

Synthesis of Two New Crown Ethers Containing Selenium and the Complexation of One of Them With Silver and Lead

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(Received: 3 September 1988; in final form: 18 November 1988)

Abstract. Two new macrocyclic crown ethers containing one or two selenium donor atoms have been prepared. Diselena-18-crown-6 (**2**) was found to transport silver ions through a methylene chloride bulk membrane at about the same rate as the analogous dithia- (**3**) and diaza-18-crown-6 (**4**) compounds and transported lead ions about the same as dithia-18-crown-6 but better than diaza-18-crown-6.

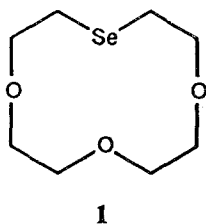
Key words. Macrocyclic compounds, selenium compounds, metal ion complexation.

1. Introduction

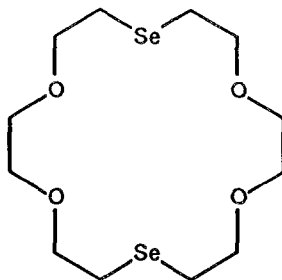
There has been considerable interest in the design of crown compounds for the selective complexation of metal cations. Since the first oxygen-containing crown ethers were reported by Pedersen [1], sulfur [2], nitrogen [3], phosphorus [4], and tin [5] have been used to replace one or all of the oxygen heteroatoms. These crown ethers show selectivity for different cations based on ring size and the heteroatom used. Substitution of either nitrogen or sulfur for oxygen in 18-crown-6 greatly influences the complexation of metal cations, weakening the complexation of K^+ and strengthening that of soft cations such as Ag^+ and Pb^{2+} . With potassium, the electrostatic forces are decreased in the aza- and thia-crowns because of decreasing electronegativity of the nitrogen and sulfur atoms [6]. With silver, the attraction by the aza and thia crowns is enhanced by the type of covalent bonding present. Replacement of oxygen by sulfur virtually destroys the ability of 18-crown-6 to complex with cations other than those, such as Ag^+ and Pb^{2+} , which show affinity for the 'soft' sulfur atoms in the thia-crown molecules [7].

This paper reports the synthesis of two selena-crown ethers (**1**) and (**2**), along with a study of the ability of (**2**) to transport Ag^+ and Pb^{2+} in a bulk liquid membrane system [7, 8]. Compound **2** was prepared in order to compare its ability to transport 'soft' cations, such as Ag^+ and Pb^{2+} , with those of the analogous sulfur (**3**) and nitrogen (**4**)-containing molecules.

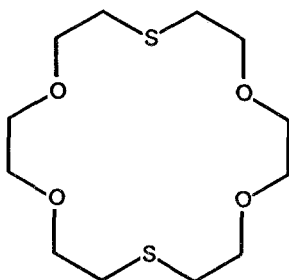
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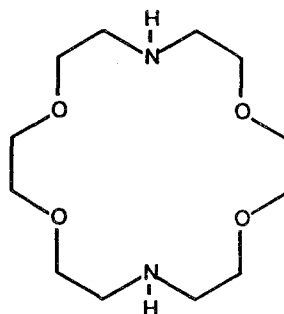
1



2



3



4

2. Experimental

All infrared (IR) spectra were obtained on a Matson FTIR spectrometer. The proton nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX-90Q spectrometer using deuteriochloroform with TMS as the solvent. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Molecular weights were determined on a Finnegan 8430 High Resolution Mass Spectrometer by the electron impact method. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Starting materials were purchased from commercial sources when available.

