Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Synthesis of metal ion-specific bindings of new functionalized aza-crown ethers

Mitsuo Toda[a]; Hiroshi Tsukube[b]; Hiroyuki Minatogawa[c]; Megumu Munakata[c]; Ken Hirotsu[d]; Ikuko Miyahara[d]; Taiichi Higuchi[d]; Kiyoshi Matsumoto[a]
[a] Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan [b] Department of Chemistry, College of Liberal Arts & Science, Okayama University, Okayama, Japan [c] Faculty of Science and Technology, Kinki University, Higashiosaka, Japan [d] Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, Japan

To cite this Article Toda, Mitsuo , Tsukube, Hiroshi , Minatogawa, Hiroyuki , Munakata, Megumu , Hirotsu, Ken , Miyahara, Ikuko , Higuchi, Taiichi and Matsumoto, Kiyoshi(1993) 'Synthesis of metal ion-specific bindings of new functionalized aza-crown ethers', Supramolecular Chemistry, 2: 4, 289 — 293

To link to this Article: DOI: 10.1080/10610279308029820

URL: http://dx.doi.org/10.1080/10610279308029820

SUPRAMOLECULAR CHEMISTRY, Vol. 2, pp. 289–293
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis of metal ion-specific bindings of new functionalized aza-crown ethers

MITSUO TODA, HIROSHI TSUKUBE[*], HIROYUKI MINATOGAWA[†], MEGUMU MUNAKATA[†], KEN HIROTSU[‡], IKUKO MIYAHARA[‡], TAIICHI HIGUCHI[‡] and KIYOSHI MATSUMOTO

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-01, Japan, [*]Department of Chemistry, College of Liberal Arts & Science, Okayama University, Okayama 700, Japan, [†]Faculty of Science and Technology, Kinki University, Higashiosaka 577, Japan and [‡]Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

(Received July 30, 1992)

The high-pressure S_NAr reaction was first applied to the synthesis of new functionalized diaza-crown ethers, which are directly connected to various heteroaromatic substituents as cation binding sites. The yields of the reaction were moderate to excellent (51% to quantitative). In a CH_2Cl_2 liquid membrane cation-transport experiment, diaza-crown ethers having 2′-thiazoyl-, 2′-benzoxazoyl-, 2′-pyrazinyl-, and 6′-pyridazinyl groups exhibited almost perfect Ag^+ ion selectivity. Cation extraction and ^{13}C-NMR titration experiments revealed that attachment of heteroaromatics to the diaza-crown ring, if in the proper position, provides excellent Ag^+ ion specificity. Since the binding and transport selectivity of these crown ethers were higher than those of the known crowns, the high-pressure technique proved a useful method for synthesis odf a new type of specific crown ethers. Single crystals of the complexes of diaza-crown ethers with silver trifluoromethanesulfonate (AgO_3SCF_3): AgTf and the corresponding metal-free diaza-crown compounds were successfully prepared. The short $Ag^+ \cdots Ag^+$ distances (2.790 and 2.969 Å) in the Ag complexes were confirmed for these Ag complexes by X-ray crystallography.

INTRODUCTION

Aza-crown compounds show quite different features from those of the conventional crown ethers. This is due not only to the soft nitrogen atoms themselves in the crown rings, but also to the fact that several functional groups can be introduced. Therefore, aza-crown compounds are expected to bind soft cations such as Ag^+ or Cu^{2+} rather than hard alkali metal or alkali earth metal cations. Though various attempts have been made, aza-crown ethers to which aryl and heteroaryl groups are directly connected to the ring nitrogen atoms are rarely known. We first applied the high-pressure technique[1,2,3] to the synthesis of these new functionalized diaza-crown ethers[4,5] which incorporated various heteroaromatic functional groups as cation binding sites. The yields were moderate to quantitative.

Transport experiments and extraction experiments[4,5] confirmed the almost perfect selectivity towards Ag^+. X-ray diffraction analysis was also performed on two silver trifluoromethanesulfonate (AgTf) complexes of **2a** and **2b**,[6] and on the corresponding metal ion free diaza-crowns. The features of the ^{13}C-NMR spectrum of the Ag complexes showed good agreement with the X-ray structure determination.

