Liquid-Liquid Extraction of Some Class *b* Metal Ions with Thiocrown Ether 1,4,8,11-Tetrathiacyclotetradecane

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Liquid-liquid extraction of some class *b* metals, silver(I), mercury(II), palladium(II) and cadmium(II) using thiocrown compound, 1,4,8,11-tetrathiacyclotetradecane (TTCT) and picrate (Pic^-) was stoichiometrically examined. Silver(I) and mercury(II) are extracted into 1,2-dichloroethane as ion-pair compounds, $[\text{Ag}(\text{ttct})_2]^+\text{Pic}^-$ and $[\text{Hg}(\text{ttct})]^{2+}\text{Pic}_2^-$ respectively. Palladium(II) is extracted into nitrobenzene as $[\text{Pd}(\text{ttct})]^{2+}\text{Pic}_2^-$ or $[\text{Pd}(\text{ttct})_2]^{2+}\text{Pic}_2^-$ depending on the concentration ratio of TTCT to palladium(II). The extraction constants for silver(I) and mercury(II) and also the distribution coefficient of TTCT in various solvents were determined. The extraction behaviors of these class *b* metals including copper(I) were compared and discussed in connection with the composition and the conceivable conformation of their extracts.

Keywords Liquid-liquid extraction, class *b* metals, thiocrown ethers, 1,4,8,11-tetrathiacyclotetradecane

The reactions of crown ethers with metal ions, especially alkali ions, have been widely studied in the fields of analytical and co-ordination chemistry.¹ The chemistry of thiocrown ether, however, has been infrequently studied, especially in analytical chemistry.^{2,3}

As thiocrown ethers contain sulfur atoms in the thioether group, they will act as softer Lewis bases than the reagents containing a mercapto group which react with class *ab* metals as well as class *b* metals. Consequently, thiocrown ethers will mainly react with softer Lewis acids and class *b* metals, rather than class *ab* metals. The difference in the affinities of the thioether group to various groups of metals is particularly interesting in connection with the selective separation of class *b* metals from class *a* and *ab* metals, especially from the first-row transition metals. In fact, it was shown that the perchlorates and picrates of class *b* metals are selectively extracted with a 1,2-dichloroethane solution of the thiocrown ether, 1,4,8,11-tetrathiacyclotetradecane (TTCT).⁴ Furthermore, the extraction and spectrophotometric determination of copper and silver with TTCT by the use of an appropriate coloured anion such as Bromocresol Green or picrate has been reported.⁵

Although the separation of class *b* metals from each other by solvent extraction will be primarily attributed to the difference of their softness, it might be made more selective by the relative sizes of the metal ion and the cavity of the macrocyclic compound, the choice of anion for formation of the ion-pair, and the kind of extraction solvents. In the present study, the stoichiometric extraction behavior of some class *b*

metals such as silver(I), mercury(II), palladium(II) and cadmium(II) into the organic solvent with TTCT were examined. The distribution of TTCT between various organic solvents and aqueous solution was also examined. The differences in the extraction behaviors of the class *b* metals were discussed in connection with the composition and the conceivable structures of the extracts.

Experimental

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). A Hiranuma mercury meter HG-1 flameless atomic absorption spectrophotometer was used for the determination of mercury(II). UV and visible absorption spectra were measured with a Hitachi 124 double beam spectrophotometer and Shimadzu self-recording spectrophotometer UV-240. The pH of aqueous phase was measured with a Hitachi-Horiba H-5 pH meter.

Reagents

The reagent, TTCT, was synthesized according to the method by Rosen and Bush⁶ and recrystallized twice from ethanol. Each metal sulfate (analytical-reagent grade) was used to prepare a 1×10^{-2} M (1 M = 1 mol dm^{-3}) stock solution. The stock solution of each metal except for silver(I) was standardized by complexometric titration. The concentration of silver(I) was

determined by potentiometric titration. Chloroform was shaken three times with 2 M hydrochloric acid, 2 M sodium hydroxide and water respectively, and then dried over anhydrous sodium sulfate and distilled. 1,2-Dichloroethane was shaken three times with 2 M potassium hydroxide and water, dried over calcium chloride, and distilled. Other reagents were of analytical-reagent grade.

