Silver(I) Ion-selective Electrodes based on Polythiamacrocycles

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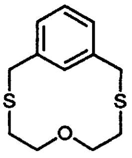
Some polythiamacrocycles having aromatic rings as macrocyclic components have been synthesised and tested as sensors in solid-state electrodes. High selectivity for Ag^+, even over that for Hg^{2+}, and excellent electrode properties have been found.

Macrocyclic polythiaethers have the ability to form complexes with transition-metal cations. We have studied 6-oxa-3,9-dithia-15-aza-bicyclo[9.3.1]pentadeca-1(15),11,13-triene[1] as a neutral carrier for a copper(II)-selective membrane electrode. The copper complex of this azadithiaether macrocycle is relatively soluble in water, so the carrier slowly exudes from the membrane limiting the electrode lifetime and performance. We have improved its electrode-sensor characteristics by replacing the pyridine moiety by a benzene group, so reducing the polarity and solubility in water. The resulting dithiaether macrocycle 6-oxa-3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (L^1) is an excellent sensor for silver(I)-selective membrane electrodes with little response towards Hg^{II}.[2] To investigate the influence of the aliphatic chain heteroatom on the electrode characteristics we have synthesised new macrocycles very similar to L^1. Systematic studies performed in this work showed that poly(vinyl chloride) (pvc) membranes containing L^1, 3,6,9-trithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (L^2) or 3,9-dithiabicyclo[9.3.1]pentadeca-1(15),11,13-triene (L^3) are suitable as sensors for silver(I)-selective membrane electrodes.

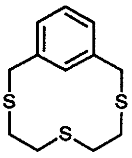
Few such electrodes are reported in the literature, all of them based on polythiacrown ether derivatives. Ion-selective membrane electrodes based on dithiacrown ethers and a monobenzocrown ether were tested as sensors for the silver(I) electrode.[3] All of them exhibit good sensitivity but no Nernstian response to the activity changes of Ag^+. Other macrocyclic molecules, basically with the same structure as the crown compounds but with lipophilic chains attached to the macrocyclic ring, have been reported and tried as sensors in Ag^+-selective polymeric membrane electrodes[4] with similar results, but these display Nernstian response. The electrode characteristics of the ion-selective membrane electrodes based on the macrocycles synthesised in the present paper have a better response than those reported before and superior to that of conventional Ag_2S-based solid-state electrodes, so their future seems promising.

Experimental

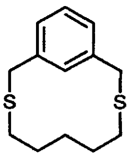
General.—Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B instrument. Proton NMR spectra were run on a Bruker WP80 54 in $CDCl_3$ solution, IR spectra on a Perkin-Elmer 1710 FT spectrophotometer as KBr pellets and mass spectra on a Hewlett-Packard HP2985 GC/MS instrument. Unless specifically mentioned, the syntheses were performed under a nitrogen atmosphere, using dehydrated and deoxygenated solvents. Solvents were placed under vacuum to eliminate the dissolved oxygen.



