SHORT PAPER

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The Ag^+ selective electrode properties of benzo-diselena selena-13-to 14-crown-4[†]

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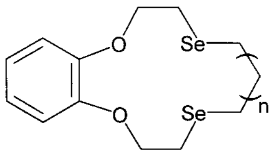
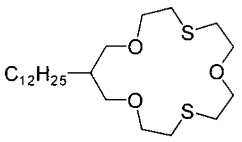
Ion selective electrodes (ISE) for Ag^+, containing 1,2-benzo-7,11-diselena-1,4-dioxacyclotridecan-2-ene (**1**) and (2,3-benzo-7,12-diselena-1,4-dioxacyclotetradecan-2-ene) (**2**) in a PVC membrane as neutral carrier, were prepared, and their selectivity coefficients for Ag^+ ($K^{pot}_{Ag,M}$) against other heavy metal ions, alkali and alkaline-earth metal ions, and ammonium ion were determined to show excellent Ag^+ selectivities.

Crown ethers have enjoyed widespread use in various fields of science and technology ever since the first preparation of such ligands by Pedersen.[1] One of the most successful applications is in analytical chemistry. In particular, the ion-selective electrode (ISE) is important in analytical applications.[2–4] For a long time, silver ion has been analysed quantitatively using the crystal membrane Ag^+-ISE made from insoluble argentiferrous salt in water.[5,6] Increasing attention has recently been focused on neutral carrier-type Ag^+-ISEs containing thiacrown ethers,[7–15] because this type of ISE often shows better selectivities than the standard solid-state electrode. Selenacrown ethers exhibit high cation binding abilities for Ag^+ which are comparable to that obtained with thiacrown ethers, but their Ag^+ selectivities as neutral carriers have scarcely been reported so far, despite the potential importance of such studies in exploring their application as neutral carrier-type Ag^+-ISEs. We have recently synthesized some selenacrown ethers and discussed their complexation behavior with cations.[16,17] In this paper we report the crystallographic structure of **2** and the Ag^+ selectivity behavior of selenacrown ethers **1** and **2** monitored by electromotive force (EMF) measurement of polymer membrane electrodes based on these Ag^+ selective ionophores. Together with the ISE behavior of reported for dodecyl-16-crown-5 (**3**)[10] (Chart 1), this study will aid our further understanding of the heteroatomcrown ether-selectivity relationship in the Ag^+-ISE.



1 n = 1

2 n = 2



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Selenacrown ethers **1** and **2** were prepared as reported[17] and their Ag^+ selectivities were evaluated by the potentiometric selectivity coefficients ($K^{pot}_{Ag,M}$) determined for polymer membranes containing these ionophores. For comparison, a representative thiacrown ether **3** was also examined under the same conditions. The potentiometric selectivity coefficients for Ag^+, which were determined by the mixed solution method, are illustrated in Fig. 1. The selectivity coefficient $K^{pot}_{Ag,M}$ represents the preference of the PVC membranes containing the selenacrown ethers for Ag^+ over the other cations. It should be kept in mind that the smaller the $K^{pot}_{Ag,M}$ value, the higher the Ag^+ selectivity.

As can be seen from Fig. 1, both polymer membranes containing **1** and **2** gave excellent log $K^{pot}_{Ag,M}$ values (< –3.8) against most of the interfering cations examined (i.e., Na^+, K^+, NH_4^+, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}), except for Hg^{2+}. It is interesting to note that, despite the different sized cavity, both **1**-, **2**- and **3**-based ISEs gave very similar characteristic ion selectivity tendencies. In spite of the different heteroatoms incorporated, both **1**- and **2**-based ISEs afford excellent Ag^+ selectivity which is comparable to the conventional dithiacrown ethers such as **3**. We have found that the partially covalent interaction between the soft Ag^+ ion and soft Se donor in 1,5,14,18-tetraselena-8,11,21,24-tetraoxacyclohexacosane give the highest complexation stability and highest selectivity for Ag^+ over the other cations.[16] Se is a softer donor than S, and interaction between Se donors and the soft Ag^+ ion is probably stronger than that between S donors and Ag^+ ion, so strong interaction may interfere with the rapid interfacial ion exchange in ISE, which in turn leads to the moderate Nernstian slope (43.0 mV/pAg for **1** and 44.1 mV/pAg for **2**) for the **1**-, and **2**-based Ag^+-ISEs.

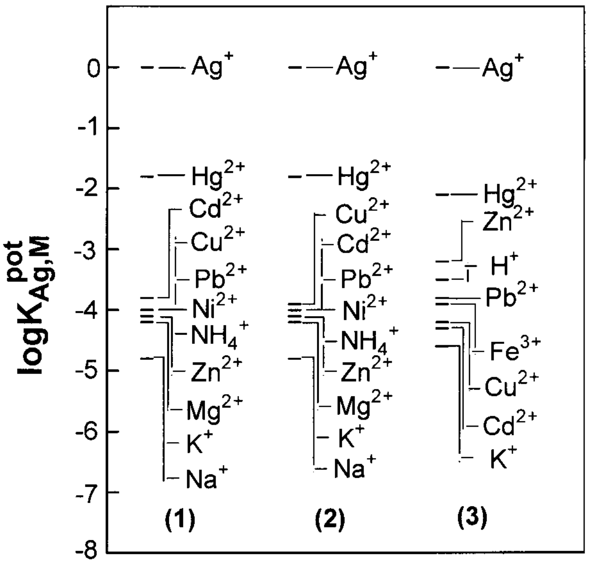

Fig. 1 Selectivity coefficients for Ag^+-selective electrodes based on **1**, **2**, and **3** (ref. 10).

