Solvent Extraction of Thallium(I) with Chelating Extractants Coordinating through Oxygen Atoms

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The solvent extraction of thallium(I) in aqueous 0.1 mol dm^{-3} sodium nitrate solutions with seven chelating extractants [(HA), 1-phenyl-1,3-butanedione (Hbza); 1,3-diphenyl-1,3-propanedione (Hdbm); 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Hbfa); 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta); 2-hydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (Hipt); 5,7-dichloro-8-quinolinol (Hdcox); and 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-buten-2-one (Hstta)] into chloroform was studied in the absence and presence of tetrabutylammonium ions (tba$^+$) or trioctylphosphine oxide (TOPO). The TlA type chelates were extracted, and, except for Hbza and Hdbm, tba$^+$TlA$_2{}^-$-type ternary complexes were extracted. However, the extraction of adduct chelates with TOPO was not obtained. A comparison of the stability, liquid–liquid partition, and acceptability of a further ligand in the organic phase was made with TlA, AgA, and LiA when A$^-$ was 1,1,1-trifuluoro-3-(2-thienyl)-2,4-butanedionate ion (tta$^-$) and the ligand was TOPO or tta$^-$.

The solvent extraction of thallium(I) with several chelating extractants into chloroform was studied by Schweitzer et al.[1,2] In these studies, thallium(I) was effectively extracted with the chelating extractants coordinating through sulfur atoms. However, it was reported that the extraction of thallium(I) with hexanoic acid was not effective.[3] Since thallium(I) is a kind of "soft acid", extraction with these extractants coordinating through sulfur atoms is assumed to be more effective than that with these coordinating through oxygen atoms. However, it was also reported that the solvent extraction of thallium(I) with 1-phenyl-1,3-butanedione (Hbza), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Hbfa), and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta), into 4-methyl-2-pentanone (MIBK) was not poor.[4] In order to determine the extractability of thallium(I) with these chelating extractants coordinating through oxygen atoms, the solvent-extraction equilibria of thallium(I) with five chelating extractants of this type [Hbza, 1,3-diphenyl-1,3-propanedione (Hdbm), Hbfa, Htta, 2-hydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (Hipt), 5,7-dichloro-8-quinolinol (Hdcox), and 1,1,1-trifluoro-4-mercapto-4-(2-thienyl)-3-buten-2-one (Hstta)] were studied. Solvent extraction with a chelating extractant coordinates through oxygen and nitrogen atoms (Hdcox), and also with a chelating extractant oxygen and sulfur atom (Hstta); this process was also examined in order to compare the results with those obtained with the chelating extractants coordinating through two oxygen atoms. The extraction of thallium(I) with these chelating extractants was also studied in the presence of trioctylphosphine oxide (TOPO) in order to determine whether an enhancement of extraction due to the adduct chelates (synergism) occurred. The extraction was also examined in the presence of tetrabutylammonium ions (tba$^+$) in order to determine whether an enhancement of the extraction due to that of anionic chelate complexes as ion-pairs with tba$^+$ (ternary complex) occurred. The extraction of thallium(I) was compared with that of silver(I) and lithium(I) when they were extracted only with Htta, with Htta and TOPO, and with Htta and tba$^+$ in order to determine the difference in the extraction behavior of these three univalent metal ions. The synergistic effect of extraction with TOPO and the extraction of anionic chelate complexes as ion-pairs with tba$^+$ (ternary complex) were also studied. A comparison was made concerning the extraction of thallium(I) with that of silver(I) and lithium(I), about the synergistic effect and the extraction of ternary complexes when the extractant was Htta.

Statistical

In the present paper, all of the species in the organic phase are denoted by the subscript "org"; those in the aqueous phase are shown without any subscript. The volumes of the two liquid phases are assumed to be the same.

The two-phase distribution and acid-dissociation equilibrium of a chelating extractant (HA) can be written as:

$$\mathrm{HA} \rightleftarrows \mathrm{HA}_{(\mathrm{org})};\quad K_\mathrm{d} = [\mathrm{HA}]_\mathrm{org}/[\mathrm{HA}] \tag{1}$$

$$\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-;\ K_\mathrm{a} = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}]. \tag{2}$$

From these equations, the concentration of extractant anion (A$^-$) can be calculated as:

$$[A^-] = [HA]_{org,init.}/\left(1+(K_d+1)[H^+]K_a^{-1}\right). \qquad (3)$$

The solvent-extraction equilibrium of thallium(I) with the anion of the chelating extractant in the aqueous phase can be written as:

$$Tl^+ + A^- \rightleftarrows TlA_{(org)};\ K_{ex1,0}=[TlA]_{org}/[Tl^+][A^-]. \qquad (4)$$

The extraction equilibrium can also be written as the extraction of Tl^+ in the aqueous phase with HA in the organic phase:

$$Tl^+ + HA_{(org)} \rightleftarrows TlA_{(org)} + H^+;$$
$$K_{ex}{}^* = [TlA]_{org}[H^+]/[Tl^+][HA]_{org}. \qquad (5)$$

Also, from Eqs. 4 and 5 the following relation is obtained: $K_{ex1,0}=K_{ex}^*K_dK_a{}^{-1}$.

Metal chelates may be formed in the aqueous phase. The equilibrium for the formation of complexes can be written as:

$$Tl^+ + nA^- \rightleftarrows TlA_n^{1-n};\ \beta_n=[TlA_n^{1-n}]/[Tl^+][A^-]^n. \qquad (6)$$

When a noncharged chelate complex which had been formed in the aqueous phase is extracted, the distribution constant between the two phases can be written as:

$$TlA \rightleftarrows TlA_{(org)};\ K_{dm} = [TlA]_{org}/[TlA]. \qquad (7)$$

When a univalent anionic complex is extracted together with a bulky cation, such as tba^+, the equilibrium may be written as:

$$Tl^+ + 2A^- + tba^+ \rightleftarrows tba^+TlA_2^-{}_{(org)};$$
$$K_{ex2,1} = [tba^+TlA_2^-]_{org}/[Tl^+][A^-]^2[tba^+]. \qquad (8)$$

