I). The values of  $\text{pH}_{1/2}$  ( $\text{pH}$  at  $\log D = 0$ ) are 5.5 for silver(I) and 4.2 for copper(I). The values of the parameter  $\alpha$ ,<sup>2)</sup> representing the softness of the metals, are 3.9 for copper(I) and 3.6 for silver(I). It would be expected that the affinity for a polythio ether (i.e. the bonding to the sulfur atoms of polythio ether), would be stronger for copper(I) than for silver(I). Consequently, formation of the copper(I) complex cation with the polythio ether will facilitate dissociation of the proton on the amino group more readily than formation of the silver(I) complex does.

Plots of the logarithmic distribution ratio of copper(I) and silver(I) vs. the logarithm of the ligand concentration in the organic phase at constant  $\text{pH}$  (7.5 for silver(I) and 6.2 for copper(I)) are shown in Fig.8-6. Straight lines with slopes of 1.1 and 0.97 were obtained for silver(I) and copper(I) respectively. Putting  $n=1$  in Eqn.(8-5) yields:

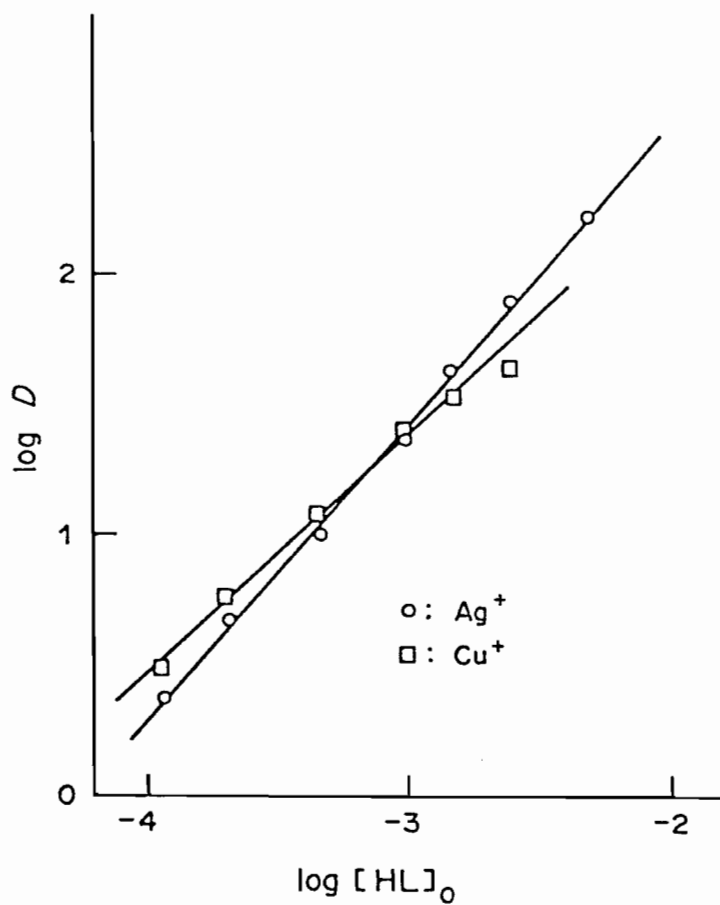
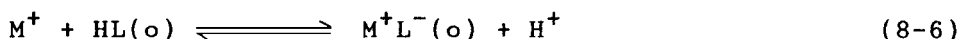


Fig.8-6. Plots of  $\log D$  vs.  $\log [HL]_0$  at pH 7.5 for silver(I) and pH 6.2 for copper(I). Concentration of silver(I) and copper(I):  $5 \times 10^{-5} M$ . (HL: 4'-PicNHBz-TTCP).



and shows that silver(I) and copper(I) form the  $M^+L^-$  without formation of an adduct. As silver(I) ion form the dimeric complex cation with Bz-TTCP as shown in Chapter 5, silver(I) may also form the dimer,  $(M^+L^-)_2$ .

#### 8.3.4 Extraction condition for the determination of silver(I)

*Extraction of silver(I) with (7), (8) and (9)* Liquid-liquid extraction of silver(I) with chromogenic thiocrown ethers (7), (8) and (9) were examined at various pH. The results are shown in Fig.8-7. In the case of the compound (9), ethylacetate was used as extraction solvent, because the precipitate of the complex formed on the interface between water and 1,2-dichloroethane. As expected from Eqn.(8-5), straight lines with the slope of +1 are obtained for (7), (8) and (9). The order of values of  $pH_{1/2}$  are same as that of  $pK_a$  values. In the case of (7) and (8), silver(I) ion was extractability more than 99% at  $pH > 8$ . Although in the case of (9), extraction of silver(I) more than 99% will demand the pH in aqueous phase to be more than 10. As many metals form the precipitate of the hydroxide at  $pH > 10$ , the compound (9) is difficult to use for the determination in practical. Figure 8-8 shows absorption spectra of (7) and (8) and their complexes in 1,2-dichloroethane. The

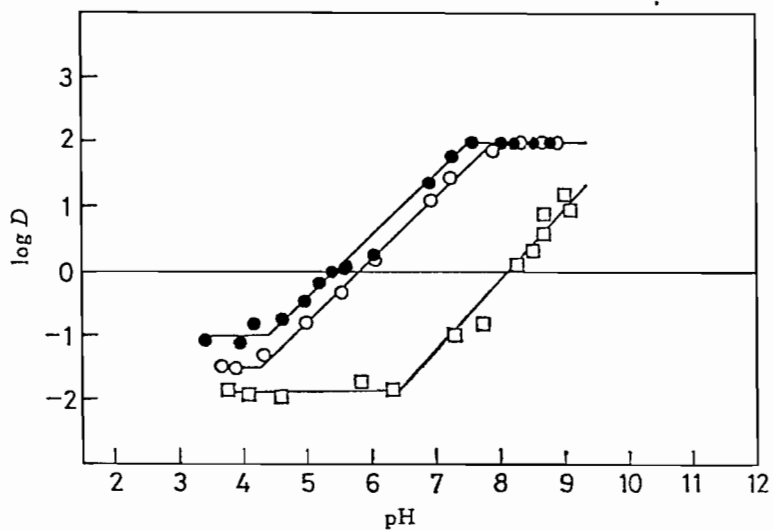


Fig.8-7. Plots of logD vs. pH. Initial concentration:  $5 \times 10^{-5} \text{M}$  silver(I). Concentration of ligand;  
 ● : (7)  $[\text{HL}]_0 = 2.5 \times 10^{-3} \text{M}$  in 1,2-dichloroethane  
 ○ : (8)  $[\text{HL}]_0 = 1.25 \times 10^{-3} \text{M}$  in 1,2-dichloroethane  
 □ : (9)  $[\text{HL}]_0 = 1.25 \times 10^{-3} \text{M}$  in ethyl acetate.

