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The Syntheses of Ortho-, Meta-, and Paracyclophane-Type Thiacrown Compounds and Their Characteristics as Extractive-Spectrophotometric Reagents for Class *b* Metals-Silver and Copper

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Ortho-, meta-, and paracyclophane-type thiacrown compounds bearing 4-(4-nitrophenylazo)phenol as a chromogenic group were synthesized, and their characteristics as extractive-spectrophotometric reagents for the class *b* metals, consisting of soft Lewis acids such as silver and copper(I), were examined. Silver and copper(I) were well extracted into chloroform with all of three reagents, though especially with the metacyclophane-type reagent. The absorption maxima of silver and copper(I) complexes with the orthocyclophane-type reagents are at the longest wavelengths among the three reagents. The orthocyclophane-type reagent is adequate for the extraction and spectrophotometric measurement of copper(I), and the metacyclophane-type reagent is suitable for that of silver. The extraction behavior of copper(II) with these three reagents has been studied in order to know if the hydroxyl group participates in the formation of the metal-thiacrown complexes.

Thiacrown ethers act as soft Lewis bases and react selectively with the class *b* metals of soft Lewis acids. The resulting thioether complex cations form ion pairs with appropriate anions, such as perchlorate and picrate, which are then extracted into suitable organic solvents.1–7) The extractive-spectrophotometric determination of silver and copper with thiacrown ethers by the use of dye anions as the pairing anions has been reported.8)

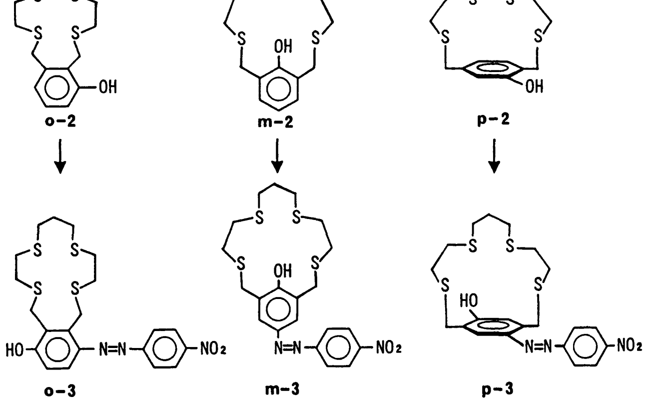
If a thiacrown ether compound itself has a chromogenic group which can function as a counter anion, that compound can be used as an extractive-spectrophotometric reagent for metal ions. Thus, the extraction with chromogenic thiacrown ethers, such as 4′-(pycrylamino)benzo-1,4,8,11-tetrathiacyclopentadec-13-ene (4′-PicNHBz-TTCP)9) and those in which a nitro group in 4′-PicNHBz-TTCP is replaced by a trifluoromethyl group,10) as well as thiacrown ethers containing a phenylazo group as a chromophore, have been reported.11)

In the present study, in order to obtain more selective and sensitive thiacrown reagents, which contain the chromogenic group also functioning as a counter anion, new ortho-, meta-, and paracyclophane-type thiacrown ether reagents were synthesized, and their characteristics as extractive-spectrophotometric reagents for class *b* metals, such as silver and copper(I), were examined. Furthermore, as it seemed interesting to know how the hydroxyl groups of the ortho-, meta-, and paracyclophane-type thiacrown ethers participate in the formation of the metal-thiacrown complexes, the extraction behavior of copper(II) has been studied.

Results and Discussion

Syntheses of Reagents. Thiacrown ether containing a hyroxyl group may be expected to be obtained by the reaction of dithiol and bis(halogenomethyl)phenol protected with a hydroxyl-protecting group such as tetrahydropyranyl ether. However, the synthesis of each isomer of bis(chloromethyl)phenol by chloromethylation into phenol or the direct bromination of dimethylphenol into the α position was very difficult. Fortunately, thiacrown ether containing a hydroxyl group **2** was obtained by the reaction of bis(bromomethyl)phenyl acetate **1** and 3,7-dithianonane-1,9-dithiol, as shown in Scheme 1.

