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Photoresponsive Crown Ethers. 13. Synthesis of Photoresponsive NS_2O Crown Ethers and Application of the Cu(I) Complexes to O_2-Binding

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Photoresponsive crown ethers with heavy metal affinity were synthesized: They are the NS_2O crowns bound to photofunctional azobenzene at 4,4′-positions *via* X(CH_2 or CO) (**1**(X=CH_2) and **1**(X CO), respectively). They efficiently extracted heavy metal ions from aqueous phase to organic(dichloromethane) phase. The continuous variation method established that both *trans*-**1** and photoisomerized *cis*-**1** bind two Cu(II) ions forming 1:1 metal/NS_2O crown complexes. The *trans*-**1**(X=CH_2)·$Cu(I)_2$ complex was irreversibly oxidized by O_2 to the $Cu(II)_2$ complex, whereas the *cis*-**1**(X=CH_2)·$Cu(I)_2$ complex bound O_2 in a partly reversible manner like Osborn's complex. Thus, a photoinduced change in the Cu(I)·····Cu(I) interatomic distance is responsible for the stability of the O_2 complex. These results show that the extraction of heavy metal ions and the O_2-complexation can be controlled by light with the mediation of photoresponsive NS_2O crown ethers.

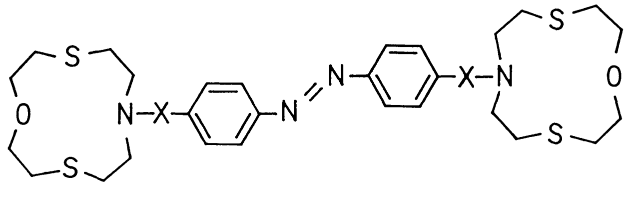
Chemical substances which exhibit photoinduced structural changes are potential candidates not only for the storage of light energy but also as mediators for the conversion of light into other forms of energy. Further, if the structural changes occurring in the photoresponsive chromophores can be transmitted 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 photoregulated ion-extraction and membrane transport.[7—12] It was shown that in these photoresponsive crown ethers, not only the binding ability but also the ion selectivity was markedly changed by photoirradiation.[7—16] Two different techniques have been developed 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. 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. It is known that a thiacrown family exhibits a significant 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. As a related system, Blank *et al.*[19] recently reported the photoresponsive binding of Zn(II) to 4,4′-bis(α-iminodiacetic acid) azotoluene. We considered that in photoresponsive thiacrown ethers, the heavy metal complexes would have affinity toward small molecules such as O_2 and CO, and thus the affinity might be also photocontrolled. With these objects in view, we synthesized **1**—**3** and evaluated the reversible O_2 binding to the Cu(I) complexes.

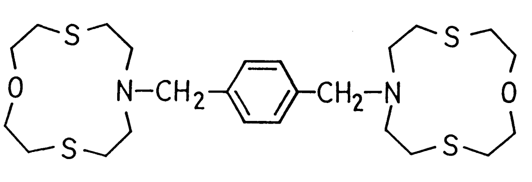
Experimental

Materials. 1-Oxa-4,10-dithia-7-azacyclododecane (NS_2O crown) was prepared from equimolar amounts of 3-oxapentane-1,5-dithiol and 1,5-dibromo-3-azapentane hydrobromide in absolute ethanol in the presence of sodium ethoxide: Mp 64—67 °C (lit,[20] 64 °C), yield 31.5%. $M^+(m/z)$: 207. IR (Nujol): ν_{NH} 3255, 3230 cm^{-1}, ν_{C-O-C} 1280, 1115 cm^{-1}. Found: C, 46.05; H, 8.36; N, 6.67; S, 30.70%. Calcd for $C_8H_{17}NOS_2$: C, 46.33; H, 8.26; N, 6.75; S, 30.92%.

