Liquid-Liquid Extraction of Some Class *b* Metal Ions with a Thiacrown Compound, 1,4,7,10,13,16-Hexathiacyclooctadecane

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The liquid–liquid extraction of various metal ions, especially of soft class *b* metal ions with a thiacrown compound, 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO) using picrate ion (Pic^-) was examined and compared with that of 1,4,8,11-tetrathiacyclotetradecane (TTCT). Although the extraction behavior of the class *a*, *ab*, and *b* metals with HTCO is fundamentally similar to that with TTCT, that of some metals belonging to class *b* metals with HTCO is different from that with TTCT. The extraction percentages of copper(II) and palladium(II) with HTCO are a few times larger than those with TTCT. Copper(I) and silver(I) are extracted with HTCO as the 1:1 complexes such as $[Cu(htco)]^+Pic^-$ and $[Ag(htco)]^+Pic^-$, respectively, regardless of the relative concentration of the ligand to the metal. On the other hand, copper(I) and silver(I) complexes with TTCT are extracted with different compositions depending upon the relative concentration of the ligand to the metal.

The extraction behavior of various metal ions, especially of the class *b* metal ions, with the thiacrown compound, 1,4,8,11-tetrathiacyclotetradecane (TTCT) was examined using perchlorate ion as the counter anion and dichloroethane or chloroform as the extraction solvent.[1,2] It was found that class *a* metal ions were not extracted at all, and *ab* metal ions, except the copper(II) ion, were hardly extracted but class *b* metal ions were extracted.

Although the formation of the metal thiacrown cation complex might be primarily governed by the softness of the metal ion to bond with the sulfur atom in a thioether type ligand (R-S-R), it will depend also on the size ratio of the metal ion to the cavity of the thiacrown ligand and on the favourable stereochemistry of the metal ion with minimal strain of the cyclic ligand molecule. Moreover, the extraction of the metal ion is associated with the formation of the ion pair between the formed metal complex cation and the counter anion and also with the affinity of the generated ion pair for the organic solvent. Consequently, it is interesting to investigate how the extraction behavior of various metals alters (especially the *b* metals) according to the number of sulfur atoms and to the number of the constituent atoms in the cyclic thiacrown ligand. This can help to separate the class *b* metals by the solvent extraction with thiacrown compounds.

In this paper, the extraction behavior of metal ions with 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO) which has six sulfur atoms in its 18-membered ring is examined and compared with that of 1,4,8,11-tetrathiacyclotetradecane (TTCT) which has four sulfur atoms in its 14-membered ring.

Experimental

Reagents. The reagent, HTCO, was synthesized according to the method by Black and McLean,[3] and recrystallized twice from ethyl acetate–hexane. The reagent, TTCT, synthesized according to the method by Rosen and Bush[4] was recrystallized three times from chloroform–ethanol. HTCO as well as TTCT were dissolved in 1,2-dichloroethane immediately prior to use. Metal sulfates (guaranteed-reagent grade) were used except for thallium(I) nitrate and the 1×10^{-2} mol dm^{-3} stock solution of each metal ion was prepared. The concentration of each metal was determined by potentiometric titration with chloride. 1,2-Dichloroethane was shaken three times with 2 mol dm^{-3} potassium hydroxide and with distilled water, dried with calcium chloride and distilled. Other reagents were of guaranteed-reagent grade.

Apparatus. A Taiyo M incubator was used for shaking the solutions. A Seiko SAS-725 atomic absorption spectrophotometer was used for the determination of metal ions. UV and visible absorption spectra were measured with a Shimadzu UV-240 recording spectrophotometer. The IR spectra of isolated metal thiacrown complexes were taken with a Hitachi 207 EPI-G2 type grating IR spectrophotometer. The pH of the aqueous phase was measured with a Hitachi-Horiba H-5 pH meter.