The cyclization reaction was achieved by the drop-by-drop addition of a benzene solution containing 1 molar equivalent of dibromide **1** and 1.5 molar equi-



Scheme 1.

valents of 3,7-dithianonane-1,9-dithiol to a sodium ethoxide solution by means of the high-dilution method. The cyclizations of *o*-, *m*-, and *p*-substituted dibromides with dithiol all produced satisfactory yields.

The reaction of hydroxy-substituted cyclophane **2** and *p*-nitrobenzenediazonium tetrafluoroborate was carried out in a dioxane-water solution under slightly alkaline conditions. The reaction mixture was acidified. A large quantity of water was added and then extracted with ethyl acetate. The solvent was removed, the residue was chromatographed on a silica-gel column, and the pure product was obtained by the recrystallization of the major band.

The orthocyclophane-type thiacrown ether **o-3** is moderately soluble in such organic solvents as chloroform, ethyl acetate, and acetone. The reagents **m-3** and **p-3** are soluble in chloroform or acetone. The proton NMR spectra of **o-3** and **m-3** are similar to each other except for that of aromatic protons, but that of **p-3** is very different from that of **o-3** or **m-3**. The benzyl proton signal of **p-3** separates into two quartets, indicating a two-AB pattern, although that of **o-3** is a doublet and that of **m-3** is a singlet. The protons of the thioether ring of **p-3** are shielded by a benzene ring and are probably affected by azo-group electrons. These proton NMR spectra are consistent with the desired configuration for each isomer; **m-3** is a symmetrical structure in which the thioether ring is coplanar for the benzene ring. **o-3** has an unsymmetrical thioether ring which is coplanar for the benzene ring. The thioether ring of **p-3** is an unsymmetrical structure and exists at the upper space of the benzene ring. It seems that the difference in the configuration of **p-3** from that of **o-3** or **m-3** causes the decrease in metal extraction to be described below.

Absorption Spectra of Three Reagents (o-3, m-3, and p-3) and of Their Silver Complexes in a 50% (v/v) Dioxane-Water Mixture. In Table 1, the absorption-spectra data for three reagents (**o-3**, **m-3**, and **p-3**), in a 50% (v/v) dioxane-water mixture are shown, along with those for their silver complexes. The absorption maxima of the three reagents in acidic media, which are present in the range of 384—400 nm, shift to longer wavelengths (537—545 nm) in alkaline media, and their molar absorptivities (ε) increase from 22000—24000 in acidic media to 34400—35800 in alkaline. These changes in the absorption spectra with the increase in the pH are almost the same as those of 4-(4-nitrophenylazo)phenol with the dimethyl substituent (2,3-dimethyl-; HL 394 nm, L^- 548 nm: 2,6-dimethyl-; HL 393 nm, L^- 556 nm: 2,5-dimethyl-; HL 398 nm, L^- 547 nm).

Table 1. Absorption Spectra Data of Reagents **3** and of Their Silver Complexes in a 50% (v/v) Dioxane-Water Mixture

	HL		L^-		AgL	
	λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε
o-3	394	24400	537	35400	525	33400
m-3	384	22000	545	35800	531	36200
p-3	400	23600	538	34400	528	31200

Concentration of **3** and silver ions: 2.5×10^{-5} M.

In the presence of the silver ion, the absorption maxima of all three reagents shift to wavelengths shorter by 10—14 nm than those of L^-. It seems that the shift shows the decrease in the resonance of the azobenzene moiety by the shift of electrons from that of *p*-nitrobenzene to the thioether ring as a result of the coordination of the silver ion to the sulfur atoms. It is interesting that the molar absorptivities for **o-3** and **p-3** silver complexes decrease, but that for **m-3** increases, compared with L^-. This seems to indicate that the phenolate ion not only functions as a counter ion, but also takes part in the bonding of the silver ion.