4,4′-Bis(1-oxa-4,10-dithia-7-azacyclododec-7-ylmethyl)azobenzene **1**(X=CH_2)) was synthesized from the NS_2O crown and 4,4′-bis(chloromethyl) azobenzene in acetonitrile in the presence of excess powdered K_2CO_3. The detailed procedure is essentially similar to that described for the synthesis of the crown ether analogue.[9] The product was isolated by a TLC method (silica gel and chloroform–ethanol (10:1 by volume)) and finally recrystallized from benzen-ligroin: Mp 117—118 °C, yield 43%. $M^+(m/z)$: 620. ^{1}H-NMR ($CDCl_3$, δ): SCH_2 and NCH_2 in the rings, 2.63—3.10, 24H; OCH_2 and $ArCH_2N$, 3.70—3.90, 12H; 3,3′-ArH, 7.44, 4H; 2,2′-ArH, 7.82, 4H.



trans-**1**(X=CH_2 or CO)



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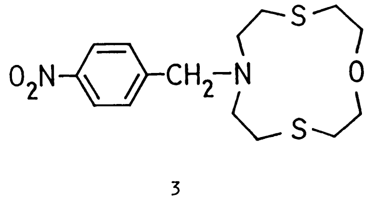

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Found: C, 57.83; H, 7.12; N, 8.87; S, 20.50%. Calcd for $C_{30}H_{44}N_4O_2S_4$: C, 58.03; H, 7.14; N, 9.02; S, 20.65%.

4,4′-Bis(1-oxa-4,10-dithia-7-azacyclododec-7-ylcarbonyl)azobenzene (**1**(X=CO)) was synthesiszed from the NS_2O crown and 4,4′-*bis(chloroformyl)azobenzene* in benzene in the presence of excess triethylamine. A similar procedure was described previously for the synthesis of the crown ether analogue.[9] The product was isolated by a TLC method(silica gel and chloroform–ethanol (10:1 by volume)) and recrystallized from benzene–ether: Mp 246—247 °C, yield 54%. M^+(*m/z*): 648. ^{1}H-NMR($CDCl_3$, δ): SCH_2, 2.5—3.2, 16H; OCH_2 and NCH_2 in the rings, 3.5—4.2, 16H; 3,3′-ArH, 7.52, 4H; 2,2′-ArH, 7.97, 4H. Found: C, 55.12; H, 6.21; N, 8.66; S, 19.56%. Calcd for $C_{30}H_{40}N_4O_4S_4 \cdot 0.25\ H_2O$: C, 55.15; H, 6.25; N, 8.57; S, 19.63%.

1,4-Bis(1-oxa-4,10-dithia-7-azacyclododec-7-ylmethyl)benzene (**2**)was prepared from the NS_2O crown and α,α′-dibromo-*p*-xylene in acetonitrile in the presence of excess powdered K_2CO_3. The method is analogous to that employed for the synthesis of **1**(X=CH_2). The product was isolated by a TLC method (silica gel and chloroform–ethanol (10:1 by volume)) and recrystallized from benzene–petroleum ether: Mp 109—110 °C, yield 34%. M^+(*m/z*): 516. ^{1}H-NMR($CDCl_3$, δ): SCH_2 and NCH_2 in the rings, 2.65—3.05, 24H; $ArCH_2N$, 3.64, 4H; OCH_2, 3.78, 8H; ArH, 7.26, 4H. Found: C, 55.84; H, 7.92; N, 5.35; S, 24.65%. Calcd for $C_{24}H_{40}N_2O_2S_4$: C, 55.78; H, 7.80; N, 5.42; S, 24.81%.

N-(*p*-Nitrobenzyl)-1-oxa-4,10-dithia-7-azacyclododecane (**3**-(X=NO_2)) was synthesized from the NS_2O crown and *p*-nitrobenzyl chloride in acetonitrile in the presence of excess powdered K_2CO_3 in a manner similar to that described previously.[9] After TLC separation (silica gel and chloroform–ethanol (10:1 by volume)), the product was recrystallized from benzen–ligroin: Mp 133—134 °C, yield 60%. M^+(*m/z*): 342. ^{1}H-NMR($CDCl_3$, δ): SCH_2 and NCH_2 in the ring, 2.61—3.00, 12H; OCH_2 and $ArCH_2N$, 3.72, 6H; *o*-ArH, 7.44, 2H; *m*-ArH, 8.08, 2H. Found: C, 52.51; H, 6.54; N, 8.19; S, 18.84%. Calcd for $C_{15}H_{22}N_2O_3S_2$: C, 52.61; H, 6.47; N, 8.18; S, 18.72%.

N-Benzyl-1-oxa-4,10-dithia-7-azacyclodedecane (**3**(X=H)) was similarly synthesized from the NS_2O crown and benzyl chloride: Mp 108—110 °C, yield 65%. Found: C, 60.66; H, 7.80; N, 4.77%. Calcd for $C_{15}H_{23}NOS_2$: C, 60.56; H, 7.79; N, 4.71%.

