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Molecular Design of Crown Ethers. 19.[1] Synthesis of Novel Disulfide- and Diselenide-Bridged Bis(benzo-12-crown-4)s and Their Ag$^+$-Selective Electrode Properties

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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 (**4**) and diselenide (**5**), have been synthesized and characterized by elemental analysis and mass, IR, UV, and ^{1}H NMR spectroscopy. An X-ray crystallographic structure was obtained for **4**. Ion-selective electrodes (ISE) for Ag$^+$, containing **4** and **5** in PVC membrane as neutral carriers, were prepared, and their selectivity coefficients for Ag$^+$ ($K^{\mathrm{pot}}_{\mathrm{Ag,M}}$) were determined against other heavy metal ions, alkali and alkaline-earth metal ions, and ammonium ion using the matched potential method. These ISEs showed excellent Ag$^+$ selectivities, log $K^{\mathrm{pot}}_{\mathrm{Ag,M}} \leq -4.0$, against most of the interfering cations examined, except for Hg$^+$ (log $K^{\mathrm{pot}}_{\mathrm{Ag,M}} \geq -1.2$). These $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ values are comparable to those reported for the representative Ag$^+$-selective thioethers **6** and **7**, revealing that both disulfide and diselenide functionalities in **4** and **5** are equally effective Ag$^+$-selective binding sites as the 1,7-dithia-4-oxa functionality in **6** and **7**, irrespective of the different atom type and relative position of the sulfur/selenium donors in the ligands. Also discussed are the steric and electronic effects of the nitro groups in **4** and **5** on the Nernstian slopes obtained with the **4**- and **5**-based ISEs.

Introduction

Crown ethers have enjoyed widespread use in various areas of science and technology ever since the first preparation of the ligand by Pedersen.[2] One of the successful applications of them is in analytical chemistry. Crown ethers are useful for separations, enrichment, and analyses of ionic species. In particular, the ion-selective electrode (ISE) is the most important target in analytical applications.[3−5] To improve or enhance the ion selectivities of crown ethers, a great deal of effort has been devoted to the design and syntheses of novel macrocycles in recent years.[4−6] In fact, a wide variety of mono- and bis(crown ether)s have been employed in the studies of ISE.[4,7−9] Especially, bis(crown ether)s, carrying two crown ether moieties at the ends of a short linker chain, have been extensively studied as neutral carriers of PVC-membrane ISEs, since they show highly selective binding of cations that can form “sandwich” complexes.

For a long time, silver ion has been analyzed quantitatively by using crystal membrane Ag$^+$−ISE made from insoluble argentiferous salt in water.[10,11] Increasing attention has recently been focused on neutral carrier-type Ag$^+$−ISEs,[7,12−22] because this type of ISEs often show better selectivities than the conventional solid-state electrode. Since dithiacrown ethers were employed in the first neutral carrier-type Ag$^+$−ISEs which showed very high Ag$^+$-selectivities against alkali metal ions,[12] thio-

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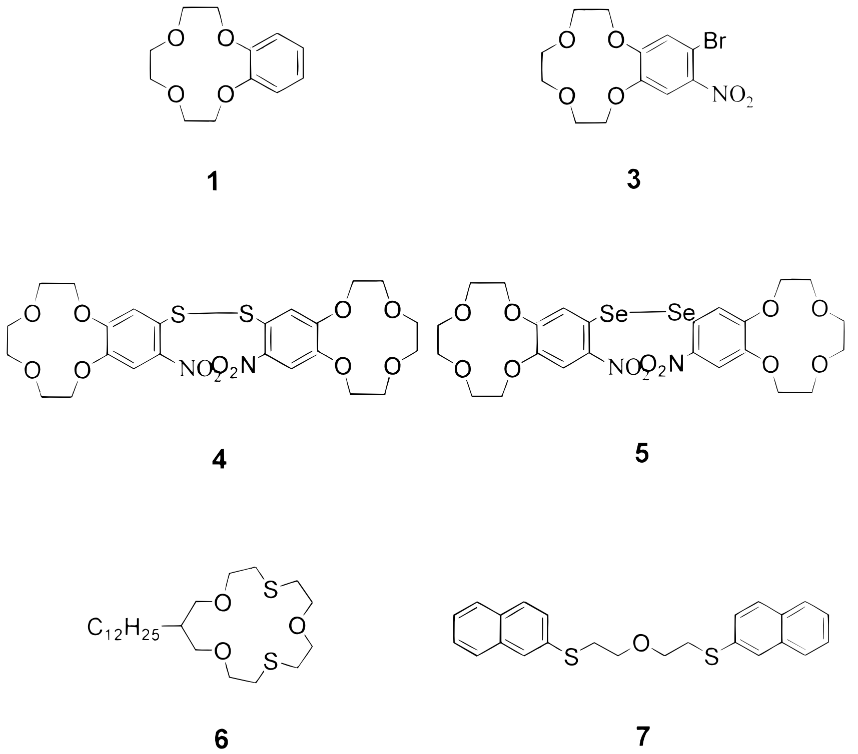
Chart 1