Extraction of metal ions

An aliquot (10 ml) of an aqueous solution containing the metal ion (5×10^{-5} M), picrate ion (1×10^{-2} M) and acetate buffer (1×10^{-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 TTCT solution of an organic solvent (1×10^{-3} M), the mixture was shaken for 30 min at 200 strokes/min at $25 \pm 0.1^\circ\text{C}$. After the mixture was centrifuged for 5 min, the pH of the aqueous phase was measured and the concentration of the metal ion was measured by atomic absorption spectrometry using the resonance line for the metal. Metal ion concentrations in organic phase were determined as follows: Five ml of the organic phase was taken and allowed to evaporate. The residue was dissolved with a small amount of concentrated nitric acid, diluted to the adequate concentration with water, and then the metal ion was determined by atomic absorption spectrometry. The concentration of the picrate ion in the aqueous phase was determined spectrophotometrically at 354 nm.

Distribution coefficient of TTCT

The distribution coefficient of TTCT was determined by the following procedure. Ten ml of the aqueous solution containing 0.1 M sodium perchlorate and 0.01 M buffer (acetic acid-sodium acetate) and 10 ml of the organic solvent containing of 5×10^{-3} M TTCT were taken in a 50 ml glass cylindrical tube and shaken for 30 min with 200 strokes/min at $25 \pm 0.5^\circ\text{C}$. After shaking, the solution was centrifuged and the aqueous phase was separated. Five ml of this aqueous phase and 5 ml of the aqueous solution containing 1.0×10^{-3} M silver nitrate standardized with sodium chloride, 0.1 M sodium perchlorate and 0.01 M buffer (acetic acid-sodium acetate) were taken in another cylindrical tube and then 10 ml of the organic solvent containing of 5×10^{-3} M TTCT were added. After shaking for 30 min with 200 strokes/min, the pH of the aqueous phase was measured, the concentration of silver(I) was measured by atomic absorption spectrophotometry, and then the distribution coefficient was calculated.

Results

Treatment of equilibrium data

If the species in the organic phase is represented by $M(\text{ttct})_m\text{Pic}_n$, the extraction equilibrium and the

Fig. 1 Equilibria involved in the liquid-liquid extraction for metal-TTCT-Pic system.

extraction constant are given by

$$M^{I+} + m \text{ttct}(o) + n \text{Pic}^- \xrightleftharpoons{K_{ex}} M(\text{ttct})_m\text{Pic}_n(o),$$

$$K_{ex} = [M(\text{ttct})_m\text{Pic}_n]_o / [M^{I+}][\text{ttct}]_o^m [\text{Pic}^-]_n \quad (1)$$

Figure 1 illustrates equilibria involved in this extraction system. Their relevant constants are as follows:

$$\begin{aligned} \beta_p &= [M(\text{OH})_p]^{(I-p)+} / [M^{I+}][\text{OH}^-]^p \\ K_c &= [M(\text{ttct})_m^{I+}] / [M^{I+}][\text{ttct}]^m \\ K_{ass} &= [M(\text{ttct})_m\text{Pic}_n] / [M(\text{ttct})_m^{I+}][\text{Pic}^-]^n \\ K_{Dc} &= [M(\text{ttct})_m\text{Pic}_n]_o / [M(\text{ttct})_m\text{Pic}_n] \\ K_{DR} &= [M(\text{ttct})]_o / [\text{ttct}] \\ K_a &= [\text{H}^+][\text{Pic}^-] / [\text{HPic}] \\ K_{Da} &= [\text{HPic}]_o / [\text{HPic}] \end{aligned}$$

As the extraction proceeded around pH 4.0 – 5.5, the concentration of picrate ion is almost the same as the initial concentration of picric acid, of which the acid dissociation constant, K_a is $10^{-0.71}$.⁷ Consequently, the equilibria involving K_a can be neglected. If it is assumed that the hydroxo complex is also present along with the free metal ion in the aqueous phase and that the species present in the organic phase is only the ion-pair, $M(\text{ttct})_m\text{Pic}_n$, the expression for the distribution ratio of metal ion is given by Eq. 2.

$$\begin{aligned} D_M &= \frac{[M(\text{ttct})_m\text{Pic}_n]_o}{[M(\text{ttct})_m\text{Pic}_n] + [M^{I+}] + \sum_p [M(\text{OH})_p]^{(I-p)+}} \\ &= \frac{[M(\text{ttct})_m\text{Pic}_n]_o}{[M(\text{ttct})_m\text{Pic}_n] + [M^{I+}](1 + \sum_p \beta_p [\text{OH}^-]^p)} \quad (2) \end{aligned}$$