Proton-Dissociation Constant. The acid dissociation constants of the reagents **3** were determined spectrophotometrically in a 50% (v/v) dioxane-water mixture, the effects of the silver ion on their pK_a values were also examined. The results are shown in Table 2. The pK_a values of **o-3** and **p-3** are similar, but that of **m-3** is somewhat small. In the presence of silver ions, the apparent pK_a value of every reagent decreases. Probably this is a result of the decrease in electron density on the phenolic oxygen atom when the electrons are shifted from the azobenzene moiety by the coordination of the silver ion. The large decrease in pK_a value for **m-3** suggests that the silver ion interacts directly with the hydroxyl group and

Table 2. Proton-Dissociation Constants of Reagents **3** in a 50% (v/v) Dioxane-Water Mixture

HL : Ag	o-3	m-3	p-3
1 : 0	9.0	8.15	8.7
1 : 1	7.55	5.3	7.2

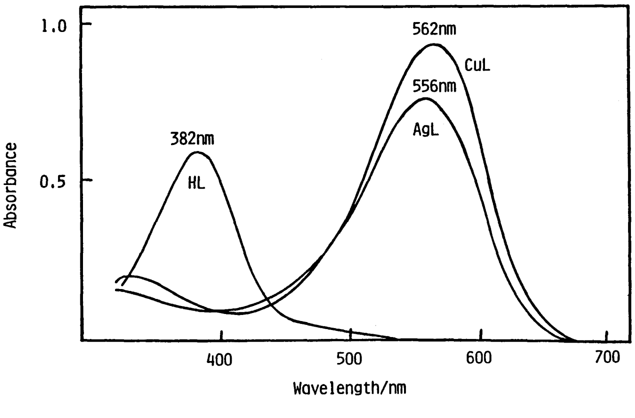


Fig. 1. Absorption spectra of **o-3** and of their silver and copper(I) complexes in chloroform. Concentration of **o-3** and metal ions: 2.5×10^{-5} M.

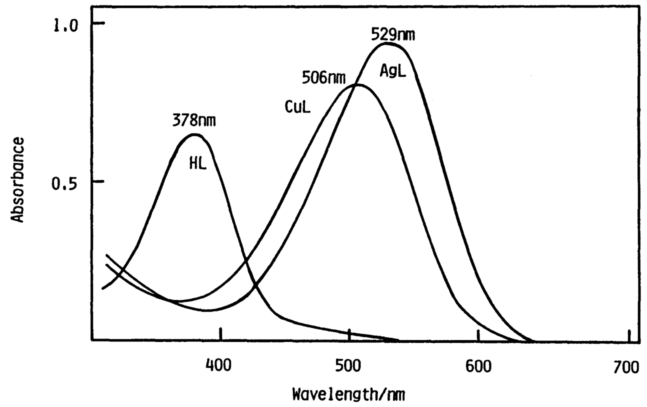


Fig. 2. Absorption spectra of **m-3** and of their silver and copper(I) complexes in chloroform. Concentration of **m-3** and metal ions: 2.5X10^{-5} M.

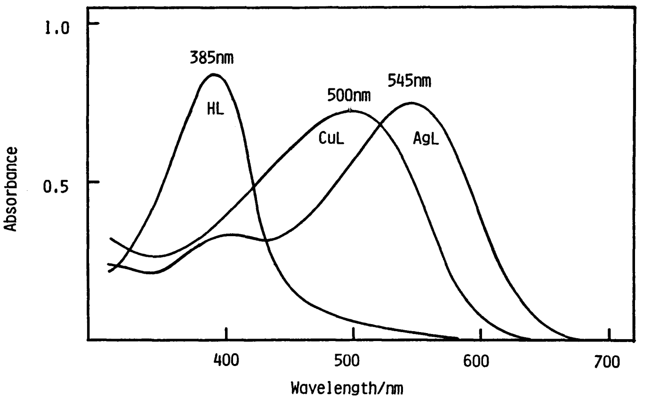


Fig. 3. Absorption spectra of **p-3** and of their silver and copper(I) complexes in chloroform. Concentration of **p-3** and metal ions: 4X10^{-5} M.