Liquid–Liquid Extraction of Various Metals. Ten ml of the aqueous solution containing 5×10^{-5} mol dm^{-3} metal ion, 1×10^{-3} mol dm^{-3} picrate ion and 1×10^{-2} mol dm^{-3} 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. For the copper(I) solution, hydroxylammonium sulfate was added to copper(II) sulfate solution to give 0.1 mol dm^{-3} hydroxylamine solution. To the resulting aqueous solution 10 ml of 5×10^{-3} or 5×10^{-4} mol dm^{-3} HTCO or TTCT 1,2-dichloroethane solution was added and the mixture was shaken for 30 min on 200 strokes/min at 25±0.1 °C. The mixture was then centrifuged for 5 min at 2000 rpm, the pH of the aqueous phase was measured and the concentration of the picrate ion in the aqueous phase was determined spectrophotometrically at 354 nm. The concentrations of the metal ion in the aqueous and organic phases were determined by atomic absorption spectrophotometry. The metal concentration in an organic phase was determined as follows: A definite quantity of the organic phase was allowed to evaporate, the residue was treated with small amounts of concentrated nitric acid and diluted with water to a standard volume and the concentration of the metal was then determined by atomic absorption spectrophotometry.

Isolation of Metal-HTCO and -TTCT Complexes. **Copper(I)-HTCO Complex:** Twenty ml of an aqueous solution containing copper sulfate (1×10^{-2} or 5×10^{-3}), hydroxylammonium sulfate (0.1 mol dm^{-3}), sodium picrate (1×10^{-2} mol dm^{-3}) and acetic acid–sodium acetate buffer (0.1 mol dm^{-3}, pH 4.4—5.0) was stirred with 20 ml of HTCO 1,2-dichloroethane solution (1×10^{-2} mol dm^{-3}) for 30 min at 25 °C in a 50 ml separation funnel. The yellow-orange deposit which formed between the two phases was filtered, washed with ethanol and 1,2-dichloroethane and dried in vacuo.

Silver(I)-HTCO Complex: The silver(I)-HTCO complex was extracted by the same method described in the isolation of copper(I)-HTCO complex, using silver nitrate instead of copper sulfate. After stirring, the mixed solution was centrifuged. When carbon tetrachloride was added to the separated organic phase, a yellow deposit was obtained. The filtered deposit was washed with ethanol and dried in vacuo.

Silver(I)-TTCT Complex: Twenty ml of the aqueous solution adjusted with acetic acid–sodium acetate to pH 5.0 containing silver sulfate (1×10^{-2} or 5×10^{-3} mol dm^{-3}) and sodium picrate (2×10^{-2} mol dm^{-3}) was placed in a 50 ml separation funnel and stirred with 20 ml of HTCO 1,2-dichloroethane solution (1×10^{-2} mol dm^{-3}) for 30 min at 25 °C. After centrifugation of the mixed solution, the organic phase was separated. On addition of 40 ml of carbon tetrachloride to the organic phase, a yellow solid deposit was obtained. It was washed with carbon tetrachloride and dried in vacuo.

Determination of the Composition of Metal Thiacrown Complexes. In order to determine the amount of the picrate ion contained in copper(I) and silver(I) thiacrown complexes, a definite amount of each complex was dissolved in DMF and the concentration of the picrate ion was spectrophotometrically determined by measuring the absorbance at 378 nm. To determine each metal ion concentration, metal thiacrown complexes were dissolved in DMF or were decomposed with sulfuric acid and then the resulting solution was then adequately diluted and the concentration of each metal was determined by atomic absorption spectrophotometry. The contents of HTCO and TTCT in the copper(I) and silver(I) complexes were estimated by subtracting of the amounts of both the metal and picrate ion from the initial amounts of the complex.