With appropriate substitutions using the above expression for K_c , K_{ass} , K_{Dc} , and K_{DR} , Eq. 2 becomes Eq. 3.

$$D_M = \frac{K_{Dc}}{(1 + \sum_p \beta_p [\text{OH}^-]^p) / K_{ass} K_c [\text{ttct}]_o^m [\text{Pic}^-]^n} \quad (3)$$

and for values $D_M < K_{Dc}$

$$D_M = \frac{K_{Dc} K_{ass} K_c [\text{ttct}]_o^m [\text{Pic}^-]^n}{K_{DR}^m (1 + \sum_p \beta_p [\text{OH}^-]^p)} \quad (4)$$

Substitution of the expression for K_{ex} into Eq. 4 leads

finally to Eq. 5.

$$D_M = \frac{K_{ex}[ttct]_o^m[Pic^-]^n}{1 + \sum_p \beta_p[OH^-]^p} \quad (5)$$

which gives the logarithmic expression, Eq. 6.

$$\log D_M = \log K_{ex} + m \log [ttct]_o + n \log [Pic^-] - \log (1 + \sum_p \beta_p [OH^-]^p) \quad (6)$$

When no hydroxo complex of the metal exists, the last term of Eq. 6 can be neglected and so Eq. 7 is obtained.

$$\log D_M = \log K_{ex} + m \log [ttct]_o + n \log [Pic^-] \quad (7)$$

Extraction of silver(I)

The relationship between the logarithm of distribution ratio ($\log D_{Ag}$) and the logarithm of the ligand concentration in the organic phase at pH 5.4 is shown in Fig. 2(a). Straight lines with the slope of +1.9 and +2.1 for 1,2-dichloroethane and chloroform respectively, were obtained, i.e., $m=2$. A logarithmic plot of D_{Ag} vs. the picrate concentration in the aqueous phase at pH 5.4 is shown in Fig. 2(b). A straight line with the slope of +1 was obtained, i.e., $n=1$. Consequently, we conclude that silver ion is extracted as the ion-pair, $[Ag(ttct)_2]^+Pic^-$. Values of $\log K_{ex}=11.7 \pm 0.2$ and 10.9 ± 0.1 for 1,2-dichloroethane and chloroform, respectively, were calculated from the extraction equilibria data.

Extraction of mercury(II)

The relationships between the logarithm of distribution ratio ($\log D_{Hg}$) and the logarithm of ligand concentration in the organic phase at pH 4.5 is shown in Fig. 3(a). A straight line with the slope of +0.8, which is close to +1, was obtained, i.e., $m=1$. A plot of $\log D_{Hg}$ vs. the logarithm of the picrate ion concentration in the aqueous phase at pH 4.6 is shown in Fig. 3(b). A straight line with the slope of +1.9 was obtained, i.e., $n=2$. We conclude that mercury(II) ion

was extracted as the ion-pair, $[Hg(ttct)]^{2+}Pic_2^-$. Mercury(II) ion is so easily hydrolyzed that it is necessary to take account of its hydroxo complexes. The value of $\log K=11.8 \pm 0.1$ in 1,2-dichloroethane was obtained by using $K_1=10^{11.03}$ and $K_2=10^{10.67}$ for mercury(II) hydroxo complexes at $\mu=0.1$, which were derived from their thermodynamic constants, $K_1=10^{11.51}$ and $K_2=10^{11.15}$.

Extraction of palladium(II)

The relationship between logarithm of the distribution ratio ($\log D_{Pd}$) and the logarithm of the initial concentration of ligand in the organic phase ($\log [ttct]_o$) at pH 4.6 is shown in Fig. 4(a). The straight line with the slope of +1 is obtained on $\log [ttct]_o < -3.7$ ($[ttct]_o/[Pd^{2+}] < 4.0$) but it becomes a horizontal line on $\log [ttct]_o > -3.7$. The formation of the palladium TTCT complex cation might be so strong that the extraction of palladium(II) on $[ttct]_o > 10^{-3.7}$ will be controlled by the ion-pair formation with picrate anion in 1,2-dichloroethane. A similar extraction of palladium(II) with TTCT was also tried by use of

Fig. 3 (a) Plot of $\log D_{Hg(II)}$ vs. $\log [ttct]_o$ at pH 4.5. (b) Plot of $\log D_{Hg(II)}$ vs. $\log [Pic^-]$ at pH 4.6. Initial concentrations: mercury(II) 1×10^{-5} M, picrate 1×10^{-3} M for (a), TTCT 5×10^{-3} M for (b). Solvent, 1,2-dichloroethane.

