STUDY ON THE STRUCTURE OF PSEUDOCROWN ETHER FORMED *IN THE REACTION OF IONOPHORE 6-O-BPY*[1] *AND* Cu^+ BY 500 MHz ^{1}H NMR SPECTROMETRY

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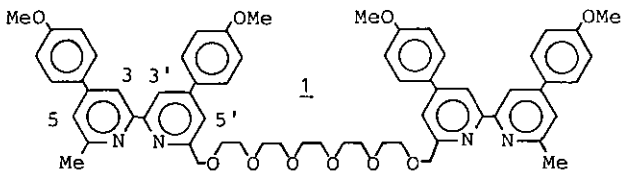
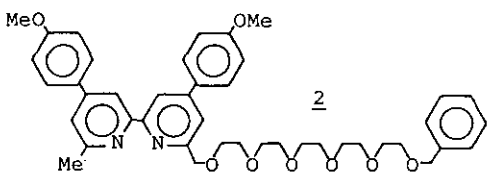
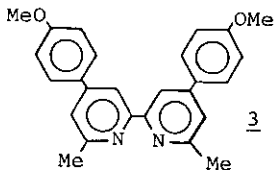
Abstract- The structures of ionophore 6-O-bpy 1 and 1-Cu^+ complex were studied by 500 MHz ^{1}H nmr spectrometry. Characteristic downfield and upfield shifts of the aromatic protons, and the methyl and the methylene protons in the picolyl moiety support strongly generation of pseudocrown structure in the 1-Cu^+ complex.

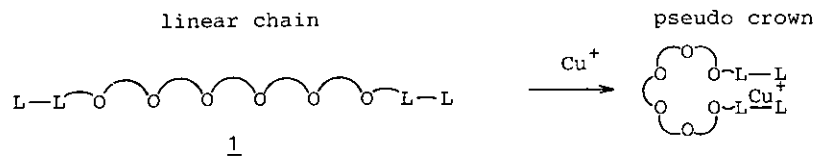
In biological systems conformational changes of enzymes, receptors, carriers, etc., often play a significant and essential role to regulate their activity according to their circumstances.[2] In the model system such as artificial ionophores, regulation of selectivity on alkali metal transport has been achieved by utilizing photo energy, pH gradient, redox system, and metal ion.[3] Recently, we have observed a dramatic enhancement of selectivity to transport the alkali metals across CH_2Cl_2 as a liquid membrane using ionophore 1 and transition metal.[3] Namely K^+ is transported ca. 10 times as much as Na^+ in the presence of Cu^+. The reason for the enhancement may be explained in terms of the conformational change of the linear ethyleneoxy chain of 1 to the cyclic(pseudocrown) form (Scheme 1). Now we wish to report 500 MHz ^{1}H nmr study on elucidating the structure of 1 and 1-Cu^+ complex to obtain a more certain evidence for generation of pseudocrown.