Results and Discussion

Liquid–Liquid Extraction of Various Metals with HTCO. The following metals were examined: Na(I) and Mg(II) as the class *a* metal; Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Tl(I) as the class *ab* metal; Cd(II), Cu(I), Ag(I), and Pd(II) as the class *b* metal. The results are shown in Table 1 with those for the extraction with TTCT.[1] It was found that the extraction

Table 1. Data for the Extraction of Various Metal Ions in the Presence of the Picrate Ion with HTCO and TTCT in 1,2-Dichloroethane Solution

Metal ion 5×10^{-5} mol dm^{-3}	Group of metal by Ahrland[a]	α value[b]	pH	Extraction (%)		
				HTCO		TTCT[c]
				5×10^{-4} mol dm^{-3}	5×10^{-3} mol dm^{-3}	5×10^{-3} mol dm^{-3}
Na(I)	*a*	~0	3.9	0		0
			5.4	0		0
Mg(II)	*a*	~0	3.9	0		0
			5.4	0		0
Mn(II)	*ab*	1.04	3.9	~0		0.5
			5.4	~0		0.8
Co(II)	*ab*	1.39	3.9	~0		0.8
			5.3	~0		0.8
Ni(II)	*ab*	1.41	3.9	~0		0.8
			5.3	~0		0.7
Cu(II)	*ab*	1.64	3.9	3	13	7.5
			5.4	4	24	5.9
Zn(II)	*ab*	1.25	3.9	~0		0.4
			5.3	~0		0.5
Tl(I)	*ab*	1.24	3.9	~0		2.2
			5.4	~0		1.0
Cd(II)	*b*	1.66	3.9	~0		0.6
			5.4	~0		0.8
Cu(I)	*b*	3.92	4.0	99		99.4
			5.4	100		99.4
Ag(I)	*b*	3.60	3.9	100		99.9
			5.4	100		99.9
Pd(II)	*b*	5.33	3.9	10	42	12.7
			5.4	11	45	14.3

a) Ref. 6. b) Ref. 7. c) Ref. 1.

behavior of the class *a*, *ab*, and *b* metal groups with HTCO is fundamentally similar to that with TTCT. That is, Na(I) and Mg(II) were not extracted at all, Mn(II), Co(II), Ni(II), Zn(II), Tl(I), and Co(II) were very weakly extracted Cu(II) and Pd(II) were extracted in some degree and Cu(I) and Ag(I) were extracted very well. The increases of both the constituent atoms of the thiacrown ring from 14 members for TTCT to 18 for HTCO and the sulfur ligand atoms from 4 for TTCT to 6 for HTCO had hardly any effect on the extraction behavior of the class *a* and *ab* metals. This fact means that the class *a* and *ab* metals except for copper(II), do not bind at all or very little with the sulfur atoms of the thioether type (R-S-R), regardless of other factors such as the number of sulfur atoms in the ligands, the number of constituent ring atoms, the molecular structure of the ligand, the kinds of the counter anion and the extraction solvent. However, the extraction behavior of some metals belonging the class *b* metals and copper(II) with HTCO is different from that with TTCT. For example, it was found that the percent extraction of Cu(II) and Pd(II) with HTCO is a few times larger than that with TTCT.

Extraction of Copper(I) and Silver(I). Copper(I) and silver(I) are almost completely extracted at pH 4.0 and 5.4 as shown in Table 1. Further, the dependence on pH and on the concentrations of the ligand and the picrate ion on the extraction of copper(I) and silver(I) were examined.

Dependence on pH: Plots of the logarithmic distribution ratio of copper(I) and silver(I) with HTCO against the pH of the aqueous phase are shown in Fig. 1. The decrease of the copper(I) extraction below pH 4 can be attributed to the decrease of the reducing power of hydroxylamine in acidic medium as well as in the case of Cu(I) extraction with TTCT.[1]

Dependence on the Concentration of the Ligand and Picrate: If the species extracted into an organic phase is represented by $M(\mathrm{htco})_m\mathrm{Pic}_n$ (Pic^-: picrate ion), the extraction equilibrium and the extraction constant, K_{ex}, are given by Eqs. 1 and 2, respectively,

$$M^n + m\,\mathrm{htco(o)} + n\mathrm{Pic}^- \overset{K_{ex}}{\rightleftharpoons} M(\mathrm{htco})_m(\mathrm{Pic})_n(\mathrm{o}) \qquad (1)$$

$$K_{ex} = [M(\mathrm{htco})_m(\mathrm{Pic})_n]_o/[M^{n+}][\mathrm{htco}]_o^m[\mathrm{Pic}]^n \qquad (2)$$

where (o) and subscript o indicate the species in the organic phase. The logarithm of the distribution ratio of a metal, $\log D_M$ is represented by the Eq. 3.

