

Short communication

Complexation of the Ammonium Cation with Dibenzo-18-crown-6: Extraction and DFT Study

Emanuel Makrlík,^{1,*} Petr Toman² and Petr Vaňura³

¹ Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Kamýcká 129, 165 21 Prague 6, Czech Republic

² Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského sq. 2, 162 06 Prague 6, Czech Republic

³ Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

* Corresponding author: E-mail: makrlik@centrum.cz

Received: 13-07-2012

Abstract

From extraction experiments and γ -activity measurements, the extraction constant corresponding to the equilibrium $\text{NH}_4^+(\text{aq}) + \mathbf{1}\cdot\text{Na}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq})$ taking place in the two-phase water - nitrobenzene system ($\mathbf{1}$ = dibenzo-18-crown-6, aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) = -0.1 \pm 0.1$. Further, the stability constant of the $\mathbf{1}\cdot\text{NH}_4^+$ complex species in water-saturated nitrobenzene was calculated for a temperature 25 °C as $\log \beta(\mathbf{1}\cdot\text{NH}_4^+) = 5.7 \pm 0.2$. Finally, by using quantum mechanical DFT calculations, the most probable structure of the $\mathbf{1}\cdot\text{NH}_4^+$ cationic complex was derived. In this complex, the “central” cation NH_4^+ is bound by three strong linear hydrogen bonds to the three corresponding ethereal oxygen atoms of the parent crown ligand $\mathbf{1}$. The interaction energy of the resulting complex $\mathbf{1}\cdot\text{NH}_4^+$ was found to be -796.1 kJ/mol, confirming the formation of the considered complex species.

Keywords: Ammonium cation, dibenzo-18-crown-6, complexation, extraction and stability constants, water-nitrobenzene system, DFT, complex structure

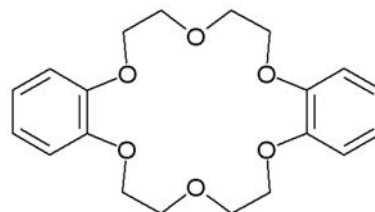
1. Introduction

The observation that macrocyclic polyethers form stable complexes with alkali and alkaline earth metal cations has stimulated a great deal of interest in these compounds for their possible applications in various branches of chemistry and biology.^{1–3} Extensive thermodynamic data suggest that the stability of macrocyclic complexes depends on the relative cation and ligand cavity size, the number and arrangements of the ligand bonding sites, the substitution on the macrocyclic ring and the solvent effects. In this context it should be noted that several reviews have covered many aspects of the chemistry of the mentioned macrocyclic compounds.^{3–6}

The dicarbollylcobaltate anion (DCC^-)⁷ and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+ , Sr^{2+} , Ba^{2+} , Eu^{3+} and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely

theoretical or analytical purposes,^{8–25} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{26–28}

In the current work, the stability constant of the cationic complex species $\mathbf{1}\cdot\text{NH}_4^+$, where $\mathbf{1}$ denotes dibenzo-18-crown-6 (see Scheme 1), in nitrobenzene saturated with water was determined. Moreover, applying quantum mechanical DFT calculations, the most probable structure of the mentioned complex species was predicted.



Scheme 1. Structural formula of dibenzo-18-crown-6 (abbrev. $\mathbf{1}$).

2. Experimental

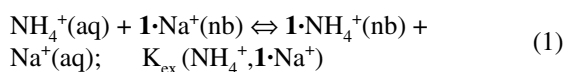
Dibenzo-18-crown-6 (abbrev. **1**; see Scheme 1) was purchased from Fluka. Cesium dicarbollycobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al.²⁹ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollycobaltate (HDCC)⁷ was prepared from CsDCC by the procedure described elsewhere.³⁰ The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.20 mol/L), yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide ²²Na⁺ was supplied by DuPont, Belgium.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of NH₄Cl of a concentration in range from 1 × 10⁻³ to 5 × 10⁻³ mol/L and microamounts of ²²Na⁺ were added to 2 mL of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations also varied from 1 × 10⁻³ to 5 × 10⁻³ mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, C₁^{in,nb}, was equal to the initial concentration of NaDCC in this medium, C_{NaDCC}^{in,nb}). The test-tubes filled with the solutions were shaken for 2 h at 25 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of sodium, D_{Na}, were determined as the ratios of the corresponding measured radioactivities of ²²Na⁺ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Previous results^{31–37} indicated that the two-phase water-NH₄Cl-nitrobenzene- **1** (dibenzo-18-crown-6) - sodium dicarbollycobaltate (NaDCC) extraction system (see Experimental), chosen for determination of the stability constant of the cationic complex **1**·NH₄⁺ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium



