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Photoresponsive Crown Ethers. 12. Photocontrol of Metal Ion Complexation with Thiacrown Ethers

Seiji Shinkai,* Yoshihiro Honda, Kaori Ueda, and Osamu Manabe*
Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852

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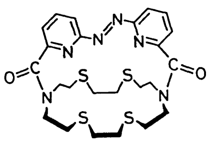
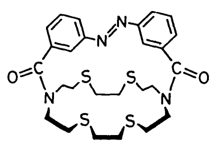
Thiacrown ethers with a photofunctional azolinkage were synthesized to control their binding ability by an on-off light switch: They are the N_2S_4 crowns capped with 2,2′-azopyridine (**1**) or azobenzene (**2**). The cis-trans isomerism occurred reversibly by photoirradiation. The binding ability, evaluated by solvent extraction, showed that (i) the order of the affinity for Hg^{2+} is *N,N′*-dibenzoylated N_2S_4 crown (**4**)≈photoirradiated **1**>*trans*-**1**>photoirradiated **2**>*trans*-**2**, (ii) neither *trans*-**2** nor **4** shows significant affinity toward heavy metal ions such as Cu^{2+}, Co^{2+}, Ni^{2+}, and Pb^{2+}, (iii) *trans*-**1** has a slight affinity (Ex% 5.9%) for Cu^{2+},whereas photoisomerized **1** shows the remarkably enhanced affinity (Ex% 93.9%) with Cu^{2+}, and (iv) such light-induced improvement is not seen for **2**. The relatively poor binding ability of **2** and **4** is rationalized in terms of the unfavorable inside-out conformation of the N_2S_4 crown ring. The remarkable affinity change in *cis*-**1** is probably due to the cooperative contribution of the thiacrown and the azopyridine cap constructing a new ligand site. **1** was used as a carrier for Cu^{2+} transport through a liquid membrane. It was found that the rate is efficiently accelerated by UV-light irradiation.

Chemical substances which exhibit photoinduced structural changes are potential candidates not only for the storage of light energy but also as mediators for the conversion of light into other forms of energy. Further, if the structural changes occurring in the photoresponsive chromophores can be transmitted to functional molecules, the fundamental functions of photoresponsive systems in nature may be mimicked in artificial systems. Azobenzene derivatives which exhibit photoinduced reversible cis-trans isomerism have frequently been employed as photoantennae which trigger subsequent events of a number of functional molecules.[1–6)]

The purpose of our investigation has been to control the functions of a crown ether family by an on-off light switch, which would lead to the photocontrol of ion-extraction and membrane transport.[7–12)] We have developed two different techniques to change the binding ability of crown ethers by light. One method is to induce a conformational change in the crown ether moiety in conjugation with a photoinduced configurational change in the azobenzene moiety. A typical example is azobenzene-bridged crown ether.[7)] The other method is associated with a change in the spatial position between two crown rings which leads to interconversion between 1:1 and 2:1 crown/cation complexes. The photoresponsiveness of azobis(benzocrown ether)s (so-called butterfly crown ethers) is a typical example.[8,11)] It was shown that in these photoresponsive crown ethers, not only the binding ability but also the ion selectivity is markedly influenced by photoirradiation[7–14)] and that in some cases an all-or-nothing change in the binding ability is observed.[15,16)] By use of such photoresponsive crown ethers, we can control the ion-extraction and membrane-transport of alkali and alkaline earth metal cations by an on-off light switch. It is known that a thiacrown family exhibits an affinity toward heavy metal cations.[17,18)] Thus, if one can extend the above concept to the thiacrown family, it would lead to photocontrol of the ion-binding ability toward heavy metal cations. With these objects in view, we synthesized thiacrown analogues **1**—**4** to test the photoresponsive binding of heavy metal cations.


trans-1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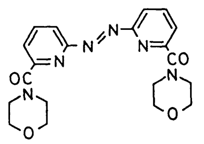
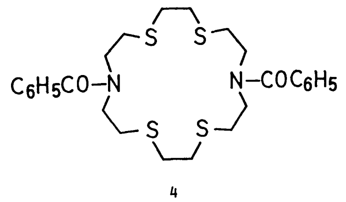

trans-3



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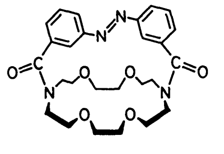
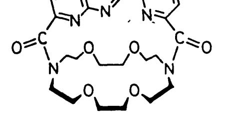
Results and Discussion