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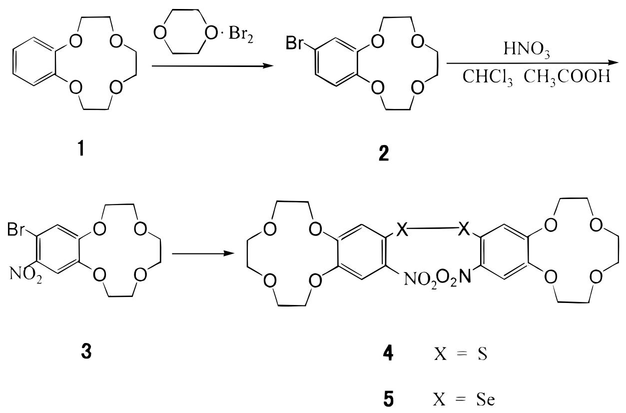
ethers have been a very important class of ionophores for Ag^+−ISEs.[7] In this context, selenium atom as a soft donor is expected to interact with soft Ag^+ ion. Indeed, we have demonstrated recently that selenacrown ethers exhibit very high binding abilities for Ag^+.[1b,23] We have also reported a thermodynamic study on the complexation of sodium ion with a series of bis(12-crown-4)s,[24] which indicates that small-sized crown ether units in a ligand molecule cooperatively bind larger sodium ion to form "1:2" sandwich complexes, giving much higher complex stability constants than that for the parent 12-crown-4. These observations together with the fact Ag^+ and Na^+ have similar radii led us to the synthetic and analytical studies of a series of novel bis(crown ether)s in which two 12-crown-4 skeleton are linked by a disulfide or diselenide for high Ag^+ selectivity.

We now wish to report the syntheses and characterization of bis(2-nitro-4,5-(1,4,7,10-tetraoxadecamethylene)-phenyl) disulfide (**4**) and bis(2-nitro-4,5-(1,4,7,10-tetraoxadecamethylene)phenyl) diselenide (**5**) and also their Ag^+ selectivities behavior monitored by electromotive force measurements of polymer membrane electrodes based on these novel Ag^+-selective ionophores. Comparison of the ISE behavior of these disulfide- and diselenide-bridged bis(benzo-12-crown-4)s with that of the parent 2,3-benzo-1,4,7,10-tetraoxacyclododeca-2-ene (**1**) and 2,3-(4′-bromo-5′-nitrobenzo)-1,4,7,10-tetraoxacyclododeca-2-ene **(3)** as well as that reported for dodecyl-16-crown-5 (**6**)[14] and acyclic dithioether (**7**)[17] (Chart 1), together with the X-ray crystallographic structure of **4**, will serve our further understanding of the structure−selectivity relationship in the Ag^+−ISE.

Scheme 1



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Results and Discussion

Syntheses. Heteroatom-bridged bis(benzo-12-crown-4)s **4** and **5** were synthesized in 71 and 31% yields, respectively, by reaction of 4-bormo-5-nitrobenzo-12-crown-4 (**3**) with Na_2S_2 or K_2Se_2, as shown in Scheme 1. The lower yield for **5** would be attributable to the larger atomic size of selenium than sulfur, which may cause steric hindrance against the adjacent nitro group. However, the incorporation of a nitro group into the benzene ring is essential, since it greatly accelerates the nucleophilic attack of disulfide or diselenide ion to the electron-deficient benzene ring.