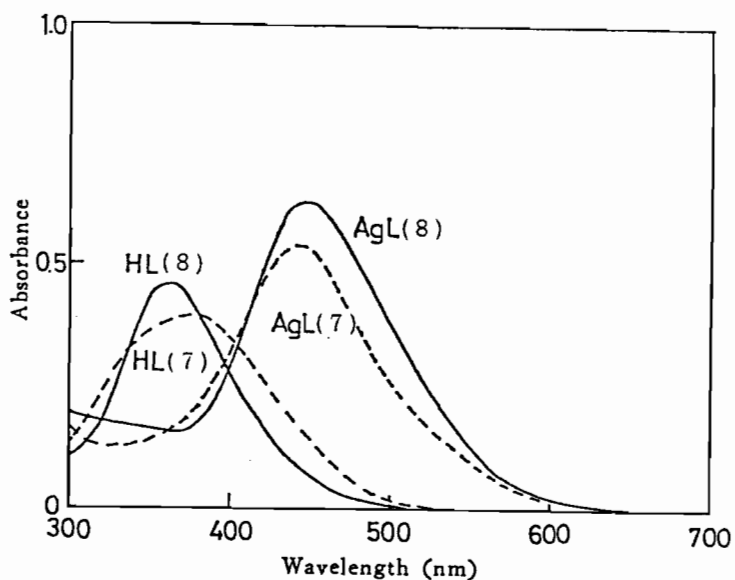


Fig.8-8. Absorption spectra of (7) and (8) and their silver(I) complexes in 1,2-dichloroethane. Reference solution: 1,2-dichloroethane. Concentration of (7) and (8):  $5 \times 10^{-6} \text{M}$ .



wavelength of absorption maximum of the compound (8) in 1,2-dichloroethane, 360nm, is shorter than that of (7). Whereas that of silver(I) complex with (8) is longer than with (7). It is expected from this result, the determination of silver(I) with (8) is more sensitive than with (7). Figure 8-9 shows the absorption spectra of silver(I) complex of (7) and (8) extracted into 1,2-dichloroethane solution against reagent blank. Absorbance at 510 nm of (8) is twice times large as that of (7). Therefore (8) is the best reagent of three compounds discussed, for the selective and sensitive determination of silver(I).

*Effect of masking agents on extraction of silver(I)*      The univalent class b metal ions silver(I) and copper(I), were completely extracted with (7) or (8) into 1,2-dichloroethane from aqueous solution at  $\text{pH} > 8.0$ . At such pH, many foreign metal ions will precipitate as their hydroxides, and interfere in the extraction of silver(I) and copper(I). Consequently, if large amounts of foreign transition metals are present, they must be masked by a suitable complexing agent. Hence, the effects of EDTA and tartrate on the extraction of silver(I) were examined by using 4'-PicNHBz-TTCP (7). The results are shown in Fig.8-10. The presence of 0.1 M EDTA shifts the extraction curve by about 5 pH units ( $\text{pH}_{1/2} = 10.8$ ). This pH effect may be due to formation of the silver(I)-EDTA complex, with an accompanying decrease in the

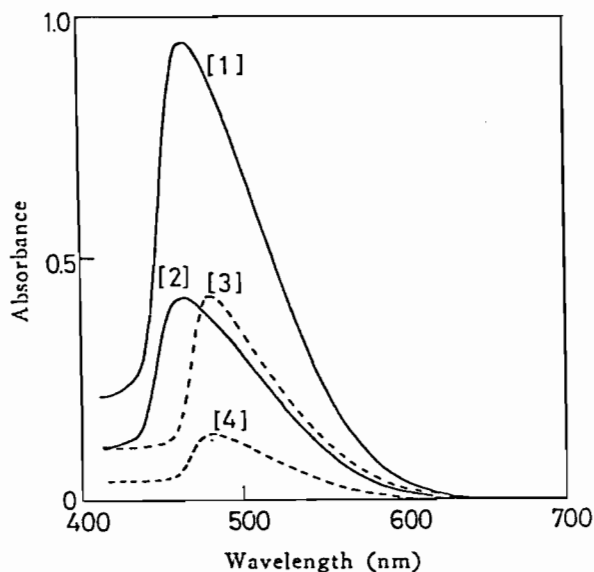


Fig.8-9. Absorption spectra of silver(I) complexes of (7) and (8) extracted into 1,2-dichloroethane solution against reagent blank at pH 9.46. Initial concentration of silver(I): [1] and [3];  $5 \times 10^{-5} \text{M}$ , [2] and [4];  $2.5 \times 10^{-5} \text{M}$ . Concentration of (7) and (8):  $1.25 \times 10^{-3} \text{M}$ . --- : (7), — : (8).

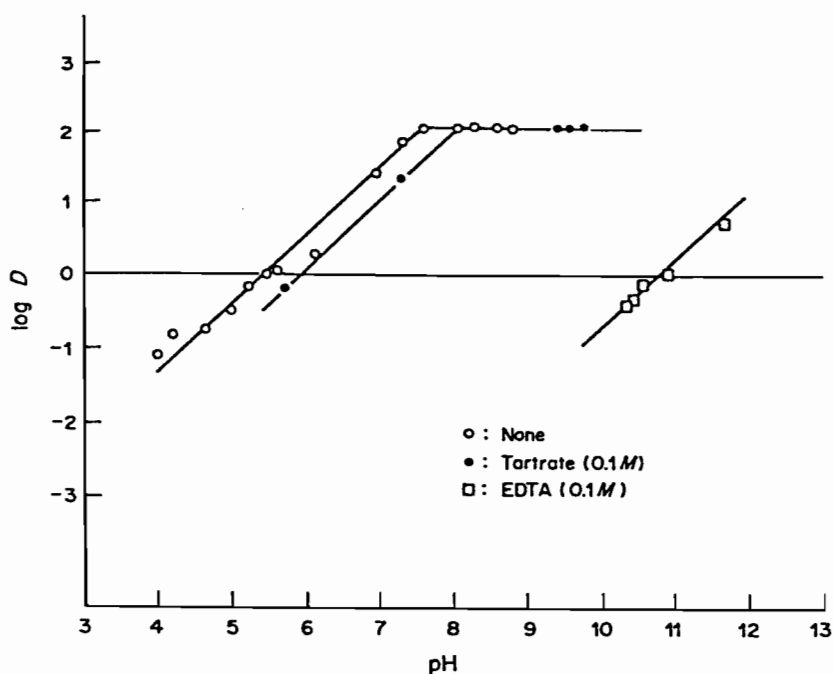


Fig.8-10. Plots of  $\log D$  vs. pH. Initial concentration:  $5 \times 10^{-5} \text{M}$  silver(I),  $2.5 \times 10^{-3} \text{M}$  4'-PicNHbz-TTCP in 1,2-dichloroethane;  $\circ$  : no masking agent,  $\square$  : 0.1M EDTA,  $\bullet$  : 0.1M tartrate.

free silver(I) ion concentration, though it is difficult to see why, since the silver(I)-EDTA complex has maximum stability at about this pH, but lower stability as the pH is decreased. On the other hand, 0.1 M tartrate does not produce so large an effect on the extraction curve for silver(I) ( $\text{pH}_{1/2}=5.8$ ), 0.1 M tartrate will serve as a suitable masking agent.

*Effect of foreign ions on extraction of silver(I)*      The interference from Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Fe(III) in the presence of 0.1 M tartrate as masking agent was examined by using (7), with a shaking time of 5 min for extraction of silver(I). The results are shown in Table 8-3. Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in a 200-fold amount relative to silver(I) do not interfere, and Mn(II) decreases the absorbance by only 3.1%. A  $5 \times 10^{-5}$  M silver(I) solution containing Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Fe(III), each at  $1 \times 10^{-2}$  M concentration, was successfully analyzed, with 0.1 M tartrate as masking agent, the silver(I) recovery being 98.6%.

Table 8-3. Effects of diverse ions.