¹H-NMR Spectra of Capped Thiacrown Ethers. We previously synthesized azobenzene-capped and azopyridine-capped crown ethers (**5** and **6**, respectively) from 1,4,10,13-tetraoxa-7,16-diaza-18-crown-6(N_2O_4 crown).[7,12)] It was found that in the ¹H-NMR spectra of these compounds the chemical shifts of the crown protons are sensitively affected by ring current of the aromatic rings. For example, *trans*-**5** gave two resolved peaks at 3.6—3.9 ppm (8H) and 4.1—4.8 ppm (16H), which were attributed to NCH_2 and OCH_2 of the crown ring, respectively.[7)] Since the crown protons of N_2O_4 crown derivatives usually appear at 3.4—3.8 ppm as a broad single peak, the downfield shift in *trans*-**5** is ascribed to the anisotropic effect of the benzene rings.


trans-5


trans-6

A similar anisotropic effect was seen for *trans*-**1** and *trans*-**2**. In contrast to a broad single peak (2.80 ppm in $CDCl_3$) observed for the methylene protons of 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (N_2S_4 crown), *trans*-**1** and *trans*-**2** gave the resolved, complex NMR spectra at 2.6—4.8 ppm (Fig. 1). The downfield chemical shifts observed at 4.6 ppm (2H) for *trans*-**1** and 3.8 ppm (4H) for *trans*-**2** would be attributed to the central methylene protons which most strongly undergo the anisotropic effect of the aromatic caps. As seen in Fig. 1, the NMR peaks of *trans*-**2** are significantly broad at 30 °C and sharpened with increasing temperature. It is conceivable that the broadening effect is induced by the steric rigidity of the bicyclic *trans*-**2**. A similar temperature-dependence is seen for the crown ether analogue *trans*-**6**. On the other hand, the NMR spectrum of *trans*-**1** had a peculiar temperature-dependence: The peaks at 30 °C were very sharp, and with increasing temperature they once became broad at the intermediate temperature region, finally being sharpened again at 117 °C. The intergral intensity of the downfield peak (around 4.6 ppm) at 30 °C corresponds to two protons. The peak is once absorbed into the main absorption band at intermediate temperature and finally separated as four proton intensity at 117 °C. According to recent X-ray crystallographic studies, most of thiacrown ethers show some disorder due to differences in the sulfide bond configuration.[19,20] It is likely on the basis of the above NMR data and the X-ray analysis[21] that the thiacrown ring of *trans*-**1** involves a few configurational isomers. We cannot explain readily, however, why the temperature dependences of the NMR spectra are so different between azopyridine-capped *trans*-**1** and azobenzene-capped *trans*-**2**.

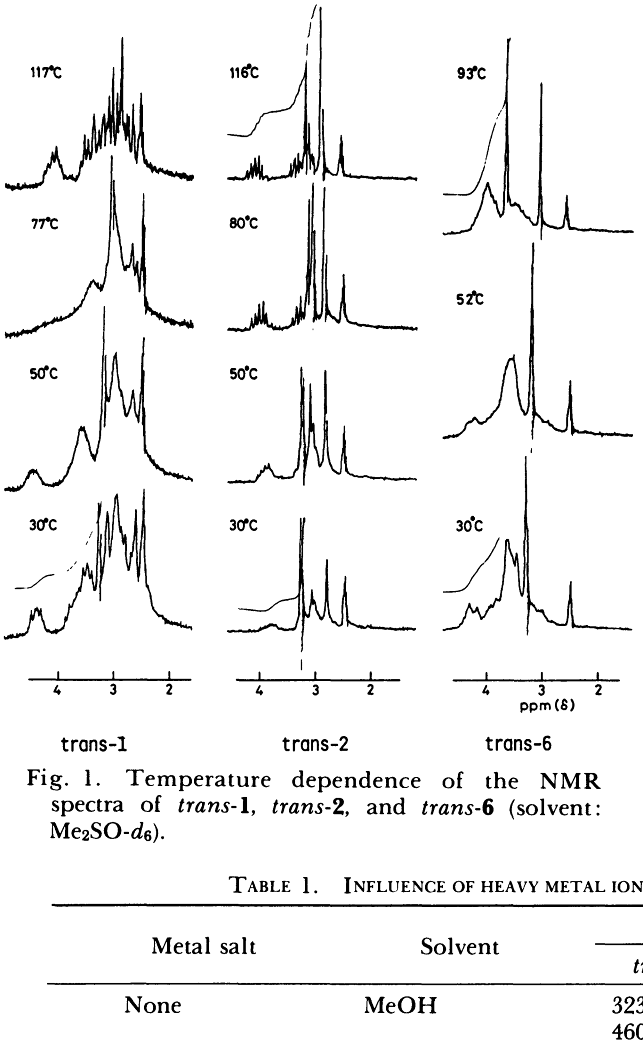


Fig. 1. Temperature dependence of the NMR spectra of *trans*-**1**, *trans*-**2**, and *trans*-**6** (solvent: Me_2SO-d_6).