Fig. 2 (a) Plots of $\log D_{Ag(I)}$ vs. $\log [ttct]_o$ at pH 5.4. $\circ$, chloroform; $\bullet$, 1,2-dichloroethane. (b) Plot of $\log D_{Ag(I)}$ vs. $\log [Pic^-]$ at pH 5.4. Initial concentrations: silver(I) 5×10^{-5} M, picrate 5×10^{-4} M for (a), TTCT 5×10^{-3} M for (b). Solvent, chloroform.

Fig. 4 (a) Plot of $\log D_{Pd(II)}$ vs. $\log [ttct]_o$ at pH 4.6. (b) Plot of $\log D_{Pd(II)}$ vs. $\log [Pic^-]$ at pH 4.6. Initial concentrations: palladium(II) 5×10^{-5} M, picrate 1×10^{-2} M for (a), TTCT 5×10^{-3} M for (b). Solvent, 1,2-dichloroethane.

Fig. 5 (a) Plot of $\log D_{\text{Pd(II)}}$ vs. $\log [\text{ttct}]_o$ at pH 4.2. (b) Plot of $\log D_{\text{Pd(II)}}$ vs. $\log [\text{Pic}^-]$ at pH 4.2. Initial concentrations: palladium(II) 5×10^{-5} M, picrate 2×10^{-2} M for (a), TTCT 2.5×10^{-3} M for (b). Solvent, nitrobenzene.

nitrobenzene in place of 1,2-dichloroethane. The results are shown in Fig. 5(a). A straight line with the slope of +1 was obtained on $\log [\text{ttct}]_o = -4.2 - -3.7$ ($[\text{ttct}]_o/[\text{Pd}^{2+}] = 1.2 - 4.0$) and one with the slope of +2 on $\log [\text{ttct}]_o = -3.7 - -3.4$ ($[\text{ttct}]_o/[\text{Pd}^{2+}] = 4.0 - 8.0$). Plots of $\log D_{\text{Pd}}$ vs. the logarithm of the concentration of the picrate ion in the aqueous phase at pH 4.5 are shown in Fig. 4(b) and 5(b). A straight line with the slope of +1.5 was obtained in the case of using 1,2-dichloroethane as an organic phase, which is not expected from the charge of palladium(II) and its reason is not obvious. However, the plot in the case of nitrobenzene gave a straight line with the slope of +2 as expected. Consequently, it was found that $[\text{Pd}(\text{ttct})]^{2+}\text{Pic}_2^-$ and $[\text{Pd}(\text{ttct})_2]^{2+}\text{Pic}_2^-$ are extracted into nitrobenzene according to the relative concentration of ligand to palladium(II).

Extraction of cadmium(II)

Very little cadmium(II) was extracted, as reported in the previous paper.⁴ It seems to form no cadmium TTCT cation complex in 1,2-dichloroethane and chloroform. To make sure, we tried to form the cadmium TTCT complex in the acetone-water or ethylacetate-water mixture solution. To the organic solvent-water mixed solution containing both cadmium oxide or sulfate and picric acid or tetraphenyl borate was added the acetone or ethyl acetate solution of TTCT, then the deposit was formed by gentle evaporation or by the addition of hexane. The composites were examined, it was found that the deposits are not cadmium-TTCT complexes but are TTCT and/or cadmium picrate.

