Pergamon

Tetrahedron Letters 42 (2001) 8047–8050

TETRAHEDRON
LETTERS

Silver ion oscillation through calix[4]azacrown tube

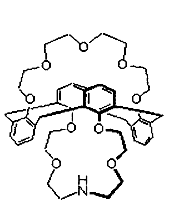
Jong Seung Kim,[a,]* Seung Hwan Yang,[a] Jeong Ah Rim,[a] Jong Yeol Kim,[b] Jacques Vicens[c] and Seiji Shinkai[d]

[a]*Department of Chemistry, Konyang University, Nonsan 320-711, South Korea*
[b]*Korea Ginseng & Tobacco Research Institute, Taejon 305-345, South Korea*
[c]*ECPM, Becquerel, F-67087 Strasbourg, Cédex 2, France*
[d]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan*

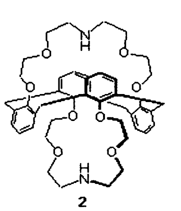
Received 1 August 2001; revised 5 September 2001; accepted 7 September 2001

Abstract—Silver ion oscillation through calixtube of 1,3-alternate calix[4]crown-5-azacrown-5 and 1,3-alternate calix[4]-bis-azacrown-5 was investigated by temperature variable ^{1}H NMR experiment. The latter (symmetrical calix-bis-azacrown-5) showed an intramolecular metal ion tunneling through π-basic calixtube while the former did not. © 2001 Elsevier Science Ltd. All rights reserved.

Calixcrown ethers have been of intensively interest in the selective metal ion recognition.[1–3] The 1,3-alternate calix[4]crown and calix[4]-bis-crown type receptors present structural peculiarities.[4] They provide two binding sites departed on both sides of the calixarene and linked to each other by a π-basic benzene tunnel.[5–8] This symmetrical arrangement is well adapted for the formation of 1:1 and 1:2 metal complexes. For example in the 1:1 complex with 1,3-calix[4]-bis-crown-5, the cation switches from one binding site to the other, so-called 'metal oscillation' through the π-basic benzene tunnel.[9] Previously, Shinkai group reported that the replacement of the central O donor atom by *N*-butyl group in a crown loop leads to 1,3-alternate calix[4]azacrowns acting as an artificial 'molecular syringe' that silver ion locates in the azacrown cavity at neutral pH, but by protonation it moves to the other part through the calixtube because of significant repulsion between $^+$N–H and the Ag$^+$ ion.[10,11] From the reported results, our curiosity has been stimulated on the Ag$^+$ ion oscillation in the 1,3-alternate calix[4]crown-5-azacrown-5 (**1**)[12–15] and in the 1,3-alternate calix[4]-bis-azacrown-5 (**2**).[12,15]



1



2

Temperature dependent ^{1}H NMR experiment showed 1:1 complex ratio between **1** and Ag$^+$ ion as shown in Fig. 1. It has been noted that the Ag$^+$ ion was not encapsulated in the center of an azacrown loop, but rather perching on the azacrown loop due to size disagreement between the azacrown cavity and the Ag$^+$ ion.[10] So, at 246 K, *meta*-hydrogen atoms (H_a and H_c) toward azacrown part were found to move downfield as two doublet peaks at δ 7.40 (H_a) and at δ 7.55 (H_c), respectively because the Ag$^+$ ion was unsymmetrically bound.[10] In contrast, H_e and H_g toward the crown-5 part seldom changed. This unusual NMR pattern has been explained by an intramolecular 'rope-jumping'[10] as shown in Fig. 2. With increasing temperature, this rope-jumping takes place more rapidly and then the speed of the motion and NMR time scale are almost identical to give a collapsing peak at 274 K. Further increases in the temperature do not seem to give an Ag$^+$ ion tunneling effect through the calixtube, which is attributable to the higher binding ability of the Ag$^+$ ion to the azacrown than to the crown ether loop. Instead, we anticipate peak coalescence by intermolecular decomplexation of the Ag$^+$ ion at over 305 K.