with the respective equilibrium extraction constant K_{ex}(NH₄⁺, **1**·Na⁺):

$$K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) = \frac{[\mathbf{1}\cdot\text{NH}_4^+]_{\text{nb}}[\text{Na}^+]_{\text{aq}}}{[\text{NH}_4^+]_{\text{aq}}[\mathbf{1}\cdot\text{Na}^+]_{\text{nb}}} \quad (2)$$

where the subscripts “aq” and “nb” denote the aqueous and nitrobenzene phases, respectively.

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms – with NH₄⁺ and Na⁺ – the very stable complexes **1**·NH₄⁺ and **1**·Na⁺.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the univalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, D_{Na} = [1·Na⁺]_{nb} / [Na⁺]_{aq}, combined with Eq. (2), we obtain the final expression for K_{ex}(NH₄⁺, **1**·Na⁺) in the form

$$K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) = \frac{1}{D_{\text{Na}}} \times \frac{C_{\text{NaDCC}}^{\text{in,nb}}}{(1 + D_{\text{Na}})C_{\text{NH}_4\text{Cl}}^{\text{in,aq}} - C_{\text{NaDCC}}^{\text{in,nb}}} \quad (3)$$

where C_{NH₄Cl}^{in,aq} is the initial concentration of NH₄Cl in the aqueous phase and C_{NaDCC}^{in,nb} denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

In this study, from the extraction experiments and γ-activity measurements (see Experimental) by means of Eq. (3), the following value of the constant K_{ex}(NH₄⁺, **1**·Na⁺) was determined as log K_{ex}(NH₄⁺, **1**·Na⁺) = -0.1 ± 0.1.

Furthermore, with respect to previous results,^{33–37} for the exchange extraction constant K_{ex}(NH₄⁺, Na⁺) corresponding to the equilibrium NH₄⁺(aq) + Na⁺(nb) ⇌ NH₄⁺(nb) + Na⁺(aq) and for the extraction constant K_{ex}(NH₄⁺, **1**·Na⁺) defined above, as well as for the stability constants of the complexes **1**·Na⁺ and **1**·NH₄⁺ in nitrobenzene saturated with water, denoted by β_{nb}(**1**·Na⁺) and β_{nb}(**1**·NH₄⁺), respectively, one gets

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{NH}_4^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) + \log K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) - \log K_{\text{ex}}(\text{NH}_4^+, \text{Na}^+) \quad (4)$$

Using the value log K_{ex}(NH₄⁺, Na⁺) = 1.3 inferred from Reference 31, the constant log K_{ex}(NH₄⁺, **1**·Na⁺) given above, log β_{nb}(**1**·Na⁺) = 7.1 ± 0.1,³⁸ and applying Eq. (4), we gain the stability constant of the **1**·NH₄⁺ complex in nitrobenzene saturated with water as log β_{nb}(**1**·NH₄⁺) = 5.7 ± 0.2. This means that in the mentioned nitrobenzene medium, the stability of the **1**·NH₄⁺ complex under study is somewhat lower than that of the cationic complex species **1**·Na⁺.

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional)^{39,40} using the Gaussian 03 suite of programs.⁴¹ The 6-31G(d) basis set was used and the optimizations were unconstrained. In order to increase the numerical ac-

curacy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by using the pruned (99,590) integration grid, having 99 radial shells and 590 angular points per shell, which was requested by means of the Gaussian 03 keyword “Int = UltraFine”.