This can also be written as the extraction of a noncharged chelate and its association with an ion-pair of the reagents as:

$$Tl^+ + A^- \rightleftarrows TlA_{(org)}$$
$$TlA_{(org)} + tba^+A^-{}_{(org)} \rightleftarrows tba^+TlA_2^-{}_{(org)}$$
$$K_{org} = [tba^+TlA_2^-]_{org}/[TlA]_{org}[tba^+A^-]_{org}. \qquad (9)$$

The extraction of an anion of chelating extractant (A^-) and that of the background salt ($X^-(NO_3{}^-)$) as ion-pairs with a bulky cation (B^+ (tba^+)) can be written as:

$$A^- + tba^+ \rightleftarrows tba^+A^-_{(org)};$$
$$K_{exAB} = [tba^+A^-]_{org}/[A^-][tba^+] \qquad (10)$$

$$NO_3{}^- + tba^+ \rightleftarrows tba^+NO_3{}^-{}_{(org)};$$
$$K_{exXB} = [tba^+NO_3^-]_{org}/[NO_3^-][tba^+]. \qquad (11)$$

Equation 8 can be rewritten by using Eqs. 4, 9, and 10 as:

$$K_{ex2,1} = K_{ex1,0}K_{org}K_{exAB}. \qquad (12)$$

The distribution ratio given by the following equation can be rewritten in several different ways:

$$D = [Tl(I)]_{org,total}/[Tl(I)]_{total}.$$

When the concentration of aqueous chelate is much lower than that of Tl^+ and the TlA chelate is the dominant chemical species in the organic phase, it is written within the limit of experimental error by using Eq. 4 as:

$$D_0{}^* = [TlA]_{org}/[Tl^+] = K_{ex1,0}[A^-]. \qquad (13)$$

However, when the first aqueous chelate is formed, it is written using Eqs. 4, 6, and 7 as:

$$D_0=[TlA]_{org}/([Tl^+]+[TlA])$$
$$=K_{ex1,0}[A^-]/(1+\beta_1[A^-])=K_{dm}\beta_1[A^-]/(1+\beta_1[A^-]). \qquad (14)$$

From Eq. 14, the following relation can be introduced:

$$K_{ex1,0} = K_{dm}\beta_1. \qquad (15)$$

When the ion-pair of the anionic chelate with tba^+ is extracted together with the noncharged chelate, the distribution ratio can be written as:

$$D = ([TlA]_{org} + [tba^+TlA_2{}^-]_{org})$$
$$/([Tl^+] + [TlA] + [TlA_2{}^-]). \qquad (16)$$

However, when $[TlA_2{}^-]$ is much lower than $[Tl^+]+[TlA]$, it can be rewritten by using Eqs. 4, 6, and 8 as:

$$D=(K_{ex1,0}[A^-]+K_{ex2,1}[A^-]^2[tba^+])/(1+\beta_1[A^-]). \qquad (17)$$

The enhancement of the extraction when the ternary complex is extracted together with the noncharged chelate can be written by using Eqs. 12, 14, and 17 as:

$$D/D_0 = 1 + K_{ex2,1}[A^-][tba^+]/K_{ex1,0} \qquad (18)$$
$$= 1 + K_{org}K_{exAB}[A^-][tba^+]. \qquad (19)$$

When tba^+ is added to the system, the free tba^+ concentration at equilibrium can be written when the ion-pairs with tba^+ in the aqueous phase are negligible as:

$$[tba^+]_{init.} = [tba^+] + [tba^+TlA_2{}^-]_{org}$$
$$+[tba^+A^-]_{org} + [tba^+NO_3{}^-]_{org}$$
$$[tba^+]= ([tba^+]_{init.} - [tba^+TlA_2{}^-]_{org})$$
$$/(1 + K_{exAB}[A^-] + K_{exXB}[NO_3{}^-]). \qquad (20)$$

Experimental

All of the reagents were of a reagent grade. The β-diketones (Hbza, Hdbm, Hbfa, and Htta) and Hdcox were obtained from Tokyo Kasei Co. The Hipt was obtained from Takasago Kôryo Co. The Hstta, and TOPO were obtained from Dojindo laboratories. The tetrabutylammonium nitrate was obtained from Kanto Chemical Co. The chloroform was washed several times with water before use. All of the solvent extraction experiments were carried out in a thermostated room at 298 K. The initial aqueous phase was a mixture of 0.1 mol dm^{-3} sodium nitrate and 0.1 mol dm^{-3} sodium hydroxide solution. The initial organic phase was a 0.1 mol dm^{-3} solution of one of the chelating extractants, except for Hdcox; the initial concentration of this reagent was 0.05 mol dm^{-3}, because of its lower solubility than 0.1 mol dm^{-3} in chloroform. The organic and aqueous solutions were placed in a stoppered glass tube (the capacity was 20 cm^3). The two phases were agitated vigorously in order to equilibrate the reagents in the two phases. Then, an aqueous solution of thallium(I) nitrate was added and a small amount of hydroxylammonium sulfate (0.001 mol dm^{-3}) was added to the thus-obtained aqueous phase. The latter was added in order to prevent the oxidation of thallium(I). The initial concentration of thallium(I) was 2×10^{-5} mol dm^{-3}. The initial volume of the two phases was made the same. Then, the two phases were again agitated for 30 min and centrifuged off. The thallium(I) in the organic phase was stripped by 1 mol dm^{-3} nitric acid. The thallium(I) in this aqueous solution and that in the equilibrated aqueous phase were determined by an atomic-absorption method. The hydrogen-ion concentration in the aqueous phase was determined by potentiometry.

In order to determine the equilibrium constant for the extraction of ion-pairs of the reagents, those of ipt$^-$ with tba$^+$ or stta$^-$ with tba$^+$ into the organic phase was determined by spectrophotometry, as follows. A portion of a 0.1 mol dm^{-3} sodium nitrate solution containing an amount of tba$^+$, and being buffered at a certain pH, was placed in a tube and a chloroform solution of Hipt or Hstta was added. The two phases were agitated for 30 min, centrifuged off, and the pH of the aqueous phase was measured. The organic phase was transferred into another tube and washed by 0.1 mol dm^{-3} acetic acid, (tba$^+$ipt$^-$), or 1 mol dm^{-3} sulfuric acid, (tba$^+$stta$^-$), solution. The thus-obtained aqueous phase was transferred into another tube and the solution was neutralized by a sodium hydrogencarbonate (tba$^+$ipt$^-$) or sodium hydroxide (tba$^+$stta$^-$) solution. After excess sodium picrate (at initial 0.01 mol dm^{-3}) was added to this neutralized aqueous solution, it was agitated with the same volume of chloroform in order to extract the tba$^+$ quantitatively as ion-pairs with picrate ion. The thus-extracted tba$^+$ was determined from the absorption of the picrate ion at 370 nm. From this amount of tba$^+$, the extraction constant (K_{exAB}) in Eq. 10 was calculated. The results are listed in Table 1.