Distribution of TTCT between aqueous solution and some organic solvents

Trace amounts of TTCT are difficult to determine by conventional analytical methods. Therefore, the fact that TTCT is almost completely extracted as

Table 1 Distribution of TTCT between aqueous and organic solutions

pH	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{CH}_2\text{ClCH}_2\text{Cl}$	CHCl_3	CCl_4
1.94			1.96	
3.00			1.99	
3.44			1.99	
3.55		1.84		2.14
3.92	1.35	1.79	2.09	2.14
4.40	1.46	1.91	1.85	1.99
4.90	1.32	1.79		2.05
5.48	1.04	1.87	1.85	2.01
Mean value	1.29	1.84	1.96	2.07
Dielectric constant	34.8	10.4	4.9	2.2

$[\text{Ag}(\text{ttct})]^+\text{Pic}^-$ into an organic solvent was adopted to the determination of TTCT. The distribution ratios of TTCT between aqueous solutions and organic solvents such as nitrobenzene, 1,2-dichloroethane, chloroform and carbon tetrachloride are shown in Table 1. The values of the distribution ratio of TTCT for each solvent are independent to pH in the range of 2 to 6 as expected, and the mean value of distribution coefficient for each solvent increases in the order of nitrobenzene < 1,2-dichloroethane < chloroform < carbon tetrachloride, which is the decreasing order of their dielectric constant values. It is obvious that the ligand, TTCT, is more soluble in the more non-polar solvents.

Discussion

Composition of metal TTCT complexes and their estimated configurations

The formation of the metal TTCT complex is primarily governed by the softness of the metal ion bonding with sulfur ligand atoms in thioether type (R-S-R). The configuration of the formed complex depends on 1) the relative size of the metal to the cavity of the ligand, 2) the favourable stereochemistry for the metal ion and the relative position of four sulfur atoms and 3) the concentration ratios of the metal and the ligand. Moreover, extraction of the metal is associated with the formation of the ion-pair between the metal TTCT complex cation and the picrate anion, and also with the affinity of the formed ion-pair to the organic solvent. In Table 2, the composition of the extracted metal TTCT complexes is summarized and also some properties of the metals are given in order to discuss the formation of metal complexes and their configurations.

Studies of the solid-state structure and the solution thermodynamic stability for copper(II) complexes with the cyclic tetrathia ether ligand, $[n]\text{aneS}_4$ ($n=12-16$), suggested that the ligand $[14]\text{aneS}_4$, that is TTCT, provides an optimum fit for planar co-ordination around copper(II).^{9,10} According to the molecular structure of $\text{Cu}^{II}(\text{ttct})(\text{ClO}_4)_2$,¹¹ the four sulfur donor

Table 2 Composition of class *b* metals-TTCT-Pic complexes with some properties of these metal ions

Metals	Classification of metals by Arhland	α Value ^a	Covalent radius Å	Composition of extracted TTCT complex	Favorable structure of metal complex
Cu(I)	<i>b</i>	3.92	1.28 ^b	[Cu(ttct)] ⁺ Pic ⁻ ^e	Tetrahedral
Ag(I)	<i>b</i>	3.60	1.52 ^c	[Ag(ttct) ₂] ⁺ Pic ⁻ ^e	Linear
Hg(II)	<i>b</i>	5.83	1.48 ^c	[Hg(ttct)] ²⁺ Pic ₂ ⁻ ^e	Tetrahedral
Pd(II)	<i>b</i>	5.33	1.31 ^c	[Pd(ttct)] ²⁺ Pic ₂ ⁻ ^f [Pd(ttct) ₂] ²⁺ Pic ₂ ⁻ ^f	Planar or tetragonal
Cd(II)	<i>b</i>	1.66	1.48 ^c	No formation	Tetrahedral
Cu(II)	<i>ab</i>	1.64	1.30 ^d	[Cu(ttct)] ²⁺ (ClO ₄) ₂ ^d	Tetragonal

a. Ref. 14.

b. Derived value from Cu(I)-S bond length, 2.39 Å reported in Ref. 13.

c. Ref. 12.

d. Derived value from Cu(II)-S bond length, 2.34 Å reported in Ref. 11.

e. In 1,2-dichloroethane.

f. In nitrobenzene.

atoms lie in a square-planar arrangement around the central copper(II) with copper-sulfur bond lengths in the range of 2.30 to 2.31 Å. If the covalent radius of sulfur atom is estimates to 1.04¹², the covalent radius of copper(II) is 1.26 Å: this value will be the optimum covalent radius of a metal fitting in the cavity of the TTCT ligand. This radius of copper(II), however, is a little shorter than its covalent radius, 1.30 Å, cited in Table 2. The copper(II)-sulfur bond may be shortened, owing to the double bond character induced by π back-donation from copper(II) to sulfur atom. If the values of the covalent radii of class *b* metals shown in Table 2 are inspected, taking account a shortening of the bond length by the some double bond formation for each class *b* metal, copper(I) and palladium(II) as well as copper(II) might be accommodated in the cavity of TTCT ligand. On the other hand, silver(I), mercury(II) and cadmium(II) will be too large to accommodate in the cavity, even if shortening of these metal-sulfur bonds by π back-donation is considered.

