J. Chem. Research (S), 1999, 284–285†

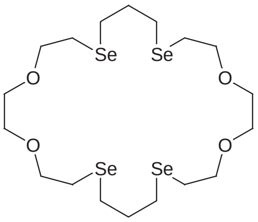
Complexation Thermodynamics of Selenacrown Ether: Origin of High Silver(I) Selectivity of 1,5,14,18-Tetraselena-8,11,21,24-tetraoxacyclohexacosane†

Yu Liu,*[a] Shu-Ping Dong,[a] Yoshihisa Inoue*[b] and Takehiko Wada[b]

[a] *Department of Chemistry, Nankai University, Tianjin 300071, China*
[b] *Department of Molecular Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita 565, Japan*

The thermodynamic parameters and relative cation selectivity for complexation of some alkali and heavy metal cations with 1,5,14,18-tetraselena-8,11,21,24-tetraoxacyclohexacosane (selena-26-crown-8) are investigated for the first time by titration calorimetry in water–acetonitrile (1 : 24 v/v) at 25 °C to show the contrasting complexation thermodynamic behaviour between Ag^+ and alkali or Tl^+ and a very high Ag^+ selectivity, originating from the exclusive contribution of the enthalpy term probably owing to the partially covalent interaction between Ag^+ and Se donor.

Thermodynamic studies of cation recognition by crown ethers started immediately after the first synthesis of the ligand in order to elucidate the nature of the cation-binding behaviour in terms of the enthalpy and entropy changes,[1] and have been of growing interest in the past three decades.[2] Therefore, enormous effort has been devoted to both the synthesis of a wide variety of crown ethers and their complexation thermodynamics to enhance the cation-binding ability and selectivity.[3] Accordingly, some selenacrown ethers have been designed and sythesized,[4–6] but their complexation thermodynamics with cations has not been reported so far, despite the importance of such studies in discussing the complexation behaviour of selenacrown ethers. In this Short Paper we wish to report the first thermodynamic study on the complexation of some alkali (Li^+, Na^+, and K^+) and heavy metal (Ag^+ and Tl^+) cations with 1,5,14,18-tetraselena-8,11,21,24-tetraoxacyclohexacosane (selena-26-crown-8) (**1**) in water–acetonitrile (1 : 24 v/v) at 25 °C. Using water–acetonitrile (1 : 24 v/v) as solvent instead of acetonitrile is mainly attributed to the low solubility of thallous nitrate in acetonitrile. On the other hand, the studies on the complexation thermodynamics with Li^+, Na^+, K^+, Ag^+ and Tl^+ have been concentrated mostly on the common crown ethers, while no attention has been paid so far to the complexation thermodynamics of selenacrown ethers. It is our specific interest to examine the binding ability and selectivity of soft cations by selenacrown ether from the thermodynamic point of view.



1

Calorimetric titrations were carried out at atmospheric pressure in a temperature-controlled water bath maintained at 25 °C, by using a TRONAC model 458 isoperibol titration calorimeter connected to a personal computer for automated titration and data processing.[7] The principle of the measurement and the detailed experimental procedures have been reported elsewhere.[8] Typically, a selenacrown ether (SeCE)[9] solution (20 mM) in aqueous acetonitrile was continuously introduced at a rate of 0.3321 $cm^3\,min^{-1}$ into a metal nitrate solution (1.1–2.5 mM) placed in the calorimeter. Assuming the conventional 1 : 1 stoichiometry [(eqn. (1)], the calorimetric data obtained for each cation–ligand combination are analysed according to the theoretical treatment reported previously.[10–12] The thermodynamic parameters (log K_s, ΔH°, ΔG° and $T\Delta S^\circ$) calculated are listed in Table 1.

$$\mathrm{M}^+ + \mathrm{SeCE} \overset{K_s}{\rightleftharpoons} [\mathrm{M}^+ \bullet \mathrm{SeCE}] \qquad (1)$$

Table 1 Complex stability constant (log K_s) and thermodynamic parameters for complexation of selena-26-crown-8 with some alkali and heavy metal cations in water–acetonitrile (1 : 24 v/v) at 298.15 K[a]

Cation	log K_s	ΔG°/kcal mol^{-1}	ΔH°/kcal mol^{-1}	$T\Delta S^\circ$/kcal mol^{-1}
Li^+	[b]	[b]	[b]	[b]
Na^+	2.45 ± 0.02	-3.34 ± 0.04	5.05 ± 0.08	8.39 ± 0.08
K^+	2.49 ± 0.08	-3.40 ± 0.08	4.97 ± 0.06	8.37 ± 0.08
Ag^+	3.77 ± 0.06	-5.14 ± 0.07	-13.38 ± 0.08	-8.24 ± 0.06
$T1^+$	2.35 ± 0.03	-3.20 ± 0.03	8.48 ± 0.04	11.68 ± 0.07

[a] Values are the averages of more than three independent measurements. [b] The ΔH value for Li^+ was too small to be determined by titration calorimetry.

As shown in Table 1, dramatic differences in the thermodynamic parameters were observed between Ag^+ and the other cations examined. For the complexation of Na^+, K^+ and Tl^+, both the enthalpy changes (ΔH°) and

---

* To receive any correspondence.