Table 3. Absorption Maxima of the Silver Complexes in Various Extraction Solvents

	λ_{max}/nm		Dielectric constant
	o-3	**m-3**	
$CHCl_3$	556	529	4.8
CH_2ClCH_2Cl	561	540	10.7
$CH_2ClCH_2Cl : C_6H_5NO_2 = 1:1$	565	548	22.7
$C_6H_5NO_2$	571	554	34.8

Concentration of **3** and silver ions : 2X10^{-5} M. **o-3** : pH 10.05 and **m-3** : pH 8.95.

Table 4. Percentages of Extraction of Silver and Copper(I) into Chloroform

	Ag (%)	Cu(I)
o-3	99.2	99.4
m-3	99.4	99.2
p-3	99.0	99.2

Concentration of **3** : 6X10^{-4} M. Concentration of metal ions: 3X10^{-5} M. pH 8.3.

Table 5. Percentages of Extraction of Silver and Copper(I) into Chloroform

	Ag (%)	Cu(I)
o-3	86.3	94.2
m-3	98.7	97.3
p-3	51.4	52.7

Concentration of **3** and metal ions : 3X10^{-5}M. pH 8.95.

that, consequently, the proton is excluded by proton-silver ion repulsion.

Liquid-Liquid Extraction Behavior of Silver and Copper(I). (i) Absorption Spectra of Silver and Copper(I) Complexes for Reagents 3: The absorption spectra of **o-3**, **m-3**, and **p-3** and of those silver and copper(I) complexes extracted into chloroform are shown in Figs. 1—3.

The absorption bands of HL have their maxima at 378—385 nm (ε=21000—25000). The absorption maxima of silver complexes for **o-3** and **p-3** exist at 556 nm and 545 nm, which are longer than those of the corresponding silver complexes in a 50% (v/v) dioxane-water solution. However, that for **m-3** in chloroform exists at a shorter wavelength than those in a 50% (v/v) dioxane-water solution. This may be attributed to the larger decrease in the resonance of the azobenzene moiety by the coordination of silver. This influence may be weakened by a polar solvent, and the effect may be larger for **m-3** than for **o-3** and **p-3**. As shown in Table 3, the absorption maxima of silver complexes for **o-3** and **m-3** are shifted to the longer wavelengths with the increase in the solvent polarity and the shift for **m-3** is larger than that for **o-3**.

(ii) The Percentage of the Extraction of Silver and Copper(I) Complexes: The percentage of the extraction of silver and copper(I) with three reagents was also examined. The results are shown in Table 4. As has been reported in previous papers,[3,9,11] silver and copper(I) were well extracted with these thiacrown compounds. Similarly, those two metals were well extracted with these three reagents **3** at 20 times the metal concentration into chloroform, as shown in Table 4. Also, as shown in Table 5, these were well extracted with **m-3** in the same concentration is that of metal ions at pH 8.95. It seems that **m-3** has an intraannular hydroxyl group; therefore, a dissociated hydroxyl group exists at a preferable position compared with that of **o-3**. The extraction with **p-3** decreases to about a half. This decrease is presumed to be accounted for as follows: two sulfur atoms of the para-substituted benzyl group exist far apart, consequently, the silver or copper(I) ion can not be coordinated by those sulfur atoms-only two sulfur atoms bonded to the trimethylene group can be coordinated. In fact, it is obvious that the internal cavity of

Table 6. Extraction Behavior of Copper(II) Complexes with **3**

	Absorption maximum/nm	% Extraction Cu(II) : HL	
		1 : 2	1 : 20
o-3	558	29	94
m-3	498	35	97
p-3	—	8	81

Concentration of Cu(II) : 3×10^{-5}M. pH 8.3

p-3 is too small for silver or copper(I), as assumed by CPK model of the space-field type.