$$\log D_M = \log K_{ex} + m\log[\mathrm{htco}]_o + n\log[\mathrm{Pic}^-] \qquad (3)$$

The extraction of copper(I) and silver(I) at pH 4.4 was examined at various concentrations of picrate ion under constant concentration of HTCO, 5×10^{-4} mol dm^{-3}. The relationships between the logarithmic distribution ratio of copper(I) and silver(I), log D_M, and the logarithm of the picrate concentration in the aqueous phase, log [Pic^-], are shown in Fig. 2. Two straight lines were obtained with slopes close to +1.0, indicating that $n=1$.

Similarly, the value of "*m*" in Eq. 3 should be given by the slope of the straight line obtained by the plots of log D_M vs. log[htco]. However, these plots gave a straight line which is independent of [htco]. As examples, plots of log D_{Ag} vs. log [htco] in various organic

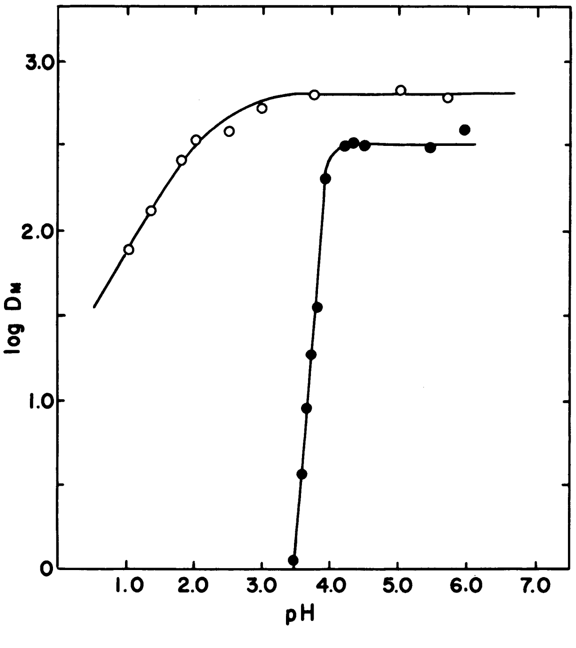

Fig. 1. Plots of distribution ratio of copper(I) (●) and silver(I) (○) vs. pH. Initial concentration: HTCO; 5×10^{-3} mol dm^{-3}, copper(I) and silver(I); 5×10^{-5} mol dm^{-3}.

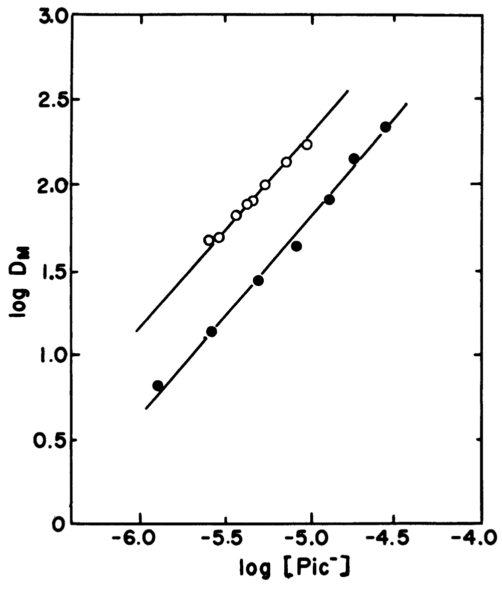

Fig. 2. Plots of logD_M vs. log[Pic^-] for copper(I) (●) and silver(I) (○). Initial concentration: HTCO; 5×10^{-4} mol dm^{-3}, copper(I) and silver(I); 5×10^{-5} mol dm^{-3}. pH 4.4.

