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PHOTORESPONSIVE CRYPTAND WITH AN AZOPYRIDINE-BRIDGE

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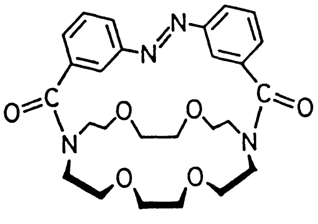
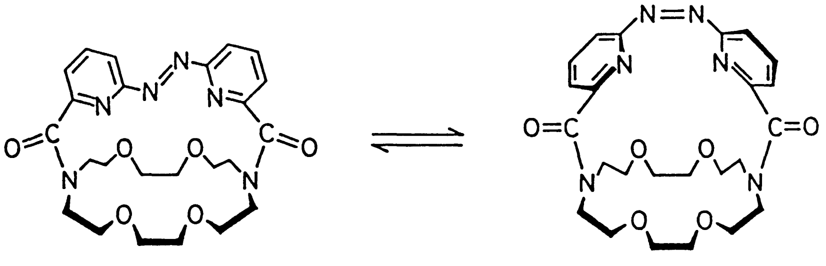
A new photoresponsive "cryptand" with an azopyridine-bridge (2) was synthesized. Trans-(2) was able to extract heavy metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, and Hg^{2+}) from aqueous solution to organic (o-dichlorobenzene + n-butyl alcohol) phase, whereas photoisomerized cis-(2) scarcely extracted heavy metal ions. The difference is rationalized in terms of the structural change of the azopyridine-bridge which is induced by photo(u.v.)-irradiation.

We previously synthesized an azobenzene-bridged crown ether (1), aiming at photocontrolling the chemical and physical functions of crown ether family compounds.[1,2] We found that the size of the crown ether of cis-(1) in which the azobenzene bridge is photoisomerized to the cis-form is somewhat greater than that of trans-(1).[1-3] This is the first example of photoresponsive crown ethers as well as others subsequently reported.[4-6]

We here wish to report a new photoresponsive "cryptand" (2) which has a crown ring bridged with an azopyridine and changes its binding ability toward heavy metal ions in response to photoirradiation. When inspecting the CPK model of (1), we noticed that the azobenzene moiety of trans-(1) stands vertically over the crown ether plane, whereas that of cis-(1) is almost parallel to the crown ether plane.[2] One may expect, therefore, that pyridine nitrogens of the azopyridine-bridge of trans-(2) are directed toward the crown ether plane, whereas those of cis-(2) would not be able to coordinate to metal ion bound into the crown ether ring. We examined whether the photoinduced structural change of the azopyridine-bridge is reflected by the binding ability of (2) through solvent extraction.



trans-(1)



trans-(2) cis-(2)

Trans-(2) was prepared from 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 and 6,6'-bis(chlorocarbonyl)-2,2'-azopyridine in chlorobenzene in the presence of triethylamine: mp 247-249°C. The product was identified by IR, elemental analysis, and mass spectrum (M^+, 498). The photoisomerization was carried out using a 500 W high-pressure Hg-lamp with a UV-D35 filter ($330 \text{ nm} < \lambda < 380 \text{ nm}$).

In the extraction of alkali metal cations with (2), we found the trend of trans (Ex, 39.8%) > cis

(29.9%) for Na^+ and cis (60.5%) > trans(22.0%) for K^+, which is similar to that with (1).[1,2] In the extraction of heavy metal cations with (1), the distinct difference in the extractability is not observed (except Pb^{2+}) between trans-(1) and cis-(1). In the extraction of heavy metal cations with (2), trans-(2) is capable of extracting heavy metal cations to considerable extents, whereas cis-(2) scarcely extracts them (except Pb^{2+})(Table 1). The anomaly of Pb^{2+} is associated with its high affinity toward the crown ether ring.[7,8] On the other hand,6,6'-bis(morpholinocarbonyl)-2,2'-azopyridine (non-crown analogue of (2)) could not extract these metal cations under the comparable extraction conditions.

Table 1. Influence of photo(u.v.)-irradiation on the extraction of heavy metal cations to the organic (o-dichlorobenzene : n-buthyl alcohol = 80 : 20 by volume) phase at 30°C.[a]

Metal	Extracted picrate (%)			
	(1)		(2)	
	dark	light[b]	dark	light[c]
Cu^{2+}	1.9	2.2	9.5	1.0
Ni^{2+}	1.0	0.4	0.6	0
Co^{2+}	3.0	2.6	3.7	0
Hg^{2+}	1.9	2.3	3.1	0
Pb^{2+}	7.9	4.3	10.8	8.8

[a] Extraction conditions for heavy metal cations: aqueous phase, $[MCl_2] = 0.010$ M, [picric acid] $= 1.00 \times 10^{-4}$ M, $[Et_4NOH] = 1.10 \times 10^{-4}$ M; organic phase, [(1) or (2)] $= 4.00 \times 10^{-3}$ M, pH 4-5.

[b] Cis-form, 76.9%. [c] Cis-form, 42.1%.

The foregoing results strongly suggest that the enhanced affinity of trans-(2) relative to cis-(2) toward heavy metal cations is due to the coordination of the azopyridine-bridge to metal cation bound into the crown ether ring. The finding substantiates that (2) acts as a photoresponsive "cryptand" for heavy metal cations.

Further evidence for the interaction of heavy metal cations with the azopyridine-bridge will be submitted as a full manuscript.

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