BINDING PROPERTIES OF SOME NEW MONO-, BIS-, AND TRIS-CROWN ETHERS FOR SILVER ION

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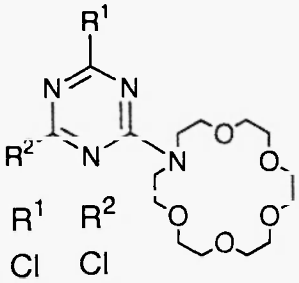
Abstract: For a variety of mono- bis- and tris-crown ethers **1** - **13**, the results of liquid membrane ion transport as well as extraction experiments are shortly described. The ^{13}C-NMR titration experiments for **1** - **13** were performed in DMF/D_2O (4/1) upon addition of silver ion. From the chemical shift changes, the binding sites of these crown ethers were deduced.

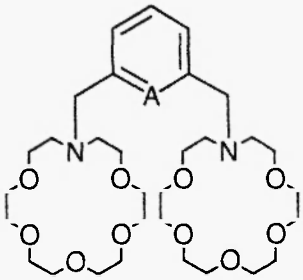
Because of the continuing interests in host-guest chemistry,[1] there were many reports regarding crown ether and related compounds that have interesting guest selectivities in metal ion binding and transport properties.[2] Recently, based upon the high-pressure S_NAr reactions, we have prepared functionalized mono- and diaza-crown ethers which are directly connected to aromatic heterocycles. Certain of them show specific binding and transport properties towards Ag^+ ion.[3, 4] To develop their selectivities for heavy metal ions and establish a recovery system for individual metal ions, it is important to understand binding fashion between a metal cation (guest) and a crown ether (host). Therefore, using ^{13}C NMR titration experiments, we have investigated binding sites of some mono-, bis-, and tris-crown ethers for silver ion.

The mono-, bis-, and tris-crown ethers **1** - **13** were prepared by conventional S_NAr reactions of the parent monoaza-18-crown-6 and 15-crown-4 ethers with the appropriate trichlorotriazine and dichlorodiazines; the high pressure conditions (0.8 GPa, 100 °C) were employed when the reations failed at nomal pressure.[4, 5] The liquid membrane ion transport and extraction experiments were performed as described before.[6]

The compounds in which an aromatic ring is bonded directly to a nitrogen atom of a crown ring (other than **5** and **6**) exhibit almost no transport and extraction properties for alkali metals such as sodium and potassium. This result is probably attributed to the reduced electron density on the nitrogen atom due to electron attracting effect of the electron deficient heteroaromatic ring thus resulting in reduced affinity with hard alkali metal ion. In contrast, the compounds **5** and **6** in which an aromatic ring is bonded indirectly to a nitrogen atom of a crown ring with interposition of methylene group exhibited relatively high transport and extraction properties for alkali metals but low selectivity (e.g. transport rate x 10^6 (mol/h) of **6** : for Na^+, 2.3, for K^+, 3.6, extraction ratio (%) of **6** : for Na^+, 5, for K^+, 32), probably because of their flexible structure. In the case of mono-, bis-, and tris-crown ethers **1**-**4** which transported selectively silver ion, the transportability increases with increasing of the number of crown ring (transport

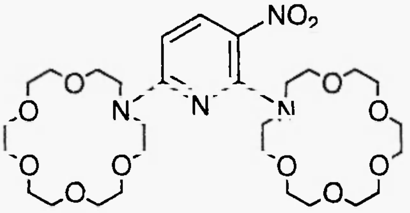


	R^1	R^2
1	Cl	Cl
2	Cl	18C
3	NEt_2	18C
4	18C	18C



5 A=CH

6 A=N



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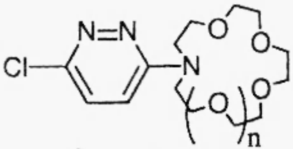
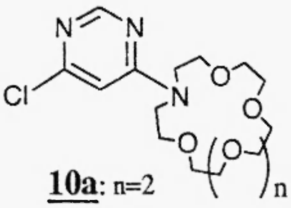
(18C: Monoaza-18-crown-6-ether)