Ion	Concentration		Absorbance	
	M	pH	at 500 nm	E%
None	-	9.60	0.588	100.0
Mn(II)	$1.0 \times 10^{-2}$	9.63	0.570	96.7
Co(II)	$1.0 \times 10^{-2}$	8.80	0.592	100.7
Ni(II)	$1.0 \times 10^{-2}$	8.83	0.590	100.3
Cu(II)	$1.0 \times 10^{-2}$	8.56	0.590	100.3
Zn(II)	$1.0 \times 10^{-2}$	9.32	0.595	101.2
Cd(II)	$1.0 \times 10^{-2}$	9.30	0.584	99.3
Fe(III)	$1.0 \times 10^{-2}$	9.63	0.586	99.7

Concentration of silver(I) :  $5 \times 10^{-5}$  M.

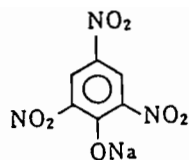
## Chapter 9.

### Effect of counter anion on extractive spectrophotometric determination of copper(II) with thiacrown compounds

#### 9.1 Introduction

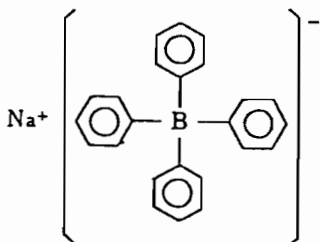
Several studies about the liquid-liquid extraction of metal ions with TTCT (1)<sup>34)</sup> and HTCO (10)<sup>37)</sup> have been reported. These studies made possible the application of thiacrown compounds to the extractive spectrophotometric determination of soft metals such as silver(I) and copper(I), by using colored anions.

In this chapter, the effects of eight counter anions on the solvent extraction of copper(II) with thiacrown compounds, TTCT and HTCO, were examined from the viewpoint of the sensitivity and the selectivity for the extractive-spectrophotometric determination of class b and ab metals. The following eight anions were examined as counter ions: perchlorate ( $\text{ClO}_4$ ), picrate (Pic), tetraphenyl borate (TPB), Bromocresol Green (BCG), Thymol Blue (TB), Hexanitrodiphenylamine (HNDPA), tetrabromophenolphthalein ethylester (TBPE) and lauryl sulfate (SLS). Their structures are shown in Fig.9-1.

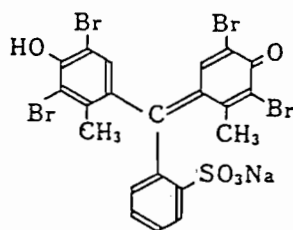


1)  $\text{ClO}_4^-$  (sodium perchlorate)

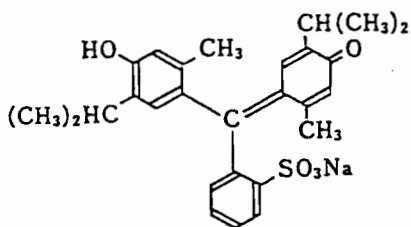
2) Pic (picric acid Na salt)



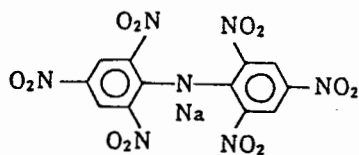
3) TPB (tetraphenylborate Na salt)



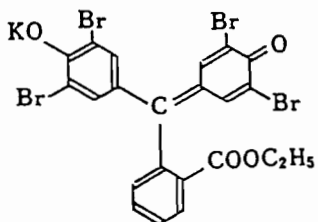
4) BCG (Bromocresol Green Na salt)



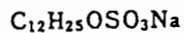
5) TB (Thymol Blue Na salt)



6) HNDPA (hexanitrodiphenylamine Na salt)



7) TBPE (tetrabromophenolphthalein ethylester K salt)



8) SLS (sodium lauryl sulfate)

Fig.9-1. Counter anions discussed in this work.

## 9.2 Experimental

An aliquot (10 ml) of the aqueous solution containing the metal ion ( $5 \times 10^{-5}$  M), the counter anion ( $5 \times 10^{-4}$  M), the buffer ( $1 \times 10^{-2}$  M, acetic acid-acetate for pH 4-6 and boric acid-borax for pH > 7) and sodium sulfate to adjust to the ionic strength 0.1 was taken in a 50 ml glass cylindrical tube with a glass stopper. After the addition of 10 ml of a 1,2-dichloroethane solution of the thiocrown ether ( $5 \times 10^{-4}$  M or  $5 \times 10^{-3}$  M), the mixture was shaken for 30 min at 200 strokes/min at  $25 \pm 0.1^\circ \text{C}$  and centrifuged for 5 min at 2000 r.p.m. After the separation, the pH of the aqueous phase was measured and the metal concentration was measured by atomic absorption spectrophotometry using the resonance line for the metal. The absorption spectra of the extracts were measured in the range 330-700 nm, against a reagent blank. For the copper(I) extraction, L-ascorbic acid solution (0.033 M) neutralized with sodium hydroxide was added into the aqueous phase to reduce copper(II) to copper(I).

### 9.3 Results and discussion

#### 9.3.1 Extraction of metals with HTCO in the presence of counter anions

Results of the extraction of metals with HTCO into 1,2-dichloroethane in the presence of TPB, HNDPA, TBPE or SLS as a counter anion are shown in Table 9-1. The extraction of various metals in the presence of TPB ion with HTCO is roughly the same as that with TTCT<sup>33</sup>). Cobalt(II), nickel(II) and zinc(II) belonging to the class ab metals are not extracted at all, regardless of counter anions, although it had been confirmed by X-ray crystallography that cobalt(II) and nickel(II) form meso octahedral complexes with HTCO in some organic solvents.<sup>17</sup>) The extraction of cobalt(II) at 30°C and 50°C were also tried, but cobalt(II) was not extracted at all. On the other hand, copper(I), silver(I) and palladium(II), belonging to class b metals, especially copper(I), seem to be extracted well and cadmium(II) are precipitated with some kinds of counter anions. For example, silver(I) and palladium(II) are precipitated with the TPB anion as their salts in the aqueous phase, and silver(I), palladium(II) and cadmium(II) are precipitated with HTCO and TBPE as ion-pair complexes on the interface. Palladium(II) and cadmium(II) also form precipitates with HTCO and HNDPA. In fact, it was found that



Table 9-1. Data for extraction of various metals in the presence of dye anions with HTCO 1,2-dichloroethane solution.

Metal ion	TPB		HNDPA		TBPE		SLS	
	pH	%E	pH	%E	pH	%E	pH	%E
Co(II)	5.5	0	6.7	0	6.8	0	5.6	0
Ni(II)	5.5	0	6.6	0	6.5	0	5.5	0
Zn(II)	5.5	0	7.3	0	7.6	0	5.6	0
Cd(II)	5.5	9.5	6.7	ppt.	6.7	ppt.	5.5	1.8
Cu(I)	5.5	99.9	7.0	99.9	7.0	98.6	5.7	99.9
Ag(I)	5.5	ppt.	6.4	99.9	6.5	ppt.	5.5	99.9
Pd(II)	6.0	ppt.	6.1	ppt.	6.1	ppt.	3.8	77.2

Table 9-2. Extraction data of copper(II) in the presence of various counter anions with HTCO 1,2-dichloroethane solution and spectrophotometric data of their extracts.