Some experiments were performed concerning the extraction of lithium(I) with Htta in a similar manner as described in a previous paper.[5]

Results

The results of the solvent extraction of thallium(I) with chelating reagents were reproducible, and the recovery of metal ions from both phases was quantitative within the limit of the experimental error.

The oxidation state of the thallium ions in the stock solution was confirmed to be +1 by a titration method with the standard potassium bromate solution.[6] The oxidation of thallium(I) to thallium(III) during solvent extraction was concluded to be negligible in systems where 0.001 mol dm^{-3} of hydroxylammonium was added into the aqueous phase. It was found that even when the concentration of hydroxylammonium was 0.01 mol dm^{-3}, the results were the same within the limit of the experimental error. Furthermore, the distribution ratio did not change during the two-phase agitation for 5 to 120 min in the presence of hydroxylammonium. Thus, the oxidation of thallium(I) during solvent extraction should be prevented by the hydroxylammonium, and the complex formation of thallium(I) with this reagent should be negligible. The addition of this reducing agent seems to be important. This is because when the extraction was made in the absence of hydroxylammonium, the distribution ratio was somewhat higher and the slope of log D vs. log [A$^-$] plot was higher than +1. These facts indicate that a part of thallium(I) was oxidized during the two-phase agitation, probably by dissolved atmospheric oxygen to thallium(III), which should be more extractable than thallium(I).

Table 1. Summary of Extraction Constant of Chelating Extractant Anion and Tetrabutylammonium Ion as Ion-Pairs
Org. phase: $CHCl_3$. Aq. phase: 0.1 mol dm^{-3} $NaNO_3$.

Extractants	pK_a	log K_d	log K_{exAB}
Hbza	8.39[a)]	3.64[a)]	—
Hdbm	8.59[b)]	5.40[f)]	—
Hbfa	6.03[a)]	2.84[a)]	4.0[h)]
Htta	6.33[a)]	1.85[a)]	4.1[i)]
Hipt	7.04[c)]	3.37[c)]	2.04
Hdcox	7.47[d)]	3.80[d)]	3.06[j)]
Hstta	3.96[e)]	4.29[g)]	6.34

K_d cf. Eq. 1, K_a cf. Eq. 2, and K_{exAB} cf. Eq. 10. a) T. Sekine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nucl. Chem.*, **35**, 3968 (1973). b) T. Sekine, M. Katori, R. Murai, and T. Saitou, *Bunseki Kagaku*, **33**, 35 (1984). c) D. Dyrssen, *Trans. R. Inst. Technol., Stockholm*, No.188 (1962). d) D. Dyrssen, M. Dyrssen, and E. Johansson, *Acta Chem. Scand.*, **10**, 341 (1956). e) E. Uhlemann and H. Müller, *Z. Chem.*, **8**, 185 (1968). f) U. Moucka and J. Stary, *Collect. Czech. Chem. Commun.*, **26**, 763 (1961). g) T. Honjo, R. Honda and T. Kiba, *Anal. Chem.*, **49**, 2246 (1977). h) Ref. 10. i) Ref. 9. j) Ref. 8.

Figures 1, 2, and 3 give the distribution ratio as a function of the concentration of the anion of the extractant in the aqueous phase, which was calculated on the basis of Eq. 3. With some extractants, such as Hdbm, the highest [A$^-$] which could be achieved was lower than the other extractants, even at the highest pH. This is because K_d in Eq. 1 is higher and K_a in Eq. 2 is lower than the other extractants. These do not allow one to achieve [A$^-$] higher than that given in Fig. 3 (see Eq. 3). The pH became too high when

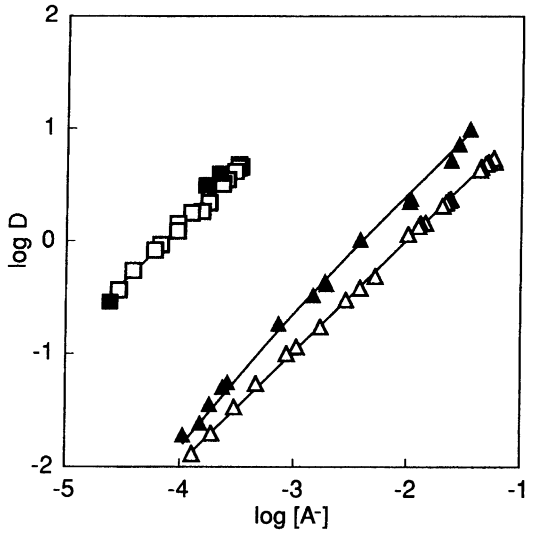

Fig. 1. Extraction curves of thallium(I) with Hdbm (squares) and Hbfa (triangles) as a function of the concentration of extractant anion in the aqueous phase in the absence (open symbols) and presence of 0.01 mol dm^{-3} (at initial) tetrabutylammonium ions (closed symbols).
Org. phase: $CHCl_3$ containing 0.1 mol dm^{-3} of Hdbm or Hbfa. Aq phase: 0.1 mol dm^{-3} $NaNO_3$.