Liquid-Liquid Extraction of Copper(II). Among the metals belonging to class *ab* metals, Co^{2+}, Ni^{2+}, and Zn^{2+} were scarcely extracted at all with 4′-(2-hydroxy-5-chlorophenylazo)Bz-TTCP[11] and 4′-PicNHBz-TTCP.[9] Only Cu^{2+} was extracted appreciably with 4′-(2-hydroxy-5-chlorophenylazo)Bz-TTCP and not with 4′-PicNHBz-TTCP. It seemed interesting to determine whether or not copper(II) can be extracted with these three reagents **3**. The absorption spectra data of copper(II) complexes for the reagents **3** in chloroform are shown in Table 6. The percentage of extraction was examined, it is also shown in Table 6. Although the percentage of the extraction of copper(II) is less than those of silver or copper(I), copper(II) is extracted in an appreciable amount. In the previous paper, we presumed that the extraction of copper(II) with 4′-(2-hydroxy-5-chlorophenylazo)Bz-TTCP is performed by the complex formation of adjacent azo and hydroxyl groups, rather than the thioether ring. However, the results of the extraction with these reagents **3** strongly suggest the formation of copper(II) complexes with the thioether ring.

Experimental

Syntheses of Reagents. Bis(bromomethyl)phenyl Acetate 1: Dimethylphenyl acetate (8.2 g, 0.05 mol) was dissolved in carbon tetrachloride (100 ml) and *N*-bromosuccinimide (17.5 g, 0.1 mol), and then benzoyl peroxide (0.2 g) was added. The reaction mixture was refluxed for 2—3 h. After cooling, the precipitate was filtered and washed with a small amount of ether. The filtrate and the washings were combined, and the solvent was removed in vacuo. The solid was recrystallized from ethanol.

2,3-Bis(bromomethyl)phenyl Acetate: Mp 100—101 °C; yield, 5.6 g (34.6%). Found: C, 37.46; H, 3.19%. Calcd for $C_{10}H_{10}Br_2O_2$: C, 37.30; H, 3.13%. IR(KBr) 1760, 1220, 1210, 1190, 620 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 324 (M+2, 28), 322 (M^+, 58), 320 (29), 280 (98), 243 (98), 241 (98), 119 (100). ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s, CH_3), 4.60 (4H, s, CH_2Br), 6.95—7.35 (3H, m, aromatic H).

2,6-Bis(bromomethyl)phenyl Acetate: Mp 119—120 °C; yield, 7.3 g (45.6%). Found: C, 37.42; H, 3.10%. IR (KBr) 1760, 1220, 1210, 1180, 590 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 324 (M+2, 6), 322 (M^+, 12), 320 (6), 280 (88), 201 (100), 199 (98). ^{1}H NMR ($CDCl_3$) δ=2.40 (3H, s, CH_3), 4.35 (4H, s, CH_2Br), 7.00—7.50 (3H, m, aromatic H).

2,5-Bis(bromomethyl)phenyl Acetate: Mp 99—100 °C; yield, 4.9 g (30.1%). Found: C, 37.07; H, 3.00%. IR (KBr) 1760, 1230, 1200, 1190, 625 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 324 (M+2, 5), 322(M^+, 9), 320 (5), 243 (44), 241 (45), 199 (100). ^{1}H NMR ($CDCl_3$) δ=2.35 (3H, s, CH_3), 4.30—4.50 (4H, d, CH_2Br), 7.05—7.35 (3H, m, aromatic H).

Hydroxy-Substituted Cyclophane (Compounds o-2, m-2, and p-2). In absolute ethanol (360 ml) under nitrogen, sodium metal (0.83 g, 36 mmol) was dissolved. To this solution, an anhydrous benzene solution (450 ml) containing dibromide **1** (3.86 g, 12 mmol) and 3,7-dithianonane-1,9-dithiol (4.10 g, 18 mmol) was added dropwise during a 6-h period at 10—15 °C. After the mixture had then been stirred overnight, the solvent was removed until the volume has only about 100 ml, and then water was added. The mixture was acidified with dilute hydrochloric acid, extracted with ethyl acetate, washed with water, and dried. The solvent was then removed, and the residue was chromatographed on a silica-gel column with chloroform-ethyl acetate (20:1 v/v) (for ortho- and paracyclophanes) or benzene (for metacyclophane) as a eluting solvent. The major band was collected. The product was pure enough for the next process. Recrystallization gave an every purer product.