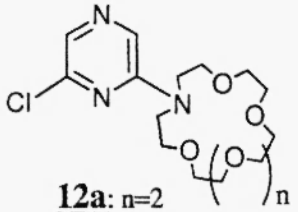
8a: n=2

8b: n=1



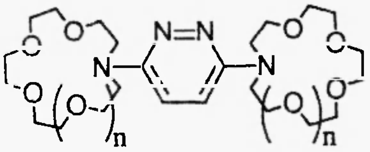
10a: n=2

10b: n=1



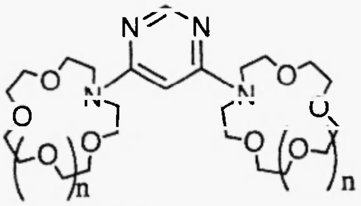
12a: n=2

12b: n=1



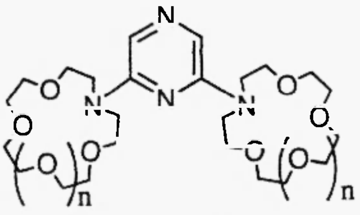
9a: n=2

9b: n=1



11a: n=2

11b: n=1



13a: n=2

13b: n=1

rate x 10^6(mol/h) for Ag^+ : 1, 0.4; 2, 2..0; 3, 2.0; 4, 3.5). It is also found that the mono-crown ethers 10, 12 and the bis-crown ethers 11, 13 having pyrimidine ring or pyrazine ring show significantly different extraction properties to mercury ions. The formers showed no extraction property, while the latters exhibited relatively high extraction properties for mercury ions (extraction ratio (%): 26-35).

Silver ion which is a soft cation is easy to interact with nitrogen atom which is softer than oxygen atom. Direct bonding of an aromatic ring to a nitrogen atom of an azacrown ether results in reduced electron density on the nitrogen atom to render it soft. As the result, such softened host compound becomes difficult to interact with hard alkali metal ion, and is likely rendered selective of soft transition metal ion. Indeed, according to the X-ray crystal structure analysis of *N,N*-dithiazolyldiaza-18-crown-6-ether,[7] a silver ion is coordinated with thiazole, nitrogen atom of a crown ring, and counter anion, and this fact is also supported by ^{13}C-NMR titration experiment.[4] ^{13}C-NMR titration experiment is a useful method for studying how metal cation and host compound form complex in solution conditions. The method involves a procedure in which a metal salt in an amount of various equivalent (0 to 9 eq.) is