Spectral Examination of Metal-Crown Interactions. In order to evaluate interactions between the thiacrown ethers and heavy metal ions, the absorption spectra were taken in methanol or *o*-dichlorobenzene(DCB)–1-butanol(*n*-BuOH) mixed solvent. The latter mixed solvent was used to compare the spectral data with the subsequent ion-extraction and thermal cis-to-trans isomerization under the consistent conditions. The results are summarized in Table 1. The absorption bands at around 325 nm and 450 nm in *trans*-**1**, *trans*-**2**, and *trans*-**3** are ascribed to π-π^* and n-π^* bands, respectively. Since **4** gives no appreciable absorption band at 300—600 nm and **2** gives no additional absorption band on the addition of heavy metal ions, a new absorption band (when it appears) can be attributed mainly to the interaction between the 2,2′-azopyridine cap with metal ions. Examination of the spectral data on *trans*-**1** and *trans*-**3** revealed that under the present conditions *trans*-**3** are capable of binding most heavy metal ions while *trans*-**1** interacts selectively with Cu^{2+} (in methanol and DCB–BuOH) and Hg^{2+} (in methanol). In these systems, the π-π^* bands shifted significantly to longer wavelength region (340—350 nm). The *trans*-**1**·Cu^{2+} complex afforded an additional, weak absorption band at around 550 nm only in

Table 1. Influence of heavy metal ions on the spectroscopic properties (30 °C)[a)]

Metal salt	Solvent	$\lambda_{max}(\varepsilon_{max})$			
		trans-**1**	*trans*-**2**	*trans*-**3**	**4**
None	MeOH	323(13200) 460(140)			
None	DCB(91):BuOH(9)	328(12700) 450(220)	325(17300) 440(370)	323(10800) 460(310)	
$CuCl_2$	MeOH	353 555		340	
$CuCl_2$	DCB(91):BuOH(9)	Sh	No	353	No
$HgCl_2$[b)]	MeOH	342		335	
$HgCl_2$	DCB(91):BuOH(9)	No	No	341	No
$CoCl_2$	DCB(91):BuOH(9)	Weak Sh	No	Sh	No
$Ni(NO_3)_2$	DCB(91):BuOH(9)	No	No	330	No
$Pb(OCOCH_3)_2$[c)]	DCB(91):BuOH(9)	No	No	Sh	No

a) [metal salt]$=1.00\times10^{-3}$ M, [**1**, **2**, **3** or **4**]$=2.50\times10^{-5}$ M. "Sh" denotes the shoulder at 350—400 nm. "No" means that the spectrum is scarcely affected by added metal ions. b) [$HgCl_2$]$=0.30$ M. c) [$Pb(OCOCH_3)_2$]$=5.51\times10^{-5}$ M.

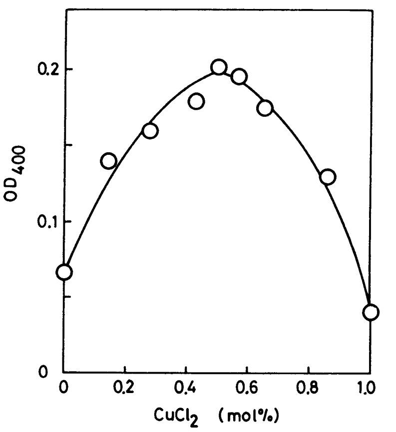


Fig. 2. Continuous variation plots of OD_{400}. 30 °C, methanol (containing 9.1 vol% dioxane), [*trans*-**1**]+[$CuCl_2$]=5.01×10^{-4} M, 0.2 cm cell.

methanol. Since such an absorption band was scarcely detected for the *trans*-**3**·Cu^{2+} complex, the band may arise from the interaction of the thiacrown moiety with Cu^{2+} bound to the azopyridine moiety of *trans*-**1**. In fact, many thiacrown ethers we recently synthesized gave a new absorption band at 500—600 nm in the presence of Cu^{2+}.[22]

The binding of Cu^{2+} to *trans*-**1** was further estimated by a continuous variation method in methanol (Fig. 2). Clearly, the absorbance at 400 nm ascribable to the complex formation provided a maximum at 0.5 mol% of $CuCl_2$, indicating that *trans*-**1** forms the 1 : 1 complex with $CuCl_2$. Here, we tried to determine the association constants (K_t) for *trans*-**1** by a spectroscopic method. They were evaluated by using Eq. 1, which holds for the formation of a 1 : 1 complex under $[\text{metal}]_0 \gg [\textit{trans}\text{-}\mathbf{1}]_0$, where OD_0 and OD are the absorbances of *trans*-**1** in the absence and the presence of metal ions, respectively, and ε is the apparent molar absorption coefficient of the *trans*-**1**·metal complexes.