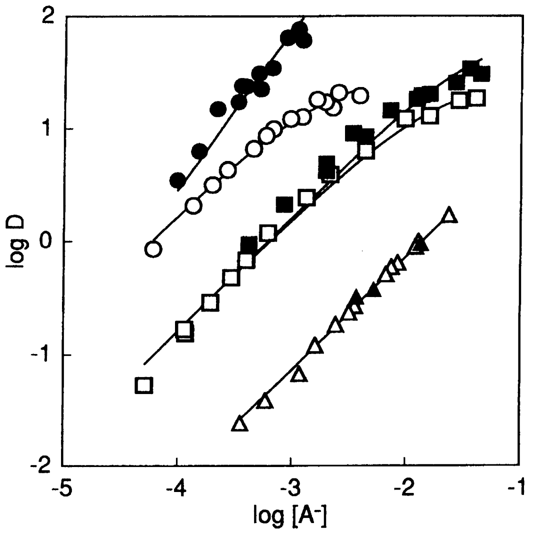

Fig. 2. Extraction curves of thallium(I) with Hbza (triangles), Hipt (squares), and Hdcox (circles) as a function of the concentration of extractant anion in the aqueous phase in the absence (open symbols) and presence of 0.01 mol dm^{-3} (at initial) tetrabutylammonium ions (closed symbols).
Org. phase: $CHCl_3$ containing 0.1 mol dm^{-3} of Hbza or Hipt or 0.05 mol dm^{-3} Hdcox. Aq phase: 0.1 mol dm^{-3} $NaNO_3$.

$[A^-]$ was higher than the value given in the figure. As can be seen from the figures, the $\log D$ vs. $\log[A^-]$ plot with the four β-diketones in the absence of tba^+ is in all cases straight lines with a slope of +1. This indicates that the extracted species was the TlA complex and that the formation of complexes with the extractant in the aqueous phase was negligible, as can be seen from Eq. 13. The values of the extraction constants ($K_{ex1,0}$ and K_{ex}^*) were determined from these data, as listed in Table 2. However, although the $\log D$ vs. $\log[A^-]$ plot with Hipt, Hdcox, and Hstta is a straight line having a slope of +1 in the lower $[A^-]$ range, the slope becomes smaller in the higher $[A^-]$ range. This can be explained by the formation of the TlA complex, also in the aqueous phase, as can be seen from Eq. 14. The extraction constant and stability constant of the complex in the aqueous phase are determined by using a least-squares computer program. They are listed in Table 2. The pH dependence of $\log D$ of these data are given in Fig. 4b in order to compare the plots in Fig. 4a, which were made by the present authors on the basis of the results of previous work.[1,2] The values of K_{ex}^* with the extractant in Fig. 4a were also calculated by the present authors from the data given in Refs. 1 and 2, as listed in Table 3. It was reported that the extracted europium(III) species with Hipt[7] and Hdcox[8] were not only the EuA_3, but also EuA_3HA. In order to examine the extraction of such self-adducts of thallium(I) with these extractants, the distribution ratio was determined by changing $[HA]_{org}$ over the range from 5×10^{-4} to 0.05 mol dm^{-3} (with Hdcox) or to 0.1 mol dm^{-3}. It was found that under these conditions, no effect of the difference in $[HA]_{org}$ was observed when $[A^-]$ was simi-

Table 2. Summary of Extraction Constant of Thallium(I) Complexes in 0.1 mol dm^{-3} $NaNO_3$–$CHCl_3$ Systems

Extractants	$\log K_{ex1,0}$	$\log K_{ex2,1}$	$\log \beta_1$	$\log K_{org}$	$\log K_{dm}$	$\log K_{ex}^*$
Hbza	1.86	—	—	—	—	−10.17
Hdbm	4.14	—	—	—	—	−9.85
Hbfa	2.03	8.21	—	2.18	—	−6.84
Htta	1.98	8.01	—	1.93	—	−6.20
Hipt	3.21	7.37	1.73	2.09	1.48	−7.20
Hdcox	4.24	10.55	2.71	3.25	1.53	−7.03
Hstta	3.32	12.71	2.01	3.05	1.31	−4.93

The values are obtained by introducing the data in Figs. 1, 2, and 3 into Eqs. 4, 5, 6, 7, 8, and 9. The $\log K_{ex1,0}$ values for the extraction of thallium(I) in 1 mol dm^{-3} $NaClO_4$–(4-methyl-2-pentanone) systems in Ref. 4 are: Hbfa; 2.83, Htta; 2.75, and Hbza; 1.28.

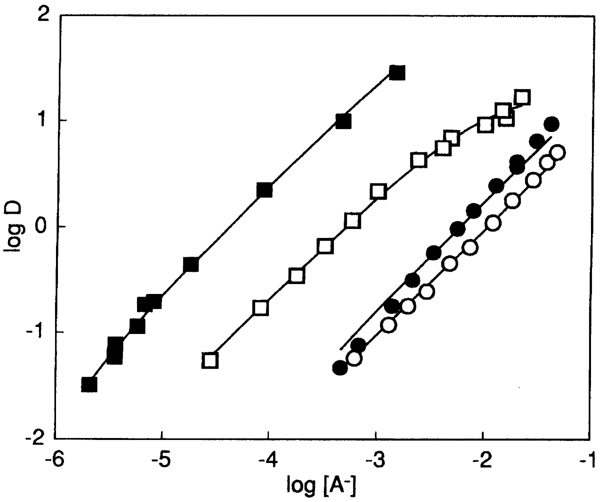

Fig. 3. Extraction curves of thallium(I) with Htta (circles) and Hstta (squares) as a function of the concentration of extractant anion in the aqueous phase in the absence (open symbols) and presence of 0.01 mol dm^{-3} (at initial) tetrabutylammonium ions (closed symbols).
Org. phase: $CHCl_3$ containing 0.1 mol dm^{-3} of Htta or Hstta. Aq phase: 0.1 mol dm^{-3} $NaNO_3$.

lar. Thus, the extraction of such a species as TlA(HA) with these extractants was negligible. The effect of the addition of TOPO or quinoline on the metal chelate extraction was negligible up to a concentration of 0.01 mol dm^{-3} with all of the chelating extractants. In other words, no synergistic effect was observed during the extraction of thallium(I) while chelating these extractants and TOPO or quinoline. The extraction in the presence of tba$^+$ is also given in Figs. 1, 2, and 3. Although extraction with Hbza and Hdbm was not affected by the addition of 0.01 mol dm^{-3} tba$^+$, extraction with Hbfa, Htta, and Hipt was to some extent enhanced by the addition of 0.01 mol dm^{-3} tba$^+$. Extraction with Hdcox was enhanced more than that observed with β-diketones and Hipt, especially in the higher range of [A$^-$]. Extraction with Hstta was enhanced much more; the distribution ratio was about one order higher by in the presence of 0.01 mol dm^{-3} tba$^+$. In order to make a statistical analysis of these data on the basis of Eqs. 12 and 17, the extraction constant of the ion-pairs of reagents in Eq. 10 was obtained with Hipt and Hstta. The constant with the other extractants and that with NO_3^- in Eq. 11 were taken from the literature. The results are shown in Tables 4a and 4b as well as in Table 1. It is indicated that the value of K_{exAB} with Hstta is more than 2-orders larger while that with Hipt is 2-orders smaller than that with Hbfa and Htta. The extraction constant ($K_{ex2,1}$) in Eq. 8, and the association constant of TlA with tba$^+$A$^-$ (K_{org}) in Eq. 9 were calculated. The concentration of free tba$^+$ to be used for these calculations was obtained on the basis of Eq. 20, which introduced the value of K_{exAB} in Table 1 and that of K_{exXB} in the literature[9] ($10^{1.3}$). The thus-obtained values of $K_{ex2,1}$ and K_{org} are listed in Table 2.