Anion	Shape	pH	%E	$\lambda_{\max}$ (nm)	$\times 10^{-4}$
ClO <sub>4</sub>	S <sup>a</sup>	5.2	3.7	-	-
Pic	P <sup>b</sup>	5.4	4.0	375	1.1
TPB	S	5.5	99.2	-	-
BCG	P	5.1	58.4	408	1.9
TB	P	5.2	86.4	393	1.4
HNDPA	P	6.7	99.9	414	3.2
TBPE	P	8.4	99.9	608	8.8
SLS	C <sup>c</sup>	5.4	25.5	-	-

a. S:Sphere.

b. P:Plane.

c. C.Chain.

66.2% of silver(I) and 46.5% of palladium(II) are transferred into the organic phase in the case of TBPE. These ion-pair complexes might dissolve in appropriate organic solvent other than 1,2-dichloroethane.

### 9.3.2 Extractive and spectrophotometric studies for copper(II) in the presence of counter anions

*Extraction behavior of copper(II)-HTCO-X* Extractive and spectrophotometric data for copper(II) in the presence of counter anion, X, including BCG, TB, Pic, and  $\text{ClO}_4$ , are shown in Table 9-2. The percent extraction of copper(II), one of the class ab metals, varies from 99.9% to 3.7% depending on the kind of counter anions. This fact suggests that the selection of the anion for the formation of ion-pair is very important for the extraction of copper(II).

Although the selective and extractive spectrophotometric determination of silver(I) and copper(I) with the thiocrown compound has been reported previously,<sup>34)</sup> it is expected that a proper combination of a thiocrown ether and an anion dye is essential to devise a more sensitive determination of copper(II) in the presence of other first transition metals without the reduction of copper(II) to copper(I). As shown in Table 9-2, the percent extraction of copper(II) under the condition of pH at which each counter anion functions as the univalent anion, decreases in the

order: TBPE, HNDPA, TPB>TB>BCG>SLS>Pic>ClO<sub>4</sub>. Although it is not obvious what kinds of nature and structure of the counter anion cause the percent extraction of copper(II) increase, the larger anion having more than two benzene nuclei, the spherical or plane anion being not long-chain, and the anion having the delocalized charge on the whole of the anion seem to be favorable to the extraction of copper(II). The highest percent extraction were obtained when TBPE was used as a counter anion.

*Absorption spectra of copper(II)-HTCO-X*                      Absorption spectra of copper(II)-HTCO-X complexes in 1,2-dichloroethane are shown in Fig.9-2 and their wavelength of the absorption maxima and their absorptivities are shown in Table 9-2. The molar absorptivity decreases in the order: TBPE>HNDPA>BCG>TB>Pic. The absorptivity of the copper(II)-HTCO-TBPE complex is 4-8 times larger than those of copper(II)-HTCO, -BCG, -TB and -Pic complexes. The copper(II)-HTCO-TBPE complex in 1,2-dichloroethane is blue, while copper(II)-HTCO-BCG, -TB and -Pic complexes are from yellow to orange. Consequently, the most sensitive extractive spectrophotometric determination of copper(II) is obtained by using HTCO as the ligand, and TBPE as the counter anion, when 1,2-dichloroethane is used as the organic solvent.

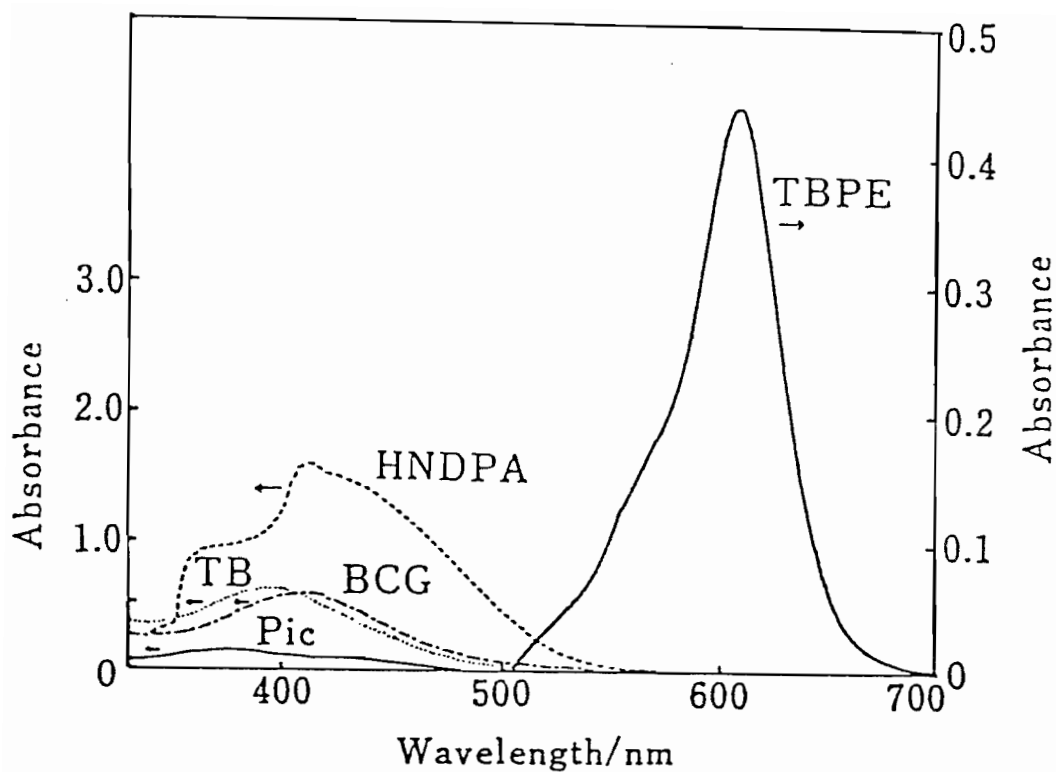


Fig.9-2. Absorption spectra of extracts in HTCO 1,2-dichloroethane solutions from aqueous copper(II) solutions containing various counter anions. Initial concentrations:  $5 \times 10^{-3} \text{M}$  HTCO,  $5 \times 10^{-4} \text{M}$  counter anion,  $5 \times 10^{-5} \text{M}$  copper(II) for Pic, BCG, TB, HNDPA and  $5 \times 10^{-6} \text{M}$  copper(II) for TBPE.

### 9.3.3 Comparison of the extraction of copper(II) with TTCT and that with HTCO in the presence of TBPE

The plots of the percent extraction (%E) of copper(II) with HTCO and TTCT vs. pH are shown in Fig.9-3. The percent extraction of copper(II) for HTCO was more than 99% at pH>7 but that for TTCT was below 75% and was irregular at pH>7. The decreases of the extraction of copper(II) for both HTCO and TTCT below pH 7 may be attributed to the protonation of TBPE anion. The acid dissociation constant of TBPE in 0.2% ethanol-water solution was determined to be  $pK_a=4.6$ . The fact that the extraction of copper(II) with TTCT is incomplete and that the extraction from the basic media is irreproducible may be due to the formation of copper(II)-TTCT-hydroxo complex. It has been reported that the copper(II)-HTCO complex cation has axially elongated octahedral structure in which the copper(II) ion is coordinated with six sulfur atoms in the HTCO molecule.<sup>26)</sup> On the other hand, copper(II)-TTCT complex cation has a square planar structure, in which the copper(II) is coordinated four sulfur atoms in the TTCT molecules and both of axial sites are occupied by two perchlorate ions<sup>16)</sup>. In the extraction of copper(II) with HTCO and TTCT, the counter anion TBPE may exist in an outer coordination sphere for hexadentate HTCO and in axial sites for tetradentate TTCT. However, in the latter case, the species such as  $OH^-$  and

