PSEUDOTHIACROWN AND PSEUDOTHIOLARIAT ETHERS FOR DOUBLE RECOGNITION SYSTEMS TOWARD COPPER(I) AND SILVER(I)

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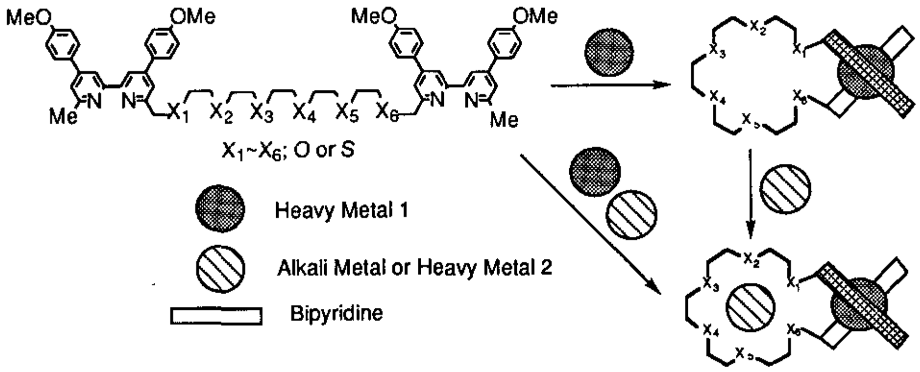
Abstract - Linear and branched polythioethers with bipyridine moieties at the termini bind Cu(I) to afford pseudothiacrown and pseudothiolariat ethers by conformational change of the polyether chain, and the pseudocrowns extract Ag(I) selectively.

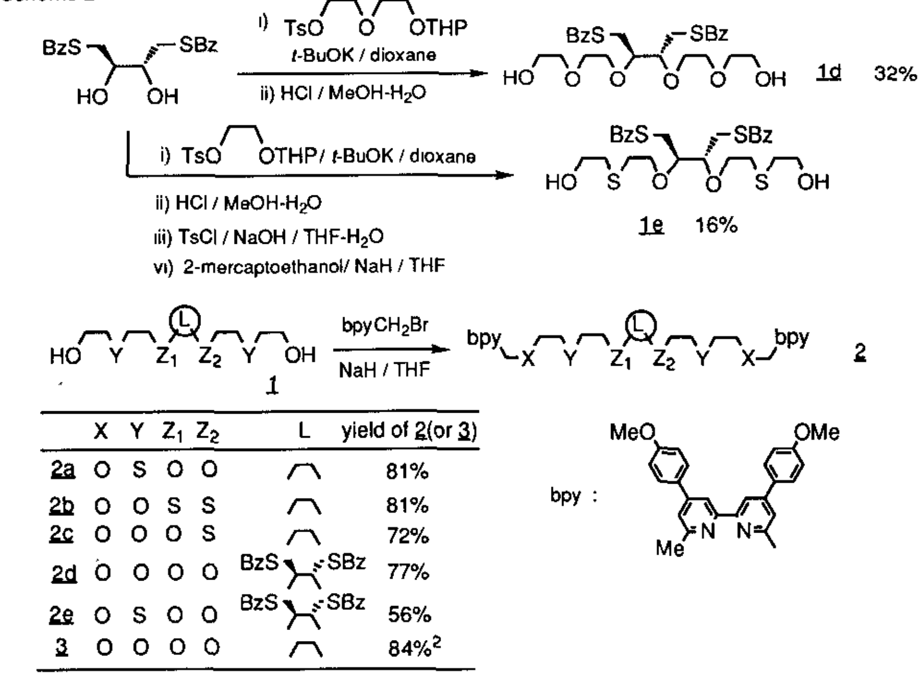
We have reported a novel concept of pseudocrown ethers, a kind of macrocyclic polyethers whose cyclic structure is kept by coordination to a metal ion instead of covalent bonding (Scheme 1).[1,2] The reported system was also the first example of an artificial allosteric ionophore which is constructed on the basis of the concept. Upon complexation of the bipyridine derivatives containing a polyether chain with Cu(I) as the effector, a dynamic conformational change from the linear to a cyclic form of the polyether moiety takes place to generate a new and selective recognition site for K^+. In this communication we report development of the methodology for the formation of a selective recognition site upon metal complexation to effect binding with heavy metal ions by the use of linear and branched polythioethers bearing bipyridines. The corresponding pseudocrowns, *pseudothiacrowns* and *pseudothiolariat ethers*, are expected to exhibit a high Ag(I) selectivity on solvent extraction of heavy metals, because thiacrown[3] and thiolariat ethers[4] are known to show such a preference. The sulfur analogs to pseudocrowns may be utilized as new double complexation systems for heavy metal ions and as novel frameworks to investigate metal-metal interaction.