Miscellaneous. The methods 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 500 W high-pressure Hg-lamp with a colour glass filter (330 nm<λ<380 nm) was used. In the solvent extraction of Cu(II) with **1**(X=CH_2), we measured the concentrations of picrate ion (by absorption spectroscopy) as well as Cu(II) (by atomic absorption spectroscopy) extracted into the dichloromethane phase. It was found that the concentration of Cu(II) is very close to that of picrate ion, indicationg that Cu(II) is extracted as Cu·picrate·Cl.

The O_2-absorption experiments of **1**—**3** were carried out by using a Thunberg cuvette. The thiacrown ether dissolved in propylene carbonate (PC) was placed in the bottom cell of the Thunberg cuvette and $[Cu(CH_3CN)_4]BF_4$ in PC was deposited in the side arm. After N_2-substitution by repeating a freezing-and-thawing, two solutions were mixed and subjected to spectral measurement at 30 °C. At this time, there was no absorption maximum at around 700 nm. An O_2 stream was introduced into the cell for 5 min at 40—50 °C, and the spectrum was recorded at 30 °C. Then, the mixture was evacuated at 1.0 mmHg for 1h at 70 °C (for *cis*-**1**, for 20 min at 40 °C in order to suppress the cis-to-trans thermal isomerization). The fraction of the oxygenation product was estimated from the decrease in the absorption band at around 700 nm.

Results and Discussion

Spectral Examination of Metal-crown Interactions. The spectroscopic properties of *trans*-**1** are summarized in Table 1. Since the π-π* band of *trans*-**1** and the n-π* band of *cis*-**1** are clearly separated, one may expect that trans-to-cis and cis-to-trans isomerizations are controlled by irradiation of UV and visible light, respectively. Under UV-light irradiation, the absorbance of the π-π* band decreased and that of the n-π* band increased gradually with tight isosbestic points and finally reached a photostationary state. The cis concentration at the photostationary state was estimated (Table 1) by the decrease in the OD of the absorption maxima, assuming that the OD of *cis*-**1** at these wavelengths is negligible in comparison with that of *trans*-**1**. The cis-forms of **1**(X=CH_2) and **1**(X=CO) isomerized thermally to the trans-forms with *k*(first-order rate constant)=0.0347 and 0.0958 h^{-1}, respectivery, at 30 °C in dichloromethane. Under visible light irradiation (200 W tungsten-lamp, 15 s at intervals of 10 min), the isomerization reaction was speeded up to 1.24 and 4.90 h^{-1}, respectively.

The addition of $CuCl_2$ to a dichloromethane solution of **1**(X=CH_2) gave rise to a new shoulder at 390—420 nm region as well as to an absorption maximum at around 700 nm. Since a similar spectral change was observed for **2**[18] and **3**, these absorption bands are attributed to the $CuCl_2$–NS_2O crown interaction. On the other hand, the spectral change of **1**(X=CO) occurred to a relatively smaller extent. We chose 390 nm to conduct the continuous variation method of *trans*- and *cis*-**1**(X=CH_2), because this band is relatively stronger than the 700 nm band and corresponds to an isosbestic point of the cis-trans isomerism. Thus, one may estimate the extent of the Cu(II)-crown association directly from the observed OD without regard to the cis percentage. Figure 1 shows that the maxima appear at $[CuCl_2]/[\mathbf{1}(X{=}CH_2)]=2$, indicating that both *trans*- and *cis*-**1**(X=CH_2) form the 2:1 copper/**1** complexes. This means that each NS_2O crown binds one Cu(II) and the composition is not changed by the photoisomerization.