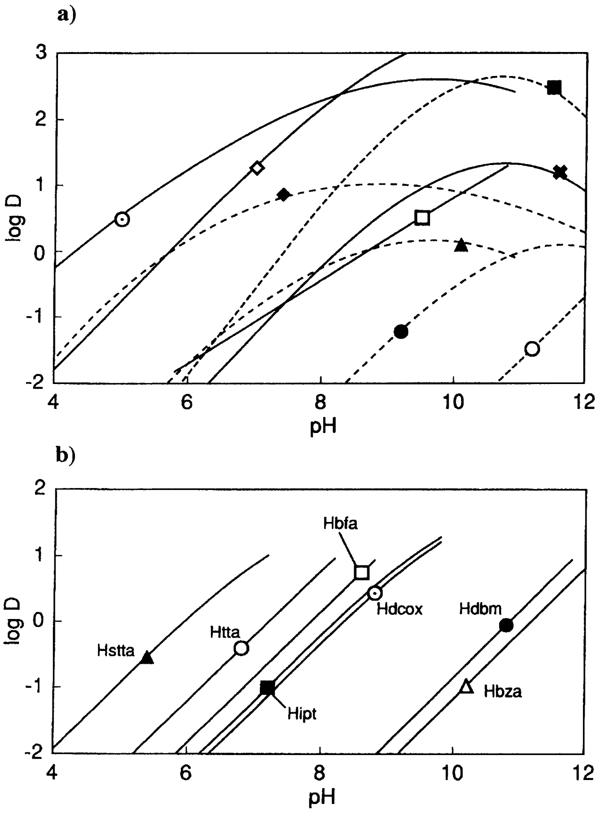

Fig. 4. a) Extraction curves of thallium(I) with several chelating extractants in the absence of tba$^+$. Data are taken from Refs. 1 and 2 and plotted by the present authors. Org. phase: $CHCl_3$ containing ■; 0.1 mol dm^{-3} sodium diethyldithiocarbamate, ◆; 0.01 mol dm^{-3} potassium xanthate, ⊙; 0.01 mol dm^{-3} diethylammonium diethyl-dithiocarbamate, ▲; 0.01 mol dm^{-3} mercapto-benzothiazole, ◇; 0.01 mol dm^{-3} diphenyl-thiocarbazone, □; 0.01 mol dm^{-3} thiooxine, ●; 0.1 mol dm^{-3} 8-quinolinol, ○; 0.01 mol dm^{-3} 1-(2-pyridylazo)-2-naphthol, and ×; 0.1 mol dm^{-3} N-benzoyl-N-phenylhydroxylamine. Aq phase: 0.1 mol dm^{-3} $NaClO_4$.
b) Extraction curves of thallium(I) with seven chelating extractants in the absence of tba$^+$. Data are taken from the present study. Org. phase: $CHCl_3$ containing △; 0.1 mol dm^{-3} Hbza, ●; 0.1 mol dm^{-3} Hdbm, □; 0.1 mol dm^{-3} Hbfa, ○; 0.1 mol dm^{-3} Htta, ■; 0.1 mol dm^{-3} Hipt, ⊙; 0.05 mol dm^{-3} Hdcox, and ▲; 0.1 mol dm^{-3} Hstta. Aq phase: 0.1 mol dm^{-3} $NaNO_3$. The curves are calculated on the basis of $D=K_{ex}^{*}[HA]_{org}[H^+]^{-1}/(1+\beta_1[A^-])$. The value of K_{ex}^{*} and β_1 are taken from Tables 1 and 2.

Discussion

The obtained results can be summarized as follows:

The extracted species of thallium(I) with the chelating extractants (HA) are in all cases in the form of TlA. The oxidation of thallium(I) to thallium(III) was negligible under the conditions of the experiments. The added

Table 3. Extraction Constant, $K_{ex}^{*}=[\mathrm{TlA}]_{org}[\mathrm{H}^{+}]/[\mathrm{Tl}^{+}][\mathrm{HA}]_{org}$, for Thallium(I) with the Chelating Extractants Coordinating through Sulfur and Sulfur or Sulfur and Nitrogen Atoms

The experimental data in Refs. 1 and 2 were calculated by the present authors on the basis of Eq. 5. Org. phase: $CHCl_3$. Aq phase: 0.1 mol dm^{-3} $NaClO_4$.

Concentration and reagents		$\log K_{ex}^{*}$
0.1 mol dm^{-3}	Sodium *N*,*N*-diethyldithiocarbamate	−6.57
0.01 mol dm^{-3}	Potassium *O*-alkyl dithiocarbonate	−3.74
0.01 mol dm^{-3}	Diethylammonium *N*,*N*-diethyldithiocarbamate	−2.43
0.01 mol dm^{-3}	2-Mercaptobenzothiazole	−5.93
0.01 mol dm^{-3}	1,5-Diphenylthiocarbazone	−3.75
0.01 mol dm^{-3}	8-Quinolinethiol	−6.49
0.1 mol dm^{-3}	8-Quinolinol	−9.48
0.01 mol dm^{-3}	1-(2-Pyridylazo)-2-naphthol	−10.67
0.1 mol dm^{-3}	*N*-Benzoyl-*N*-phenylhydroxylamine	−7.27

Table 4. Solvent Extraction of Tetrabutylammonium Ion (tba^{+}) and Chelating Extractant Anion as Ion-Pairs

a) Org. phase: $CHCl_3$ initially containing 0.1 mol dm^{-3} Hipt. Aq phase: 0.1 mol dm^{-3} $NaNO_3$.