In order to investigate the metal ion tunneling based on the concept of 'molecular syringe' reported by Shinkai,

---

* Corresponding author. Tel.: +82-41-730-5240; fax: +82-41-733-5240; e-mail: jongskim@konyang.ac.kr

0040-4039/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(01)01712-9

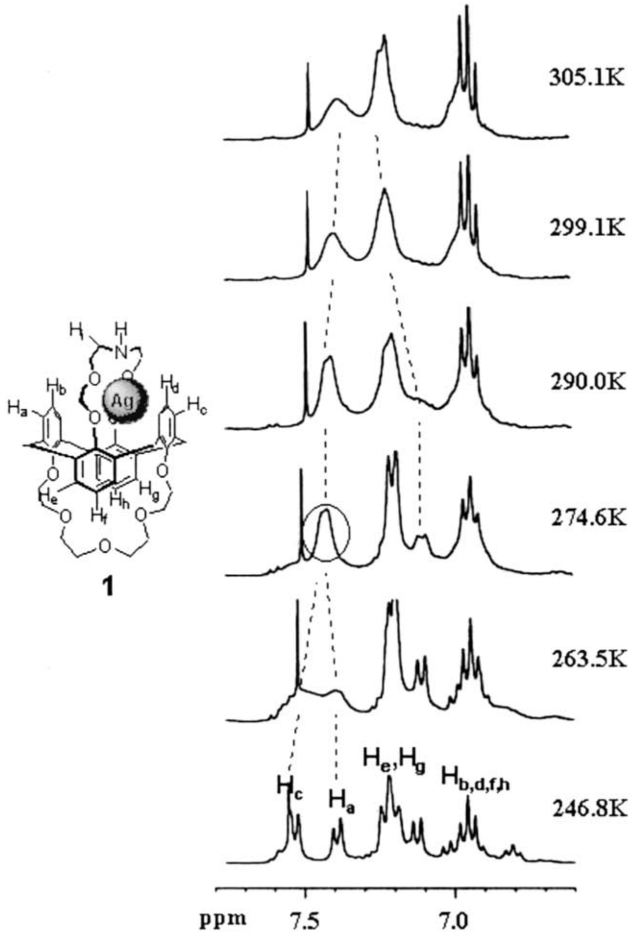


Figure 1. Temperature variable ^1H NMR spectra (600 MHz) of $\mathbf{1}\cdot Ag^+$, $CDCl_3:CD_3OD=4:1$, guest: AgO_3SCF_3.

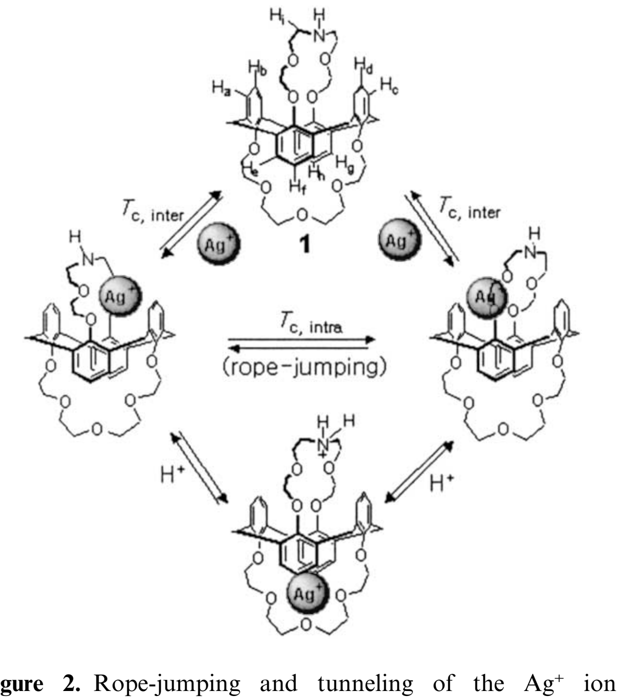


Figure 2. Rope-jumping and tunneling of the Ag^+ ion through calixazacron-5 by protonation (CF_3CO_2H). $T_{c,intra}$ denotes intramolecular coalescence temperature. $T_{c,inter}$ denotes intermolecular coalescence temperature.

