

Molecular Design of Crown Ethers. 19¹. Synthesis of Novel Disulfide- and Diselenide-Bridged Bis (benzo-12-crown-4)s and their Ag⁺ Selective Electrode Properties

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Abstract: Two novel heteroatom-bridged bis (benzo-12-crown-4 ether)s, *i.e.* bis [2-nitro-4,5-(1,4,7,10-tetraoxadecamethylene)phenyl] disulfide **1** and diselenide **2**, have been synthesized. X-ray crystallographic structure was obtained for **1**. Ion selective electrodes (ISE) for Ag⁺, containing **1** and **2** in PVC membrane as neutral carriers, were prepared, and their selectivity coefficients for Ag⁺ ($K_{Ag,M}^{pot}$) were determined against other heavy metal ions, alkali and alkaline-earth metal ions, and ammonium ion. These ISEs showed excellent Ag⁺ selectivities, $\log K_{Ag,M}^{pot} \leq -3.8$, against most of the interfering cations examined, except for Hg⁺.

Keywords: Heteroatom-bridged bis (benzo-12-crown-4 ether)s, ion selective electrodes, selectivity coefficients.

Crown ethers have enjoyed widespread use in various fields since the very first preparation of the ligand by Pedersen. One of the great applications of them is in analytical chemistry. In particular, the ion-selective electrode is a most important target in analytical applications^{2,3}. A wide variety of monocyclic crown ethers and bicyclic crown ethers have been employed in the studies of the ion-selective electrode in recent years³⁻⁵. Especially, bicyclic crown ethers have been extensively studied as a neutral carrier of PVC membrane ion-selective electrodes, which have reflected the high selectivity of the bicyclic crown ethers for the respective metal ions. Since dithiacrown ethers gave the first neutral carrier Ag⁺ selective electrodes with a discrimination of alkali metal ions, thioethers became very important compounds as ionophores for Ag⁺ selective electrodes. On the other hand, selenacrown ethers exhibit strong cation binding with Ag⁺ as well as thiocrown ethers, so we hoped to synthesize a series of thia- and seleno-bridged bis (crown ether)s, which are different from corresponding normal bis (crown ether)s, in order to investigate their Ag⁺ selectivity as ionophores. In the present communication, we report the synthesis of 2,2'-dinitro-4,5,4',5'-bis (1,4,7,10-tetraoxacyclododeca-2-ene) -dibenzo-disulfide **1**, and 2,2'-dinitro-4,5,4',5'-bis (1,4,7,10-tetraoxacyclododeca-2-ene) -dibenzo-diselenide **2**, and their Ag⁺ selectivity behavior monitored by electromotive force (EMF) measurements of polymetric membrane electrodes based on the Ag⁺ ionophores. The results of the ion-selective electrode obtained and the crystal structure analysis of compound **1**, together with those

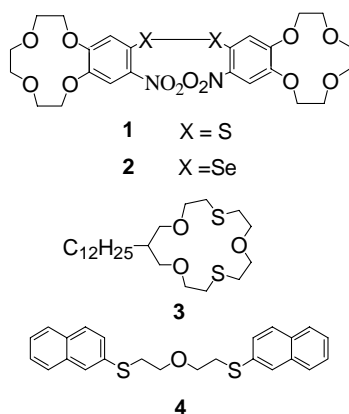
for dodecyl 16-crown-5 **3**⁶ and noncyclic dithioether **4**⁷ (**Chart 1**), will serve our further understanding of this Ag⁺ selective electrode behavior of heteroatom-bridged bis (benzo-12-crown-4)s. It is another point of interest to examine the effect of different steric position of sulfur atom upon Ag⁺ selectivities of ligands.