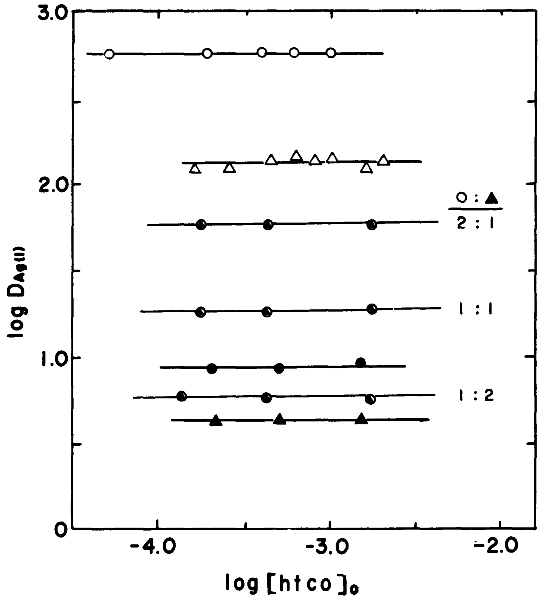

Fig. 3. Plots of $\log D_{Ag(I)}$ vs. $\log [htco]_o$ for various organic solvents. Initial concentration: silver(I); 5×10^{-5} mol dm^{-3}, picrate; 5×10^{-4} mol dm^{-3}. Organic solvent: ○; 1,2-dichloroethane, △; chloroform, ●; benzene, ▲; carbon tetrachloride, ◉; mixture of 1,2-dichloroethane and carbon tetrachloride. pH: 5.4.

solvents such as 1,2-dichloroethane, chloroform, benzene and carbon tetrachloride, are shown in Fig. 3. The straight lines are independent of the concentration of HTCO and the values of $\log D_{Ag}$ increase in the order of 1,2-dichloroethane>chloroform>benzene>carbon tetrachloride, which is the order of their dielectric constants. The reason that values of the $\log D_{Ag}$ are below 1.0 for benzene and carbon tetrachloride will be owing to the formation of the yellow precipitate on the boundary of two layers. It is thought that the solubility of their ion-pair compound, $[M(htco)_m]^+Pic^-$, is limited in solvents having a low dielectric constant. This supposition is also supported by the facts that the values of the $\log D_{Ag}$ in a mixture of 1,2-dichloroethane and carbon tetrachloride do not vary with the concentration of HTCO and that their values decrease with the increase of the fraction of carbon tetrachloride in the mixture as shown in Fig. 3. The reason why the values of $\log D_M$ for copper(I) and silver(I) do not depend on the concentration of HTCO can be explained as follows. The ability of the complex formation of HTCO to copper(I) and silver(I) is so high that the equilibrium of

$$M^+ + m\,\text{htco} \rightleftharpoons [M(htco)_m]^+ \qquad (4)$$

lies far to the right. Therefore, it is considered that the concentration of uncomplexed copper(I) or silver(I) in the aqueous phase is too low to be determined by atomic absorption spectrophotometry. Thus, the

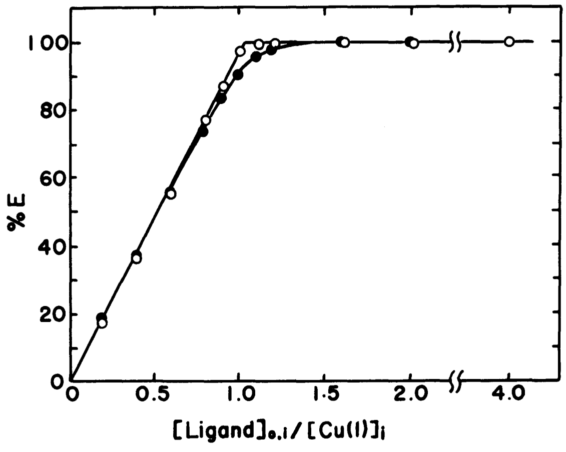

Fig. 4. Molar ratio study for copper complexes with HTCO (○) and TTCT (●). Initial concentration: copper(I); 5×10^{-5} mol dm^{-3}, picrate; 5×10^{-4} mol dm^{-3}. pH: 4.0.