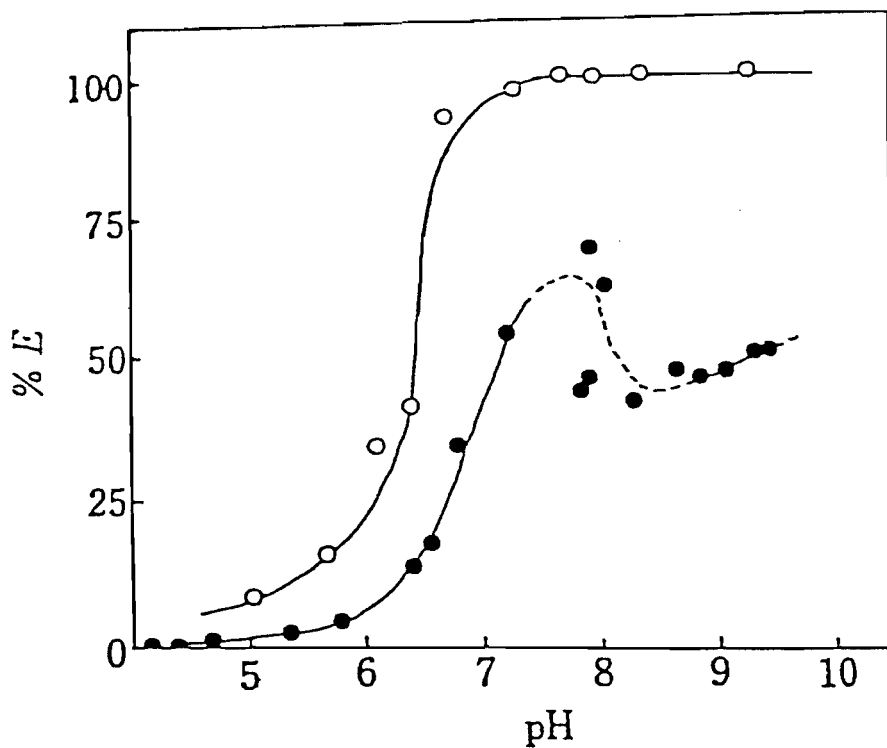


Fig.9-3. Plots of %E of copper(II) vs. pH. Initial concentrations:  $1 \times 10^{-5}$  M copper(II),  $5 \times 10^{-3}$  M HTCO and TTCT,  $3 \times 10^{-4}$  M TBPE. ○ : HTCO, ● : TTCT.

H<sub>2</sub>O may also compete to occupy the axial sites of the plane, so that the poor extraction from the basic media may be due to the formation of complexes such as copper(II)-TTCT-(OH)<sub>2</sub>, copper(II)-TTCT-OH-TBPE and copper(II)-TTCT-OH-H<sub>2</sub>O-TBPE.

The composition of the Cu(II)-HTCO-TBPE complex extracted into 1,2-dichloroethane solution was examined by the molar ratio method. As shown in Fig.9-4a and 4b, the break points appear at  $[\text{HTCO}]_{\text{o},i}/[\text{copper(II)}]_{\text{aq},i}=1$  and  $[\text{TBPE}]_{\text{aq},i}/[\text{copper(II)}]_{\text{aq},i}=2$ . Therefore, the ratio of copper(II):HTCO:TBPE, might be 1:1:2, that is, the extracted species can be assumed to be  $[\text{Cu(II)htco}]^{2+}(\text{TBPE})^{-2}$ . The gradual increase of %E over each break point, as seen in Fig.4a and 4b, may be because the formation of the 1:1 cationic complex,  $[\text{Cu(II)htco}]^{2+}$ , between copper(II) and HTCO, and the formation of the ion-pair,  $[\text{Cu(II)htco}]^{2+}$  and  $\text{TBPE}^{-}$  are not so strong.

More than 99% copper(II) is extracted with HTCO in the presence of TBPE at pH>7. The molar absorptivity of the extract is so high that the sensitive and selective extractive-spectrophotometric determination of copper(II) without the reduction to copper(I) is expected.

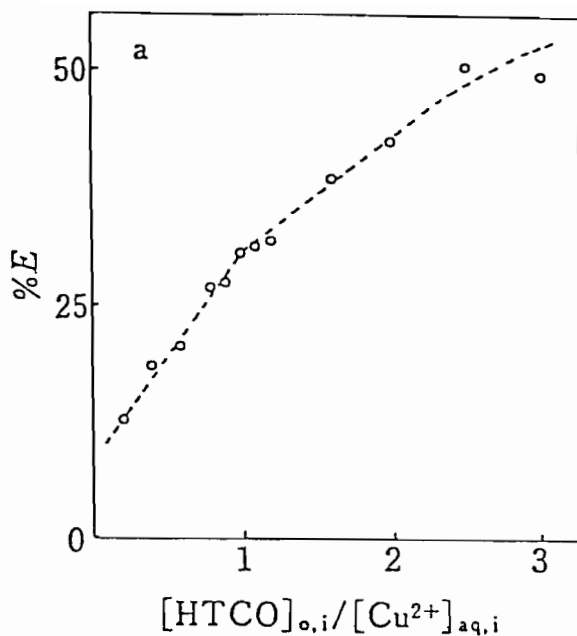


Fig.9-4a. Plots of %E of copper(II) vs. molar ratio of HTCO to copper(II) at pH 8.5. Initial concentrations:  $5 \times 10^{-5} M$  copper(II),  $5 \times 10^{-4} M$  TBPE.

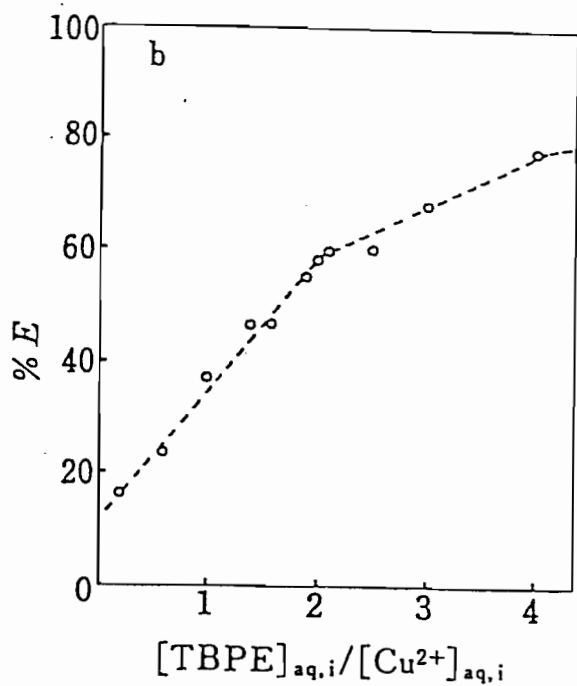


Fig.9-4b. Plots of %E of copper(II) vs. molar ratio of TBPE to copper(II) at pH 8.5. Initial concentration:  $5 \times 10^{-5} M$  copper(II),  $5 \times 10^{-3} M$  HTCO.



## Chapter 10.

### Extraction and spectrophotometric determination of silver(I) with HTCO

#### 10.1 Introduction

Silver(I) ion is extracted with a tetrathio ether and appropriate counter anion. It is expected that the combination of a polythio ether which can encircle the silver(I) ion and a counter anion of high absorptivity will make possible the sensitive and selective determination of silver(I) ion. In this chapter, the extraction and spectrophotometric determination of silver(I) with HTCO and TBPE as counter anion was examined. The extraction system was applied to the determination of silver(I) in standard steel sample.