The reaction of ethylene thioglycol oligomers (**1**)[5] with 6 - bromomethyl - 6' - methyl - 4, 4' - bis(4 - methoxyphenyl) - 2, 2' - bipyridine[1,2] gave the desired polythioethers (**2**) as precursors for pseudothiacrowns and pseudothiolariat ethers in good yields (Scheme 2).[6]

Scheme 1



Scheme 2



	X	Y	Z_1	Z_2	L	yield of 2(or 3)
2a	O	S	O	O		81%
2b	O	O	S	S		81%
2c	O	O	O	S		72%
2d	O	O	O	O	BzS SBz	77%
2e	O	S	O	O	BzS SBz	56%
3	O	O	O	O		84%[2]

To solutions of compounds (**2**) was added Cu(I) to give red solutions with λ_{max} at *ca.* 475 nm[7] assigned to a metal-to-ligand-charge-transfer (MLCT) band,[8] indicative of tetrahedral complexes of bipyridines with Cu(I). In ^{1}H nmr spectra, upfield shifts of the picolyl methyl and methylene protons (e.g. $\Delta\delta$ 0.40, 0.39 ppm in **2a**) were observed upon the addition of Cu(I). The shifts caused by magnetic anisotropy of the bipyridines also suggest an exclusive formation of a tetrahedral complex.[2,9] Spectroscopic titrations (uv-vis, and ^{1}H nmr) supported a 1:1 stoichiometry of a ligand and Cu(I). Even at Cu(I) to a ligand ratio of 2.5 : 1, only one species was detected by ^{1}H nmr spectroscopy. Hence, stable pseudothiacrowns should be produced. Ag(I) complex of **2a** is also formed easily. Electronic absorption spectroscopy indicated that at a lower concentration of $1.5\text{x}10^{-5}$ M **2a** binds Ag(I), and the 1:1 complex is stable in the presence of excess Ag(I)[7]. However, in ^{1}H nmr titration at a higher concentration of $2 \text{ x } 10^{-3}$ M **2a** we observed upfield shifts of the methylene and methyl protons adjacent to the bipyridine rings up to a 1:1 ratio and a successive increase of the δ values up to 2:1. The spectrum does not change over a ratio of 2:1. The upfield shifts probably result from tetrahedral complexation with Ag(I) in a similar fashion to the Cu(I) complex.[10-12] The successive downfield shifts should be attributed to a linear structure of a 2:1 complex, because a ring current of the one bipyridine ring can not affect the magnetic environment of the other. The different observation between uv-vis and nmr is well explained by the difference of **2a** and Ag(I) concentrations, because formation of a 2:1 complex becomes more favorable at a higher concentration, compared to the case of a 1:1 complex. ^{1}H Nmr spectroscopy also indicated that the bipyridine moieties bind Cu(I) more strongly than Ag(I). The spectrum of a 1:1 mixture of Ag(I) and **2a** was immediately and completely changed into the characteristic spectrum of the Cu(I) complex by the addition of Cu(I). On the other hand, peaks of ^{1}H nmr spectrum of a 1:1 mixture of Cu(I) and **2a** were sharpen on the addition of Ag(I), although the chemical shifts were not changed significantly. Additionally, the broad signal of the picolyl methylene protons was split into a AB like pattern, which is probably attributed to kinetic inertness of the Cu(I)-Ag(I) complex. Broadening of nmr signals caused by lability of a complex is often observed in similar bipyridine Cu(I) complexes.[11,13] Since no exchange between Cu(I) bound by the bipyridines and free Ag(I) was supported by ^{1}H nmr spectroscopy described above, the spectral change after the addition of Ag(I) is presumably caused by interaction between the pseudo ring and Ag(I).[14]

