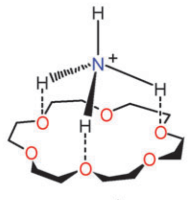
Surprisingly stable ammonium ion complex of a non-cyclic crown-type polyether: solid and solution studies†

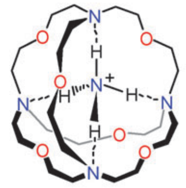
Ki-Min Park,*[a] Hyun Jee Kim,[a] Suk-Hee Moon,[b] Jagadese J. Vittal,[ac]
Jong Hwa Jung[a] and Shim Sung Lee*[a]

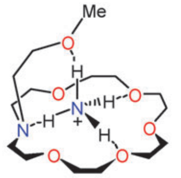
Received (in Victoria, Australia) 29th January 2010, Accepted 22nd February 2010
First published as an Advance Article on the web 11th March 2010
DOI: 10.1039/c0nj00074d

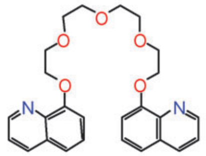
The first crystal structure of an NH_4^+ ion complex with 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (L), a representative non-cyclic analogue of 18-crown-6, is reported along with the characteristics of the complex's solution; very interestingly, L forms a more stable complex with the NH_4^+ ion than does 18-crown-6 by the formation of unique recognition tetrahedral-type hydrogen bonds.

Discovery of the remarkable complexing abilities of macrocyclic polyethers toward metal cations, NH_4^+ derivatives and other neutral molecules has provided new challenges in chemistry during the last four decades.[1–4] Non-cyclic, crown-type polyethers have also attracted much attention because of their similar behaviour to crown ethers, and they seem to provide model compounds in the areas of stereoselective complexation, cation transport and enzyme chemistry.[2d,5–9] The recognition of organic cations, particularly NH_4^+ species, *via* hydrogen bonding is of significant interest. In terms of molecular geometry, how can the cyclic and non-cyclic polyethers bind to ammonium (or alkyl ammonium) ions with tetrahedral shapes? In this view, the elucidation of the crystal structure of the NH_4^+ ion complex of 18-crown-6 (**1**),[4] exhibiting a tripod arrangement of $^+NH\cdots O$ hydrogen bonds on one face of the macrocyclic cavity in a perching mode, has provided not only the answer to this old question but also the inspiration for progress in the recognition of biomolecules for many chemists.[2–4] In this case, the fourth N–H is not involved in a direct interaction and points away from the crown ring. In fact, host molecules with three-dimensional structures, such as 'soccer ball' cryptand (**2**)[10] and lariat crown (**3**),[11] show steric feasibility for the tetrahedral recognition of the NH_4^+ ion, thus enhancing their binding affinity and selectivity.


18-Crown-6·NH_4^+ complex (**1**)


Cryptand·NH_4^+ complex (**2**)


Lariat crown·NH_4^+ complex (**3**)


L

Among the non-cyclic, crown-type polyethers, 1,13-bis-(8-quinolyl)-1,4,7,10,13-pentaoxatridecane [**L** (in this work), Kryptofix-5® (commercial name)][6] is a representative example due to its similar behaviour to 18-crown-6 and because it has the attractive capability of forming pseudo-cyclic complexes with cationic guests in a manner similar to cyclic species.[2d,6–9] In general, however, the affinity of open chain polyether ligands for alkylammonium guests is much weaker, and the complexation process thus much less effective.[2d,7]

A similar question to the structural aspects of the NH_4^+ complex of 18-crown-6 can be raised for **L**. It should be noted that the complexation of **L** with some metal cations, alkylammoniums and small neutral organic molecules has already been extensively investigated.[2d,6–9] In addition, its stoichiometric complexation with the NH_4^+ ion was introduced by Vögtle *et al.* as early as 1977.[6] It is amazing that no crystal structure of its NH_4^+ ion complex has ben available until now, even though the knowledge of such structural information is a prerequisite for progress in the recognition of organic and biomolecules.

In an extension of our work on the complexation of **L**,[9] we were able to prepare crystals of the complex of **L** with the NH_4^+ ion that were suitable for X-ray analysis. Herein, we report the preparation and crystal structure of the NH_4^+ ion complex of **L**. The photophysical and thermal properties of the complex are also described. In addition to the solid state study, NMR titrations of **L** and 18-crown-6 with the NH_4^+ ion in acetonitrile were undertaken to compare their stability constants of complexation.