The structure of **2** was determined by X-ray analysis (Fig. 2). All atoms except for Se(1A), C(9A), C(10A), C(11A), C(12A) and Se(2A) are located in a plane (Fig. 3). Unlike ordinary oxacrown ethers, two Se atoms in **2** are situated on opposite sides of the plane, and their separation is the greatest [Se(1A) – Se(2A): 6.472Å] of all the pairs of atoms in the ring.

Experimental

Membrane electrode: The typical procedure for membrane preparation is as follows: Poly(vinyl chloride) (PVC) (132 mg, 32.9%), dibulyl phthalate (DBP) (264 mg, 65.8%), potassium tetrakis(*p*-chlorophenyl)borate (KTClPB) (1.2 mg, 50 mol% relative to the crown ether), and crown ether (1%) were dissolved in THF 5 ml. This solution was then poured into a flat-bottomed Petri dish of 32 mm inner diameter and 50 mm height.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

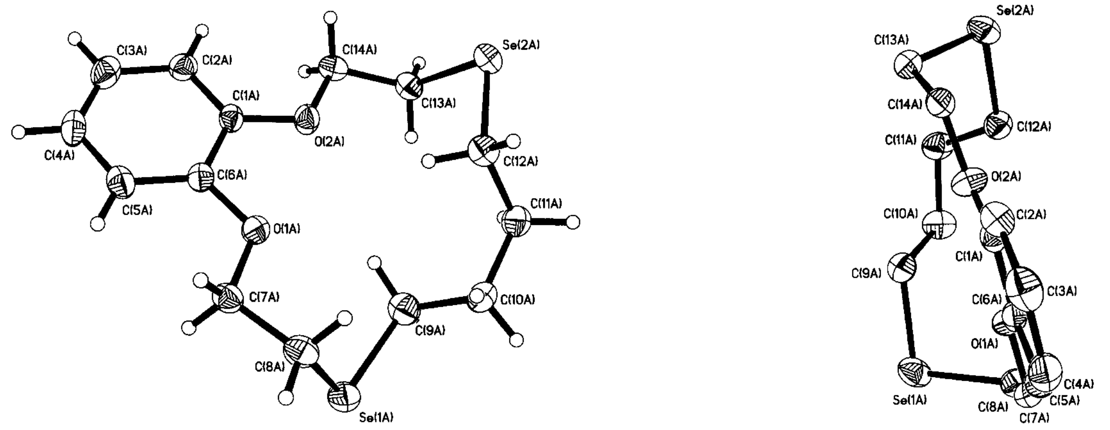

Fig. 2 and **Fig. 3** X-ray structure of **2**.

Gradual evaporation of the solvent at room temperature gave a transparent, flexible membrane of about 0.3 mm in thickness. A disk of 7 mm in diameter was cut from the PVC membrane and incorporated into a PVC tube tip with 5% THF solution in water. After injection of $AgNO_3$ 0.01 M of aqueous solution as the internal solution, the electrode was conditioned by soaking in $AgNO_3$ 0.01 M aqueous solution for 2 h. The external reference electrode was a double junction type Ag/AgCl glass electrode. The composition of electrochemical cell is given as Ag·AgCl|0.01 M $AgNO_3$ |PVC membrane|sample solution|1 M KNO_3|4 M KCl|Hg_2Cl_2·Hg.

EMF measurements: All EMF (electromotive force) measurements were made at 25 ± 0.1 °C, using a pH/mV meter. Sample solutions were magnetically stirred and kept in a thermostated water bath. The EMF values were corrected by subtracting the liquid–junction potential between the external reference electrode and the sample solution in the high Ag^+ concentration.

*Crystal data for **2**:* Data collection was carried out on a BRUKER SMART 1000 instrument; $C_{14}H_{20}O_2Se_2$, M_r = 378.22, MoKα radiation, $\mu = 4.952$ mm^{-1}, $\lambda = 0.71073$ Å, $0.67° < \theta < 25.03°$, monoclinic, space group $P2_1/c$, $a = 30.764(3)$, $b = 11.2260(12)$, $c = 8.6989(10)$ Å, $\beta = 96.990(2)°$, $V = 2981.9(6)$ Å^3, Z = 8, $D_c = 1.685$g cm^{-3}, $\mu = 4.952$ mm^{-1}, F(000) = 1504, $T = 293(2)$ K, reflections collected 15123, independent reflections 5272 ($R_{int} = 0.0499$), full-matrix least-squares refinement on F^2, data/restraints/parameters 5272/0/325, goodness-of-fit 1.055. The structure was solved by direct methods using SHELXS–97[18] and SHELXL–97.[19] The final R indices were $R1 = 0.0447$, $wR_2 = 0.1119$ and (all data) $R1 = 0.0721$, $wR_2 = 0.1228$. Largest diff. Peak and hole in eÅ^{-3} max = 0.714, min = –0.823.

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Supporting information available: Crystal data and structure refinements, bond lengths and angles, atomic coordinates, anisotropic displacement, and H-atom coordinates for **2**.

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