Scheme 1



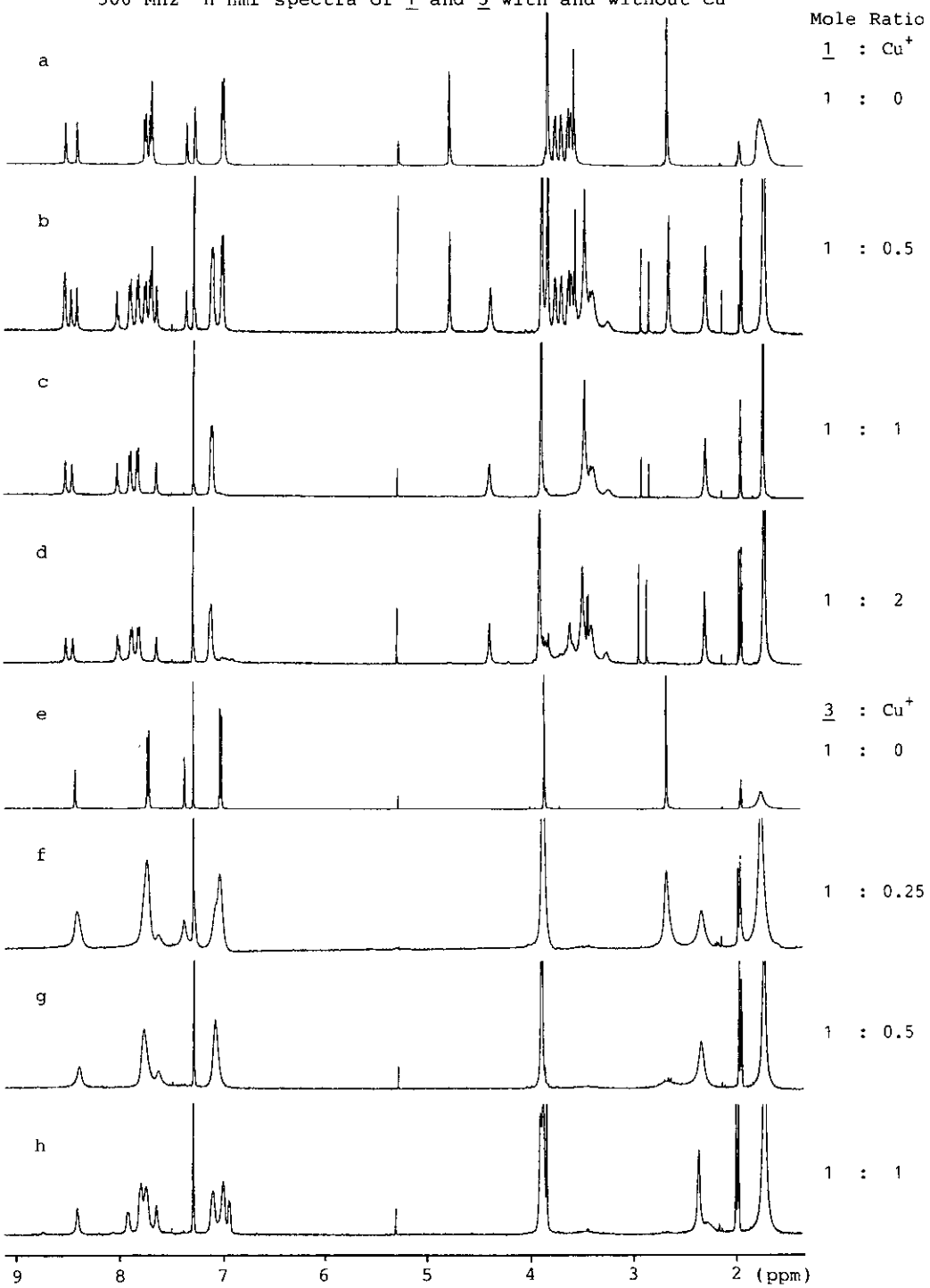
1

L-L: bipyridine

1-Cu^+

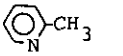
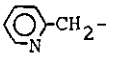
500 MHz ^1H nmr spectra[4] of 1 and a mixture of 1 and CuCl at various mole ratios in $CDCl_3$-CD_3CN(95:5) at 23°C are shown in Fig. 1. Well resolved signals of the ethyleneoxy groups of 1 at a region ca. 3.6 - ca. 3.9 ppm and characteristic signals of two kinds of the pyridine protons at an aromatic region ca. 6.9 - ca. 8.6 ppm are observed as seen in Fig. 1a. Assignment of these protons in 1, 2, 3, 1-Cu^+, and 3-Cu^+ was carried out unambiguously by comparison with those of $Cu(I)bpy_2ClO_4$[5](Table 1). Complexation of 1 and Cu^+ is apparently supported by the observation of downfield shift of the aromatic protons, especially for H-5 and H-5'(7.36 ⟶ 7.65 ppm and 7.69 ⟶ 8.03 ppm, respectively), which is caused by binding of a cation, i.e. Cu^+. The picolyl methyl and the methylene protons at the pyridine ring of 1 appear at 2.69 and 4.81 ppm, respectively. The chemical shifts of these signals, however, are moved remarkably to upfield(2.33 and 4.42 ppm, respectively) upon the addition of Cu^+ into a solution of 1 due to ring current of the pyridine(vide infra). It is worthwhile to point out that on the addition of Cu^+ a signal with an averaged chemical shift between 1 and 1-Cu^+ complex does not appear, especially for the aromatic, the picolyl methyl, or the methylene protons, but a new signal, which is assigned to that of 1 bound to Cu^+, is observed instead, revealing inertness of 1-Cu^+ on the nmr time scale. Furthermore formation of the 1:1 complex is strongly supported by this nmr method, because the signals of free ligand 1 disappeared almost completely at a mole ratio of 1:1 and the chemical shifts of the aromatic protons and methyl or methylene protons adjacent to the aromatic rings are constant even in the presence of excess Cu^+. Supposing that the 1:1 complex of 1 and Cu^+ is formed with a tetrahedral geometry, which is often seen in solution and in a solid state for bipyridyl derivatives,[5,6] the methylene and the methyl protons are located close to and just above a plane of the bipyridine by consideration based on the observation of the space filling model. Consequently the chemical shifts are moved considerably toward upfield by magnetic anisotropy of the pyridine ring