Metal Ion Catalyses in the Thermal Cis-to-Trans Isomerization. We have described that the photoinduced cis-trans interconversion of **1** occurs reversibly. It is known that some heavy metal ions can catalyze the thermal isomerization of azo-linkages[12,21,22] 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. From Table 2, most of the heavy metal ions used are capable of catalyzing the thermal isomerization and, in particular, Cu(II) provides the greatest catalytic effect. We thus carried out further detailed investigation on the Cu(II) catalysis. In Fig. 2, the first-order rate constants for **1** are plotted against the Cu(II) concentration. The plots for **1** give a biphasic dependence which consists of no rate increase at $[CuCl_2]/[\mathbf{1}]<2$ and marked rate increase at $[CuCl_2]/[\mathbf{1}]>2$. The result suggests that Cu(II) is selectively bound to the two NS_2O crown ethers in the first phase and the interaction with the azo

TABLE 1. λ_{max} AND ε_{max} OF *trans*-**1**, CIS/TRANS RATIO AT THE PHOTOSTATIONARY STATE, AND FIRST-ORDER RATE CONSTANTS(k) FOR THERAMAL ISOMERIZATION[a)]

Crown	Solvent	$\lambda_{max}(\varepsilon_{max})$	cis/trans[b)]	$k^{c)}/h^{-1}$
1(X=CH_2)	CH_2Cl_2	325(20000) 436(520)	68/32	0.0347
1(X=CH_2)	PC[d)]	330(22900) 440(770)	72/28	
1(X=CO)	CH_2Cl_2	330(28600) 445(780)	49/51	0.0958
1(X=CO)	PC[d)]	330(29000) 435(870)	63/37	

a) 30 °C. b) It takes about 10 min for 2.50×10^{-5} M(1M=1 mol dm^{-3}) of the crown solutions to reach the photostationary state by light from a 500 W high-pressure Hg-lamp through a glass filter (330 nm<λ<380 nm). c) CH_2Cl_2 containing 3.1 vol% of ethanol. d) Propylene carbonate.

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	**1**(X=CH_2)	**1**(X=CO)
None	0.0347	0.0958
$CuCl_2$	1.15	0.594
$HgCl_2$	0.067	0.126
$CoCl_2$	0.033	0.358
$Ni(OCOCH_3)_2$	0.033	0.094

a) Solvent: dichloromethane: ethanol=96.9: 3.1 by volume, [metal salt]=1.00×10^{-4} M. [**1**]=2.50×10^{-5} M.

linkage which is associated with the rate enhancement begins at [$CuCl_2$]/[**1**]>2. This is second evidence that each NS_2O crown binds one Cu(II).

Solvent Extraction of Heavy Metal Ions. In Table 3, the influence of photoirradiation on the extractability of **1** and related compounds **2** and **3**(X=NO_2) is summarized. **3**(X=NO_2) was mainly used because of the analogy between NO_2 and azobenzene as electron-withdrawing substituents. It is seen from extractabilities (Ex%) of **2** and **3**(X=NO_2) that Hg(II) has a contrasting characteristic to other metal ions: Cu(II), Co(II), Ni(II), and Pb(II) give the smaller Ex% in **3**(X=NO_2) than in **2**, while the Ex% for Hg(II) is slightly enhanced in **3**(X=NO_2). The result means that the basicity of the nitrogen in the NS_2O crown ring plays a decisive role in the complexation with the four metal ions, while the affinity with the sulfur atoms is most important in the Hg(II)-binding. Most important in Table 3 is the fact that the Ex% for **1** is scarcely affected by photoirradiation. This means that two NS_2O crown rings act rather independently. We previously examined the photoresponsive behaviors of 4,4′-bis(1,4,7,10-tetraoxa-13-azacyclopentadec-13-ylmethyl)-azobenzene and 4,4′-bis(1,4,7,10-tetraoxa-13-azacyclopentadec-13-ylmethyl)azobenzene and 4,4′-bis(1,4,7,10-tetraoxa-13-azacyclopentadec-13-ylcarbonyl)azobenzene (monoaza-15-crown-5 analogues of **1**(X=CH_2) and **1**(X=CO)).[9)] The photoisomerized cis-forms of these

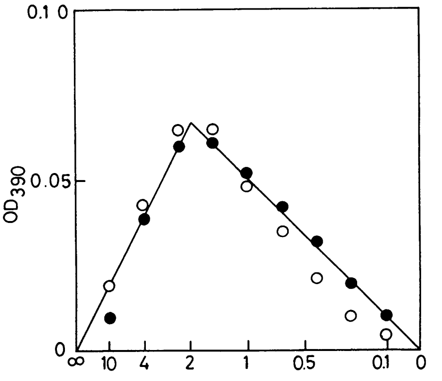


Fig. 1. Continuous variation plots of OD_{390}. 30 °C, CH_2Cl_2 (containing 3.1 vol% ethanol), [**1**(X=CH_2)]+[$CuCl_2$]=2.50×10^{-5} M.
● *trans*-**1**(X=CH_2); ○ Photoirradiated **1**(X=CH_2) where cis/trans=68/32.

