

SELECTIVE RECOGNITION FOR HEAVY AND TRANSITION METALS BY NOVEL POLYETHERS BEARING BIPYRIDINES, AND MOLECULAR CHIRALITY OF PSEUDOCROWN STRUCTURE IN THE Cu(I) COMPLEX

Tatsuya Nabeshima,* Tadashi Inaba,† Naomichi Furukawa,†*
Shunji Ohshima, Toshiyuki Hosoya, and Yumihiko Yano

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract: Bisbipyridine derivatives linked by polyether chain **1** showed selective binding behavior to Zn(II) and Cu(I). The strength of the affinity is larger than that of 6, 6'-dimethylbipyridine derivative **2** because of the chelate effect of **1**. Molecular chirality of the pseudocrown ether, **1**-Cu(I) complex, was observed by ¹H NMR spectroscopy at -28°C in the presence of Pirkle's reagent.

Conformational change of apoproteins induced by some external stimuli plays an essential role to modulate activity of allosteric enzymes and some cooperative biological systems.¹⁾ Recently we have synthesized oligoethylene glycol derivatives **1** which have two kinds of binding sites for metals (polyether chain for alkali metals, and bipyridines moiety for transition metals) and can bind two different metals simultaneously.^{2 - 4)} Transport selectivity for *alkali metals* was dramatically enhanced by the addition of Cu(I) to **1b** due to conformational change of the polyether moiety (formation of pseudocrown structure). Here we report selective recognition of *transition metals* by polyethers **1**, and appearance of molecular chirality accompanied by the conformational change of the binding site for alkali metals in complexation with Cu(I). Generation of chirality by the reaction between achiral species might be utilized for transfer or modulation of chiral information, which is one of the most interesting and important targets in host-guest chemistry.

Binding affinity of bipyridine derivatives **1** - **2**⁵⁾ and pentaglyme to heavy metals was estimated by solvent extraction experiment in a biphasic system (a dichloromethane solution of a ligand and an aqueous solution of a metal ion) under conditions shown in Table 1. A clear organic layer was obtained by centrifugation, after vigorous mixing for 11 h.

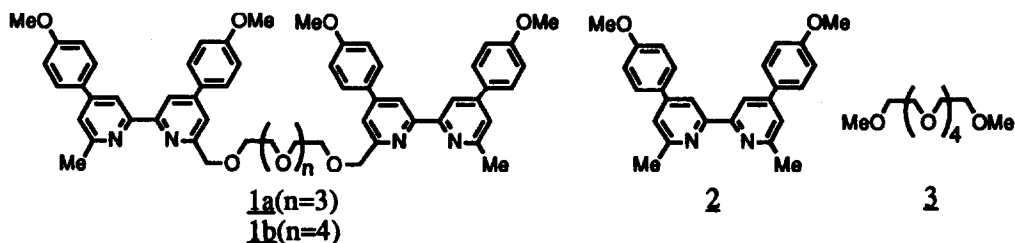


Table 1 Extraction of Transition Metals by Bipyridine Derivatives at 25°C.

	E(%) ^{a)}					
	Fe ³⁺	Co ²⁺	Ni ²⁺	Zn ²⁺	Mn ²⁺	Cr ³⁺
1a^{b)}	0.01	0.15	0.1	15.3	0	0
1b^{b)}	0.09	0.39	0.4	15.4	0.07	0
2^{c)}	0.01	0	0	6.8	0	0
3^{b)}	0.03	0	0	0.05	0	0

a) Determined by atomic absorption spectroscopy; aqueous phase (10 ml) containing 0.001 M metal nitrate, adjusting the pH at 5.5 by using bis-tris buffer.

b) Organic phase (CH₂Cl₂, 10 ml) containing the ligand, 7 x 10⁻⁴ M, or c) 1.4 x 10⁻³ M.