---

[a] *Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University, Jinju 660-701, South Korea. E-mail: kmpark@gnu.ac.kr, sslee@gnu.ac.kr; Fax: +82 55-753-7614; Tel: +82 55-751-6021*
[b] *Subdivision of Food Science, Kyungnam College of Information and Technology, Busan 616-701, South Korea*
[c] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore*

† Electronic supplementary information (ESI) available: Details of experimental, X-ray crystallographic data, ORTEP diagram, crystal packing structure, FAB mass spectra, photos of **L** and [**L**·NH_4]PF_6 in the solid state after excitation, ^1H NMR titration spectrum for **L** and 18-crown-6 with NH_4PF_6, and their fitting plot of WinEQNMR, and TG-DTA data of [**L**·NH_4]PF_6. CCDC 760717. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00074d

Slow evaporation of an acetonitrile solution of **L** with one equiv. of NH_4PF_6 afforded colorless crystals of the complex that were suitable for X-ray analysis‡ in a quantitative yield. The complex crystallised in a 1 : 1 complex of formula $[\mathbf{L}\cdot NH_4]PF_6$ (Fig. 1). In association with the NH_4^+ ion, **L** differs from 18-crown-6 in the solid state. Comparing the crystal structures of the NH_4^+ ion complexes of 18-crown-6[4] and **L**, it is noteworthy that one $^+$N–H in $[\text{18-crown-6}\cdot NH_4]^+$ remains uncoordinated to 18-crown-6, while all four $^+$N–H moieties are coordinated to **L** in $[\mathbf{L}\cdot NH_4]^+$, despite cyclic ligands being stronger than non-cyclic examples towards most common metal and organic cations. In $[\mathbf{L}\cdot NH_4]^+$, the NH_4^+ ion is in the centre of the complex surrounded by **L** in a helical manner. Notably, the NH_4^+ ion is strongly hydrogen bonded by two ether oxygens ($^+N\cdots O$ distances are 2.991(3) Å for $^+$N3–H3B···O2 and 2.898(3) Å for $^+$N3–H3C···O4) and two hetero nitrogens ($^+N\cdots N$ distances are 2.849(3) Å for $^+$N3–H3A···N1 and 2.842(3) Å for $^+$N3–H3D···N2) of **L**. These observed distances for $[\mathbf{L}\cdot NH_4]^+$ (average 2.895 Å) are not significantly different from those of $[\text{18-crown-6}\cdot NH_4]^+$ ($^+N\cdots O$ distance 2.84–2.86 Å).[4] Three other oxygen atoms (O1, O3 and O5) in $[\mathbf{L}\cdot NH_4]^+$ are in the range 2.924–3.061 Å from the NH_4^+ nitrogen. In addition, the observed large dihedral angle (67.7°) between the two quinoline groups in **L** may be induced by the formation of effective $^+$N–H···N-type hydrogen bonds. As a result, the nitrogen atoms in the quinoline group provide not only better hydrogen bonding sites but also stronger donors than those offered by ether oxygens.

On the other hand, the complexed ligand is characterised by the torsion angles between two adjacent donors. In $[\mathbf{L}\cdot NH_4]^+$, as might be expected, all the donors are associated with a *gauche* conformation upon complexation with the NH_4^+ ion. No intramolecular π–π interaction between pairs of quinoline groups are observed (Fig. 1c). Instead, intermolecular π–π interactions between the quinoline moieties of adjacent complexes occur with distances of 3.478(6) and 3.523(7) Å (ESI, Fig. S1a†). Consequently, unlike 18-crown-6, open chain ligand **L** adopts a helical structure to optimise the tetrahedral interactions: the NH_4^+ guest in $[\mathbf{L}\cdot NH_4]^+$ is found to be almost fully encircled by the open chain molecule and lies roughly in parallel with the average plane of the ligand (Fig. 1b and c).