RESULTS AND DISCUSSION

Synthesis of new functionalized aza-crown ethers

A variety of functionalized diaza-crown ethers were readily prepared from commercially available diaza-crown ethers (Scheme 1). The yields are summarized in Table 1. Generally the reaction gave 15-, 18- and 21-membered diaza-crown ethers as well as piperazine derivatives in moderate to excellent yields. We also tried this S_NAr reaction under ordinary pressure for comparison. When diaza-crown **1b**, 2-bromothiazole and triethylamine were reacted in a sealed tube, less than 2% yield of **2b** was obtained. The earlier methods (ring closure after introduction of functional group) required high dilution conditions and additional procedures, and the products were obtained in lower yields. Thus, our procedure would afford a convenient method for construction of the unique aza-crown ethers and ligand topologies.

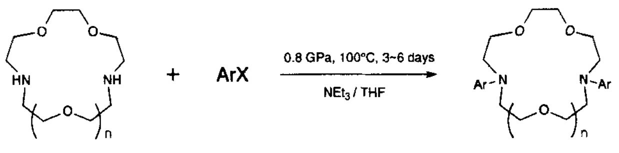
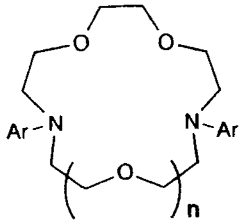
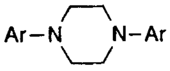
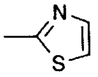
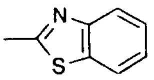
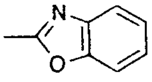
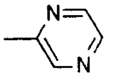
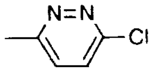
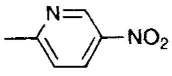
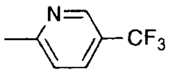
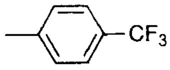


Table 1 Structure and yields (%, in parentheses) of diaza-crown compounds

				
Ar	*n = 1*	*n = 2*	*n = 3*	
—H	**1a**	**1b**	**1c**	**1d**
	**2a** (89)	**2b** (82)	**2c** (92)	**2d** (94)
	**3a** (100)	**3b** (74)	-	-
	**4a** (95)	**4b** (64)	-	-
	**5a** (82)	**5b** (86)	-	**5d** (96)
	**6a** (80)	**6b** (81)	-	-
	**7a** (95)	**7b** (77)	-	-
	**8a** (83)	**8b** (85)	-	**8d** (72)
	**9a** (92)	**9b** (79)	-	**9d** (100)

Structures of 2a and 2b and their silver complexes

Transport, extraction and ^{13}C-NMR experiments on these diaza-crown ethers towards metal ions were carried out.[4,5] Our new functionalized compounds exhibited almost perfect Ag^+ ion selectivity. Changes in ^{13}C-NMR chemical shifts when silver perchlorate was added are suggestive of the binding sites and their make-up. After several attempts we succeeded in isolating single crystals of two silver ion complexes, the AgTf complex of **2a** and **2b** (Fig 1). Interestingly, they had 1:2 complex structures of crown and silver salts. The manner of attachment of the siler ions showed quite good agremeent with ^{13}C-NMR results. The binding sites of the two functionalized diaza-crown ethers to silver atoms were two nitrogen atoms of the crown-ring and an additional two thiazolyl nitrogens. However, the structures of these two binuclear Ag^+ complexes are quite different in symmetry. The complex of **2b** has an exactly centrosymmetrical co-ordination structure and the $Ag^+ \cdots Ag^+$ separation is 2.790 Å. Remarkably, this is shorter than in metallic silver (2.889 Å). Each silver is basically co-ordinated by two nitrogen atoms of the thiazole and crown ring. In contrast to the **2b** complex, in the **2a** complex two Ag atoms are closely spaced ($Ag^+ \cdots Ag^+$, 2.969 Å) but in an asymmetrical fashion (Fig 1). One silver is strongly linked to two thiazole nitrogens, and to an oxygen of the counteranion. The second silver interacts with a nitrogen and three oxygen atoms of the diaza-crown ring, and with an oxygen of the counteranion. In the solid state, the conformational structures of **2a** and **2b** (Fig 2) are not different enough to explain the remarkably different structures between the **2a**·AgTf and **2b**·AgTf complexes. In the case of the **2a**·AgTf complex, Ag^+ ion binding presumably changes the orientation of the thiazole-