$\log [tba^{+}]_{init.}$	pH	$\log [ipt^{-}]$	$[tba^{+}]_{org}$	[tba]	$\log K_{exAB}$
−2.0	9.30	−2.14	7.22×10^{-3}	2.73×10^{-3}	2.20
−2.3	9.34	−2.11	3.71×10^{-3}	1.41×10^{-3}	2.16
−2.7	9.39	−2.06	1.41×10^{-3}	5.88×10^{-4}	2.01
−3.0	9.40	−2.05	7.14×10^{-4}	2.94×10^{-4}	2.02
−3.0	9.94	−1.60	7.61×10^{-4}	2.60×10^{-4}	1.88
−3.3	9.03	−2.37	3.64×10^{-4}	1.57×10^{-4}	2.19
−3.7	9.40	−2.05	1.47×10^{-4}	6.14×10^{-5}	2.00

Average of $\log K_{exAB}$ is 2.07.

b) Org. phase: $CHCl_3$ initially containing 0.1 mol dm^{-3} Hstta. Aq phase: 0.1 mol dm^{-3} $NaNO_3$.

$\log [tba^{+}]_{init.}$	pH	$\log [stta^{-}]$	$[tba^{+}]_{org}$	[tba]	$\log K_{exAB}$
−2.3	3.03	−6.38	3.42×10^{-3}	1.10×10^{-3}	6.43
−2.7	3.22	−6.19	1.50×10^{-3}	4.31×10^{-4}	6.37
−3.0	3.29	−6.12	7.51×10^{-4}	2.06×10^{-4}	6.34
−3.0	3.25	−6.16	6.96×10^{-4}	2.12×10^{-4}	6.27
−3.3	3.28	−6.13	3.53×10^{-4}	9.80×10^{-5}	6.34
−3.7	3.39	−6.02	1.29×10^{-4}	3.33×10^{-5}	6.30

Average of $\log K_{exAB}$ is 6.34.

hydroxylammonium in the aqueous phase prevented the oxidation of thallium(I) to thallium(III), but did not interfere with the extraction of thallium(I). When the concentrations of the anions of the extractant ($[A^{-}]$) were similar, the extraction of thallium(I) was better in the order Hdcox > Hdbm > Hstta > Hipt > Hbfa≃Htta > Hbza. The formation of chelates in the aqueous phase was found only with Hdcox, Hipt, and Hstta when $[A^{-}]$ was high.

The addition of TOPO and quinoline into the systems of the present study caused no enhancement of extraction. Thus, the formation of adduct chelates with TOPO and with quinoline should be negligible in all the cases.

The addition of tba^{+} did not enhance extraction with Hbza and Hdbm, but it did enhance extraction with Hbfa, Htta, Hipt, Hdcox, and Hstta. The enhancement of extraction by the addition of tba^{+} was larger in the order Hstta > Hdcox > Hipt≃Hbfa≃Htta. It is known that thallium(I) is coordinated more easily by the ligands, which combine with the metal ion through sulfur and/or nitrogen atoms, than those through oxygen atoms. The Hstta coordinates with thallium(I) through the oxygen and sulfur atoms. Thus, it could form the anionic chelate complex more easily. This should be the reason why the extraction of the ternary complex is better with this extractant than with those coordinating through two oxygen atoms, such as Htta. Complex formation with Hdcox should be made through the nitrogen and oxygen atoms; this can coordinate with thallium(I) more easily than those which coordinate through two oxygen atoms. This should also be the reason why the extraction of the ternary complex with Hdcox is better than that with the extractants coordinating through two oxygen atoms. Extraction with Hbza and Hdbm is not enhanced by the addition of 0.01 mol dm^{-3} tba$^+$. The negligible extraction of the ternary complexes with these extractants has been pointed out concerning other metal ions; this was explained to be due to the poor extraction of the ion-pairs, tba$^+$A$^-$, of these reagents,[10] and, thus, the equilibrium given by Eq. 9 is very unfavorable. On the other hand, with Hstta, the ion-pairs, tba$^+$stta$^-$, are very well extracted into chloroform, as can be seen from K_{exAB} in Table 1. Thus both K_{exAB} and K_{org} are larger with Hstta than the other extractants, except for K_{org} with Hdcox, which is very favorable for the extraction of the ternary complex with Hstta, as can be seen from Eq. 8.

If the extracted species is only the noncharged complex (TlA), and the formation of complexes in the aqueous phase are negligible, the $\log D$ vs. $\log[\mathrm{A}^-]$ plot should be a straight line with a slope of +1, while if the ternary complex is mainly extracted, the plot should be a straight line with a slope of +2, as can be seen from Eq. 17. However, with all of the extractants used in the present study, the slope of the extraction curve in the presence of tba$^+$ is only slightly larger than +1, except for Hstta and Hdcox, with which the slope is nearly +1. This should be due to the fact that the extraction of the tba$^+$TlA$_2{}^-$ species is not much better than that of the TlA species, as can be seen from Eq. 17.

The degree of enhancement due to extraction of the ternary complex in the present study could be classified into two groups. The extractions with the β-diketones and Hipt belong to group 1; the extractions with the other two (Hdcox and Hstta) belong to group 2. It is clear that the value of K_{org} is lower with the extractants of group 1 than group 2. The higher K_{org} values of Hdcox and Hstta are very important in order to understand the difference in the enhancement when tba$^+$ is added. As can be seen from Eqs. 14, 17, 18, and 19, and from Table 2, the value of K_{org} of Hdcox is rather similar to that of Hstta. However, the value of K_{exAB}, the extractability of A$^-$ with tba$^+$, is three-orders larger with stta$^-$. Although it is generally expected that the slope of the plot $\log D$ vs. $\log[\mathrm{A}^-]$ is +2 when the extracted species is mainly tba$^+$TlA$_2{}^-$, as can be seen from Eq. 17, the two extraction curves with Hstta (one is obtained in the absence of tba$^+$ and the other is obtained in the presence of 0.01 mol dm^{-3} tba$^+$ in the initial aqueous phase in Fig. 3) are nearly parallel, except in the lowest $[\mathrm{A}^-]$ range. Thus, the slope of the extraction curve with Hstta in the presence of tba$^+$ is also +1 when $[\mathrm{A}^-]$ is higher. This can be explained by the following equation, which is introduced from Eqs. 10, 11, 19, and 20, and the value of $K_{\mathrm{exXB}}=10^{1.3}$:

$$D/D_0=1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A}^-][\mathrm{tba}^+]_{\mathrm{init.}}/(3+K_{\mathrm{exAB}}[\mathrm{A}^-]). \tag{21}$$