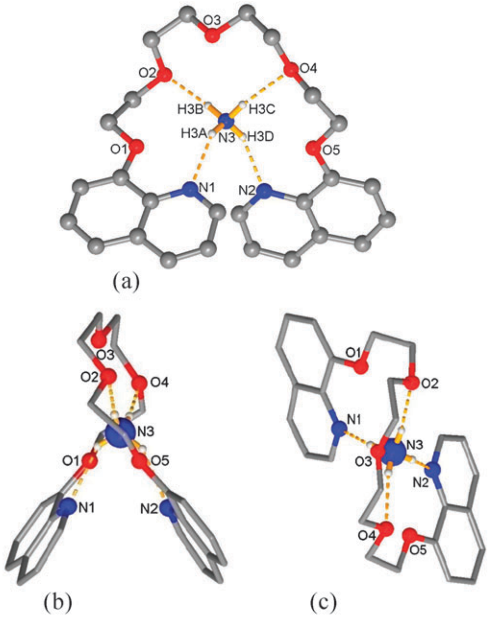


Fig. 1 The crystal structure of $[\mathbf{L}\cdot NH_4]PF_6$: (a) general view, (b) side view and (c) top view.

For comparison, NMR solution titrations of **L** and 18-crown-6 with NH_4PF_6 were carried out in CD_3CN (Fig. 2; ESI, Fig. S5 and S7†), because no NMR titration and thermodynamic data[12] in acetonitrile for both ligands are available in literature. The signals of the aliphatic (H_{1-4}) and aromatic (H_{a-f}) protons in **L** were well resolved and identified. Contrary to the case of **L**, 18-crown-6 showed only one singlet peak due to the high symmetry of the molecule. Upon the stepwise addition of NH_4^+, in both cases, every proton in each ligand shifted, suggesting stable complexation for the fast exchanging system. The titration curves [plotting δΔ (ppm) *vs.* added equivalents of NH_4PF_6] for each proton clearly showed an inflection point at a mole ratio of 1.0, indicating that the stoichiometry of the complexes is 1 : 1 in solution, which is the same as that in the solid state. In the case of **L**, the order of magnitude of the chemical shift variation was $H_f > H_e \gg H_a, H_d, H_{2-4} > H_b, H_1 > H_c$. Upon complexation, NH_4^+ causes a much larger downfield shift for H_f and H_e in the aromatic region than it does for the aliphatic protons. Thus, the NH_4^+ appears to be more strongly coordinated by N donors, while the O donors interact with the NH_4^+ relatively weakly. Once again, all the NMR data agree with the binding mode seen in the solid state, suggesting that the solid state structure of $[\mathbf{L}\cdot NH_4]^+$ is also retained in solution. The affinity of NH_4^+ towards **L** in a 1 : 1 ratio was also observed by FAB mass spectrometry measurements, $[\mathbf{L}\cdot NH_4]^+$ *m*/*z* 466.

On the basis of curve-fitting analysis of the ^{1}H NMR titration curves using the WinEQN MR program,[13] the stability constants (log *K*) for the 1 : 1 complexes of $[\text{18-crown-6}\cdot NH_4]^+$ and $[\mathbf{L}\cdot NH_4]^+$ were determined (Table 1). Surprisingly, **L** (log K = 4.24) forms a more stable complex with the NH_4^+ ion than does 18-crown-6 (log K = 3.59), and the difference between the two values is quite significant. As mentioned for $[\text{18-crown-6}\cdot NH_4]^+$, the NH_4^+ ion engages in three H-bonds

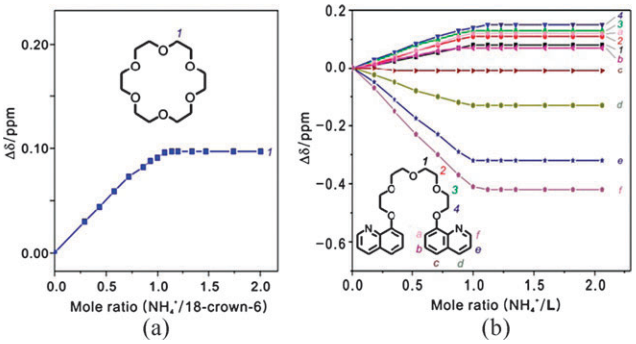


Fig. 2 NMR titration curves for (a) 18-crown-6 and (b) **L** with NH_4PF_6 in CD_3CN.

Table 1 Stability constants for the complexation of NH_4PF_6 with 18-crown-6 and **L** in CD_3CN-d_3 at room temperature

Ligand	Log *K*	Ratio	Method
18-crown-6	3.59	1 : 1	NMR
L	4.24	1 : 1	NMR

with three oxygen atoms among the six donors (O_6) in the ring, and one of the NH functionalities is not involved in binding. In the case of **L**, however, the non-cyclic chain, with seven donors (N_2O_5), is able to wrap around and hydrogen bond with the remaining NH functionality, forming a more stable complex than normally expected for non-cyclic donors.