#### 10.2 Experimental

##### 10.2.1 Liquid-liquid extraction of silver(I)

An aqueous solution containing  $5 \times 10^{-5}$  M (or  $5 \times 10^{-6}$  M) silver(I) ion and  $1 \times 10^{-2}$  M buffer was prepared; its ionic strength was kept at 0.1 with sodium sulfate. The buffer solutions were prepared with sulfuric acid at pH1-3, acetic acid-sodium acetate at pH3-6 and borax-boric acid at pH6-9.

TBPE as acid form was dissolved in 1,2-dichloroethane. A 10 ml of the aqueous solutions was placed in a 50 ml glass cylindrical tube with a glass stopper. After the addition of 10 ml of the 1,2-dichloroethane solution containing  $5 \times 10^{-4}$  M HTCO and  $5 \times 10^{-4}$  M TBPE, the mixture was shaken for 30 min at 200 strokes/min at  $25 \pm 0.1^\circ\text{C}$  and then centrifuged for 5 min at 2000 r.p.m. The absorption spectra of the 1,2-dichloroethane were measured against a reagent blank in the range from 500 to 700 nm. The pH of the aqueous phase was measured, and silver(I) concentration of the aqueous phase was measured by means of atomic absorption spectrometry.

#### 10.2.2 Preparation of a standard sample solution of steel

The standard sample of steel NBS-159 (0.1g) was dissolved in 20 ml of (1+4) nitric acid by heating. After the addition of 10 ml of (1+9) sulfuric acid, the solution was heated gently until fumes of sulfuric acid had been evolved. The residue was cooled to room temperature, and then the walls of the beaker were washed with a small portion of water. After the addition of several drops of hydrogen-peroxide solution (30%), the solution was heated gently until fumes of sulfuric acid had been evolved. The residue was cooled and then dissolved in water. Finally the solution was diluted to 100 ml with water.

### 10.2.3 Determination of silver(I) in the standard sample of steel

An aliquot of the sample solution was neutralized with sodium hydroxide solution and the pH of the solution was adjusted to 6.4 with the acetate buffer solution. In order to prevent the deposition of ferric hydroxide, 0.01 M tartrate was added to the solution which was then diluted to 50 ml with water. A 10 ml of this solution was shaken with 10 ml of 1,2-dichloroethane containing  $5 \times 10^{-4}$  M HTCO and  $5 \times 10^{-4}$  M TBPE in a 50 ml glass cylindrical tube equipped with a glass stopper. After shaking for 10 min and standing, 1,2-dichloroethane phase was placed in a 1 cm cell. The absorbance at 608 nm was measured against the 1,2-dichloroethane.

## 10.3 Results and discussion

### 10.3.1 Effect of pH

The extraction of silver(I) with HTCO and TBPE from the aqueous solution into 1,2-dichloroethane was examined in the pH range 1-9. Relationship between the extractability of silver(I) (E%) and pH in the aqueous phase is shown in Fig.10-1. Silver(I) ion is extracted more than 98% in the range of  $\text{pH} > 6$ . As decreasing the pH ( $< 6$ ), extraction percent decreases to 15-20% at  $\text{pH} 1-2$ . The mechanism of the

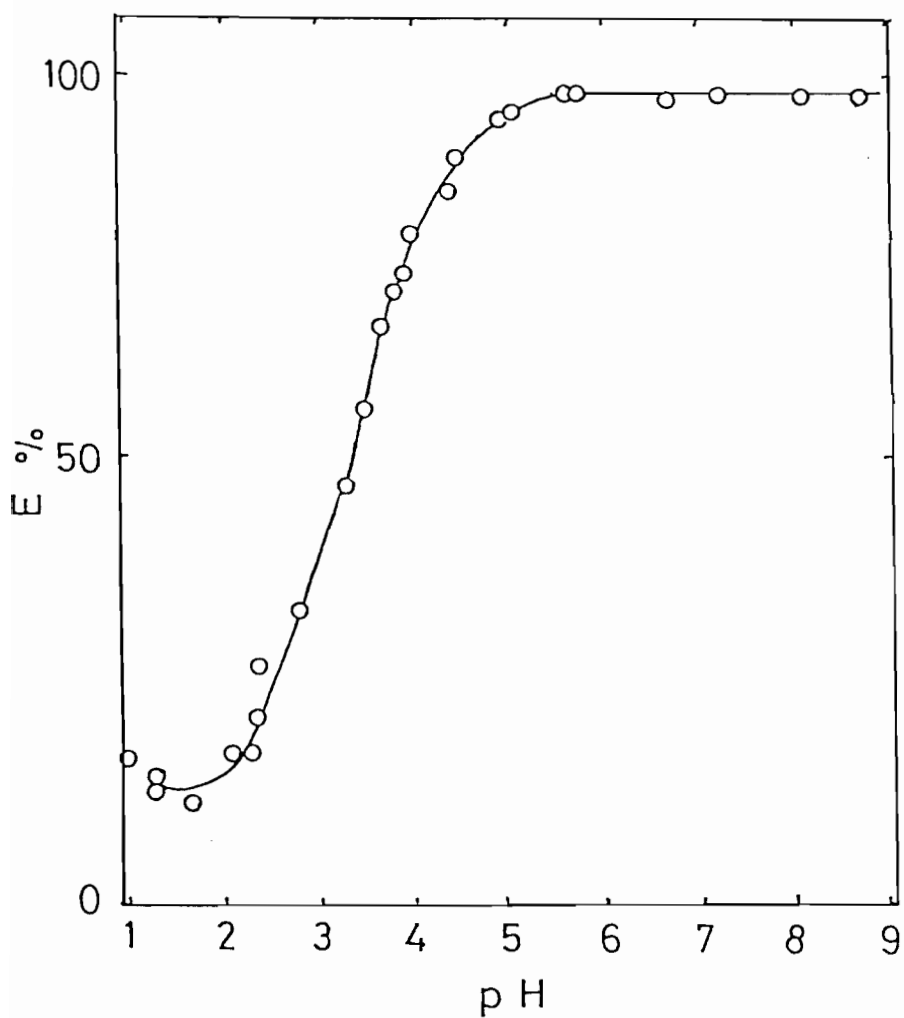


Fig.10-1. Plots of extraction percent (E%) vs. pH. Initial concentrations:  $5 \times 10^{-5} \text{M}$  silver(I),  $5 \times 10^{-4} \text{M}$  HTCO,  $5 \times 10^{-4} \text{M}$  TBPE.

extraction is considered as follows: a silver(I) ion forms the complex cation with the cyclic hexathio ether HTCO. The ion pair of the complex cation and the anion of TBPE is distributed to organic phase. Therefore pH in the aqueous phase will affect the extraction percent following the acid dissociation of TBPE. The acid dissociation constant ( $K_a$ ) of TBPE in 0.2% ethanol-water solution was determined spectrophotometrically to be  $pK_a=4.6$ .