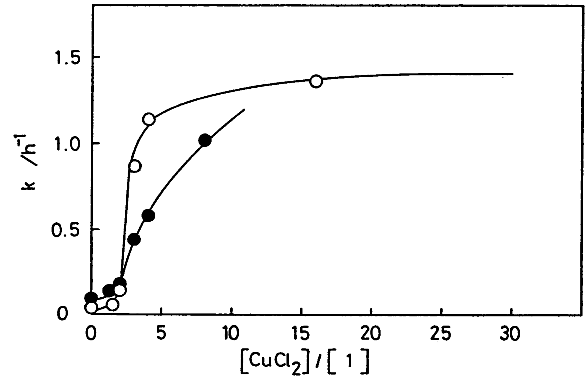
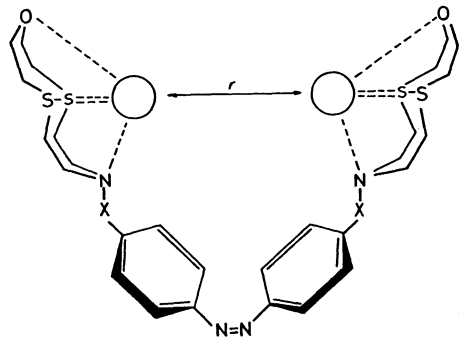


Fig. 2. Influence of added $CuCl_2$ on the thermal cis-to-trans isomerization (30 °C). ○ and ● [**1**(X=CH_2)]=[**1**(X=CO)]=2.50×10^{-5} M, (respectively) in CH_2Cl_2 containing 3.1 vol% ethanol.

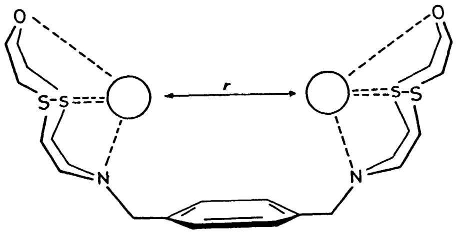
TABLE 3. INFLUENCE OF PHOTOIRRADIATION ON THE EXTRACTION OF HEAVY METAL IONS TO THE ORGANIC PHASE (DICHLOROMETHANE) WITH **1**, **2**, AND **3**(X=NO_2) AT 30 °C[a)]

Crown	Extracted picrate/%				
	Cu^{2+}	Hg^{2+}	Co^{2+}	Ni^{2+}	Pb^{2+}
trans-**1**(X=CH_2)	77.6	78.2	17.9	20.3	38.5
Photoirradiated **1**(X=CH_2)[b)]	86.4	84.4	20.4	28.0	35.1
trans-**1**(X=CO)	14.2	18.6	13.7	12.7	
Photoirradiated **1**(X=CO)[c)]	15.0	19.6	14.7	13.1	
2	100	74.0	22.8	25.6	73.9
3(X=NO_2)	10.2	91.4	14.2	14.9	17.5

a) Extraction conditions: aqueous phase, [metal salt]=0.010 M, [picric acid]=1.00×10^{-4} M, pH4.0—4.1 with Et_4NOH(*ca.* 10^{-4} M); organic phase, [**1** or **2**]=6.06×10^{-4} M or [**3**(X=NO_2)]=1.21×10^{-3} M. Chloride salts are used except Pb^{2+}(acetate salt). b) cis-Form 76%. c) cis-Form 49%.



cis-1(X=CH$_2$)·Cu(I)$_2$ complex



2·Cu(I)$_2$ complex

Fig. 3. Ear-muff conformation of the Cu(I) complexes of **2** and *cis*-**1**(X=CH$_2$).

crown ethers bound Rb$^+$ and Cs$^+$ with relatively large ion radii more efficiently than the trans-forms, but no significant difference could be seen for Na$^+$. One may presume, therefore, that the caity constructed by two intramolecular crown rings is pretty large. The ion radius of Cu(II) (0.76—0.87 Å) is much smaller than that of Na$^+$ (1.13—1.16 Å). Provided that the cis-forms of **1**(X=CH$_2$) and **1**(X=CO) construct the cavity similar to these crown ethers, it is very likely that two NS$_2$O crown rings in *cis*-**1** cannot coordinate to one Cu(II) ion cooperatively.