It was previously reported that copper(I) is almost completely extracted (on $E\% > 99.4$) as 1:1 copper TTCT complex, [Cu(ttct)]⁺Pic⁻ into 1,2-dichloroethane or chloroform.⁴ The average copper(I)-sulfur bond length in the complex, [Cu(ttct)]⁺ClO₄⁻, is 2.32 Å:¹³ this value is almost identical with that of 2.303 Å found in the corresponding copper(II) complex. Consequently, copper(I) must be able to fit in the cavity of TTCT ligand. However, in the solid state of the complex, [Cu(ttct)]⁺ClO₄⁻, the tetrahedral arrangement which copper(I) favours strongly is accomplished by three sulfur atoms from one TTCT ligand molecule and a fourth sulfur atom from an adjacent TTCT molecule; therefore, a 3:1-coordinate polynuclear copper(I) complex is formed.¹³ Although it is not obvious whether such a configuration holds or not in organic solvents, it is likely that the fourth co-ordination site of copper(I) is replaced by the solvent molecule, holding on the tetrahedral structure, and that the mononuclear copper(I) TTCT complex is highly extracted in organic solvents.

Fig. 6 Schematic representation of possible configuration of silver(I) and palladium(II) TTCT complex cations.

—||—, -CH₂-CH₂-; —|||—, -CH₂-CH₂-CH₂-.

The composition of the extracted silver TTCT complex, [Ag(ttct)₂]⁺Pic⁻, is different from that of the copper(I) TTCT complex, [Cu(ttct)]⁺Pic⁻. The cavity of the TTCT ligand will not be enough to accommodate the silver(I) which is much larger than copper(I). Moreover, silver(I) favours a linear type complex. From these reason, TTCT may act as monodentate ligand in its *exo* form¹⁵ and then silver(I) may form a 1:2 linear complex rather than a sandwich complex as depicted in Fig. 6(a) and (b), respectively.

Mercury(II) is extracted as the 1:1 complex, [Hg(ttct)]²⁺Pic₂⁻, whose composition is different from 1:2 silver complex, [Ag(ttct)₂]⁺Pic⁻. The mercury(II)-sulfur covalent bond will be rather strong, as the α value of mercury(II) is the largest among the class *b* metals. Moreover, the size of mercury(II) is so large that mercury(II) will not be able to accommodate in the cavity of TTCT ligand. Therefore, it is supposed that the 1:1 complex in organic solvents will hold a square-pyramidal configuration in its solid-state¹⁶, in which four sulfur atoms will occupy the basal plane and fifth site will be occupied by the solvent molecule or picrate ion.

The size of palladium(II) seems to be on the border line of fitting or not in the cavity of TTCT ligand. For the 1:1 complex, $[\text{Pd}(\text{ttct})]^{2+}\text{Pic}_2^-$, extracted into nitrobenzene under relatively low concentration of the ligand, palladium(II) will lie on the plane or little above the plane formed with four sulfur donor atoms (Fig. 6(c)). However, for the 1:2 complex, $[\text{Pd}(\text{ttct})_2]^{2+}\text{Pic}_2^-$, extracted into nitrobenzene under relatively high concentration of the ligand, the planar conformation in which TTCT ligands on the *exo* form will function as the bidentate ligands as depicted in Fig. 6(e) rather than the sandwich conformation (Fig. 6(d)).

As shown in Table 2, cadmium(II) is classified as a class *b* metal, but its softness, which is represented by its α value, is much less than those of other class *b* metals such as silver(I), copper(I), mercury(II) and palladium(II). Moreover, the covalent radius of cadmium(II), 1.48 Å is too larger to accommodate in the cavity of TTCT ligand. Thus cadmium(II) seems not to form its TTCT complex cation, and hence will not be extracted into organic solvents.

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