Experimental

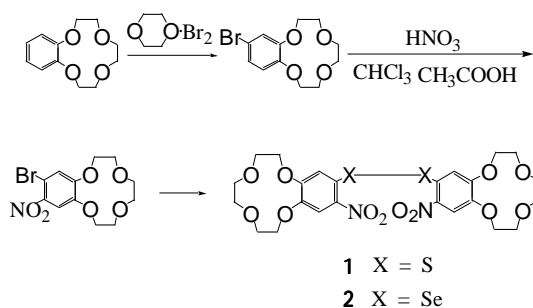
2,2'-Dinitro-4,5,4',5'-bis (1,4,7,10-tetraoxacyclododeca-2-ene) –dibenzo-disulfide **1**, and 2,2'-dinitro-4,5,4',5'-bis (1,4,7,10-tetraoxacyclododeca-2-ene) –dibenzo -diselenide **2** were synthesized and characterized by elemental analysis and mass, IR, UV, and ¹H NMR spectroscopy. Crystals of **1** suitable for X-ray crystallography were grown by slow evaporation from an acetonitrile solution of **1**. The coated-wire ISEs based on **1** and **2** were constructed according to the procedure reported previously⁸. All EMF measurements were made at 25 ± 0.1°C, using a pH/mV meter. The potentiometric selectivity coefficient $K_{Ag,M}^{pot}$ determined here are defined in the Nicolsky-Eisenman equation:

$$E = E^o + \frac{2.303RT}{F} \log \left[a_{Ag} + K_{Ag,M}^{pot} (a_M)^{1/Z_M} \right]$$

Chart 1



Scheme 1



Results and Discussion

Synthesis. Heteroatom-bridged bis (benzocrown ether)s **1** and **2** were synthesized in 71 and 31% yields, respectively, by reaction of 4-bromo-5-nitro-12-crown-4 with Na₂S₂ or K₂Se₂, as shown in **Scheme 1**. The lower yield obtained for **2** would be attributable to the larger atomic size of selenium than sulfur, which may cause steric hindrance against the adjacent nitro group. However, it is essential to incorporate a nitro group into the benzene ring, which in turn accelerates the nucleophilic attack of disulfide or diselenide

ion to the electron-deficient benzene ring. **Ag⁺ Selectivity.** The Ag⁺ selectivities of the heteroatom-bridged bis (benzo-12-crown-4)s **1** and **2** were evaluated by the potentiometric selectivity coefficients ($K_{Ag,M}^{pot}$) determined for polymer membranes containing these ionophores. For comparison purpose, two representative thioether **3** and **4** were also examined under the same conditions. The potentiometric selectivity coefficients for Ag⁺ are illustrated in **Figure 1**. As can be seen from **Figure 1**, both polymer membranes containing **1** and **2** gave excellent $\log K_{Ag,M}^{pot}$ values ([-3.8) against most of the interfering cations examined (*i.e.*, Na⁺, K⁺, NH₄⁺, Mg²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Pb²⁺), except for Hg²⁺. It is interesting to note that, despite the different heteroatoms incorporated, both **1**- and **2**-based ISEs gave characteristic ion selectivity tendencies which resemble each other but distinctly differ from the ISEs containing thioethers **3** and **4**. It should be also noted that the disulfide ligand **1** is distinctly different from the conventional 1,4- and 1,7-dithiaethers in the position and nature of two sulfur donors, yet it affords the excellent Ag⁺ selectivity which is comparable to the conventional dithiacrown ethers such as **3**. Probably, the interaction of soft sulfur donors with soft Ag⁺ ion is much stronger than that with other heavy metal, alkali metal, alkaline earth, and ammonium ions, and the position of sulfur donors in a ligand is not very important for most sulfur-containing ionophores.

Figure 1 Selectivity coefficients for Ag⁺ selective electrodes based on **1**, **2**, **3**, and **4**.