Although a possible influence of a polar solvent on the detailed structures of **1** and its complex with NH_4^+ could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.^{42–49}

In the model calculations, we optimized the molecular geometries of the parent crown ligand **1** and the $\mathbf{1}\cdot\text{NH}_4^+$ complex species. The optimized structure of the free ligand **1** is illustrated in Figure 1.

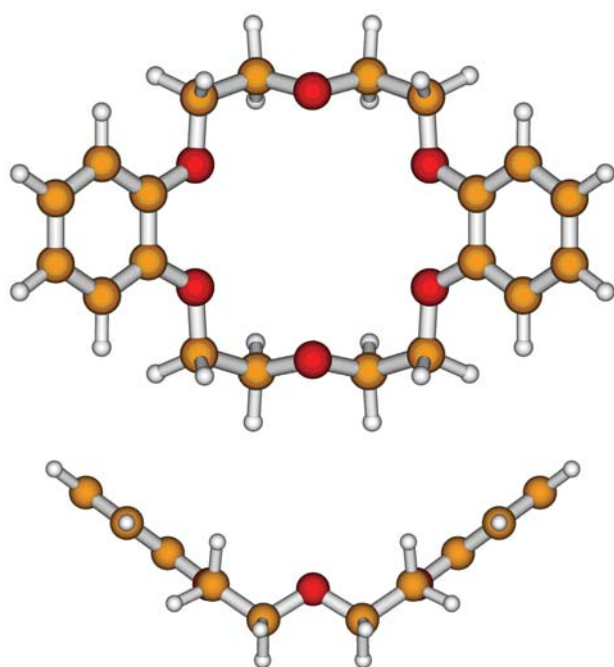


Figure 1. Two projections of the DFT optimized structure of free ligand **1** [B3LYP/6-31G(d)].

In Figure 2, the structure obtained by the full DFT optimization of the $\mathbf{1}\cdot\text{NH}_4^+$ complex is depicted, together with the lengths of the corresponding hydrogen bonds (in Å; $1\text{Å} = 0.1\text{ nm}$). In the $\mathbf{1}\cdot\text{NH}_4^+$ cationic complex species, which is most energetically favoured, the “central” cation NH_4^+ is bound by three strong linear hydrogen bond interactions to the two (Ar-O-CH₂) ethereal oxygens (1.83 and 1.83 Å) and to one (CH₂-O-CH₂) ethereal oxygen atom (1.84 Å) of the parent crown ligand **1**.

Finally, the interaction energy, $E(\text{int})$, of the $\mathbf{1}\cdot\text{NH}_4^+$ complex [calculated as the difference between the pure electronic energies of the complex $\mathbf{1}\cdot\text{NH}_4^+$ and isolated **1** and NH_4^+ species: $E(\text{int}) = E(\mathbf{1}\cdot\text{NH}_4^+) - E(\mathbf{1}) - E(\text{NH}_4^+)$] was found to be -796.1 kJ/mol , which confirms the for-

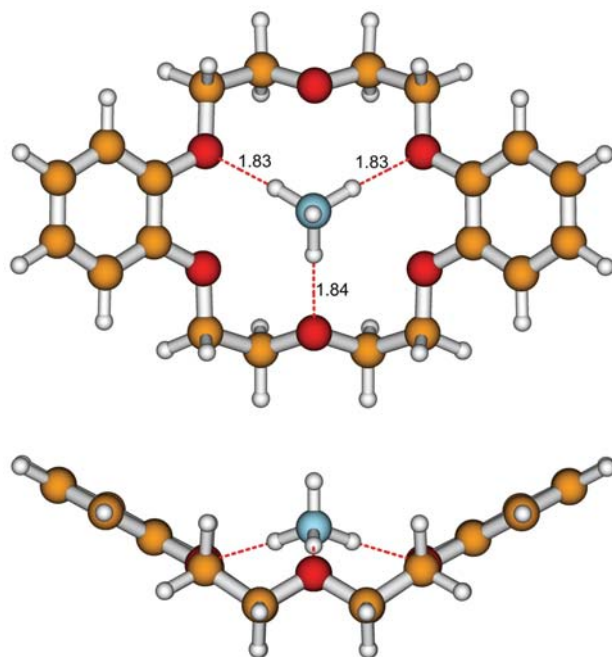


Figure 2. Two projections of the DFT optimized structure of the $\mathbf{1}\cdot\text{NH}_4^+$ complex [B3LYP/6-31G(d)].

mation of the considered cationic complex species $\mathbf{1}\cdot\text{NH}_4^+$.