The results indicate, together with the result of the continuous variation experiment (Fig. 1), that both *trans*- and *cis*-**1** form the 2:1 (*i.e.*, 1:1 metal/crown) complexes with metal ions. Based on the foregoing informations, we conducted photocontrol studies of reversible O$_2$ adsorption to the **1**(X=CH$_2$)·Cu(I)$_2$ complex.

Oxygen Adsorption to the Cu(I)-complexes of 1, 2, and 3. The preparation of complexes which contain two transition metal ions separated by distances of 3.5—6 Å has been of much concern in recent years. Interest in such complexes stems from their potential for the functionality to flank small molecules in a sandwich manner as a so-called cascade complex.[23] In particular, the systems which are capable of binding O$_2$ or N$_2$ are of special interest because of their relevance to biological systems, such as haemocyanin, hemerythrin, and perhaps nitrogenase. There are several precedents for bi-metallic copper complexes which bind O$_2$ or CO, although the revesibility is not satisfactory yet.[18,24–26] Osborn *et al.*[18] reported **2**·Cu(I)$_2$ complex, in which the oxygenation-deoxygenation sequence in the solid state can be repeated several times although the reversibility in solution is not as complete as in the solid state.

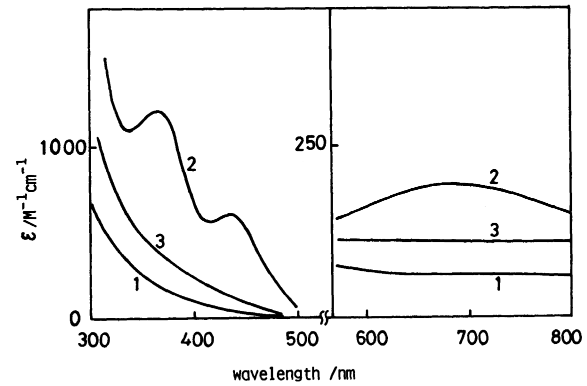


Fig. 4. Spectral change for the reaction of **2**·Cu(I)$_2$ (1.00×10^{-3} M) and O$_2$ in propylene carbonate. **2**·Cu(I)$_2$; was prepared from 1.00 mM of **2** and 4.00 mM of [Cu(CH$_3$CN)$_4$]BF$_4$. 1, **2**·Cu(I)$_2$; 2, after introduction of O$_2$; 3, after evacuation.

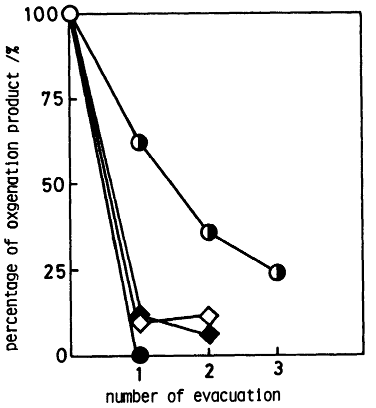


Fig. 5. Reversibility in O$_2$-binding in propylene carbonate.
◐ [**2**]=1.00×10^{-3} M, [Cu(CH$_3$CN)$_4$·BF$_4$]=4.00×10^{-3} M; ◇ [**3**(X=NO$_2$)] and ◆ [**3**(X=H)]=1.00×10^{-3} M, [Cu(CH$_3$CN)$_4$·BF$_4$]=3.83×10^{-3} M; ● [*trans*-**1**(X=CH$_2$)]=2.50×10^{-4} M, [Cu(CH$_3$CN)$_4$·BF$_4$]=2.66×10^{-3} M.