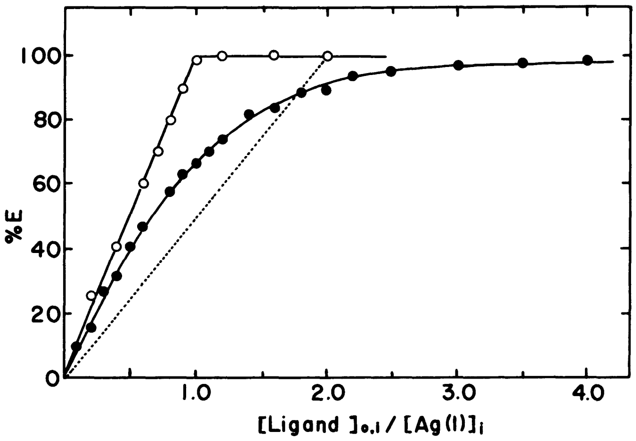

Fig. 5. Molar ratio study for silver(I) complexes with HTCO (○) and TTCT (●). Initial concentration: silver(I); 5×10^{-5} mol dm^{-3}, picrate; 5×10^{-4} mol dm^{-3}. pH: 4.0 Dotted line represents the case of formation of the stable 1:2 complex alone.

extractions of these metals appear to depend only upon the distribution of the ion-pair complex, $M(htco)_m{}^+Pic_n{}^-$.

In order to determine the value of m, the molar ratio method was tried. The plots of the %E for copper(I) vs. the ratio of $[htco]_{o,i}$ or $[ttct]_{o,i}$ to $[Cu(I)]_i$ and similar plots for silver(I) are shown in Figs. 4 and 5, respectively. The subscript i represents the initial concentration. In Fig. 4, the %E of copper(I) increases linearly with the increase of the ratio, $[htco]_{o,i}/[Cu(I)]$, and reaches almost 100% at the ratio=1. The distinct break point at $[htco]_{o,i}/[Cu(I)]_i=1$ means $m=1$. It is obvious that copper(I) forms the very stable 1:1 cationic complex, $[Cu(htco)]^+$, and the ion pair, $[Cu(htco)]^+Pic^-$, which is effectively extracted into 1,2-dichloroethane. The fact that the break point for HTCO is clearer than for TTCT as shown in Fig. 4

Table 2. Composition of Copper(I) and Silver(I) Complexes with HTCO

Metal	Initial condition	Metal:HTCO:Pic (Found)	Proposed formula
Cu(I)	Cu : HTCO = 1 : 1	1.0 : 1.0 : 0.9	[Cu(htco)]Pic
	Cu : HTCO = 1 : 2	1.0 : 1.1 : 0.9	[Cu(htco)]Pic
Ag(I)	Ag : HTCO = 1 : 1	1.0 : 0.9 : 0.9	[Ag(htco)]Pic
	Ag : HTCO = 1 : 2	1.0 : 0.8 : 0.9	[Ag(htco)]Pic

Table 3. Composition of Copper(I) and Silver(I) Complexes with TTCT

Metal	Initial condition	Metal:TTCT:Pic (Found)	Proposed formula
Cu(I)	Cu : TTCT = 1 : 1	1.0 : 1.3 : 1.0	[Cu(ttct)]Pic
	Cu : TTCT = 1 : 2	1.0 : 1.6 : 0.9	[Cu(ttct)]Pic + [Cu(ttct)$_2$]Pic
Ag(I)	Ag : TTCT = 1 : 1	1.0 : 0.4 : 0.8	[Ag$_2$(ttct)]Pic$_2$
	Ag : TTCT = 1 : 2	1.0 : 0.6 : 0.8	[Ag$_2$(ttct)]Pic$_2$ + [Ag(ttct)]Pic

indicates the copper(I)–HTCO complex is more stable than the copper(I)–TTCT complex. From both Eq. 3 and the result shown in Fig. 2, log K_{ex}=8.7±0.4 for the extraction of copper(I) with HTCO was estimated, of which value is larger than the value, 7.3±0.3 for copper(I)–TTCT.[1]