Amount of metal ions thus extracted into the organic layer was determined by atomic absorption spectroscopy, giving extractability (Table 1).⁶⁾ Remarkably high selectivity to Zn(II) ion among metals examined here was observed in bipyridine derivatives **1** (a, 15.3%; b, 15.4%) and **2** (6.8%). In the case of Cu(I) we adopted different conditions to determine the binding strength because of the following reasons. Inorganic Cu(I) salt was easily oxidized to the corresponding Cu(II) salt by molecular oxygen and solubility of Cu(I) salt (e.g. CuI) to water is extremely low. However Cu(I) complexes of **1** and **2** are soluble in CHCl₃, or CH₂Cl₂, and resist the oxidation more strongly than the Cu(I) salt. Consequently the binding affinity was determined by measuring UV-VIS spectra of the organic layer, after vigorously stirring 1 : 2 (or 1 : 4) mixture of CuI and **1** (or **2**)⁷⁾ with an equal volume of an aqueous bis-tris buffer solution (pH 5.5). Large amount of Cu(I) remained in the organic layer even after 12-h stirring (**1a**, ~100%; **1b**, ~100%; **2**, 54%). In contrast to the case of the bipyridine derivatives, almost none of metal ions studied here was extracted by pentaglyme (e.g. 0.05% in Zn(II); <1% in Cu(I)). Therefore it is assumed that only the bipyridine moieties act as ligands for heavy metal ions and that the high selectivity to Zn(II) and Cu(I) is caused basically by the properties of the bipyridine moieties, that is, steric effect of the substituents at 6 and 6' positions of the bipyridines is favorable to stable and exclusive formation of tetrahedral complexes⁸⁾ in **1** and **2**. Among the bipyridine derivatives, **1** (bipyridines with polyether linkage) show higher extractability toward Cu(I) and Zn(II) than **2**. The difference between **1** and **2** can be ascribed to chelate effect in **1**. From the CPK model inspection of the Cu(I) complexes of **1**, the length of the polyether chains is suitable for complexation without strain. Vapor pressure osmometry clearly indicated quantitative formation of 1 : 1 complex between Cu(I) and **1b**, supporting the presence of the chelate effect, too.

When the Cu(I) complexes are inert, there must be two optical isomers having pseudocrown structure (Fig. 1), whose cavity may provide a chiral recognition field.