we took ^1H NMR of **1**, $\mathbf{1}\cdot Ag^+$ and $\mathbf{1}\cdot(H^+)\cdot Ag^+$ consecutively and the results are depicted in Fig. 3. When the nitrogen atom in the azacrown loop is protonated, the Ag^+ ion would be pushed out through the π-basic cavity to the crown-5 loop due to an electrostatic repulsion.[10] For the Ag^+ ion complex, H_a (Ar–H_{meta}) shifted downfield from δ 7.11 to δ 7.41. When it was protonated, H_i (CH_2-NH-CH_2) also shifted downfield from δ 2.85 to δ 3.14. In addition, H_e towards crown-5 loop remarkably changed by $\Delta\delta=0.40$, while H_a slightly changed by $\Delta\delta=0.11$, which can indicate Ag^+ ion tunneling by an electrostatic repulsion between quaternary ammonium cation and Ag^+ ion. These results are quite consistent with those reported by Shinkai group.

Unlike **1**, the X-ray crystal structure of **2** has a D_{2h}-symmetrical tube-shaped π-basic cavity composed of four benzene rings.[15] Therefore, for **2** we have examined the possibility of the intramolecular metal ion tunneling as observed in the conventional calix-bis-crown-5.[9] Fig. 4 indicates temperature variable ^1H NMR spectra of $\mathbf{2}\cdot Ag^+$ complex. At 246 K, complexed Ar–H_{meta} (H_a) and uncomplexed Ar–H_{meta} (H_c) are separated due to the slow rope-jumping and then finally collapsed at 274 K, which is similar to those of $\mathbf{1}\cdot Ag^+$.

Further increase of the temperature up to 305 K provided the other collapsing mode of Ar–H_{meta} ($H_{a,c}$ and

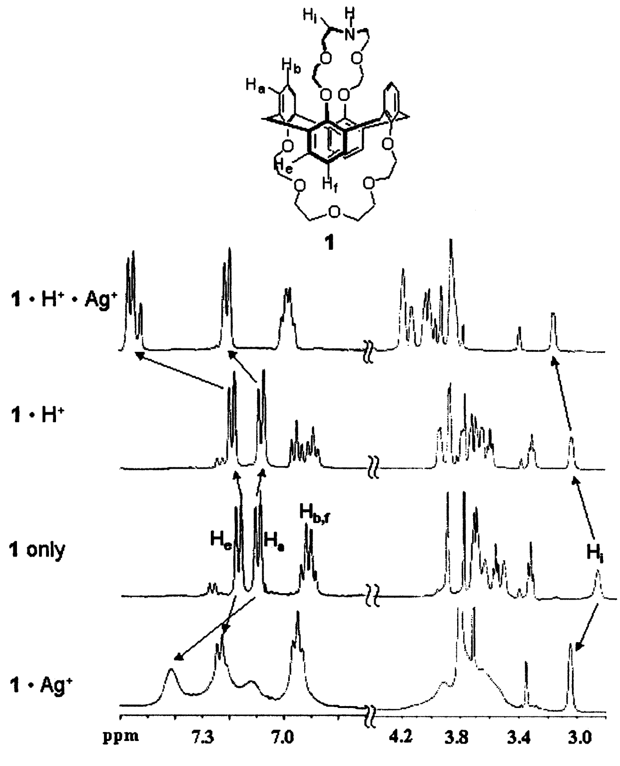


Figure 3. Partial spectra for protonation of $\mathbf{1}\cdot Ag^+$. 600 MHz ^1H NMR, $CDCl_3:CD_3OD=4:1$, guest ion: AgO_3SCF_3, H^+: CF_3CO_2H.