The photoluminescence properties of **L** and [**L**·NH_4]PF_6 were also investigated, both in solution and in the solid state (Fig. 3). **L** exhibits indigo-violet photoluminescence dominated by emissions at 380 and 407 nm in solution and the solid state, respectively, due to a π–π* transition of the quinoline moiety. Upon complexation with NH_4^+ ions, the maxima of the emission spectra in solution and in the solid state are shifted to 392 and 480 nm, respectively. In other words, when [**L**·NH_4]$^+$ is generated, the red-shift value observed in the solid state ($\Delta\lambda_{em}$ = 73 nm) is much larger than that seen in solution ($\Delta\lambda_{em}$ = 12 nm), indicating that the observed π–π interactions between quinoline moieties in the solid state are more effective than those in solution. This is due to the presence of intermolecular π–π interactions between quinoline moieties in the solid state, as mentioned in the single-crystal structure analysis (ESI, Fig. S1†).

To examine the effect of the hydrogen bonds on its thermal properties, a crystalline sample [**L**·NH_4]PF_6 was characterised by TGA and DTA (ESI, Fig. S9†). The TGA curve shows a first mass loss of 2.67% from 166 to 200 °C that corresponds to the complete loss of one NH_4^+ ion (expected mass loss 2.62%), encapsulated by **L** *via* four strong hydrogen bonds. This thermal behaviour may be induced by the four hydrogen bonds between **L** and NH_4^+ in the solid state mentioned above in the crystal structure analysis.

In summary, the preparation and structural characterisation of the NH_4^+ ion complex with non-cyclic crown-type polyether **L** has been reported. Unlike 18-crown-6, which shows a perching-type of hydrogen binding with the NH_4^+ ion, **L** adopts a helical structure in order to optimise tetrahedral recognition in the solid state. This conformation serves the reason why the non-cyclic ligand shows a rather larger affinity for the NH_4^+ ion than does 18-crown-6 in solution. Photoluminescence and TGA studies support the notion that the non-cyclic ligand interacts efficiently with the NH_4^+ ion and stabilises its hydrogen-bonded complex.

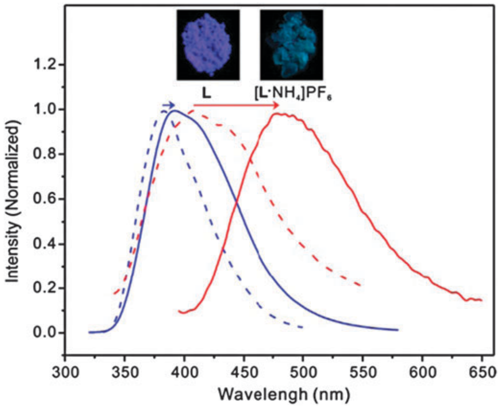


Fig. 3 Photoluminescence spectra of **L** (---) and [**L**·NH_4]PF_6 (—) in the solid state (red) and in solution (acetonitrile, blue) (λ_{ex} = 302 nm).

This research was supported by grant no. R32-2008-000-20003-0 from the WCU project of MEST and KOSEF through Gyeongsang National University.

Notes and references

‡ Crystal data for [**L**·NH_4]PF_6: $NH_4·C_{26}H_{28}N_2O_5·PF_6$, *M* = 611.52, monoclinic, *a* = 9.7803(6), *b* = 18.3376(12), *c* = 16.0545(11) Å, β = 101.608(1)°, *U* = 2820.4(3) Å^3, *T* = 298(2) K, space group $P2_1/c$ (no. 14), *Z* = 4, μ = 0.179 mm^{-1}, 17 031 reflections measured, 6178 unique (R_{int} = 0.0435). Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0537 ($I > 2\sigma(I)$) and wR_2 = 0.1706 (all data) with GOF = 1.041.†