### 10.3.2 Composition of the extracted species

The composition of the silver(I)-HTCO-TBPE complex extracted into 1,2-dichloroethane was examined by the molar ratio method. As shown in Figs.10-2a and 2b, the break points appear at  $[HTCO]_{o,i}/[silver(I)]_{aq,i}=1$  and  $[TBPE]_{o,i}/[silver(I)]_{aq,i}=1$ . Therefore, the molar ratio of silver(I):HTCO:TBPE might be 1:1:1, that is, the extracted species can be assumed to be  $[Ag(I)htco]^+TBPE^-$ . The cavity of HTCO is large enough to wrap around the silver(I) ion. It has been reported that the silver(I)-HTCO complex cation has an octahedral structure in which silver(I) ion is coordinated with six sulfur atoms in the HTCO molecule.<sup>24)</sup>

On the other hand, the size of silver(I) ion is too large to fit into the cavity of cyclic tetrathio ethers such as TTCT(1) and Bz-TTCP(2). As described in Chapter 5, silver(I) ion formed the dimeric complex cations with these

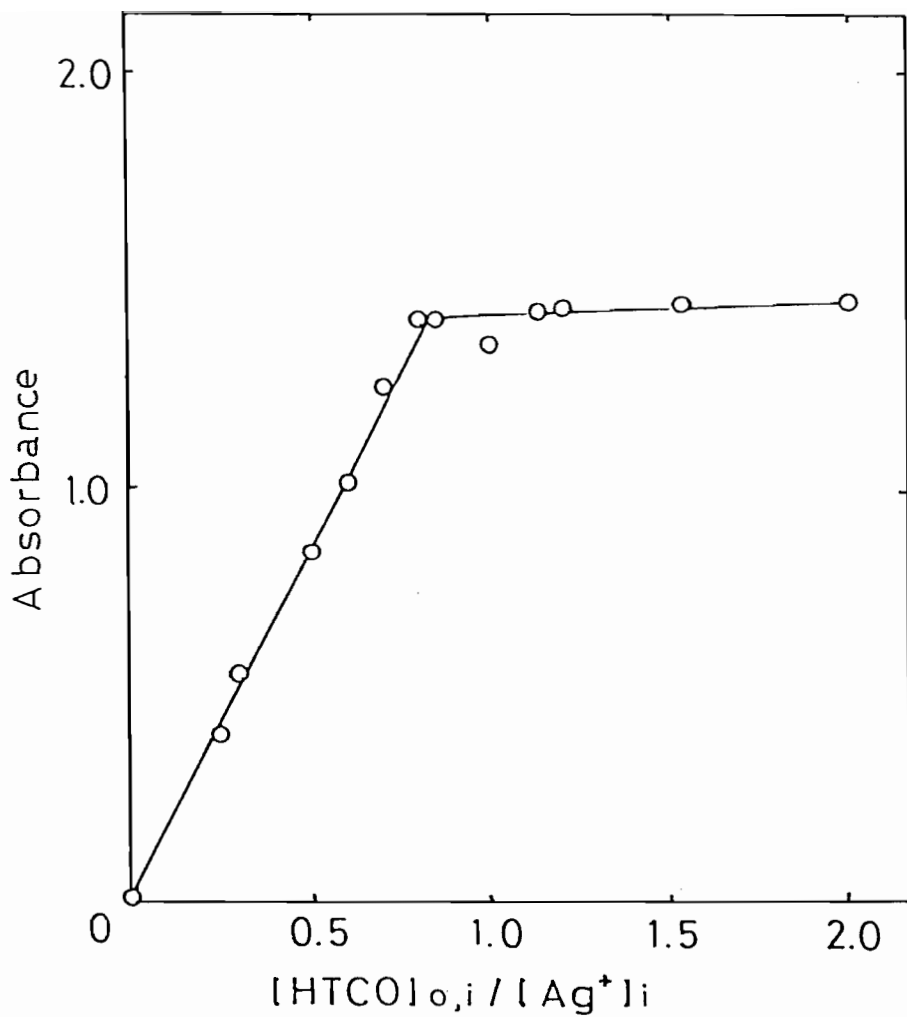


Fig.10-2a. Molar ratio methods at pH6.0. Initial concentration:  $5 \times 10^{-5} M$  silver(I),  $5 \times 10^{-4} M$  TBPE.

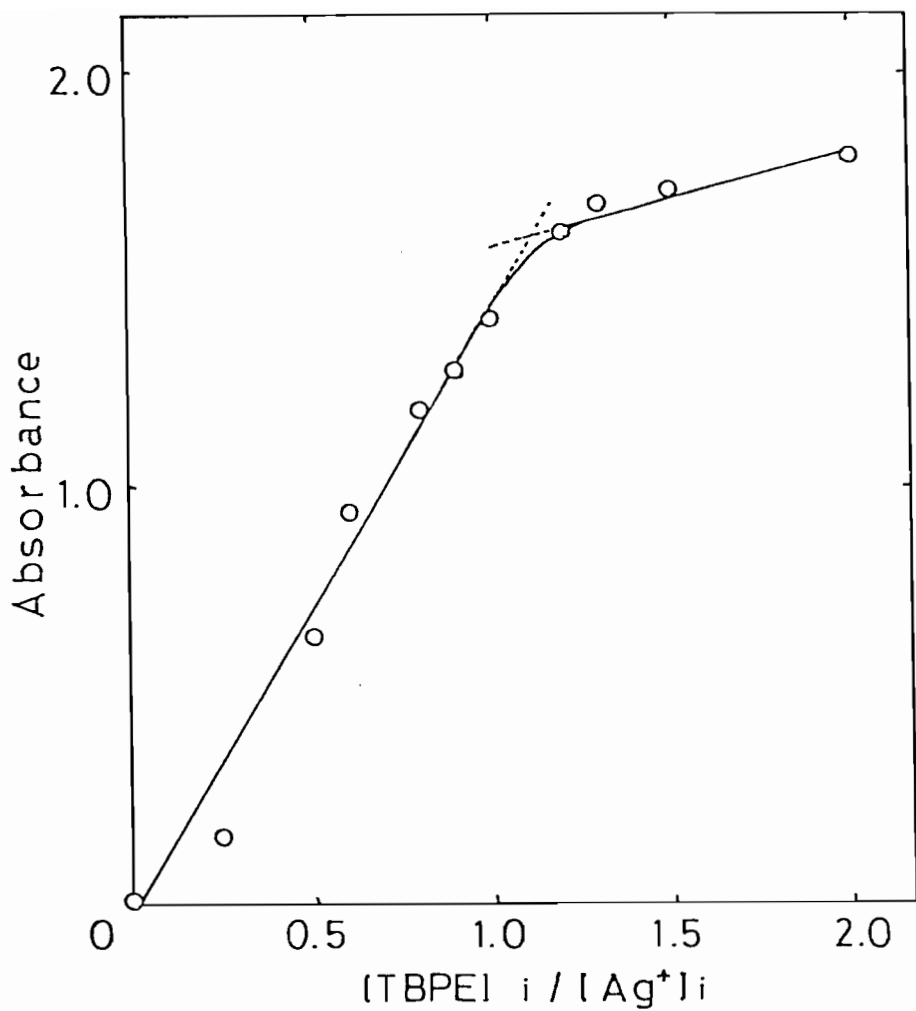


Fig.10-2b. Molar ratio methods at pH6.0. Initial concentration:  $5 \times 10^{-5} M$  silver(I),  $5 \times 10^{-4} M$  HTCO.

ligands, such as  $[\text{Ag}_2(\text{ttct})_2]^{2+}$  and  $[\text{Ag}_2(\text{bz-ttcp})_2]^{2+}$ . Two silver(I) ions are sandwiched between two ligand molecules in the complex cation. It has been reported the extractability of HTCO is superior to that of TTCT.<sup>37)</sup> The stable silver(I)-HTCO complex cation with anion of TBPE extracted into 1,2-dichloroethane is expected in this extraction system.