4. Acknowledgements

This work was supported by the Grant Agency of Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Project No.: 42900/1312/3114 “Environmental Aspects of Sustainable Development of Society,” by the Czech Ministry of Education, Youth and Sports (Project MSM 6046137307) and by the Czech Science Foundation (Project P 205/10/2280). The computer time at the MetaCentrum (Project LM 2010005), as well as at the Institute of Physics (computer Luna/Apollo), Academy of Sciences of the Czech Republic, is gratefully acknowledged.

5. References

1. C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 2495–2496.
2. C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
3. I. M. Kolthoff, *Anal. Chem.* **1979**, *51*, 1R–22R.
4. J. J. Christensen, D. J. Eatough, R. M. Izatt, *Chem. Rev.* **1974**, *74*, 351–384.
5. J. S. Bradshaw, R. M. Izatt, *Acc. Chem. Res.* **1997**, *30*, 338–345.
6. R. M. Izatt, K. Pawlak, J. S. Bradshaw, R. L. Bruening, *Chem. Rev.* **1991**, *91*, 1721–2085.
7. E. Makrlík, P. Vaňura, *Talanta* **1985**, *32*, 423–429.

8. E. Makrlík, P. Vaňura, P. Selucký, *J. Solution Chem.* **2009**, 38, 1129–1138.
9. E. Makrlík, P. Vaňura, P. Selucký, *J. Solution Chem.* **2010**, 39, 692–700.
10. E. Makrlík, P. Vaňura, P. Selucký, V. A. Babain, I. V. Smirnov, *Acta Chim. Slov.* **2009**, 56, 718–722.
11. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 470–474.
12. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 485–490.
13. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 922–926.
14. E. Makrlík, P. Toman, P. Vaňura, R. Rathore, *Acta Chim. Slov.* **2010**, 57, 948–952.
15. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2011**, 58, 176–180.
16. E. Makrlík, P. Vaňura, P. Selucký, Z. Spíchal, *Acta Chim. Slov.* **2011**, 58, 600–604.
17. E. Makrlík, P. Toman, P. Vaňura, R. Rathore, *Acta Chim. Slov.* **2011**, 58, 611–615.
18. E. Makrlík, P. Vaňura, P. Selucký, Z. Spíchal, *Acta Chim. Slov.* **2011**, 58, 860–865.
19. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2012**, 59, 189–193.
20. E. Makrlík, P. Toman, P. Vaňura, *Acta Chim. Slov.* **2012**, 59, 199–202.
21. E. Makrlík, P. Vaňura, J. Budka, P. Selucký, *Monatsh. Chem.* **2010**, 141, 31–33.
22. E. Makrlík, P. Vaňura, Z. Sedláková, *J. Radioanal. Nucl. Chem.* **2009**, 280, 607–611.
23. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 283, 571–575.
24. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 284, 137–142.
25. E. Makrlík, P. Toman, P. Vaňura, *J. Radioanal. Nucl. Chem.* **2011**, 289, 667–670.
26. V. N. Romanovskiy, I. V. Smirnov, V. A. Babain, T. A. Todd, R. S. Herbst, J. D. Law, K. N. Brewer, *Solvent Extr. Ion Exch.* **2001**, 19, 1–21.
27. J. D. Law, R. S. Herbst, T. A. Todd, V. N. Romanovskiy, V. A. Babain, V. M. Esimantovskiy, I. V. Smirnov, B. N. Zaitsev, *Solvent Extr. Ion Exch.* **2001**, 19, 23–36.