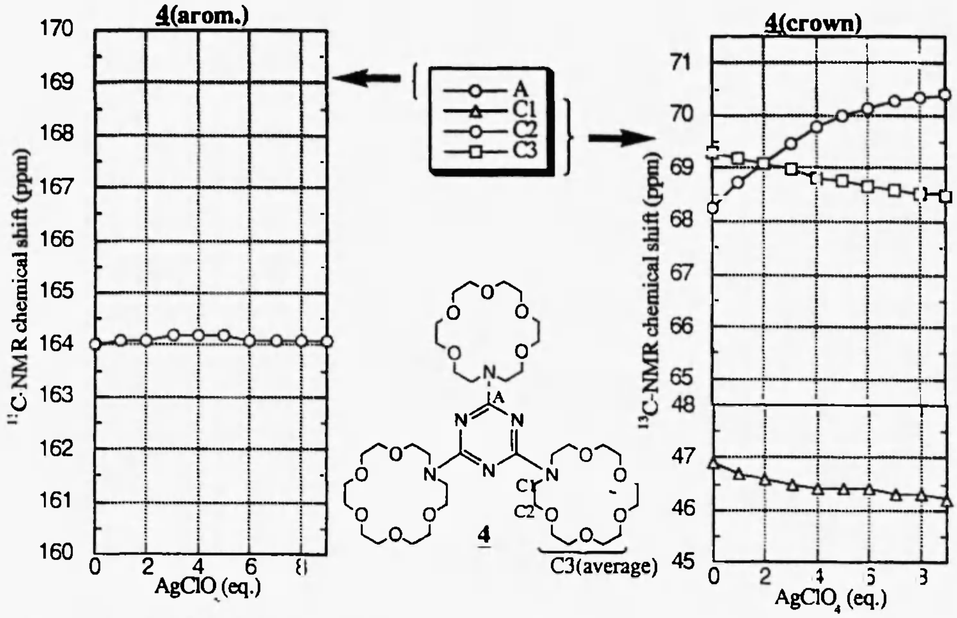


Figure 1. ^{13}C-NMR Titration Experiment of **4**

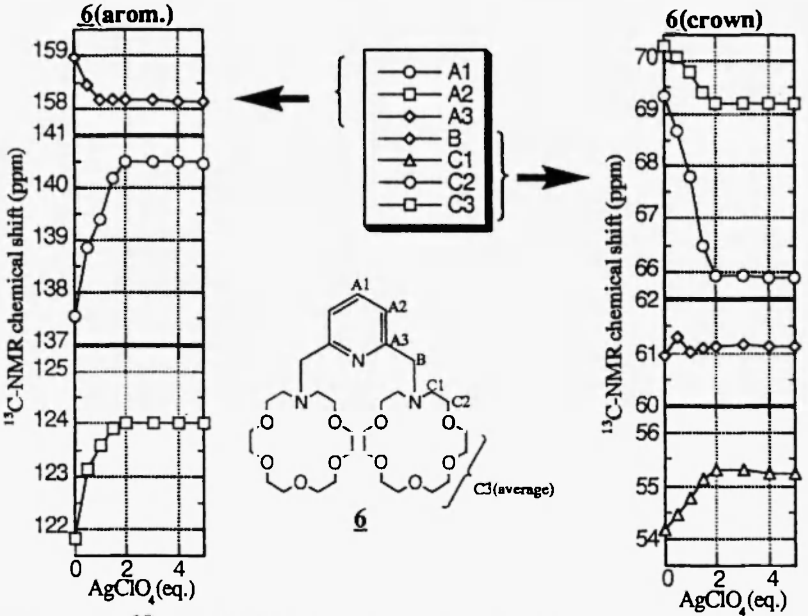


Figure 2. ^{13}C-NMR Titration Experiment of **6**

added to an host compound in DMF/D$_2$O (4/1), ^{13}C-NMR spectrum is measured, and change in chemical shift is compared.

Although ^{13}C-NMR titration experiment was carried out using a guest of silver perchlorate for all the host compounds 1 - 13, only the representative and typical results (figures) are described to save space. The host compounds 1 - 4 having a triazine ring gave a result that aromatic ring and nitrogen atom of the crown ring were not involved in binding, being different from previous results (Fig. 1). Because electron density decreases at the cation binding site, the chemical shift of the adjacent carbon is