It occurred to us that as the ability of the bi-metallic complexes to bind O$_2$ is largely governed by the distance between two metal ions, a change in this would directly induce a change in the stability of the O$_2$-complex. Molecular models show that for preferred ear-muff conformation of **2** (Fig. 3) the two Cu(I) ions are separated by 3.5—5 Å: the later X-ray study of the **2**·Cu(I)$_2$·OH complex gave a distance of 3.384 Å.[27] We estimated on the basis of the CPK model building that the Cu(I)···Cu(I) interatomic distance in the *cis*-**1**(X=CH$_2$)·Cu(I)$_2$ complex is in the range 3.0—9.0 Å. The wide distance range is due to the conformational freedom of the thiacrowns. The ear-muff conformation of **1**(X=CH$_2$) and **2** may not be the stable one, but one may expect for the O$_2$-complexes the "lock-in" effect[8,16] of O$_2$ that enforces the ear-muff conformation. Therefore, the Cu(I) complex of **1**(X=CH$_2$) and **2** may allow the reversible binding of O$_2$ only when it is photoisomerized to cis and adopts the preferred ear-muff conformation (Fig. 3). On the other hand, such favorable distance between the two intramolecular Cu(I) ions is not expected for the complex with *trans*-**1**(X=CH$_2$).

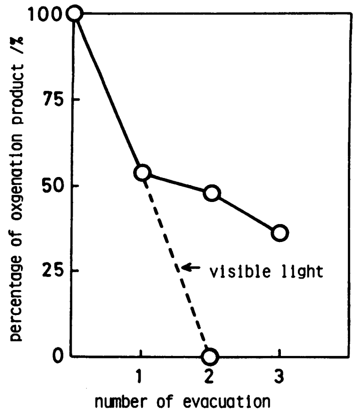


Fig. 6. Reversibility in O_2-binding to *cis*-**1**(X=CH_2) in propylene carbonate. [photoirradiated **1**(X=CH_2) (*cis* 72%)]=2.50×10^{-4} M, [$Cu(CH_3CN)_4\cdot BF_4$]=2.66×10^{-3} M. Photoirradiation was carried out before mixing with the Cu(I) solution.

In an optical cell, the appropriate amount of thiacrown ethers (*trans*-**1**, **2**, and **3**) was mixed with [$Cu(CH_3CN)_4$]BF_4 in propylene carbonate (PC) under anaerobic conditions. An oxygen stream was introduced into the optical cell at 40—50 °C for 5 min and the mixture was subjected to spectral measurement at 30 °C. A new broad absorption maximum appeared at around 700 nm (Fig. 4), which was scarcely affected by further introduction of oxygen. This band is attributable either to a reversible oxygenation product (Cu(I)·····O_2·····Cu(I)) or to an irreversible oxidation product (Cu(II)).[18,24–26] The fraction of the reversible oxygenation product was evaluated from the disappearance of the absorption maximum on evacuation[18] (1.0 mmHg, 70 °C, 1 h). The results are illustrated in Fig. 5. When the treatment was repeated several times, oxygen was newly introduced after evacuation. It is seen from Fig. 5 that the Osborn's complex **2**·$Cu(I)_2$(λ_{max} of the O_2-complex 686 nm) is capable of binding O_2 in a reversible manner for several times: the fractions of the oxygenated product are 62 (1st evacuation), 36 (2nd evacuation), and 23% (3rd evacuation). Thus, the reversibility becomes inferior as the repeated number of evacuation and the irreversible oxidation product is accumulated. The reversibility of the mononuclear complexes **3**·Cu(I) (λ_{max} of the O_2-complex 694 nm for **3**(X=NO_2) and 684 nm for **3**(X=H)) was found to be much inferior: 9 (1st evacuation) and 11% (2nd evacuation) for **3**(X=NO_2) and 12 (1st evacuation) and 6% (2nd evacuation) for **3**(X=H). As expected, no decrease in the absorbance was observed for the *trans*-**1**(X=CH_2)·$Cu(I)_2$ complex ((λ_{max} 710 nm), indicating that the irreversible oxidation to Cu(II) is the sole reaction path.

In contrast, we found that *cis*-**1**·$Cu(I)_2$ complex ((λ_{max} 708 nm) is capable of forming the significant fraction of the reversible oxygenation product. The evacuation was carricd out under milder conditions (1.0 mmHg, 40 °C, 20 min) where the progress of the thermal cis-to-trans isomerization is almost negligible (k=0.12 h^{-1} at 40 °C: for the conditions see the figure caption to Fig. 5). We used photoisomerized **1**(X=CH_2) containing 72% of *cis*-**1**(X=CH_2) at the beginning. We observed 54% decrease in the absorbance after first evacuation. This value indicates that 75% of *cis*-**1**(X=CH_2) form the oxygenation product (Fig. 6). Second and third evacuations gave 48 and 36% decrease, respectively. In a separate study, we irradiated the sample by visible light for 5 min after first evacuation. The spectral measurement showed that by this treatment the remaining cis-form has been isomerized to the trans-form. Then, O_2 was introduced. As shown in Fig. 6, no oxygenated product was detected on second evacuation. The marked difference in the reversibility between the the *trans*- and *cis*-**1**(X=CH_2)·$Cu(I)_2$ complexes suggests that this process may be controlled by a light switch through the photoinduced cis-trans interconversion of **1**(X=CH_2).