$$\frac{OD-OD_0}{[\text{metal}]_0}=\varepsilon K_t[\textit{trans}\text{-}\mathbf{1}]_0-K_t OD \qquad (1)$$

In methanol solvent, new absorption maxima appeared on the addition of $CuCl_2$ and $HgCl_2$ at 353 and 342 nm, respectively (Table 1). Thus, the wavelengths at the maximum or near the maximum were used to follow the spectral changes in methanol. In DCB–BuOH mixed solvent, the addition of $CuCl_2$ developed a shoulder at around 400 nm, so that we chose the 380 nm band where the spectral change seemed most apparent. The plots of $[\text{metal}]_0$ *vs*. OD, which showed saturation curves (Fig. 3), were analyzed according to Eq. 1, resulting in good linear relationships between $(OD-OD_0)/[\text{metal}]_0$ and OD with $r>0.98$. We here assume that $HgCl_2$ also forms the 1 : 1 complex with *trans*-**1**. The K_t values were determined from the slopes (*i.e.*, $-K_t$) by least-squares analysis: For $CuCl_2$ $K_t=8660\ M^{-1}$ (methanol) and 686 M^{-1} (DCB-*n*-BuOH); for $HgCl_2$ 18 M^{-1} (methanol).[†]

Metal Ion Catalyses in the Thermal Cis-to-Trans Isomerization. **1**, **2**, and **3** in DCB-*n*-BuOH (9 : 1 by volume) could be isomerized to the *cis*-forms by UV-light irradiation (330 nm<λ<380 nm) without degradation. We found, however, that the *cis* concentration of **2** (azobenzene-capped) at the photostationary state is high (70%), whereas those of **1** (azopyridine-capped) and **3** are only 24 and 18%, respectively. We thus looked for other wavelengths which might improve the *cis* concentrations of **1** and **3**, but failed.

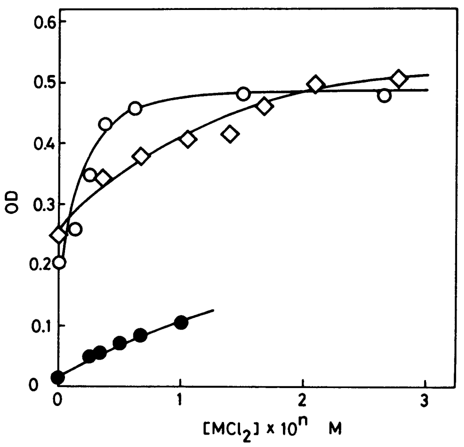


Fig. 3. OD of new absorption bands based on the complex formation with *trans*-**1** plotted against metal ion concentrations (30 °C). ○ $CuCl_2$–MeOH, [*trans*-**1**]=4.14×10^{-5} M, *n* (in abscissa)=3 and OD (in ordinate) is at 353 nm; ● $CuCl_2$–DCB: *n*-BuOH (9:1 by volume), [*trans*-**1**]=3.88×10^{-5} M, *n* (in abscissa)=3 and OD (in ordinate) is at 380 nm; ◇ $HgCl_2$–MeOH, [*trans*-**1**]=4.14×10^{-5} M, *n* (in abscissa) =1 and OD (in ordinate) is at 350 nm.

TABLE 2. INFLUENCE OF HEAVY METAL IONS ON THE FIRST-ORDER RATE CONSTANTS (k, h^{-1}) FOR THE THERMAL CIS-TO-TRANS ISOMERIZATION(30 °C)[a)]

Metal salt	Azo compound		
	1	**2**	**3**
None	0.0765	0.0133	0.0921
$CuCl_2$	0.220	0.308	
$HgCl_2$	0.088	0.020	
$CoCl_2$	0.078	0.023	
$Ni(NO_3)_2$	0.080	0.068	
$Pb(OCOCH_3)_2$	0.075[b)]	0.015[b)]	

a) Solvent: *o*-dichlorobenzene : 1-butanol=91 :9 by volume, [metal salt]=1.00×10^{-3} M, [**1**]=[**3**]=3.87×10^{-5} M, [**2**]=3.24×10^{-5} M. b) [$Pb(OCOCH_3)_2$]=5.51×10^{-5} M.