Ag^+ Selectivity. The Ag^+ selectivities of heteroatom-bridged bis(benzo-12-crown-4)s **4** and **5** were evaluated by the potentiometric selectivity coefficients ($K_{Ag,M}^{pot}$) determined for polymer membranes containing these ionophores. For comparison purpose, the parent benzo-12-crown-4 **1** and its bromo,nitro-derivative **3** as well as the representative thioether **6** and **7** were examined under the same conditions. The polymer membrane was com-

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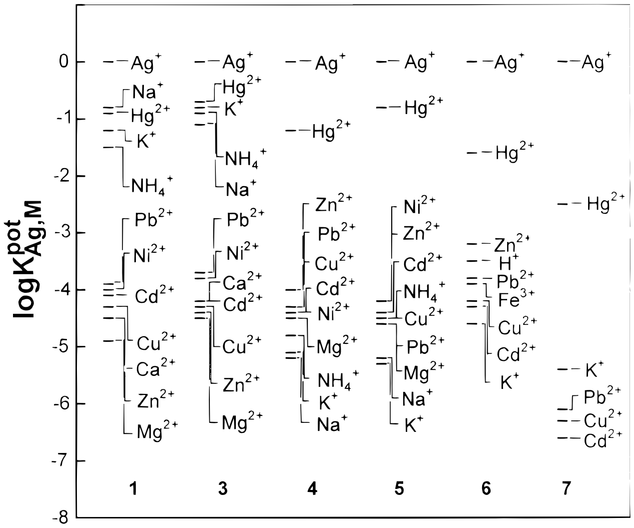

Figure 1. Selectivity coefficients for Ag^+-selective electrodes based on **1**, **3**, **4**, **5**, **6** (ref 14), and **7** (ref 17).

posed of PVC as the support, dibutyl phthalate (DBP) as the membrane solvent, and a mono- or bis(crown ether) as the ionophore. The membranes also contained a small amount of potassium tetrakis(*p*-chlorophenyl)borate (KTClPB) for the purpose of reducing membrane resistance and suppressing permeation of counteranions in the aqueous phase into the membrane phase. The potentiometric selectivity coefficients for Ag^+, which were determined by the matched potential method, are illustrated in Figure 1. The selectivity coefficient ($K^{pot}_{Ag,M}$) represents the preference of the ISE (or PVC membrane) containing the heteroatom-bridged bis(benzo-12-crown-4) for Ag^+ over the other cations. Thus, the coefficient $K^{pot}_{I,M}$ defines the ability of an ISE (or membrane) to distinguish different ions in the same solution. The smaller the $K^{pot}_{I,M}$ value, the greater the electrode preference for the primary ion (I^+) over the interfering ion (M^{n+}).[8]

As can be seen from Figure 1, both polymer membranes containing **4** and **5** gave excellent $\log K^{pot}_{Ag,M}$ values (≤ -4.0) 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 heteroatoms incorporated, both **4**- and **5**-based ISEs gave characteristic ion selectivity tendencies which resemble each other but distinctly differ from the ISEs containing thioethers **6** and **7** or the benzo-12-crown-4's **1** and **3**. The performance of the present ISEs is generally superior to that displayed by conventional Ag_2S-based electrode or the **6**-based ISE and is satisfactory as Ag^+–ISE, although acyclic dithioether **7** shows better performance. The fact that polymer membranes containing **1** and **3** gave greater $\log K^{pot}_{Ag,M}$ values (≥ -1.5) against Na^+, K^+, NH_4^+, and Hg^{2+} than those of **4**- and **5**-based ISEs and similar $\log K^{pot}_{Ag,M}$ values against Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} means that **1**-, **3**-, **4**-, and **5**-based ISEs primarily possess moderate to high Ag^+ selectivities and only weakly responds to alkaline-earth metal ions and other transition metal ions (i.e. Mg^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}). Na^+, K^+, NH_4^+, and Hg^{2+} give serious interference for **1** and **3**. One possible explanation is that hard divalent cations, possessing high hydration energies, cannot strongly interact with 12-crown-4 and/or disulfide/diselenide moiety in the ionophore, while less heavily hydrated soft cations, such as Ag^+ or Hg^{2+}, coordinate to soft sulfur or selenium donors, which may be assisted by further ligation of the 12-crown-4 moieties. However, the assistance seems only optional judging from the very high Ag^+-selectivities observed for **4** and **5**. It should be also noted that the disulfide ligand **4** 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 **6**, except for Hg^{2+}. 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. In this context, the poorer Ag^+ selectivities over Hg^{2+} of **4** and **5** than those reported for **6** and **7** are intriguing and would be attributed to the 1,2-disulfur/diselenium donor arrangement.