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

entropy changes (ΔS°) are positive. This means that the complexation with Na^+, K^+ and Tl^+ is an endothermic process and is driven exclusively by the entropic gain. The large positive entropy changes clearly indicate that the complexation causes extensive desolvation of cation and ligand, which overcomes the entropic losses arising from the host–guest association and possible structural freezing upon complexation. The oversized cavity of selena-26-crown-8 obviously makes the operation of the size-fitting interaction difficult, giving rise to the very similar stability constants for Na^+, K^+ and Tl^+. The too-small cation size, high hydration energy and reduced coordination number of Li^+ are considered to be jointly responsible for the negligible heat production upon calorimetric titration.

It is very interesting and significant that Ag^+ shows completely different thermodynamic behaviour upon complexation. The much stronger, partially covalent interaction between the selenium donors and Ag^+ leads to the highly negative ΔH° of $-13.38\,\mathrm{kcal\,mol^{-1}}$ which far exceeds the entropic loss ($T\Delta S^\circ = -8.28\,\mathrm{kcal\,mol^{-1}}$) from the substantial structural freezing caused by complexation of Ag^+ in the cavity, eventually giving the highest complex stability ($\Delta G^\circ = -5.14\,\mathrm{kcal\,mol^{-1}}$) and highest selectivity (of up to 26) for Ag^+ over the other cations.

It is clearly demonstrated that the interaction of soft selenium donors with the soft Ag^+ cation leads to the largest enthalpic gain (ΔH°) and the large, but relatively much smaller, entropic loss ($T\Delta S^\circ$), which is in sharp contrast to the complexation thermodynamic behaviour of hard alkali cations. Although the detailed mechanism of complexation cannot be elucidated from the thermodynamic data only, these contrasting results may be attributed to the switching of the donor atom involved and the different degree of original hydration to the free donor atoms. A plausible explanation is that this mixed-donor ligand, possessing both soft Se and hard O donor atoms in the same macrocycle, switches the acting donor, depending on the cation to be accommodated. Thus, soft cations interact predominantly with the soft Se donors which are not hydrated originally, and are expected to produce much heat through the formation of partially covalent bonds which accompany only a small extent of dehydration. In contrast, hard alkali cations, which are heavily hydrated originally, interact preferentially with the hard O donors located at the transanular position of the ligand, and the replacement of water of hydration around the cation with the ligand's O, and probably Se, donors does not produce much heat but releases the hydration water from both cation and ligand through the wrapping complexation by the large macrocycle, affording the highly positive entropy changes. Further experiments to elucidate this mechanism switching and the somewhat different behaviour of Tl^+ are currently in progress.

This work was supported by the National Outstanding Youth Fund (Grant No. 29625203) and Natural Science Foundation (Grant No. 29676021) of China, Transcentury Training Program Foundation for the Talents of the State Education Commission of China, and Natural Science Fund of Tianjin Municipality (Grant No. 973602211), which are gratefully acknowledged.

Received, 13th October 1998; Accepted, 18th December 1998
Paper E/8/07947A

References

1 R. M. Izatt, J. H. Rytting, D. P. Nelson and B. J. Haymore, *Science*, 1968, **164**, 443.
2 Y. Inoue and T. Wada, *Adv. Supramol. Chem.*, 1997, **4**, 55.
3 R. M. Izatt, *Chem. Rev.*, 1995, **95**, 2529.
4 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. D. Johnston and B. M. Pinto, *J. Am. Chem. Soc.*, 1989, **111**, 6582.
5 S. Tomoda and M. Iwaoka, *J. Chem. Soc., Chem. Commun.*, 1990, 231.
6 S. Muralidharan, M. Hojjatie, M. Firestone and H. Freiser, *J. Org. Chem.*, 1989, **54**, 393.
7 Y. Liu, B.-H. Han, Y. Inoue and M. Ouchi, *J. Org. Chem.*, 1998, **63**, 2144.
8 Y. Liu, X.-P. Bai, Y. Inoue and M. Ouchi, *J. Phys. Chem. B*, 1998, **102**, 4871.
9 W.-P. Li, X.-F. Liu and H.-S. Xu, *Acta Chim. Sinica* (*Huaxue Xuebao*), 1994, **52**, 1082.
10 (*a*) L. D. Hansen, E. A. Lewis and D. J. Eatough, in *Chemical Analysis*, ed. J. K. Grime, vol. 79, Analytical Solution Calorimetry, Wiley, New York, 1985, ch. 3, pp. 57–95; (*b*) D. J. Eatough, E. A. Lewis and L. D. Hansen, in *Chemical Analysis*, ed. J. K. Grime, vol. 79, Analytical Solution Calorimetry, Wiley, New York, 1985, ch. 5, pp. 137-161.
11 Y. Liu and J. Hu, *Acta Phys. Chem. Sinica* (*Wuli Huaxue Xuebao*), 1987, **3**, 11 (*Chem. Abstr.*, 1987, **106**, 202750n).
12 Y. Liu, L.-J. Zhang, Y.-M. Li, Y.-T. Chen, S. Huang, J. Meng, Y. Inoue and M. Ouchi, *Thermochim. Acta*, 1995, **253**, 93.