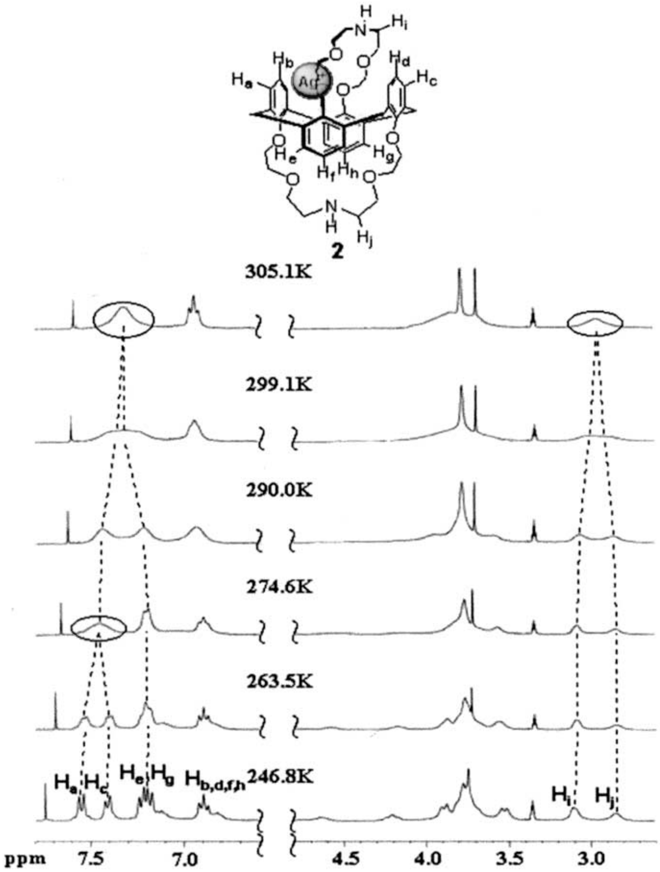


Figure 4. Temperature variable ^{1}H NMR spectra (600 MHz) of **2**·Ag^{+}. $CDCl_3$: $CD_3OD=4:1$.

$H_{e,g}$), which clearly implicates that there is a significant intramolecular Ag^{+} ion tunneling through the π-basic tube. In this NMR time scale, the Ag^{+} ion oscillation through the calixtube is slow enough to be distinguishable at below 305 K. For this metal ion oscillation, it is immediately evident that the NMR pattern of H_i and H_j adjacent to the nitrogen atom of the azacrown loop. H_i shifted downfield due to the complexation with Ag^{+} ion. Two separated peaks of H_i and H_j did not change until 274 K at which the peak coalescence takes place by rapid rope-jumping. They were finally observed to collapse at 305 K, which can support the intramolecular Ag^{+} ion moving through the calixtube passage as discussed above. Ag^{+} ion oscillation mechanism through the calix[4]-bis-azacrown-5 channel is depicted in Fig. 5.

In conclusion, dynamic ^{1}H NMR spectroscopy with temperature variation showed that the silver ion oscillates intramolecularly between the two azacrown cavities of the symmetrical calix-bis-azacrown-5 (**2**) through a π-basic calixtube, whereas it stops in the azacrown cavity in the case of unsymmetrical calix-azacrown (**1**).