The steric effect of the nitro groups in **4** 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 $K^{pot}_{Ag,M}$ values were obtained in the ISE experiments described above. Even so, the electron-withdrawing effect of nitro group in **4** 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. The only observable effect is the moderate Nernstian slopes (41.5 and 39.8 mV/pAg) for the **4**- and **5**-based PVC membrane electrodes. This would be attributed to the strong coordination interaction between soft Ag^+ ion and soft sulfur/selenium donors, which decelerates the interfacial ion exchange in ISE, affording the non-Nernstian response upon measurement of Ag^+ ion. Although the $K^{pot}_{Ag,M}$ profile shown in Figure 1 may differ from the "real" cation selectivities of **4** and **5**, the Ag^+–ISEs based on these ligands give excellent $K^{pot}_{Ag,M}$ values and will be useful for the practical purpose.

Ionophore **5** is a bis(benzocrown ether) linked with two selenium atom. Selenium is a softer donor than sulfur, and interaction between selenium donors and soft Ag^+ ion is stronger than that between sulfur donors and Ag^+ ion. Strong interaction may interfere the rapid interfacial ion exchange in ISE, which in turn leads to the moderate Nernstian slope (39.8 mV/pAg) for the **5**-based Ag^+–ISE.

Experimental Section

General Remarks. Melting points, measured with an XT-4 apparatus, are uncorrected. ^1H NMR spectra were recorded on a Bruker AC-P200 instrument at 200 MHz in $CDCl_3$ solution, using tetramethylsilane as an internal reference. Infrared and ultraviolet spectra were recorded on Shimadzu IR-435 and Shimadzu UV-2401/PC instruments, respectively. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. Mass spectra were measured by using a JEOL JMS-DX-303 instrument.

Materials. Starting materials were commercial available unless otherwise noted. 2,3-Benzo-1,4,7,10-tetraoxacyclododeca-2-ene[25] (**1**) and 4′-bromobenzo-1,4,7,10-tetraoxacyclododeca-2-ene[26] (**2**) were prepared according to the literature procedures.

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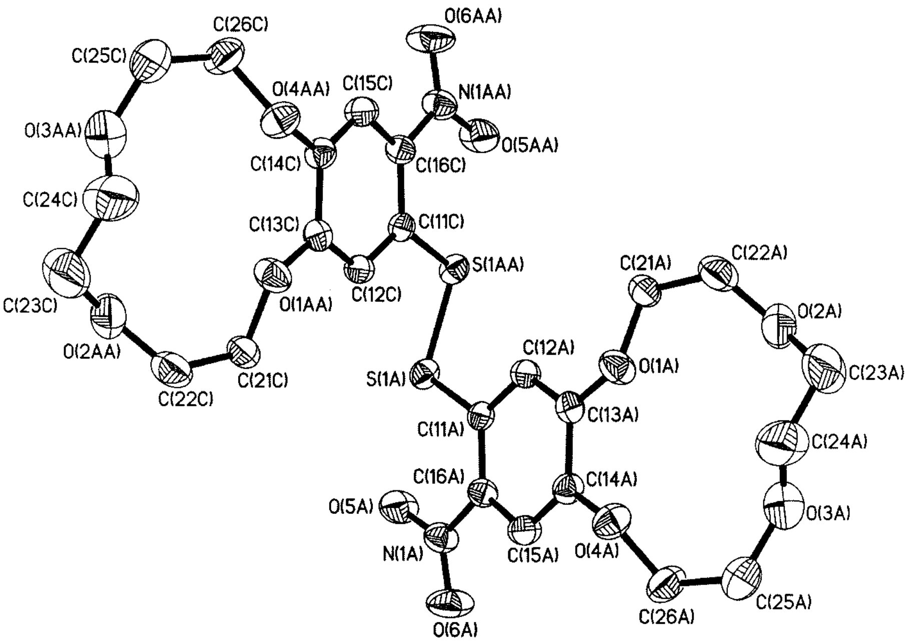

Figure 2. X-ray structure of **4**. Steric position between nitro-groups and sulfur atoms: (a) bonds distances, [S(1A)−O(5A)] 2.56 Å; [S(1A)−N(1A)] 3.09 Å; [S(1A)−O(6A)] 4.29 Å; [S(1AA)−N(1A)] 5.02 Å; (b) bonds angles, [S(1AA)−S(1A)−O(5A)] 173.86°; [S(1AA)−S(1A)−N(1A)] 155.79°; [S(1AA)−S(1A)−O(6A)] 156.13°.