Fig. 1 Molecular Chirality of Pseudocrown Ether

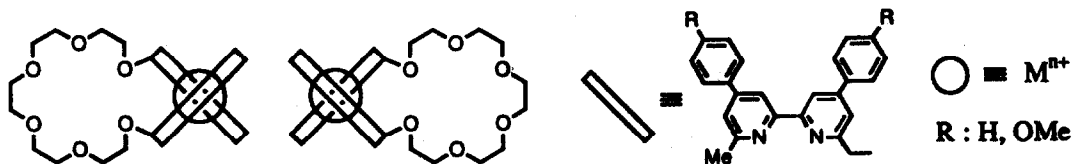
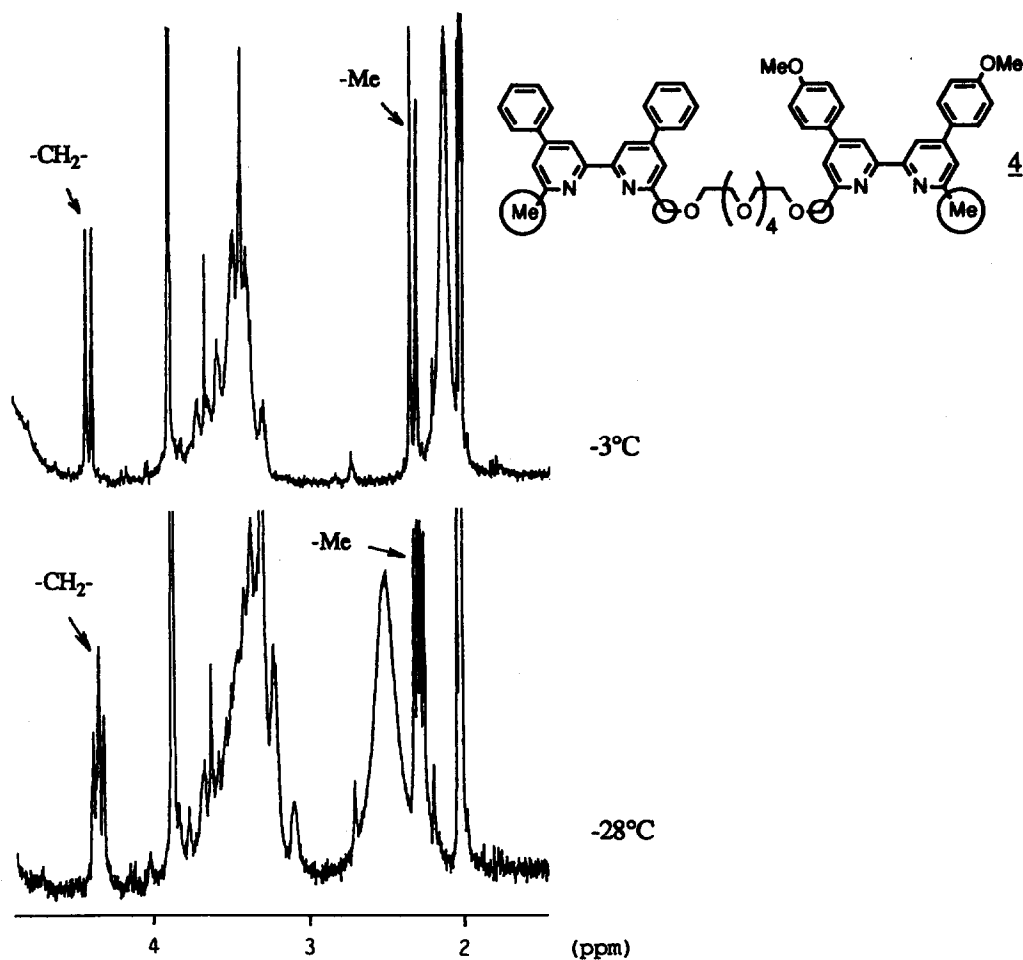
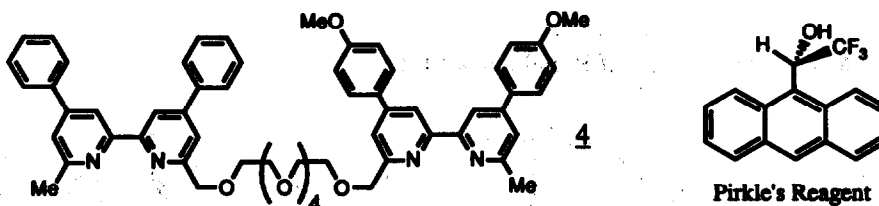


Fig. 2 ^1H NMR Spectra of **4**-Cu(I) in the Presence of Pirkle's Reagent.
($\text{CDCl}_3 : \text{CD}_3\text{CN} : \text{CD}_3\text{OD} = 85 : 5 : 10$)





Measurement of 500 MHz ^1H NMR of the complexes was carried out at various temperatures in the presence of excess amount of Pirkle's reagent ((S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol),⁹⁾ which was used for characterization of chiral bipyridine derivatives.^{10 - 12)} As seen in Fig. 2, Cu(I) complex of unsymmetrical ligand **4** showed apparent splittings of signals of the bipyridine moieties at -28°C , while **1b** complex did not (not shown) probably because of the higher symmetry. Most characteristic splittings indicating the molecular chirality is that the two signals of methyl protons at 6 positions of the bipyridine moieties at -3°C are split into four sharp lines at -28°C , where rotation of C-C bond between the methyl carbon and the C6 of the bipyridine should not be frozen. The splitting observed at low temperature can be explained by restriction of racemization by ligand exchange. We are now investigating application to chiral molecular recognition induced by external stimuli by a series of the pseudocrowns.

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References and Notes

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- 6) $E(\%) = \{([M^{n+}]_0 - [M^{n+}]_{aq}) / 7 \times 10^{-4} M\} \times 100$; $[M^{n+}]_0$: initial conc. of metal ion in aq. phase; $[M^{n+}]_{aq}$: conc. of metal ion in aq. phase after extraction.
- 7) Solvent system: 0.02% CH_3CN in CH_2Cl_2 (8 ml); $[1]$ (or $[2]/2$) = 1.75×10^{-4} M; excess amount of bipyridines was used to achieve exclusive complexation between one Cu(I) and two bipyridine moieties.
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