28. R. S. Herbst, D. R. Peterman, R. D. Tillotson, L. H. Delmau, *Solvent Extr. Ion Exch.* **2008**, 26, 163–174.
29. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, 90, 879–896.
30. E. Makrlík, *Collect. Czech. Chem. Commun.* **1992**, 57, 289–295.
31. J. Rais, *Collect. Czech. Chem. Commun.* **1971**, 36, 3253–3262.
32. E. Makrlík, F. Božek, *Polish J. Chem.* **1998**, 72, 949–952.
33. E. Makrlík, J. Hálová, M. Kyrš, *Collect. Czech. Chem. Commun.* **1984**, 49, 39–44.
34. E. Makrlík, P. Vaňura, *J. Radioanal. Nucl. Chem.* **1996**, 214, 339–346.
35. M. Daňková, E. Makrlík, P. Vaňura, *J. Radioanal. Nucl. Chem.* **1997**, 221, 251–253.
36. E. Makrlík, P. Vaňura, M. Daňková, *J. Radioanal. Nucl. Chem.* **1999**, 240, 579–583.
37. E. Makrlík, P. Vaňura, *Monatsh. Chem.* **2006**, 137, 157–161.
38. E. Makrlík, P. Vaňura, *Unpublished results.*
39. C. Lee, W. Yang, R. G. Parr, *Phys. Chem. B* **1988**, 37, 785–789.
40. A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648–5652.
41. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
42. J. Kříž, J. Dybal, E. Makrlík, *Biopolymers* **2006**, 82, 536–548.
43. J. Kříž, J. Dybal, E. Makrlík, P. Vaňura, J. Lang, *Supramol. Chem.* **2007**, 19, 419–424.
44. J. Kříž, J. Dybal, E. Makrlík, P. Vaňura, *Supramol. Chem.* **2008**, 20, 387–395.
45. J. Kříž, J. Dybal, E. Makrlík, J. Budka, P. Vaňura, *Supramol. Chem.* **2008**, 20, 487–494.
46. J. Kříž, J. Dybal, E. Makrlík, J. Budka, *J. Phys. Chem. A* **2008**, 112, 10236–10243.
47. J. Kříž, J. Dybal, E. Makrlík, J. Budka, P. Vaňura, *J. Phys. Chem. A* **2009**, 113, 5896–5905.
48. J. Kříž, P. Toman, E. Makrlík, J. Budka, R. Shukla, R. Rathore, *J. Phys. Chem. A* **2010**, 114, 5327–5334.
49. J. Kříž, J. Dybal, E. Makrlík, P. Vaňura, B. A. Moyer, *J. Phys. Chem. B* **2011**, 115, 7578–7587.

Povzetek

Iz eksperimentov ekstrakcije in meritev γ -aktivnosti smo določili konstante ekstrakcije za ravnotežja $\text{NH}_4^+(\text{aq}) + \mathbf{1}\cdot\text{Na}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{NH}_4^+(\text{nb}) + \text{Na}^+(\text{aq})$ v dvofaznem sistemu voda-nitrobenzen ($\mathbf{1}$ = dibenzo-18-crown-6, aq = vodna faza, nb = faza nitrobenzene), $\log K_{\text{ex}}(\text{NH}_4^+, \mathbf{1}\cdot\text{Na}^+) = -0.1 \pm 0.1$. Pri 25 °C smo določili konstanto stabilnosti kompleksa $\mathbf{1}\cdot\text{NH}_4^+$ v nitrobenzene, nasičenem z vodo, ki znaša $\log \beta(\mathbf{1}\cdot\text{NH}_4^+) = 5.7 \pm 0.2$. Z uporabo kvantno mehanskih DFT izračunov smo določili najbolj verjetno strukturo $\mathbf{1}\cdot\text{NH}_4^+$ kationskega kompleksa. Ugotovili smo, da je »centralni« kation NH_4^+ s tremi močnimi linernimi vodikovimi vezmi vezan na tri eterske kisikove atome crownskega liganda $\mathbf{1}$. Energija interakcije kompleksa $\mathbf{1}\cdot\text{NH}_4^+$ znaša -796.1 kJ/mol, kar potrjujeje strukture privzete konformacije kompleksa.