It is known that some heavy metal ions can catalyze the thermal isomerization of azo-linkages,[2,23] probably because of the stabilization of the transition-state through metal ion coordination to the azo linkages. In Table 2, typical first-order rate constants in the presence of metal ions are summarized. As the rate constant for **1** (0.0765 h^{-1}) is comparable with that for **3** (0.0921 h^{-1}), steric inhibition due to the rigidity arising from the thiacrown moiety is unlikely. Similarly, the rate constant for **2** (0.0133 h^{-1}) is comparable with that for the azobenzene-capped crown ether analog (0.0562 h^{-1} at 40 °C in DCB)[7]. From Table 2, most of the heavy metal ions used are capable of catalyzing the thermal isomerization and, in particular, Cu^{2+} provides the greatest catalytic effect. We thus carried

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[†] 1 M=1 mol dm^{-3}.

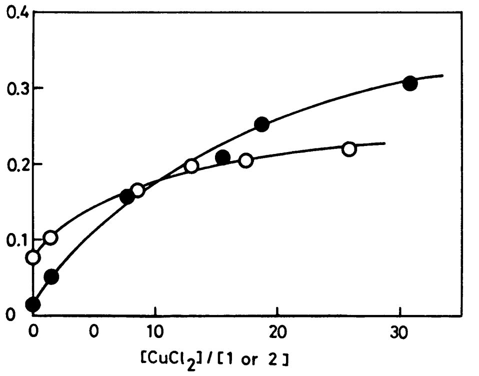

Fig. 4. Influence of added CuCl$_2$ on the thermal cis-to-trans isomerization in DCB–*n*-BuOH (9:1 by volume) at 30 °C. ○ [**1**]=3.87×10^{-5} M; ● [**2**]=3.24×10^{-5} M.

out further detailed investigation on the Cu^{2+} catalysis. In Fig. 4, the first-order rate constants for **1** and **2** are plotted against the Cu^{2+} concentration. The plots for **1** and **2** seem to afford a simple saturation curve.

The Cu^{2+}-catalyzed isomerization in Fig. 4 is expressed by Scheme 1, where K_c is the association constant with the *cis*-forms and k_0 and k are the first-order rate constants in the absence and the presence of metal ions, respectively.

$$\begin{tikzcd} cis\text{-form} + \mathrm{Cu}^{2+} \arrow[r, shift left, "K_c"] \arrow[d, "k_0"] & cis\text{-form}\cdot\mathrm{Cu}^{2+} \arrow[l, shift left] \arrow[d, "k_c"] \\ trans\text{-form} & trans\text{-form} \end{tikzcd}$$

Scheme 1.

K_c and k_c can be evaluated by using Eq 2,[24] which holds for the formation of a 1:1 complex under $[\mathrm{Cu}^{2+}] \gg [cis\text{-form}]$, where $q=(k_c/k_0)-1$ and k_c is the first-order rate constant for the complex.

$$\frac{k_0}{k-k_0} = \frac{1}{qK_c}\cdot\frac{1}{[\mathrm{Cu}^{2+}]} + \frac{1}{q} \tag{2}$$

From the plots of $k_0/(k-k_0)$ against $[\mathrm{Cu}^{2+}]_0^{-1}$, we determind $(qK_c)^{-1}$ (slope) and q^{-1} (intercept) by the least-squares procedure ($r>0.99$). Thus, K_c and k_c were calculated from these two terms: $K_c=2190$ M^{-1} and $k_c=0.294$ h^{-1} for *cis*-**1**: $K_c=1726$ M^{-1} and $k_c=0.472$ h^{-1} for *cis*-**2**.

The rate values show that the rate constants for the Cu^{2+}-complexes of *cis*-**1** and *cis*-**2** are greater by 3.8-fold and 34.5-fold, respectively, than those for the uncomplexed *cis*-forms. On the other hand, the K_c value for *cis*-**1** is greater by 3.2-fold than the K_t value for *trans*-**1**. Previously, we estimated the K_c value for the azopyridine-capped crown ether analog (**6**) from a similar kinetic method.[12] In **6**, the azopyridine is the main association site with Cu^{2+}, so that we considered the K_c to be the true association constant with the *cis*-form. In **1**, however, one must take the another interaction with the thiacrown moiety (at least partially) into account which would not be reflected by the kinetics. Thus, the K_c values determined here mainly reflect the interaction with the azo moietics and should be considered to be the "kinetic" association constants.