in 1, which is the case in this study. Linewidths of the signals of 1-Cu^+ complex are less broadening compared to those of 2 and 3 complexes, indicating that rates of ligand exchange of the former complexes are slower than the latter, that is, 1-Cu^+ complex is more inert than 2 and 3 complexes. Surprisingly about half of 2 still remains as a free form even at a mole ratio(2:Cu^+) of 1:0.5, which is an appropriate value for generation of

Fig. 1
500 MHz ^{1}H nmr spectra of 1 and 3 with and without Cu^+



2·2-Cu^+ complex with a tetrahedral configuration using two bipyridines in the two different molecules. The results obtained in this study suggest that there is a strong chelating effect on formation of the tetrahedral 1-Cu^+ complex despite of steric hindrance at the 6- and 6'-positions of the bipyridines, because the two bipyridine moieties exist at very close together intramolecularly. In other words intermolecular complexation can be ruled out in 1 and pseudocrown structure is readily generated by binding of the two bipyridines in the same molecule with Cu^+. Generation of pseudocrown structure reported previously[3] is ascertained by this nmr experiment, which also shows that 1 can be used as a novel tool for indication of Cu^+ in solution because of its strong chelating effect.

Table 1 ^{1}H Nmr chemical shifts(ppm) of 1, 3, and their Cu^+ complexes[a]

Coumpounds	H-3	H-3'	H-5	H-5'		
1	8.42	8.53	7.36	7.69	2.69	4.81
1-Cu^+	8.48	8.54	7.65	8.03	2.33	4.42
3	8.45		7.38		2.70	
3-Cu^+ [b]	8.41		7.64		2.36	

a) in $CDCl_3$-CD_3CN(95:5) at 23°C, TMS was used as an internal standard.

b) Mole ratio of 3 to Cu^+ is 1 : 0.5.

REFERENCES AND NOTES

1. Pentaethylene glycol bis[6-methyl-4,4'-bis(4-methoxyphenyl)-2,2'-bipyridine-6'-yl]methoxy ether; 6-O- means there are 6 oxygen atoms in the ethyleneoxy chains of 1.
2. See, for example, E. E. Conn, P. K. Stumpf, G. Bruening, and R. H. Doi. 'Outline of Biochemistry,' 5th ed., John Wiley & Sons, New York, 1987, Chapter 4.
3. T. Nabeshima, T. Inaba, and N. Furukawa, Tetrahedron Lett., 1987, 28, 6211, and references therein.
4. 500 MHz ^{1}H nmr spectra were recorded on a Bruker AM-500.
5. S. Kitagawa, M. Munakata, and N. Miyaji, Inorg. Chem., 1982, 21, 3842.
6. M. Munakata, S. Kitagawa, A. Asahara, and H. Masuda, Bull. Chem. Soc. Jpn, 1987, 60, 1927, and references therein.

Received, 31st October, 1988