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 are "active" for small molecules and others as seen in metalloproteins. We thus consider that the activities of heavy metal ions could be photocontrolled by use of thiacrown ethers or azacrown ethers linked to photofunctional groups. One example is the reversible O_2-binding reported here. Although the frameworks of the photoresponsive thiacrown ethers are still to be improved, the results indicate that the affinity of heavy metal ions with O_2 can be controlled, in principle, by switching the light source on and off. Further investigation is currently in progress in this laboratory.

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References

1) D. Balasubramanian, S. Subramani, and S. Kumar, *Nature (London)*, **254**, 252 (1975).

2) K. Kano, Y. Tanaka, T. Ogawa, M. Shimomura, Y. Okahata, and T. Kunitake, *Chem. Lett.*, **1980**, 421.

3) A. Ueno, J. Anzai, T. Osa, and Y. Kodama, *Bull. Chem. Soc. Jpn.*, **50**, 2995 (1977).

4) A. Ueno, H. Yoshimura, R. Saka, and T. Osa, *J. Am. Chem. Soc.*, **101**, 2779 (1979).

5) M. Irie and K. Hayashi, *J. Macromol. Sci., Chem.*, **A13**, 511 (1979).

6) C. D. Eisenbach, *Makromol. Chem.*, **179**, 2489 (1978).

7) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, and O. Manabe, *Tetrahedron Lett.*, **1979**, 4569; S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa, and O. Manabe, *J. Am. Chem. Soc.*, **102**, 5860 (1980).

8) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, and O. Manabe, *J. Am. Chem. Soc.*, **103**, 111 (1981).

9) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 3279.

10) S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, **104**, 1967 (1982).

11) S. Shinkai, K. Shigematsu, M. Sato, and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2735.

12) S. Shinkai, T. Kouno, Y. Kusano, and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2741.

13) I. Yamashita, M. Fujii, T. Kaneda, S. Misumi, and T. Otsubo, *Tetrahedron Lett.*, **1980**, 541.

14) M. Shiga, M. Takagi, and K. Ueno, *Chem. Lett.*, **1980**, 1021.

15) S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *Tetrahedron Lett.*, **23**, 2581 (1982); Idem, *J. Am. Chem. Soc.* **105**, 1851(1983).

16) J.-P. Desvergne and H. Bouas-Laurent, *J. Chem. Soc., Chem. Commun.*, **1978**, 403.

17) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).

18) J. E. Bulkowski, P. L. Burk, M.-R. Ludmann, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, **1977**, 498.

19) M. Blank, L. M. Soo, N. H. Wasserman, and B. F. Erlanger, *Science*, **214**, 70 (1981).

20) D. S. C. Black and I. A. McLean, *Aust, J. Chem.*, **24**, 1401 (1971).

21) D. P. Fisher, V. Piermattie, and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **99**, 2811 (1977).

22) A. Nakamura, M. Aotake, and S. Otsuka, *J. Am. Chem. Soc.*, **96**, 3456 (1974).

23) J.-M. Lehn, *Acc. Chem. Res.*, **11**, 49 (1978) and references cited therein.

24) J. Powell and C. J. May, *J. Am. Chem. Soc.*, **104**, 2636 (1982).

25) H. M. J. Hendricks, J. J. M. W. Birker, J. van Rijn, G. G. Vershoor, and J. Reedijk, *J. Am. Chem. Soc.*, **104**, 3607 (1982).

26) M. S. Haddad, S. R. Wilson, D. J. Hodgson, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **103**, 384 (1981).

27) P. L. Burk, J. A. Osborn, M.-T. Youinou, Y. Agnus, R. Louis, and R. Weiss, *J. Am. Chem. Soc.*, **103**, 1273 (1981).