Solvent Extraction of Heavy Metal Ions. The binding ability of **1**, **2**, and **4** was estimated by solvent extraction of heavy metal ions from water to an organic phase (DCB: *n*-BuOH=4:1 by volume). We employed picrate ion (Pic) which is one of the most convenient counteranions for solvent extraction. In the extraction of Cu^{2+} and Hg^{2+}, however, the aqueous phase after the treatment gave an absorption band at around 350 nm (*vide supra*), which partially overlapped with the absorption band of picrate ion. We thus employed Methyl Orange (MO: λ_{max} 466 nm) for Cu^{2+} and Hg^{2+}. To make all the extraction data comparable, we determined the extractability (Ex%) of Hg^{2+} with picrate ion by correcting the 350 nm band, but the accuracy of the Hg^{2+}-picrate system must be somewhat inferior to others. The results, together with the detailed extraction conditions, are summarized in Table 3.

The examination of Table 3 reveals that (i) except for Hg^{2+}, **4** generally acts as a poor ligand for heavy metal ions, (ii) Hg^{2+} is bound not only to **4** but also to **1** and **2**, and the Ex%'s for **1** (but not so much for **2**) are improved by UV-light irradiation, (iii) neither **2** nor **4** binds Cu^{2+} appreciably, indicating that the small Ex% of *trans*-**1** for Cu^{2+} is probably due to the interaction with the azopyridine moiety, (iv) most significantly, the Ex% of **1** for Cu^{2+} dramatically enhanced by UV-light irradiation (5.9%→93.9%). The binding ability of **4** with Hg^{2+} can be rationalized either by the

TABLE 3. INFLUENCE OF PHOTOIRRADIATION ON THE EXTRACTION OF HEAVY METAL IONS TO THE ORGANIC PHASE(*o*-DICHLOROBENZENE: 1-BUTANOL=4:1 BY VOLUME) WITH **1**, **2**, AND **4** AT 30 °C[a)]

Crown	Counteranion	Extracted counteranion/%				
		Cu^{2+}	Hg^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}
trans-**1**	Pic		18	1.7	0	5.5
	MO	5.9	13.8			
Photoirradiated **1**[b)]	Pic		37	1.7	2.4	5.5
	MO	93.9	28.1			
trans-**2**	Pic		0—3	0	0	0
	MO	0	6.8			
Photoirradiated **2**[c)]	Pic		0—3	0	2.7	1.4
	MO	0	8.2			
4	Pic		22	0	1.2	0
	MO	0	30.5			

a) Extraction conditions: aqueous phase, [metal salt]=0.010 M, [Pic(picric acid)]=1.00×10^{-4} M or [MO(Methyl Orange)]=8.90×10^{-5} M, pH 4.2—4.3 with Et$_4$NOH(*ca.* 10^{-4} M); organic phase, [crown]=1.00×10^{-3} M. b) *cis*-Form 27%. c) *cis*-Form 53%.

general affinity between sulfur and Hg^{2+} or by the relatively large Hg^{2+} radius. The ion radius of Hg^{2+} (1.10—1.16 Å) is comparable with that of Na^+ (1.13—1.16 Å), whereas except for that of Pb^{2+} (1.32—1.63 Å), those of other metal ions (0.76—0.84 Å) are comparable with that of Li^+ (0.73—0.88 Å). Anyway, the absence of the significant affinity for other heavy metal ions (even for Cu^{2+}) is unexpected. Recently, the crystal structure of 1,4,7,10,13,16-hexathiacyclooctadecane (hexathia analog of 18-crown-6) was reported by Harman *et al.*[20] They found the sulfur atoms in a gauche configuration in the thiacrown ether at the position where the corresponding oxygens in the conventional crown ether would be anti. As a result, the thiacrown ether has both endo- and exodentate-sulfur atoms, resulting in a tendency for bridging two metal ions rather than chelating to one as conventional crown ethers do. If **4** adopts a similar conformation in solution (and probably it does[21]), it is unlikely that the four sulfur atoms coordinate to one metal ion. The examination of the CPK model suggests that, assuming *sp*^{3} for the amide nitrogens, the boat-form of **4** in which the four sulfur atoms can coordinate to one metal ion is highly crowded, whereas the crowding is somewhat relaxed in the chair-form in which only two sulfur atoms can coordinate to one metal ion. It seems to us, therefore, that the coordination of the four sulfur atoms of the N_2S_4 crown to one metal would be energetically unfavorable. The low association tendency of **2** with Hg^{2+} relative to **4** would be ascribed to further deformation of the thiacrown ring by the azobenzene cap. Further details of the relation between the crown structure and the metal selectivity will be described elsewhere.[21]

Finally, we would like to consider the photoirradiation effect on **1**. Based on the spectral change in the azopyridine moiety (Fig. 3), we estimated the association constants of *trans*-**1** in methanol for Cu^{2+} and Hg^{2+} to be 8660 and 18 M^{-1}, respectively. Contrary to these association constants, Hg^{2+} gave the greater Ex% values than Cu^{2+} (Table 3). The discrepancy is accommodated by taking the contribution of the thiacrown moiety into account: that is, the spectroscopically-determined association constants mainly reflect the interaction with the azoarene caps, whereas the interaction with the thiacrown moiety, which is not detected by spectroscopy, is expected for Hg^{2+}.