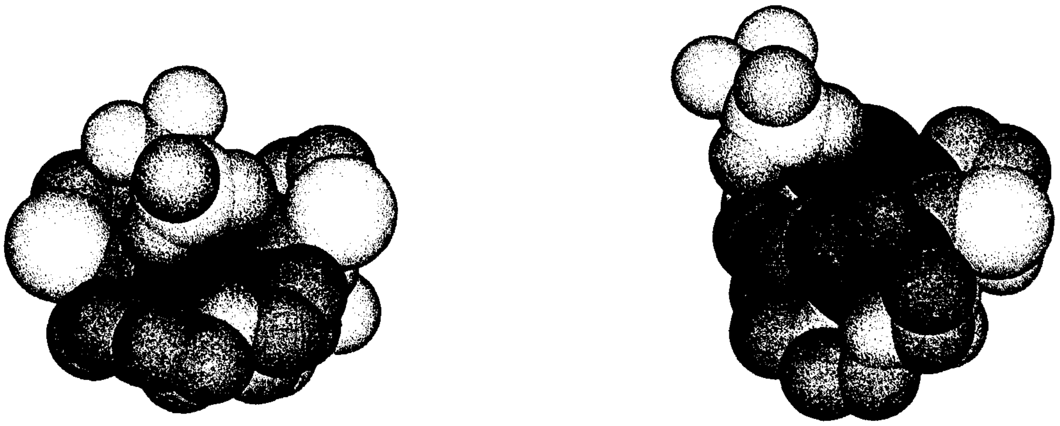
Space filling model of view 1

Space filling model of view 2

Cylindrical bonds model of view 1

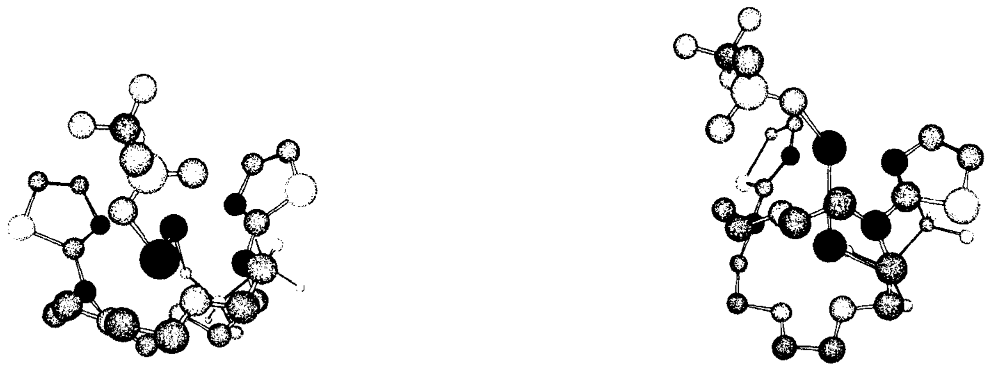
Cylindrical bonds model of view 2

Structure of **2a**



Space filling model of view 3

Space filling model of view 4

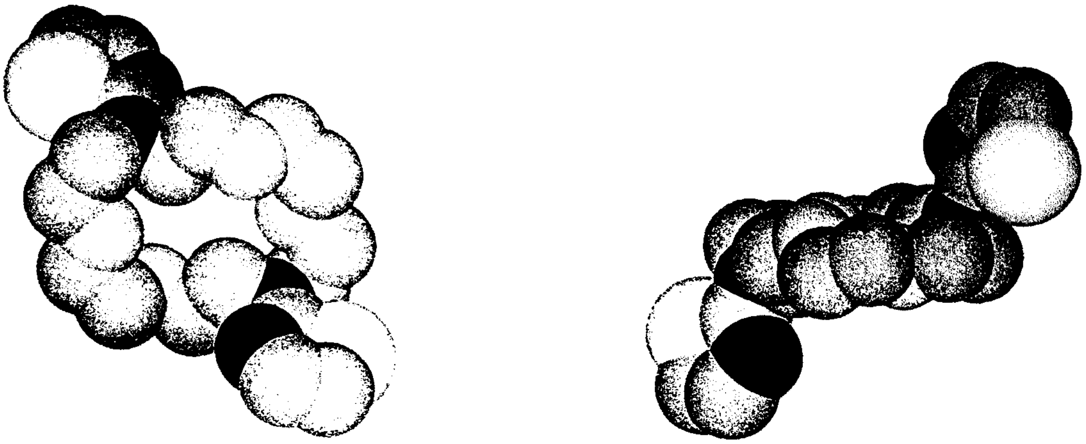


Cylindrical bonds model of view 3

Cylindrical bonds model of view 4

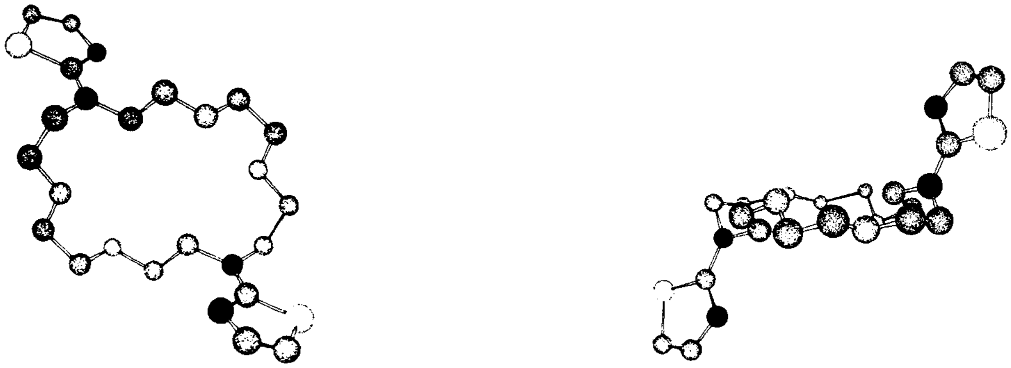
Structure of the 2:1 AgO_3SCF_3 complex of **2a**

Figure 1 Structure of **2a** and its 2:1 AgO_3SCF_3 complex. All hydrogen atoms are omitted for clarity.



Space filling model of view 1