2,3-(4′-Bromo-5′-nitrobenzo)-1,4,7,10-tetraoxacyclododeca-2-ene (3). To 2.0 g (6.6 mmol) of **2** dissolved in a mixture of 35 mL of chloroform and 30 mL of acetic acid was added dropwise 10 mL of nitric acid (65%) over a 5 min period. The mixture was stirred for 24 h at room temperature, then neutralized with aqueous Na_2CO_3 and the chloroform layer separated. The aqueous layer was extracted with chloroform, and the combined chloroform extracts were dried over $MgSO_4$. After evaporation of $CHCl_3$, the hot liquid was poured into ethanol to give a yellow crystal, which was recrystallized from methanol to yield 1.8 g (78.3%) of pure compound: mp 115−117 °C; ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 4 H), 3.90 (t, 4 H), 4.30 (t, 4 H), 7.20 (s, 1 H), 7.65 (s, 1 H).

Bis(2-nitro-4,5-(1,4,7,10-tetraoxadecamethylene)phenyl) Disulfide (4). $Na_2S{\cdot}9H_2O$ (0.48 g, 2 mmol) and sulfur power (0.064 g, 2 mmol) were added to methanol (4 mL), and the mixture was refluxed for 1 h. After cooling, the solution was filtered to give a transparent brownish red solution. The solution was added dropwise into a solution of 1.39 g (4 mmol) of **3** dissolved in 30 mL of hot methanol, and then the mixture was stirred under reflux for 1 h. After standing for 1 h, the resultant solution was filtered and the precipitates collected were washed with water and methanol to give 0.85 g (70.8%) of yellow crystals: mp 193.5−195.5 °C; MS *m/z* 600 (M^+), 301; UV−vis λ_{max}(CH_3CN)/nm (ϵ/M^{-1} cm^{-1}) 231.5 (23 500), 267.5 (25 380), 313.0 (12 250), 373.0 (11 740); FT-IR (KBr) ν/cm^{-1} 3390.0, 2912.5, 1595.1, 1506.3, 1482.0, 1363.1, 1267.6, 1200.2, 1140.7, 1113.8, 1071.0, 1046.8, 1020.3, 919.0, 894.7, 817.5, 544.6; ^{1}H NMR δ 3.69 (s, 8 H), 3.79 (t, $J = 3.6$ Hz, 8 H), 4.20 (m, 8 H), 7.32 (s, 2 H), 7.92 (s, 2 H). Anal. Calcd for $C_{24}H_{28}O_{12}N_2S_2$: C, 48.00; H, 4.67; N, 4.67. Found: C, 47.92; H, 4.61; N, 4.94.

Bis(2-nitro-4,5-(1,4,7,10-tetraoxadecamethylene)phenyl) Diselenide (5). Absolute ethanol (15 mL) was added with magnetic stirring to 0.187 g (3.25 mmol) of 94% potassium borohydride and 0.385 g (4.88 mmol) of selenium, and the mixture was heated to reflux with stirring for 2 h, with passing nitrogen gas into the solution in order to dissolve selenium and to expel H_2Se (caution).[27] The brownish red ethanolic solution of K_2Se_2 was then ready for further use.