As shown in Fig. 5, the results of the molar ratio study for silver(I) to HTCO and TTCT seem to be different. In the case of HTCO, a distinct break point is found at [htco]$_{o,i}$/[Ag(I)]=1, which indicates that the extracted species is [Ag(htco)]Pic. On the other hand, in the case of TTCT, it seems to form the more stable [Ag(ttct)$_2$]Pic than [Ag(ttct)]Pic which may form on the ratio of [ttct]$_{o,i}$/[Ag(I)]<1. This estimation accords with the previous report[5] that silver(I) is extracted as the ion-pair complex compound, [Ag(ttct)$_2$]$^+$Pic$^-$, under the presence of the excess TTCT. The composition of the extracted silver(I) complex species seems to be different between TTCT and HTCO. The comparison of the curves of silver(I)–HTCO and –TTCT in Fig. 5, indicates that the 1:1 silver(I)–HTCO complex is more stable than the 1:1 or 1:2 silver(I)–TTCT complex.

Isolated Copper(I) and Silver(I) Complexes with HTCO and TTCT. The results of the determination of the compositions of copper(I) and silver(I)–HTCO and –TTCT complexes isolated from their extracts into 1,2-dichloroethane solution are shown in Table 2 for HTCO complexes and Table 3 for TTCT complexes. As seen in Table 2, regardless of the initial concentration ratios of copper(I) to HTCO, the molar ratio of copper(I), HTCO and picrate ion of the isolated complex is 1:1:1, corresponding to a proposed formula [Cu(htco)]Pic. This accords with the results of the above mentioned solvent extraction. Similarly, the composition of silver(I)–HTCO complex is [Ag(htco)]Pic, regardless of the initial concentration ratio of silver(I) to HTCO. However, as seen in Table 3, the composition of the copper(I) and silver(I)–TTCT complexes was not simple. Increasing the initial concentration of TTCT increases the content of TTCT and the complex seems to be a mixture of [Cu(ttct)]Pic and [Cu(ttct)$_2$]Pic. According to the study of the extraction equilibria for the copper(I)–TTCT–Pic complex,[1] it was estimated that copper(I) is extracted as the 1:1:1 complex, [Cu(ttct)]$^+$Pic$^-$, into 1,2-dichloroethane solution, regardless of the initial concentration of TTCT. Probably, the extracted 1:1:1 complex transforms to the 1:2:1 complex, [Cu(ttct)$_2$]$^+$Pic$^-$, under the condition of the excess TTCT in the 1,2-dichloroethane solution.

In the case of silver(I), the obtained complexes will be the mixture of [Ag$_2$(ttct)]Pic$_2$ and [Ag(ttct)]Pic. The complex, [Ag(ttct)$_2$]Pic could not be obtained.

References

1) K. Saito, Y. Masuda, and E. Sekido, *Anal. Chim. Acta*, **151**, 447 (1983).

2) K. Saito, Y. Masuda, and E. Sekido, *Bull. Chem. Soc. Jpn.*, **57**, 189 (1984).

3) D. St. C. Black and I. A. McLean, *Tetrahedron Lett.*, **1969**, 3961.

4) W. Rosen and D. H. Bush, *J. Am. Chem. Soc.*, **91**, 4694 (1969).

5) E. Sekido, K. Saito, Y. Naganuma, and H. Kumazaki, *Anal. Sci.*, **1**, 363 (1985).

6) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., London*, **12**, 265 (1958).

7) S. Yamada and M. Tanaka, *J. Inorg. Nucl. Chem.*, **37**, 587 (1975).