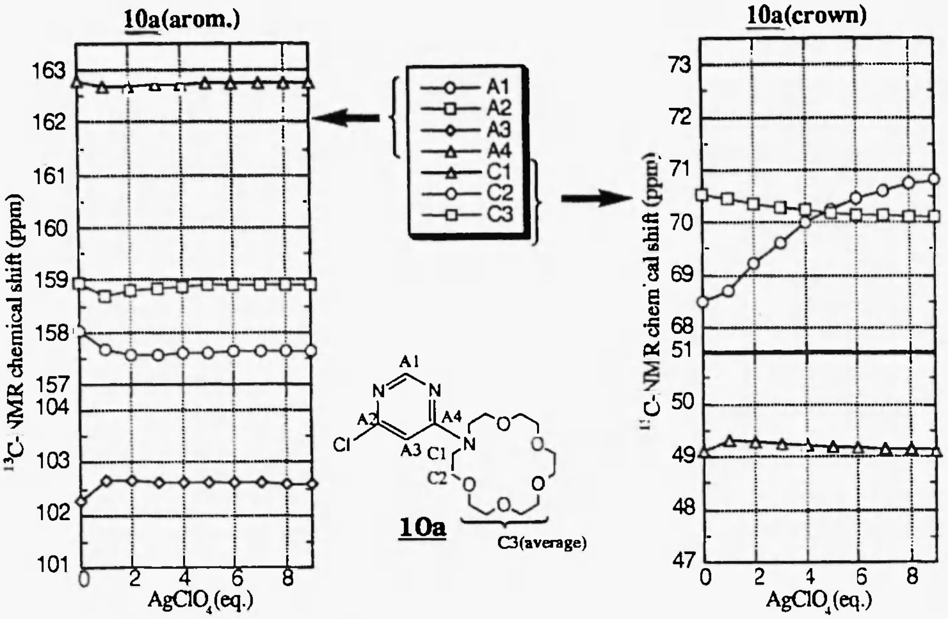


Figure 3. ^{13}C-NMR Titration Experiment of **10a**

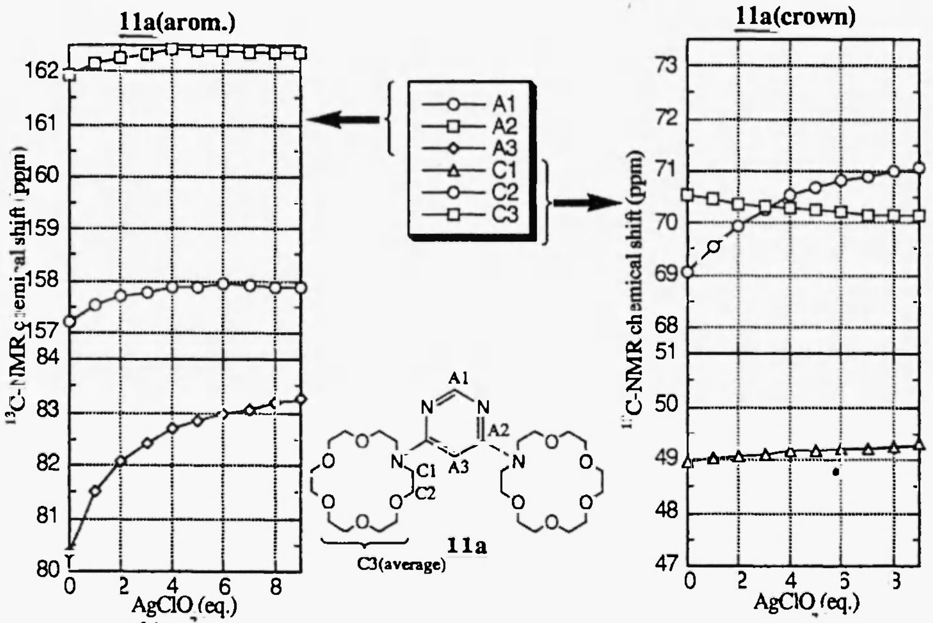


Figure 4. ^{13}C-NMR Titration Experiment of **11a**

subjected to lower field. Therefore, the presence of a carbon of high field shift suggests existence of counter anion located near the carbon. The host compounds **5**, **6**, and **7** exhibit low field shift both at C1 (positions 2 and 18) of crown ring and at aromatic ring, whereas the host compounds **1** - **4** and **7** show low field shift at C2 (positions 3 and 17) of crown ring. (Fig. 2) Therefore, the binding sites for silver ion are considered to be at positions 4 and 16 oxygen atoms of a crown ring for **1** - **4**, at position 1 nitrogen atom of a crown ring and aromatic ring for **5** and **6**, and at positions 1, 4 and 16 nitrogen/oxygen atoms of a crown ring and aromatic ring for **7**.

The nitrogen atom of a crown ring of the compounds **5** and **6** coordinates to silver in usual fashion. In contrast, the nitrogen atom of the compounds **1**- **4** is not the case, probably because triazine ring is highly π-electron-deficient and thus highly electron-withdrawing so that the electron density of the nitrogen is too low to coordinate with silver ion.

Next, the mono- and bis-crown ethers **8a** -**13a** having pyridazine, pyrimidine, or pyrazine ring as spacer were subjected to ^{13}C-NMR titration experiment. (Fig. 3 and 4). The results show that, for all these compounds, the low field shift was not observed at C1 (positions 2 and 18) , while the low field shift was observed only at C2 (positions 3 and 17) of a crown ring. Thus, the electron-withdrawing property of pyridazine, pyrimidine, and pyrazine ring is so significant as to render nitrogen atom of a crown ring impossible to coordinate with silver ion. On the other hand, the low field shift was observed at aromatic ring except **10a**. Therefore, the binding site to silver ion is located probably only at oxygen atoms of positions 4 and 16 of a crown ring for the compound **10a**, and at oxygen atoms of positions 4 and 16 of a crown ring and aromatic ring for the compounds **8a**, and **11a** - **13a**.

In the cases of the compounds **5**, **6** where the chemical shift changes remain constant after addition of two equivalent of silver perchlorate, the formation of relatively stable 1:2 complex of the compounds **5**, **6** with silver ion is apparent. The equilibrium is presumably to be on the complex side.

In summary, the result suggesting that two crown rings enclose cooperatively a guest silver ion is obtained. The guest capture capability increases more than mere increment of host site, and therefore the construction of bis- or tris-crown ethers is useful strategy for designing of molecules having highly increased guest capture capability.

Further work is in progress on the synthetic and binding aspects of bis- and tris-crown ethers having other heterocycles than triazine, pyrazine, and pyridazine as a spacer which will be a subject of future communications.

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