2.1. PREPARATION OF 4,7,10-TRIOXA-1-SELENACYCLODODECANE (1) (1-SELENA-12-CROWN-4)

Gaseous hydrogen selenide was bubbled into 500 mL of ethanol, which had previously been treated with 1.4 g (0.06 mole) of sodium, until the gas appeared in the bleach trap (the bleach solution turned red). The ethanol solution was heated to reflux, whereupon 7.08 g (0.03 mole) of tetraethylene glycol dichloride in 225 mL of ethanol was added slowly over a 15 hour period under a nitrogen purge. The resulting mixture was refluxed for 24 hours under a nitrogen atmosphere and cooled. The reaction mixture turned from yellow to black due to exposure to a small amount of air. The mixture was stirred with Norit and filtered through Celite.

The solvents were evaporated under reduced pressure and the residue was purified on silica gel using 1 : 1 hexane/ethyl acetate as the eluant to give 1.22 g (16.7%) of a pale yellow oil; IR (neat): 1455, 1365, 1290, 1124, 1101, 980 cm^{-1} ; NMR (δ) 3.94 (t, 4H), 3.65 (s, 8H), 2.84 (t, 4H). Exposure to air oxidized the selenium in the crowns leaving red selenium on the silica gel column. This method of purification lowered the yields by a significant amount.

Anal. Calc. for $\text{C}_8\text{H}_{16}\text{O}_3\text{Se}$: C, 40.17; H, 6.74; mol. wt. 240. Found: C, 39.97; H, 6.72; MS, 240.

2.2. PREPARATION OF 4,7,13,16-TETRAOXA-1,10-DISELENACYCLOOCTADECANE (2) (1,10-DISELENA-18-CROWN-6)

To 600 mL of ethanol, which had previously been treated with 3.8 g (0.17 mole) of sodium metal and 2.3 g of potassium chloride, was added gaseous hydrogen selenide as above. The ethanol solution turned cloudy white. Triethylene glycol dichloride (11.53 g, 0.062 mole) in 200 mL of ethanol was added in the same way as described above. The ethanol solution was refluxed for 3 days and treated with Norit as above to give a light yellow solid, 3.35 g (27.8%); mp 91–92° (recrystallized from ethanol); IR: 1455, 1325, 1265, 1115, 1095, 1060, 1030, 1000 cm^{-1} ; NMR (δ) 3.78 (t, 8H); 3.62 (s, 8H); 2.84 (t, 8H).

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{O}_4\text{Se}_2$: C, 36.93; H, 6.20; mol. wt. 392. Found: C, 37.16; H, 6.21; MS, 391, 392, 393.

2.3. CATION TRANSPORT STUDIES OF 2

Membrane transport experiments were carried out using a bulk liquid membrane as has been described in Refs. [7, 8]. The following metal compounds were obtained in the highest grade available and were used without further purification: AgNO_3 (Baker), $\text{Pb}(\text{NO}_3)_2$ (Baker), $\text{Cd}(\text{NO}_3)_2$ (B&A), $\text{Zn}(\text{NO}_3)_2$ (Mallinckrodt), $\text{Ni}(\text{NO}_3)_2$ (Baker), and spectroquality methylene chloride (Em Omnisolve). All aqueous solutions were prepared using distilled deionized water.

3. Results and Discussion

Earlier, dithia-18-crown-6 (3) was found to transport silver and lead ions from an aqueous source phase into a neutral aqueous receiving phase through a methylene chloride bulk membrane [7, 8] with flux values (J_M) of 76 and $271 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$, respectively [7]. As expected, similar transport results were found for diselena crown 2, i.e., 65 and $288 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$ for Ag^+ and Pb^{2+} , respectively. Transport by the corresponding diaza crown, (4), was found to be similar for Ag^+ ($J_M = 82 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$), but poorer for Pb^{2+} ($J_M = 18 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$) [7]. The low transport of Pb^{2+} by 4 may be explained by a competitive transport of H^+ from the acidic (pH = 3.8) Pb^{2+} source phase. This competitive transport is not found with the neutral thia and selena crown ethers. Cadmium, nickel and zinc ions were not transported by 2.

Acknowledgement

This work was supported by U.S. Department of Energy, Office of Basic Energy Sciences, Contract No. DE-FG02-86 ER 13463.

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