For the Hg^{2+}-binding to *trans*-**1**, one may consider the cooperative coordination of the thiacrown and the azopyridine-cap, because the Ex% of *trans*-**1** (Pic 18%, MO 13.8%) is significantly higher than that for *trans*-**2** (Pic 0—3%, MO 6.8%). Interestingly, we found that the Ex% of **1** for Cu^{2+} is remarkably enhanced by UV-light irradiation and a similar improvement is also seen for Hg^{2+}. When taking the low *cis* concentration (27%) in the extraction solution into account, the improvement is quite dramatic. The results strongly suggest that in *cis*-**1** the thiacrown and the azopyridine cap cooperatively build a ligation site with a strong coordination ability. At present, we can only speculate on the structure from the CPK model: the azopyridine-cap in *trans*-**1** stands vertically over the thiacrown ether plane.[21] whereas that in *cis*-**1** is almost parallel to the thiacrown plane. Therefore, one (or two) pyridine nitrogen in the *cis*-cap is directed towards two adjacent sulfur atoms in the thiacrown ring. In this case, the metal cation undergoes the cooperative coordination both from the pyridine nitrogen and the sulfur atoms. Although further study is needed to clarify the structure of the binding site, the results indicate that **1** has a dramatic photoresponsiveness in the binding to Cu^{2+}.

TABLE 4. PHOTOCONTROL OF Cu^{2+} TRANSPORT ACROSS A LIQUID MEMBRANE (30 °C)[a]

Condition	Transport rate/mol h^{-1}	
	Method I[b]	Method II[c]
Dark	1.4×10^{-8}	*ca.* 2×10^{-10}
UV light[d]	6.3×10^{-9}	1.2×10^{-9}
UV and visible lights[e]	7.0×10^{-9}	1.2×10^{-9}

a) The membrane phase (10 ml, *o*-dichlorobenzene: 1-butanol=4:1 by volume) : [**1**]=3.00×10^{-4} M. b) IN aqueous phae: [$CuCl_2$]=0.010 M, [picrate]=1.00×10^{-3} M, [CH_3COONH_4]=0.010 M. OUT aqueous phase: water. The rate was estimated from the absorption maximum of picrate ion. c) IN aqueous phase: [$CuCl_2$]=0.010 M. OUT aqueous phase: water. The rate was estimated from the absorption band of Cu^{2+}-PAN complex (see Experimental). d) The membrane phase was irradiated through a color glass filter (330 nm<λ<380 nm) for 10 min at intervals of 60 min. e) UV(10 min)→dark(50 min)→visible(10 min)→dark (50 min)→repeated.

Photocontrol of Cu^{2+} Transport. Since the large difference in Ex% was found for the extraction of Cu^{2+} with **1**, we attempted the photocontrol of Cu^{2+} transport across a liquid membrane at 30 °C. The results are summarized in Table 4.

When picrate ion as a counteranion was added to the IN aqueous phase (method I), the rate under UV-light irradiation was smaller than that in the dark. We observed, however, that in the transport under UV-light irradiation the membrane phase rapidly colors yellow. This indicates that Cu^{2+}-picrate salt, which is efficiently extracted with *cis*-**1** into the membrane phase, is not released to the OUT aqueous phase. We found that *cis*-**1** can be isomerized to *trans*-**1** (half-life, *ca.* 2 min at 30 °C) by irradiation of a 200-W tungsten lamp even in the presence of Cu^{2+} ion. Therefore, we alternately irradiated the membrane phase by UV and visible lights in order to facilitate the ion-release by the isomerization to *trans*-**1**, but the rate was scarcely improved.

We previously experienced that hydrophobic counteranions facilitate the ion-extraction but rather decelerate the rate of the ion-release from the membrane phase.[8] We thus carried out the Cu^{2+} transport without any hydrophobic counteranions (method II). Although the absolute values of the Cu^{2+} transport were relatively small, the rate under UV-light irradiation was significantly enhanced compared with that in the dark. Visible light had no effect on the transport rate. Probably, the rate enhancement in method II is attributed to the improved extraction efficiency by photoisomerized *cis*-**1**. In other words, the extraction of Cu^{2+} to the membrane phase from the IN aqueous phase is rate-determining through the transport system.