### 10.3.3 Absorption spectra of extracted species

Absorption spectra of silver(I)-HTCO-TBPE complex in 1,2-dichloroethane are shown in Fig.10-3. The shape of the absorption spectrum is similar to that of the anion ( $\text{TBPE}^-$ ) in ethanol-water solution. Some colored anions such as Bromocresol Green, picrate, Thymol Blue hexanitrodiphenylamine and TBPE were examined as counter anions. The absorptivity of silver(I)-HTCO-TBPE complex is 3-8 times larger than those of the other colored anions. The molar absorptivity of silver(I)-HTCO-TBPE at the wavelength of absorption maxima (608 nm) is  $8.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The verification of Beer's law was carried out under the condition shown in Fig.10-3. The system obeys Beer's law (at 608 nm) in the range of  $1 \times 10^{-6} \text{ M} - 3 \times 10^{-5} \text{ M}$  (0.1-3ppm). A Beer's law plot gave a reproducible, rectilinear calibration graph.



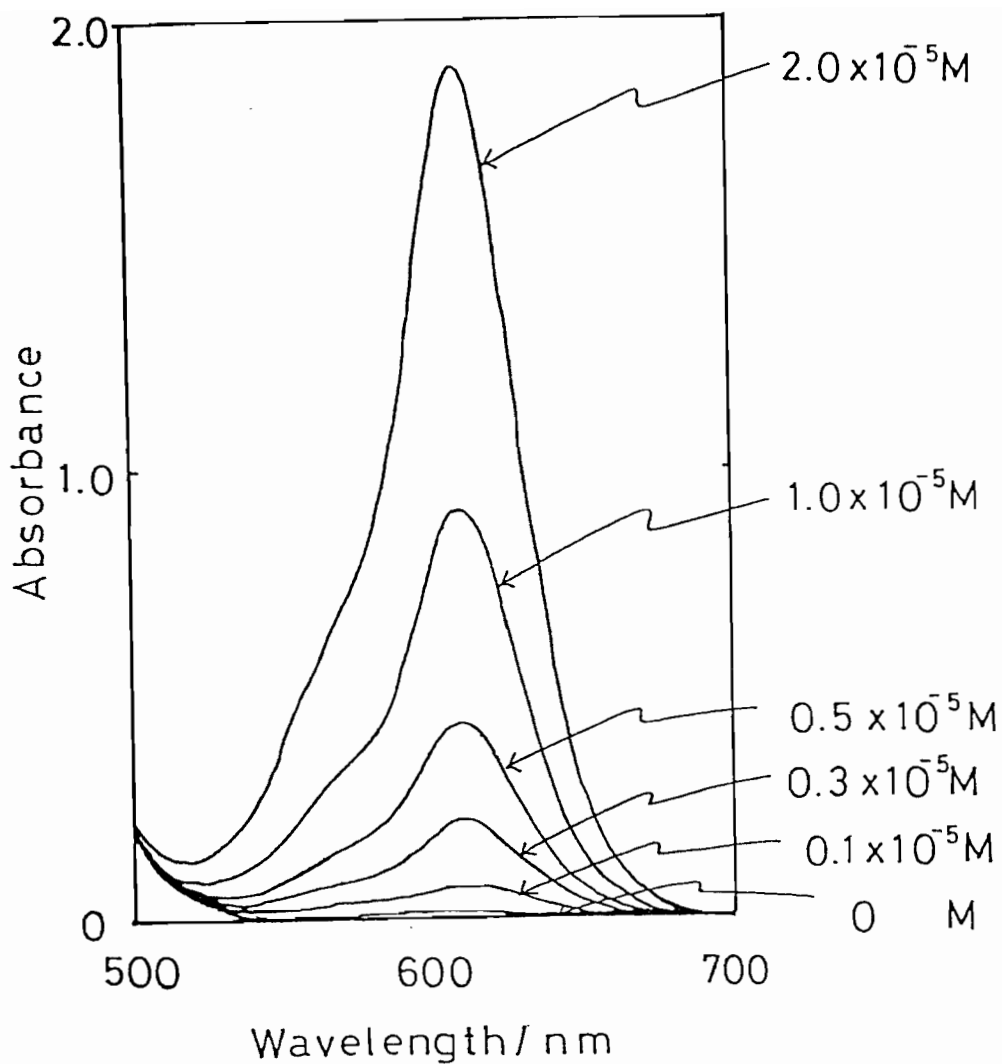


Fig.10-3. Absorption spectra of extracted species against 1,2-dichloroethane at pH 6.4. Initial concentration:  $5 \times 10^{-4} \text{ M}$  HTCO,  $5 \times 10^{-4} \text{ M}$  TBPE.

#### 10.3.4 Effect of foreign ions

The interference from Mg(II), Co(II), Ni(II), Mn(II), Fe(III), Cu(II), Zn(II) and Cd(II) was examined, with shaking time of 5 min for extraction of silver(I). The results are shown in Table 10-1. These metal ions in a 1000-fold amount relative to silver(I) ion do not interfere seriously. Negative errors caused by these metals are within 3.3%. In the case of Fe(III), the pH value of the aqueous phase was so high, depositions of ferric hydroxide and silver(I) oxide might decrease the absorbance. However, a 500 fold excess of Fe(III) did not interfere the determination of silver(I) when the pH value of aqueous phase was 5.69. When high concentration of foreign metal ions exist in the aqueous phase, they will precipitate as their hydroxides, and interfere the determination. The use of tartrate as masking agent is recommended.

#### 10.3.5 Application

The standard sample of steel NBS-159 contains silver(I) were used in this study. The proposed extractive spectrophotometric method was applied to the determination of silver(I) in the sample solution. The chemical composition of the sample is shown in Table 10-2. The proposed method gave a average value for five measurements, 0.094% m/m of silver(I) content. This value shows a reasonable agreement

with the standard value of 0.090% m/m.

Table 10-1. Effects of diverse ions.

Ion	Concentration, M	pH	Absorbance at 608 nm	%E
None	-	6.42	0.473	100.0
Mg(II)	$5 \times 10^{-3}$	6.38	0.462	97.9
Co(II)	$5 \times 10^{-3}$	6.20	0.457	96.6
Ni(II)	$5 \times 10^{-3}$	6.08	0.462	97.7
Mn(II)	$5 \times 10^{-3}$	6.39	0.468	98.9
Fe(III)	$5 \times 10^{-3}$	9.78	0.388	82.0
Cu(II)	$5 \times 10^{-3}$	6.75	0.476	100.0
Zn(II)	$5 \times 10^{-3}$	6.22	0.464	98.1
Cd(II)	$5 \times 10^{-3}$	6.25	0.475	100.0

Concentration of silver:  $5 \times 10^{-6}$  M.

Table 10-2. Chemical composition  
of steel sample NBS-159.

Chemical composition (weight percent)			
C	0.521	Cu	0.181
Si	0.258	P	0.036
Mn	0.807	V	0.054
Ni	0.137	Mo	0.141
Cr	1.00	Ag	0.090
S	0.027		

Table 10-3. Analysis of steel standard sample  
for silver.

Ag(weight percent)		
standard value	previous work pic	present work TBPE
0.090	0.093	0.094
	$\epsilon_{pic}=1.8 \times 10^4$	$\epsilon_{TBPE}=8.8 \times 10^4$

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8. Liquid-Liquid Extraction of Copper(II) with Cyclic and Acyclic Tetrathio Ethers,  
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