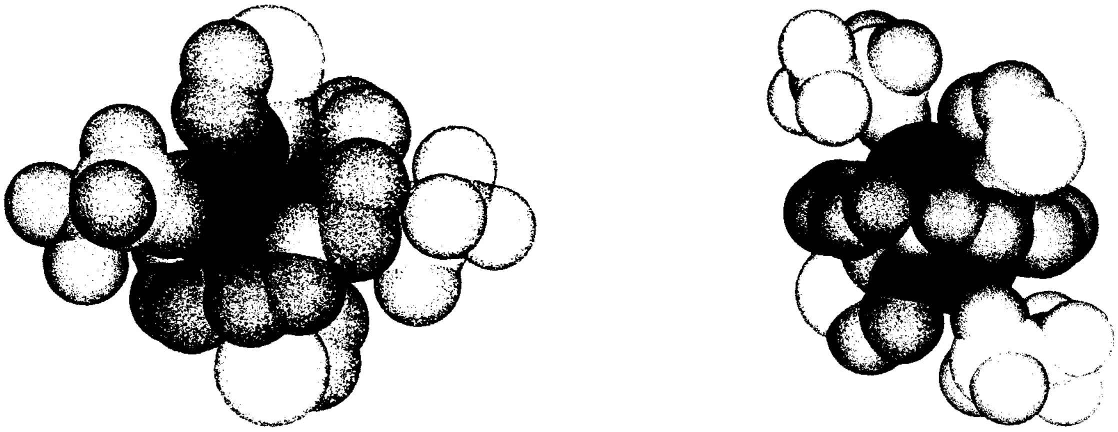
Space filling model of view 2



Cylindrical bonds model of view 1

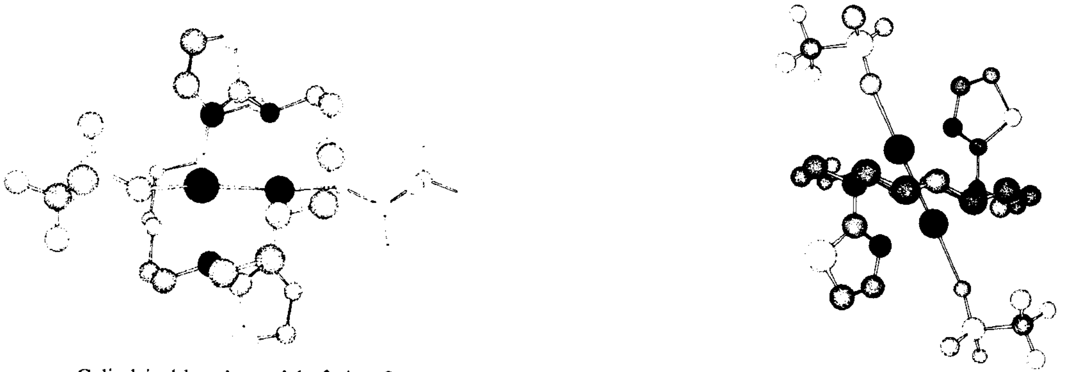
Structure of **2b**

Cylindrical bonds model of view 2



Space filling model of view 3

Space filling model of view 4



Cylindrical bonds model of view 3

Cylindrical bonds model of view 4

Structure of 2:1 AgO_3SCF_3 complex of **2b**

Figure 2 Structure of **2b** and its 2:1 AgO_3SCF_3 complex. All hydrogen atoms are omitted for clarity.

functionalized sidearms upon complexation in solution. It is indeed the case that a guest cation can organize a ligand conformation.