o-2: Yield, 3.11 g (74.9%). Recrystallization from methanol-methyl acetate (1 : 1); mp 112—113 °C. Found: C, 51.75; H, 6.30%. Calcd for $C_{15}H_{22}OS_4$: C, 51.98; H, 6.40%. IR (KBr) 3425, 1580, 1465, 1200, 765 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 348 (M+2, 5), 346 (M^+, 26), 211 (17), 167 (92), 107 (100). ^{1}H NMR ($CDCl_3$) δ=1.55—2.10 (2H, m, CH_2-$\mathbf{CH_2}$$CH_2$), 2.50—3.10 (12H, overlapping t and s, $\mathbf{CH_2}$-$CH_2$$\mathbf{CH_2}$, $\mathbf{CH_2CH_2}$), 3.75—4.10 (4H, d, CH_2Ar), 6.55—7.20 (3H, m, aromatic H).

m-2: Yield, 3.58 g (86.2%). Recrystallization from ethanol; mp 94—95 °C. Found: C, 51.99; H, 6.18%. IR(KBr) 3325, 1460, 1410, 1200, 750 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 348 (M+2, 22), 346 (M^+, 100), 286 (15), 184 (50), 120 (88), 91 (82). ^{1}H NMR ($CDCl_3$) δ=1.40—1.90 (2H, m, $CH_2$$\mathbf{CH_2}$-$CH_2$), 2.30—2.75 (12H, overlapping t and s, $\mathbf{CH_2}$$CH_2$$\mathbf{CH_2}$, $\mathbf{CH_2CH_2}$), 3.80 (4H, s, CH_2Ar), 6.65—7.30 (3H, m, aromatic H).

p-2: Yield, 3.49 g (84.0%). Recrystallization from acetonitrile; mp 96—97 °C. Found: C, 51.91; H, 6.31%. IR (KBr) 3245, 1580, 1430, 1230, 720 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 348 (M+2, 20), 346 (M^+, 97), 286 (8), 198 (16), 167 (96), 107 (100). ^{1}H NMR ($CDCl_3$) δ=1.25—1.80 (2H, m, $CH_2$$\mathbf{CH_2}$$CH_2$), 2.15—2.65 (12H, overlapping t and s, $\mathbf{CH_2}$$CH_2$$\mathbf{CH_2}$, $\mathbf{CH_2CH_2}$), 3.60—3.85 (4H, d, CH_2Ar), 6.80—7.25 (3H, m, aromatic H).

***p*-Nitrophenylazo Reagents 3 (Compounds o-3, m-3, and p-3).** Phenolic cyclophane **2** (1.04 g, 3.0 mmol) was dissolved in dioxane (60 ml), and then 0.05 M sodium hydroxide solution (60 ml) was added. To this solution, *p*-nitrobenzenediazonium tetrafluoroborate (0.77 g, 3.3 mmol) dissolved in water (150 ml) was added dropwise at 5—10 °C. During this addition, the reaction mixture was kept homogeneously at pH 8—9 by the use of dioxane and a dilute sodium hydroxide solution. Then the solution was stirred at room temperature for 1 h and acidified with dilute hydrochloric acid. A large quantity of water was added, the mixture was extracted with ethyl acetate and dried. The solvent was removed, and the residue was chromatographed on a silica-gel column with chloroform-ethyl acetate (20:1 v/v) (for ortho- and paracyclophanes) or chloroform (for metacyclophane) as a eluting solvent. The major band was collected and recrystallized.