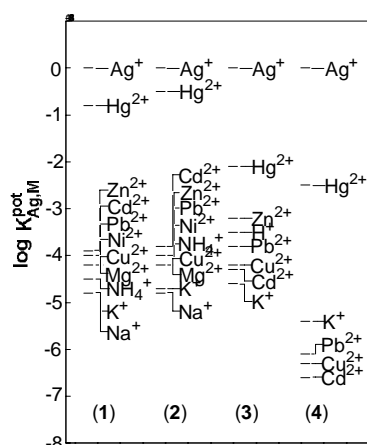
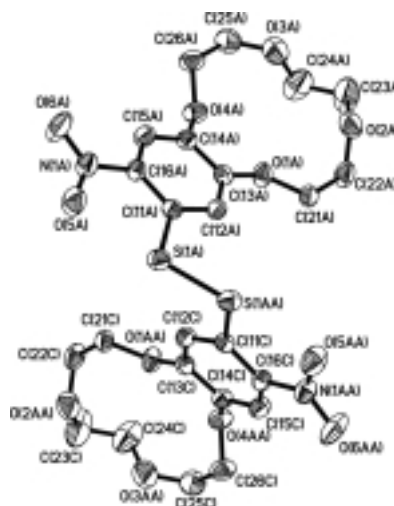


Figure 2 X-ray structure of **1**. Steric position between nitro-groups and sulfur atoms: a, bonds distances, [S(1A)-O(5A)] 2.56 Å; [S(1A)-N(1A)] 3.09 Å; [S(1A)-O(6A)] 4.29 Å; [S(1AA)-N(1A)] 5.02 Å. b, bonds angles, [S(1AA)-S(1A)-O(5A)] 173.86°; [S(1AA)-S(1A)-N(1A)] 155.79°; [S(1AA)-S(1A)-O(6A)] 156.13°.



The steric effect of the nitro groups in **1** may be evaluated approximately by the X-ray crystallographic structure shown in **Figure 2**. Although the nitro group closely

located to the sulfur donor would cause some steric hindrance upon ligation to Ag^+ , there is enough space around the sulfur atom to accommodate Ag^+ and indeed excellent $K_{\text{Ag},M}^{\text{pot}}$ values were obtained in the ISE experiments described above. Even so, the electron-withdrawing effect of nitro group in **1** must be disadvantageous for the interaction of sulfur donor with Ag^+ cation, but the other interfering cations also suffer similar unfavorable electronic effect and eventually the net effect could be negligible.

Acknowledgments

This work was supported by the National Outstanding Youth Fund, Natural Science Foundation of China, Tianjin Natural Science Fund, Transcentury Qualified Personal Fund of Tianjin Education Committee (Sun-light Plan), and Transcentury Qualified Personal Fund of State Education Committee of China, which are gratefully acknowledged.

References and Notes

1. a) Part 17, Y. Liu; X.P. Bai; Y. Inoue; M. Ouchi. *J. Phys. Chem. B*, **1998**, *102*, 4871; Part 18, Y. Liu; H.Y. Zhang. *Chin. J. Chem.* **2000**, in press. b) Complexation Thermodynamics of Crown Ethers. Part 6, see Y. Liu; B.H. Han; Y. Inoue; M. Ouchi. *J. Org. Chem.* **1998**, *63*, 2144.
2. E. Bakker; P. Bühlmann; E. Pretsch. *Chem. Rev.* **1997**, *97*, 3083.
3. P. Bühlmann; E. Pretsch; E. Bakker. *Chem. Rev.* **1998**, *98*, 1593.
4. J. Casabo; F. Teixidor; L. Escriche; C. Vinas; C. Pérez-Jiménez. *Adv. Mater.* **1995**, *7*, 238.
5. K. Kimura; T. Shono. In *Cation Binding by Macrocycles*; Y. Inoue; G. W. Gokel. Ed.; Marcel Dekker, Inc. New York, **1990**, P 429.
6. M. Oue; K. Kimura; K. Akama; M. Tanaka. *Chem. Lett.* **1988**, 409.
7. W. Wroblewski; Z. Brzozka. *Sens. Actuators*, **B** **1995**, *24–25*, 183.
8. H. Tamura; K. Kimura; T. Shono. *Anal. Chem.*, **1982**, *54*, 1224.
9. Crystallographic parameters for **1** have been deposited in the editorial office of CCL.

Received 3 August 1999