Since $[\mathrm{tba}^+]_{\mathrm{init.}} \gg [\mathrm{Tl}^+]_{\mathrm{init.}}$, the term $[\mathrm{Tl}^+]_{\mathrm{init.}}$ is not given in Eq. 21. Since the value of K_{exAB} with stta$^-$ is $10^{6.34}$, when $[\mathrm{A}^-]$ is high the following approximation is possible:

$$3+K_{\mathrm{exAB}}[\mathrm{A}^-] \fallingdotseq K_{\mathrm{exAB}}[\mathrm{A}^-]. \tag{22}$$

On the basis of Eq. 22, Eq. 21 can be rewritten as:

$$\begin{aligned} D/D_0 &= 1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A}^-][\mathrm{tba}^+]_{\mathrm{init.}}/(K_{\mathrm{exAB}}[\mathrm{A}^-]) \\ &= 1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{tba}^+]_{\mathrm{init.}} \end{aligned} \tag{23}$$

As can be seen from Eq. 23, the enhancement (D/D_0) should be approximately constant, even when the value of $[\mathrm{A}^-]$ is different and the $[\mathrm{tba}^+]_{\mathrm{init.}}$ is constant. This is the reason why the two extraction curves with Hstta in the absence and presence of tba$^+$ are parallel.

Schweitzer et al. made a comprehensive study of the solvent extraction of thallium(I) with several chelating extractants mainly coordinating with the metal ion through two sulfur atoms or sulfur and nitrogen atoms.[1,2] They gave results only in a numerical form in their papers. In order to compare these previous results with those in the present study, both series of data are given in the $\log D$ vs. pH plot form in Figs. 4a and 4b. As can be seen from Fig. 4a, the extractions with these chelating extractants are effective, and three of them extract thallium(I) quantitatively ($\log D>2$) by a single extraction. On the other hand, in the present study, the highest distribution ratio at the highest $[\mathrm{A}^-]$ is about 10 in the absence of tba$^+$. As has already been stated, the extraction of thallium(I) when $[\mathrm{A}^-]$ is similar is better in the order Hdcox>Hdbm>Hstta>Hipt>Hbfa$\simeq$Htta>Hbza. However, as can be seen form Fig. 4b, extraction is better when $[\mathrm{HA}]_{\mathrm{org,init.}}$ is 0.1 mol dm^{-3}, in the order Hstta>Htta>Hbfa>Hipt$\simeq$Hdcox>Hdbm>Hbza. Since the initial concentration of Hdcox is 0.05 mol dm^{-3}, the extraction with Hdcox should be slightly better than this order. It can be seen from Figs. 4a and 4b that the extractants studied in the present work are to some extent effective reagents for thallium(I), except for Hbza and Hdbm; for these two reagents, the pH should be higher than 11 for good extraction. However, even at the maximum, the extraction does not exceed 90%, in contrast to the extractants shown in Fig. 4a; these reagents, which coordinate through sulfur atoms or sulfur and nitrogen atoms, can extract more than 99% by a one-batch operation.

The extraction data with Hbza, Hbfa, and Htta into MIBK were reported from our laboratory.[4] However, since the solvent and the aqueous phases (1 mol dm^{-3} NaClO$_4$ in this previous work) are different, no further comparison is made here. The extraction curves, $\log D$ vs. pH, in this previous study are rather similar to those in Fig. 4b.

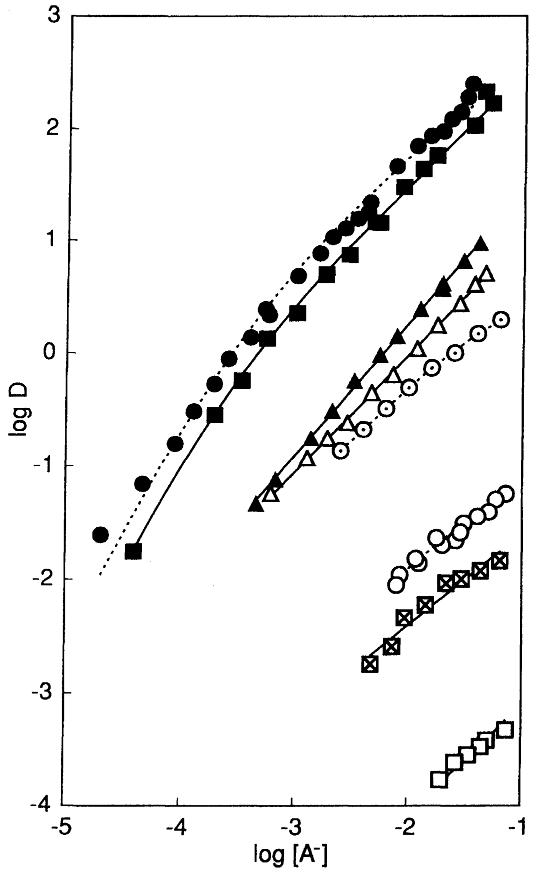

Fig. 5. Extraction of thallium(I) (triangles), silver(I) (circles), and lithium(I) (squares) with Htta in the absence and presence of tba^+ or TOPO. The curves are calculated on the basis of Eq. 17 and those for the data in the presence of TOPO are calculated by $D=K_{ex1,0}[tta^-](1+\beta_{(org)1}[TOPO])$ where $\beta_{(org)1}=[M(tta)TOPO]_{org}/[M(tta)]_{org}[TOPO]_{org}$. The open symbols were obtained in the absence of tba^+ and TOPO. The closed symbols were obtained in the presence of 0.01 mol dm^{-3} tba^+ for Tl(I) and Li(I) or 0.001 mol dm^{-3} tba^+ for Ag(I). ⊙ (Ag(I)) and ⊠ (Li(I)) are obtained in the presence of 0.01 mol dm^{-3} TOPO in the org. phase. (The value of silver(I) are calculated on the basis of the data in Ref. 12.)
Org. phase: $CHCl_3$ containing 0.1 mol dm^{-3} Htta. Aq phase: 0.1 mol dm^{-3} $NaNO_3$. The data of silver(I) are obtained from Refs. 12 and 15.