Solvent extraction was carried out to examine affinity of pseudothiacrowns and pseudothiolariat ethers to heavy metals.[15] Cu(I) complexes of **2a~e** do not extract Ni(II), Pb(II), Mn(II), and Co(II) at all. However, the extractabilities of these complexes toward Ag(I) are 72, 31, 29, 25, and 197 %, respectively. In contrast, **3**-Cu(I) exhibits a very low value (4 %) toward Ag(I). This result suggests that coordination of the sulfur atom(s) of pseudothiacrown is important for the selectivity. The large value of the **2e**-Cu(I) complex (197 %) shows that the pseudothiolariat ether can extract two Ag(I) ions. Compared to the lower values of **2a**-Cu(I) (72 %) and **2d**-Cu(I) (25 %), the higher affinity of **2e**-Cu(I) may be rationalized by an effective coordination of the sulfur atoms in the ring[3] and side arm[4] to Ag(I) ions. In the absence of Cu(I), the extractabilities of **2a~e** to Ag(I) are 135, 119, 108, 118, and 167%, suggesting concomitant formation of the 2:1 complexes seen in the nmr titration. Importantly, in **2a~d**, a large *negative allostery* of Ag(I) recognition was performed using Cu(I) as an effector. Noteworthy is that small but distinct enhancement, *positive allosteric effect*, of the value in **2e** by the addition of Cu(I) was observed.

Construction of more effective allosteric systems using these pseudo cyclic frameworks and detailed characterization of the Cu(I)-Ag(I) complexes are currently investigated in our laboratory.

REFERENCES AND NOTES

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6. These compounds were identified by ^{1}H nmr, ir, and/or ms spectroscopy.
7. Cu complexes: λ_{max} (ε) in 2%MeCN-CH_2Cl_2 for **2a**,**b** and 2%MeCN-$CHCl_3$ for **2c~e**: **2a** 475nm (11200), **2b** 475nm (12200), **2c** 477nm (11500), **2d** 476nm (12300), **2e** 476nm (10100). Ag complex of **2a**: 343nm (59000) in 2%MeCN-CH_2Cl_2.
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14. In the ^{1}H nmr experiments, $AgNO_3$ and CuCl were used. Interestingly, a 1:1:1 mixture of **2a**, $AgNO_3$, and CuCl gave a small amount of precipitates but increase of $AgNO_3$ caused an apparent increase of the precipitates. Namely, this qualitative observation implies that almost all AgCl is captured by **2a** and dissolved in the 1:1:1 system.
15. Extractabilities were defined as a following equation and determined by atomic absorption spectroscopy. Extractability (%) = $[\text{metal nitrate}]_{org} / (3.0 \times 10^{-4}) \times 100$, $[\text{metal nitrate}]_{org}$: concentration of metal nitrate in the organic phase(1,2-dichloroethane). In the case of Cu(I) complexes; $[\text{metal nitrate}]_0$ (initial concentration of metal nitrate in the aqueous phase), [ionophore] (concentration of ionophore in 1,2-dichloroethane), and [CuCl] (initial concentration of CuCl in the aqueous phase) are 1.2×10^{-3}, 3.0×10^{-4} and 6.0×10^{-4} M, respectively. 1.8×10^{-3} M was employed as $[\text{metal nitrate}]_0$ for Ag(I), because an equal amount of Ag(I) to Cl^- was completely precipitated as AgCl. In the absence of CuCl $[\text{metal nitrate}]_0$ is 1.2×10^{-3} M. For an apparatus see ref 2.

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