In conclusion, the thiazole-functionalized arms are confirmed to play important roles in these two binuclear complexes, and the size of the crown ring significantly influences the structure of the complexes. Theoretical calculations on the relative stabilities among possible conformations of these AgTf complexes are envisaged in order to explain the structural difference described above.

EXPERIMENTAL SECTION

Solvents and reagents including diaza-crown ethers **1a**–**1c** are commercially available and were used without any additional purification.

General procedure for synthesizing functionalized diaza-crown ethers

A mixture of non-functionalized diaza-crown ether **1a** (1.37 mmol), the heteroaromatic halide (chloride or bromide) (5.48 mmol), an excess of triethylamine (10.7 mmol), and 8 ml of THF in a polytetrafluoroethylene tube, was compressed to 0.8 GPa (8 kbar) at 100°C for a few days. After cooling and depressurization, solvent and unreacted triethylamine were evaporated. The quarternary salt precipitated and was removed by filtration and the product was isolated by chromatography on silica gel.

Isolation of the AgTF complex of 2a

In a 30 ml two-necked pyrex flask, 111.4 mg (0.29 mmol) of **2a** and 215.3 mg (0.938 mmol, 2.89 equiv.) of AgTf were dissolved in 10 ml of dry THF. After stirring overnight at room temperature under an argon atmosphere, the mixture was filtered and the solid was washed with 50 ml of dichloromethane. The filtrate was evaporated and 208.5 mg of crude product was obtained. Recrystallization from dichloromethane–hexane gave complex crystals as colourless prisms. m.p. 180–183°C decomposed. Anal. calcd. for $C_{18}H_{24}O_9N_4S_4F_6Ag_2$: C, 24.06; H, 2.69; N, 6.24. Found: C, 23.88; H, 2.57; N, 6.06.

Isolation of the AgTf complex of 2b

The reaction was carried out in dry THF using **2b** as above. Colourless plates, m.p. 163–164°C were obtained. Anal. calcd. for $C_{20}H_{28}O_{10}N_4S_4F_6Ag_2$: C, 25.49; H, 2.99; N, 5.94. Found: C, 25.21; H, 2.87; N, 6.03.

ACKNOWLEDGEMENT

This research was supported in part by Shimazdu Science Foundation and a Sasakawa Scientific Research Grant from the Japan Science Society to M.T., Grant-In-Aid for Scientific Research (No. 04303003, 04453023) to K.M. and (No. 04804037) to H.T. and from the Ministry of Education, Science and Culture, Japan and The Salt Science Research Foundation (No. 92002) to H.T.

REFERENCES

1 Matsumoto, K.; Sera, A.; Uchida, T.; *Synthesis 1*, **1985**. Matsumoto, K.; Sera, A.; *Synthesis* 999, **1985**.
2 Noble, W.; Kelm, H.; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 841. Matsumoto, K.; Acheson, R.M.; in *Organic Synthesis at High Pressure*, John-Wiley, New York, 1991.
3 Ibata, T.; Isogai, Y.; Toyoda, J.; *Chem. Lett.* **1987**, 1187. Matsumoto, K.; Toda, M.; Hashimoto, S.; *Chem. Lett.* **1991**, 1283. Matsumoto, K.; Hashimoto, S.; Hasimoto, M.; Toda, M.; Otani, S.; *Syn. Commun.* **1992**, *22*, 787.
4 Matsumoto, K.; Minatogawa, H.; Munakata, M.; Toda, M.; Tsukube, H.; *Tetrahedron Lett.* **1990**, *31*, 3923.
5 Tsukube, H.; Minatogawa, H.; Munakata, M.; Toda, M.; Matsumoto, K.; *J. Org. Chem.* **1992**, *57*, 542.
6 Hirotsu, K.; Miyahara, I.; Higuchi, T.; Toda, M.; Tsukube, H.; Matsumoto, K.; *Chem. Lett.* **1992**, 699.