The solvent-extraction behavior of thallium(I) is different from that of two other unipositive metal ions: silver(I) and lithium(I).[11] Figure 5 compares the solvent extractions of these three metal ions with Htta. The equilibrium constants for lithium(I) were calculated from these data, as given in Table 5. The extraction of Tl^+ with Htta in the absence of tba^+ is much better than Ag^+ and even better than Li^+. The even better extraction of Tl^+ than Li^+ is probably due to the fact that the Tl(tta) complex is much more stable than the Li(tta) complex. The extraction is better when $K_{dm}\times\beta_1$ is greater, as can be seen from Eq. 15. Thus, the higher β_1 of the Tl(tta) complex than that of the Li(tta) complex should be more favorable for the extraction of thallium(I). It is also probable that K_{dm} of Tl(tta) is higher than that of Li(tta). However, the reason for the difference in the extraction behavior of thallium(I) and silver(I) should be more complicated. The stability constant of Ag(tta) is higher than that of Tl(tta). This can be estimated as follows. The extraction curve of thallium(I) with Htta in Fig. 5 is approximately a straight line having a slope of +1 up to $[A^-]$ is 0.05 mol dm^{-3}. If the formation of the Tl(tta) complex in the aqueous phase would not be negligible, the slope should become lower than +1, as can be seen Eq. 14. If the deviation in the plot $\log D$ vs. $\log[A^-]$ from the straight line with a slope of +1 would be, for example, $10^{0.1}$ or 1.26, it should be recognized from the figure. From this, the estimated upper limit of the β_1 value of the Tl(tta) complex can be calculated on the basis of Eqs. 13 and 14, as:

Table 5. Summary of Equilibrium Constants for the Extraction of Univalent Metal Ions with Htta and Tetrabutylammonium Ions
Org. phase: $CHCl_3$. Ap hase: 0.1 mol dm^{-3} $NaNO_3$ initially containing 0.01 mol dm^{-3} (for Tl(I) and Li(I)) or 0.001 mol dm^{-3} (for Ag(I)) tetrabutylammonium ions.

	Tl(I)	Ag(I)[b)]	Li(I)
$\log K_{ex1,0}$	1.98	0.14	−2.08
$\log K_{ex2,1}$	8.01	10.9	9.61
$\log\beta_1$	<0.7[a)]	1.1	—
$\log K_{org}$	1.93	6.25	7.59

a) Estimated upper limit. See the text. b) Taken from Refs. 12 and 15; the data of Tl(I) and Li(I) are obtained in the present study.

$$D_0^*/D_0=1+\beta_1[A^-]<1.26, \tag{24}$$

where D_0^* is defined in Eq. 13. When 0.05 mol dm^{-3} is introduced in $[A^-]$ in Eq. 24, the upper limit of β_1 is calculated to be smaller than 5.2 ($\beta_1<5.2$ or $\log\beta_1<0.7$). On the other hand, it was reported in a previous paper[12)] that the β_1 of the Ag(tta) complex is $10^{1.10}$, which is about two-times larger than this estimated upper limit of β_1 of Tl(tta). From these facts, it should be reasonable to estimate that the lower limit of the K_{dm} of the Tl(tta) complex on the basis of Eq. 15 to be $10^{1.3}$. This is because $K_{ex1,0}$ of Tl(tta) is $10^{1.98}$ and $K_{ex1,0}=\beta_1\times K_{dm}$, as can be seen from Eq. 15. Thus, it can be estimated using the Tl(tta) complex that $\beta_1<10^{0.7}$ and $K_{dm}>10^{1.3}$. The K_{dm} of the Ag(tta) complex in the chloroform-aqueous 0.1 mol dm^{-3} sodium perchlorate system was estimated to be $10^{-0.96}$.[12)] This indicates that the value of K_{dm} of Tl(tta) should be more than 180-times larger than that of the Ag(tta) complex. The K_{dm} of a noncharged metal complex should be dependent on the overall effect of the hydrophobic and hydrophilic character of the molecule if no solvation in the organic phase occurs. The volume of the Tl(tta) complex should not be very much different from the volume of the Ag(tta) complex, and, thus, the hydrophobic tendency of these two should not be very much different. Thus, the reason why K_{dm} of the Tl(tta) complex is greater than that of the Ag(tta) complex should be due to the fact that Ag(tta) complex is hydrated more strongly than is the Tl(tta) complex. Such an effect due to the difference of hydration of the extractable complex on the solvent extraction of divalent metal ions with β-diketones was previously pointed out.[13,14]

The distribution ratio of lithium(I) with Htta is about one order higher than that of thallium(I) in the presence of 0.01 mol dm^{-3} tba$^+$; upon the addition of 0.01 mol dm^{-3} tba$^+$, the distribution ratio increased by six orders. In other words, the Li(tta) complex is a very good accepter of tba$^+$tta$^-$. Furthermore, the extraction of silver(I) with Htta in the presence of 0.001 mol dm^{-3} tba$^+$ is one order better than that of thallium(I) in the presence of 0.01 mol dm^{-3} tba$^+$. The acceptability of the Ag(tta) complex is also much higher than that of the Tl(tta) complex; the K_{org} of Ag(tta) complex is more than four-orders larger than that of the Tl(tta) complex, though it is more than one order smaller than that of the Li(tta) complex. It was pointed out that there was a similar tendency in the acceptability of certain metal chelates with a further ligand; when a metal chelate forms more stable adduct with a solvating reagents, such as TOPO, and show a larger synergistic effect them a certain other metal chelate, it forms a more stable anionic complex with the anion of the chelating reagent in the tba$^+$A$^-$ ion-pairs, and shows a higher extractability of the ternary complex than the other metal chelate.[15] Both the Ag(tta)[12] and Li(tta)[16] complexes form stable adducts with TOPO, but, as is described, the Tl(tta) complex does not form adducts with TOPO.

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