o-3: Recrystallization from acetonitrile; yield, 0.87 g (58.5%). Mp 219—220 °C. Found: C, 50.73; H, 4.90; N, 8.59%. Calcd for $C_{21}H_{25}N_3O_3S_4$: C, 50.88; H, 5.08; N, 8.48%. IR (KBr) 3280, 1580, 1330, 1280, 1240 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 495 (M$^+$, 3), 301 (16), 267 (32), 167 (68), 61 (100). ^{1}H NMR ($CDCl_3$: DMSO-d_6=1:1) δ=1.75—2.10 (2H, m, $CH_2CH_2CH_2$), 2.70—3.10 (12H, overlapping t and s, $CH_2CH_2CH_2$, CH_2CH_2), 4.10 (2H, s, CH_2Ar), 4.55 (2H, s, CH_2Ar), 6.85—6.95 (1H, d, aromatic H), 7.60—7.70 (1H, d, aromatic H), 7.95—8.20 (4H, q, aromatic H).

m-3: Recrystallization from acetonitrile; yield, 0.35 g (23.4%). Mp 162—163 °C. Found: C, 51.00; H, 4.97; N, 8.56%. IR (KBr) 3300, 1510, 1345, 1295, 1285 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 495 (M$^+$, 5), 269 (15), 194 (13), 107 (65), 61 (100). ^{1}H NMR ($CDCl_3$) δ=1.30—1.85 (2H, m, $CH_2CH_2CH_2$), 2.35—2.80 (12H, overlapping t and s, $CH_2CH_2CH_2$, CH_2CH_2), 3.90 (4H, s, CH_2Ar), 7.80—8.50 (6H, m, aromatic H).

p-3: Recrystallization from acetonitrile and water; yield, 0.49 g (33.0%). Mp 145—146 °C. Found: C, 50.77; H, 5.00; N, 8.57%. IR (KBr) 3450, 1525, 1340, 1280, 1260 cm^{-1}. MS (70 eV) *m/z* (rel intensity) 495 (M$^+$, 17), 301 (35), 268 (100), 167 (98), 107 (99). ^{1}H NMR (pyridine-d_5) δ=1.50—1.70 (2H, m, $CH_2CH_2CH_2$), 2.20—2.95 (12H, m, $CH_2CH_2CH_2$, CH_2CH_2), 3.78 and 4.48 (2H, AB-q, *J*=13.9, CH_2Ar), 3.80 and 5.17 (2H, AB-q, *J*=14.0, CH_2Ar), 7.51 (1H, s, aromatic H), 8.11 and 8.41 (4H, q, aromatic H), 8.25 (1H, s, aromatic H).

Reagent and Apparatus. Metal solution: Copper(II) sulfate, an analytical-grade reagent, was used to prepare the 1×10^{-2} M stock solution, which was then standardized by EDTA titration. A 1×10^{-2} M stock solution of silver nitrate commercially available for volumetric analysis was used.

The other reagents and all of the apparatus used were the same as have been described in a previous paper.$^{11)}$

Proton-Dissociation Constant. The proton dissociation constants of thiacrown ether reagents were determined spectrophotometrically in a 50% (v/v) dioxane-water mixture by means of a method similar to that described in the previous paper.$^{11)}$ The ionic strength was adjusted to 0.1 with sodium sulfate.

Extraction of Metals. An aliquot (10 ml) of an aqueous solution containing the metal ion and the buffer solution was placed in a 20-ml cylindrical glass tube equipped with a stopper. The ionic strength was kept at 0.1 with sodium sulfate. To obtain a copper(I) solution, enough hydroxylamine sulfate was added to the copper(II) sulfate solution.

After the addition of 10 ml of the reagent **3** solution, the mixture was shaken for 30 min at 200 strokes/min and centrifuged for 5 min. The absorbance of the organic phase was measured at the wavelength of each absorption maximum against a reagent blank. The metal concentrations in the organic phase were determined as follows: 5 ml of the organic phase was taken and allowed to evaporate. The residue was dissolved with a small amount of concentrated nitric acid and diluted adequately with water, and then the metal ion was determined by means of atomic absorption spectrometry.

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