To 6 mL of an ethanolic potassium diselenide solution, prepared above, was added dropwise to 0.4 g (1.15 mmol) of **3** in 15 mL of hot ethanol, and the solution was heated to reflux for 8 h. After cooling, the solvents were removed in vacuo and the residue was extracted with $CHCl_3$. Evaporation of the $CHCl_3$ gave solid residue, which was purified by column chromatography on silica (200−300 mesh, ethyl acetate) and then recrystallized from methanol to give yellow crystal **5** (0.25 g, 31.3%): mp 167−169 °C; MS *m/z* 694 (M^+); UV−vis λ_{max}(CH_3CN)/nm (ϵ/M^{-1} cm^{-1}) 229.0 (10 740), 270.0 (8450), 319.5 (6110), 386 (4940); FT-IR (KBr) ν/cm^{-1} 3404, 2903.5, 1637.1, 1591.4, 1553.6, 1500.9, 1396.2, 1311.7, 1266.6, 1192.4, 1136.5, 1099.5, 1071.5, 1021.8, 912.9, 826.3, 751.3, 655.5; ^{1}H NMR δ 3.69 (s, 8 H), 3.77 (t, $J = 4$ Hz, 8 H), 4.21 (m, 8 H), 7.39 (s, 2 H), 7.97 (s, 2 H). Anal. Calcd for $C_{24}H_{28}O_{12}N_2Se_2$: C, 41.50; H, 4.03; N, 4.03. Found: C, 41.33; H, 4.21; N, 4.12.

Silver Selectivity Evaluated by Potentiometric Selectivity Coefficient. Membrane Electrode. The typical procedure for membrane preparation is as follows: Poly(vinyl chloride) (PVC) (132 mg, 32.9%), dibutyl phthalate (DBP) (264 mg, 65.8%), potassium tetrakis(*p*-chlorophenyl)borate (KTClPB) (1.2 mg, 50 mol % to the crown ether), and crown ether (1%) were dissolved in 5 mL of THF. This solution was then poured into a flat-bottomed Petri dish of 32 mm inner diameter and 50 mm height. 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 PVC tube tip with 5% THF solution in water. After injection of 0.01 M aqueous solution of $AgNO_3$ as the internal solution, the electrode was conditioned by soaking in 0.01 M aqueous solution of $AgNO_3$ for 2 h. The external reference electrode is 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.

Selectivity Coefficients. The potentiometric selectivity coefficient $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ determined here are defined in the Nicol-

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(27) Excess hydrogen selenide was trapped by passing it into a 5% aqueous lead acetate solution.

sky−Eisenman equation:

$$E = E° + \frac{2.303RT}{F}\log[a_{\mathrm{Ag}} + K^{\mathrm{pot}}_{\mathrm{Ag,M}}(a_{\mathrm{M}})^{1/Z_{\mathrm{M}}}]$$

where E represents the experimentally observed potential, R the gas constant, T the thermodynamic temperature in K, F the Faraday constant, a_{Ag} the Ag^+ activity, a_{M} the activity of the foreign cation, and Z_{M} the charge of the foreign cation. The selectivity coefficients were determined by a matched potential method.[28] In the matched potential method, selectivity coefficients are defined as the ratio of the primary ion concentration to the interfering ion concentration which gives the same potential change in a reference solution. To determine the selectivity coefficient by this method, one would measure the change in potential upon changing the primary ion concentration. The interfering ion would then be added to an identical reference solution until the same potential change is obtained. The change in potential must be produced in a constant initial background of the primary ion (10^{-5} M) and must be the same in both cases. In this method, there is no need to take the valence of ions consideration, and therefore, it does not assume that the slopes for both primary and interfering ions are the same or even Nernstian.

Crystallographic Structural Determination. Crystals of **4** suitable for X-ray crystallography were grown by slow evaporation from an acetonitrile solution of **4**. X-ray crystallographic data were obtained on a Bruker SMART 1000 instrument. Structures were solved with the SHELXS-97 software. Crystal, data collection, and refinement parameters are given in Table 1.

Table 1. Crystal Data and Data Collection Parameters

data	**4**
formula	$C_{24}H_{28}N_2O_{12}S_2$
formula wt (g/mol)	600.60
T (K)	293(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	$P2/n$
a (Å)	18.0838(18)
b (Å)	5.5517(5)
c (Å)	27.489(3)
α (deg)	90
β (deg)	100.612(2)
χ (deg)	90
V (Å^3)	2712.6(5)
Z	4
D_c (Mg/m^3)	1.471
F(000)	1256
cryst size (mm)	0.02 × 0.25 × 0.25
θ range (deg)	2.29−25.03
reflns collected	10798
independent reflns	4804 (R_{int}=0.0753)
obsd reflns	2624
data/restraints/parameters	4808/0/362
goodness-of-fit on F^2	0.919
R1	0.0497
R_w2	0.1052

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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 **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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