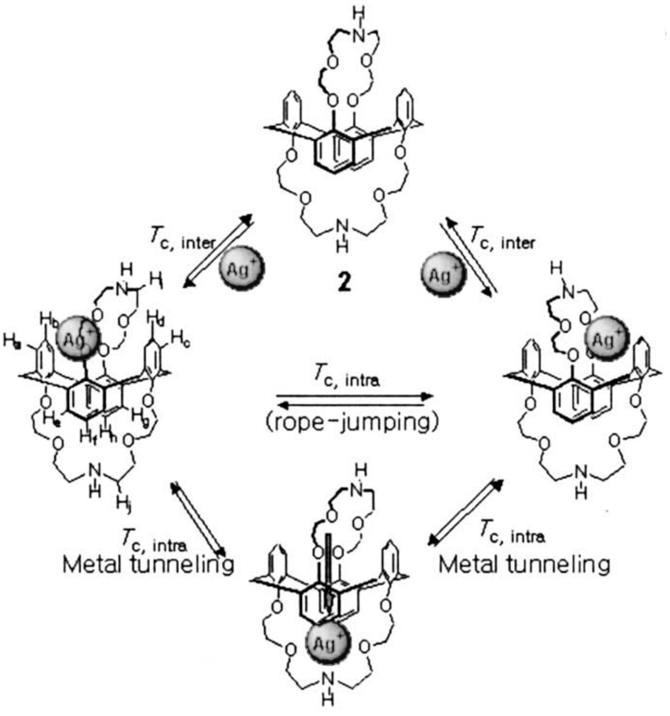


Figure 5. Ag^{+} ion oscillation through calix[4]-bis-azacrown-5 (**2**) channel.

Acknowledgements

This work was supported by Grant 2000-1-12300-001-3 from the Basic Research Program of the Korea Science and Engineering Foundation. We thank the Korea Basic Science Institute in Taejon, Korea, for use of the Bruker ARX-600 NMR spectrometer.

References

1. Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989.
2. Gutsche, C. D. In *Synthesis of Macrocycles*: *Design of Selective Complexing Agents*; Izatt, R. M.; Christensen, J. J., Eds.; Wiley: New York, 1987; p. 93.
3. Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, 1998.
4. Thuéry, P.; Nierlich, M.; Lamare, V.; Dozol, J. F.; Asfari, Z.; Vicens, J. *J. Incl. Phenom.* **2000**, *36*, 375–408.
5. Kim, J. S.; Lee, W. K.; Kim, J. G.; Suh, I. H.; Yoon, J. Y.; Lee, J. H. *J. Org. Chem.* **2000**, *65*, 7215.
6. Asfari, Z.; Naumann, C.; Vicens, J.; Nierlich, M.; Thuéry, P.; Bressot, C.; Lamare, V.; Dozol, J. F. *New J. Chem.* **1996**, *20*, 1183.
7. Arnaud-Neu, F.; Asfari, Z.; Souley, B.; Vicens, J. *New J. Chem.* **1996**, *20*, 453–463.
8. Asfari, Z.; Abidi, R.; Arnaud-Neu, F.; Vicens, J. *J. Incl. Phenom. Macro. Chem.* **1992**, *13*, 163.
9. Koh, K. N.; Araki, K.; Shinkai, S.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **1995**, *36*, 6095–6098.

10. Ikeda, A.; Tsudera, T.; Shinkai, S. *J. Org. Chem.* **1997**, *62*, 3568–3574.
11. Bissell, R. A.; Cordova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133.
12. Kim, J. S.; Lee, W. K.; No, K.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **2000**, *41*, 6095–6098.
13. Kim, J. S.; Suh, I. H.; Kim, J. K.; Cho, M. H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2307.
14. Kim, J. S.; Pang, J. H.; Yu, I. Y.; Lee, W. K.; Suh, I. H.; Kim, J. K.; Cho, M. H.; Kim, E. T.; Ra, D. Y. *J. Chem. Soc., Perkin Trans. 2* **1999**, 837.
15. Kim, J. S.; Jensen, W. P.; Lee, C. H.; Lee, J. H.; Kim, M. J.; Kim, J. G.; Suh, I. H. *Acta Crystallogr.* **2000**, *C56*, 379–381.