1 (*a*) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 2495; (*b*) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7077.
2 (*a*) G. W. Gokel, in *Crown Ethers and Cryptands*, ed. J. F. Stoddart, The Royal Society of Chemistry, Cambridge, 1994, ch. 6, pp. 253; (*b*) N. K. Dalley, in *Synthetic Multidentate Macrocyclic Compounds*, ed. R. M. Izatt and J. J. Christensen, New York Academic Press, New York, 1978, pp. 270; (*c*) R. Hilgenfeld and W. Saenger, *Top. Curr. Chem.*, 1982, **101**, 1; (*d*) F. Vögtle, H. Sieger and W. M. Müller, *Top. Curr. Chem.*, 1981, **98**, 107; (*e*) M. R. Truter, *Struct. Bonding*, 1973, **16**, 71; (*f*) H. Tsukube, in *Cation Binding by Macrocycles*, ed. Y. Inoue and G. W. Gokel, Marcel Dekker, New York, 1990, ch. 3, pp. 99.
3 I. Goldberg, Complexes of Crown Ethers with Molecular Guests, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London, 1984, vol. 2, pp. 261.
4 (*a*) J. M. Timko, S. S. Moore, D. M. Walba, P. C. Hiberty and D. J. Cram, *J. Am. Chem. Soc.*, 1977, **99**, 4207; (*b*) O. Nagano, A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 790; (*c*) K. N. Trueblood, C. B. Knobler, D. S. Lawrence and R. V. Stevens, *J. Am. Chem. Soc.*, 1982, **104**, 1355; (*d*) S. S. Lee, J. H. Jung, D. J. Chang and B. Y. Lee, *Bull. Korean Chem. Soc.*, 1990, **11**, 521; (*e*) D. Braga, M. Gandolfi, M. Lusi, D. Paolucci, M. Polito, K. Rubini and F. Grepioni, *Chem.–Eur. J.*, 2007, **13**, 5249.
5 Y. Suzuki, T. Morozumi and H. Nakamura, *J. Phys. Chem. B*, 1998, **102**, 7910.
6 B. Tümmler, G. Maass, E. Weber, W. Weher and F. Vögtle, *J. Am. Chem. Soc.*, 1977, **99**, 4683.
7 (*a*) B. Tümmler, G. Maass, F. Vögtle, H. Sieger, U. Heimann and E. Weber, *J. Am. Chem. Soc.*, 1979, **101**, 2588; (*b*) R. Wakita, M. Miyakooshi, Y. Nakatsuji and M. Okahara, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1991, **10**, 127.
8 (*a*) W. Saenger and H. Brand, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **35**, 838; (*b*) W. Saenger, I. H. Suh and G. Weber, *Isr. J. Chem.*, 1979, **18**, 253; (*c*) G. Weber and W. Saenger, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 424; (*d*) J. Pickardt and S. Wiese, *Z. Naturforsch., B*, 2000, **55**, 971; (*e*) G. Weber and W. Saenger, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **35**, 1346.
9 (*a*) Y. Kang, S.-T. Moon, S. Park, J. Kim, S. S. Lee and K.-M. Park, *Bull. Korean Chem. Soc.*, 2007, **28**, 873; (*b*) K.-M. Park, S.-T. Moon, Y. J. Kang, H. J. Kim, J. Seo and S. S. Lee, *Inorg. Chem. Commun.*, 2006, **9**, 671; (*c*) I. Yoon, Y. H. Lee, J. H. Jung, K.-M. Park, J. Kim and S. S. Lee, *Inorg. Chem. Commun.*, 2002, **5**, 820; (*d*) S. S. Lee, J. H. Jung, S. H. Yu and M. H. Cho, *Thermochim. Acta*, 1995, **259**, 133.

10 B. Metz, J. M. Rosalky and R. Weiss, *J. Chem. Soc., Chem. Commun.*, 1976, 533b.

11 (*a*) R. A. Schultz, E. Schelgel, D. M. Dishong and G. W. Gokel, *J. Chem. Soc., Chem. Commun.*, 1982, 242; (*b*) R. A. Schultz, B. D. White, D. M. Dishong, K. A. Arnold and G. W. Gokel, *J. Am. Chem. Soc.*, 1985, **107**, 6659.

12 R. M. Izatt, J. D. Lamb, N. E. Izatt, B. E. Rossiter, Jr., J. J. Chritensen and B. L. Haymore, *J. Am. Chem. Soc.*, 1979, **101**, 6273.

13 (*a*) H. J. Schneider, R. Kramer, S. Simova and U. Schneider, *J. Am. Chem. Soc.*, 1998, **110**, 6422; (*b*) M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.