Conclusions. In this article we have indicated that the concept to photocontrol the chemical and physical functions of a crown ether family can be extended to a thiacrown ether family which acts as receptors for heavy metal ions. Being different from "inactive" alkali metal ions, some kinds of heavy metal ions show various catalytic activities as seen in metalloproteins. We thus consider that the catalytic activities of heavy metal ions could be photocontrolled by use of thiacrown ethers or azacrown ethers as photoresponsive mediators. Although the frameworks of the photoresponsive thiacrown ethers are still to be improved, the results indicate that the binding ability towards heavy metal ions can be controlled, in principle, by switching the light source on and off. Further investigation is currently in progress in this laboratory.

Experimental

Materials. The preparation of 6,6′-bis(morpholinocarbonyl)-2,2′-azopyridine (**3**) was described previously.[12]

1,4,10,13-Tetrathia-7,16-diazacyclooctadecane (N_2S_4 crown) was prepared from equimolar amounts of 1,2-ethanedithiol and bis(2-bromoethyl)amine hydrobromide in ethanol in the presence of sodium ethoxide; mp 128—129 °C (lit,[25] 124 °C), yield 14%, M^+ 326. ^{1}H-NMR ($CDCl_3$, δ): NH, 2.03, 2H; NCH_2 and SCH_2, 2.80, 24H. Found: C, 43.92; H, 7.97; N, 8.53%. Calcd for $C_{12}H_{26}N_2S_4$: C, 44.13; H, 8.02; N, 8.58%.

Compound **1** was synthesized from equimolar amounts of the N_2S_4 crown and 6,6′-bis(chloroformyl)-2,2′-azopyridine according to the high dilution method in chlorobenzene in the presence of excess triethylamine. The procedure is essentially similar to that described for the synthesis of *trans*-**6**[12]: mp 249—251 °C (dec), yield 33%, M^+ 562. ^{1}H-NMR ($CDCl_3$, δ): N_2S_4 crown protons, 2.4—4.0 and 4.4—4.8, 22H and 2H, respectively; pyridine protons, 7.8—8.2, 6H. Found: C, 51.16; H, 5.23; N, 14.80%. Calcd for $C_{24}H_{30}N_6S_2O_4$: C, 51.22; H, 5.37; N, 14.93%.

Compound **2** was synthesized from equimolar amounts of the N_2S_4 crown and 3,3′-bis(chloroformyl)azobenzene in chlorobenzene in the presence of excess triethylamine. The product was purified by a TLC method (silica gel and chloroform); mp 256—258 °C, yield 24%, M^+ 560. IR (KBr disk): $\nu_{C=O}$ 1635 cm^{-1}. ^{1}H-NMR (Me_2SO-d_6, δ): N_2S_4 crown protons, 2.6—3.4 and 3.6—4.0, 20H and 4H, respectively; benzene protons, 7.64 (4H), 7.96 (2H), and 8.12 (2H). Found: C, 55.51; H, 5.74; N, 10.00%. Calcd for $C_{26}H_{32}N_4O_2S_4$: C, 55.68; H, 5.75; N, 9.99%.

Compound **4** was obtained by the treatment of the N_2S_4 crown with benzoyl chloride in benzene in the presence of excess triethylamine. The product was recrystallized from benzene; mp 105—107 °C, yield 51%, M^+ 534. Found: C, 58.16; H, 6.51; N, 4.95%. Calcd for $C_{26}H_{34}N_2O_2S_4$: C, 58.39; H, 6.41; N, 5.24%.

Miscellaneous. The method of solvent extraction and the rate determination of thermal cis-to-trans isomerization were described previously.[7—12] As a UV-light source for the trans-to-cis isomerization, a 100-W high-pressure Hg-lamp with a color glass filter (330 nm$<\lambda<$380 nm) was used.

Transport of Cu^{2+} across a liquid (DCB: n-BuOH=4:1 by volume) membrane with the aid of **1** was examined with a U-tube. The U-tube (10 mm diameter) was immersed in a thermostated (30 °C) water bath. The transport system consisted of 10 ml of the liquid membrane and IN and OUT aqueous phases (5 ml each). The membrane phase was stirred at a constant speed (180 rpm). When required, the tube was irradiated either by a 100-W high-pressure Hg-lamp or by a 200-W tungsten lamp. In method I, the rate of Cu^{2+} transport was estimated from the absorption maximum of picrate ion. In method II, the aliquots of the OUT aqueous phase were treated with 1-(2-pyridylazo)-2-naphthol (PAN) and the rate was determined from the absorption band at 550 nm using a calibration curve. Further details of the transport methods are recorded in footnotes to Table 4.

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