L^1



L^2



L^3

Synthesis of Macrocyclic Compounds L^1–L^3.—Under a nitrogen atmosphere and high dilution conditions, a solution (A) of KOH (0.04 mol) and bis(2-mercaptoethyl) ether (L^1), bis(2-mercaptoethyl) sulphide (L^2) or penta-1,5-dithiol (L^3) (0.02 mol) in butan-1-ol (50 cm^3) was mixed over butan-1-ol (1.5 l) with a solution (B) of α,α′-dichloro-*m*-xylene (0.02 mol) in butan-1-ol (50 cm^3) at a rate of 3 cm^3 h^{-1}. The KCl formed was filtered off and the resulting solution evaporated to dryness. The oily material was extracted with benzene (150 cm^3), washed with Na_2CO_3 and water and dried (Na_2SO_4, 8 h). The dry residue was dissolved in benzene (5 cm^3) and chromatographed over neutral Al_2O_3. The fraction eluted with benzene was separated and taken to dryness. The resulting yellowish oily material was poured onto light petroleum (b.p. 40–60 °C, 50 cm^3) and a white crystalline compound appeared. Yields: L^1, 22; L^2, 30; L^3, 30% [Found: C, 59.95; H, 6.80% M 240. $C_{12}H_{16}OS_2$ (L^1) requires C, 59.90; H, 6.65%, M 240.4. Found: C, 56.33; H, 6.55%; M 256. $C_{12}H_{16}S_3$ (L^2) requires C, 56.20; H, 6.30%; M 256.5. Found: C, 65.60; H, 7.80. $C_{13}H_{18}S_2$ (L^3) requires C, 65.50; H, 7.60%]. Principal IR absorptions: L^1, $\nu(CH_2)$ 2933, $\nu(OCH_2)$ 2875, $\nu(CH_2OCH_2)$ 1070 and $\nu(CS)$ 707; L^3, $\nu(CH_2)$ 2920, $\nu(CH)$ 3030 and $\nu(CS)$ 704 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): L^1, δ 2.57 (4, t, CCH_2O), 3.01 (4, t, SCH_2C), 3.78 (4, s, SCH_2Ph), 7.20 (2, m, Ph), 7.21 (1, m, Ph) and 7.63 (1, s, Ph); L^2, δ 2.18 (4, t, CCH_2S), 2.38 (4, t, SCH_2C), 3.74 (4, s, SCH_2Ph), 6.93 (1, s, Ph) 7.33 (2, m, Ph), 7.40 (1, m, Ph); L^3, δ 1.10 (4, q, CCH_2C), 1.37 (2, q, CCH_2C), 2.31 (4, t, SCH_2C), 3.75 (4, s, SCH_2Ph), 7.2 (2, m, Ph), 7.2 (1, m, Ph) and 7.54 (1, s, Ph). The ^{13}C NMR spectra were in accord with the proposed formulae.

Fabrication of Electrodes.—The sensor membranes were prepared and assembled as previously described.[5–7] The sensor material (macrocycles, 7%) with dioctyl phthalate (31%) as plasticizer and pvc (62%) were dissolved in tetrahydrofuran. The sensor solution was poured dropwise onto a conductive circular flat cavity (0.2 mm deep) drilled in the end of an electrode body tube sealed with a layer of conducting polymer material. After drying the thickness of the resulting convex

Table 1 Electrode characteristics

Sensor	L^3	L^1	L^2
Detection limit (mol dm^{-3})	6.7×10^{-7}	3.0×10^{-7}	1.4×10^{-6}
Slope (mV per decade)	56	59	59
Time response (s)	<5	<5	<10
pH interval	1.8–8.5	2.5–8.5	2.5–8.3
Lifetime (month)	>9	>13	>8

Table 2 Selectivity coefficients ($K^{pot}_{A/B}$)

Sensor	L^3	L^1	L^2
Ca^{2+}	3.6×10^{-6}	1.1×10^{-5}	1.8×10^{-5}
Zn^{2+}	3.9×10^{-6}	2.7×10^{-6}	1.2×10^{-6}
Mg^{2+}	4.4×10^{-6}	4.9×10^{-6}	5.5×10^{-6}
Sr^{2+}	4.6×10^{-6}	1.0×10^{-5}	1.6×10^{-5}
Ni^{2+}	4.9×10^{-6}	1.8×10^{-6}	9.8×10^{-6}
Pb^{2+}	6.3×10^{-6}	1.2×10^{-5}	7.9×10^{-6}
Na^{+}	7.4×10^{-6}	1.3×10^{-5}	1.3×10^{-5}
Cu^{2+}	8.9×10^{-6}	7.9×10^{-6}	3.1×10^{-5}
Cd^{2+}	9.3×10^{-6}	3.9×10^{-5}	5.5×10^{-5}
K^{+}	1.2×10^{-5}	1.7×10^{-5}	5.7×10^{-5}
Co^{2+}	1.4×10^{-5}	2.5×10^{-6}	1.5×10^{-5}
Tl^{+}	4.5×10^{-5}	1.3×10^{-5}	1.4×10^{-4}
Hg^{2+}	2.3×10^{-3}	5.0×10^{-3}	8.0×10^{-3}

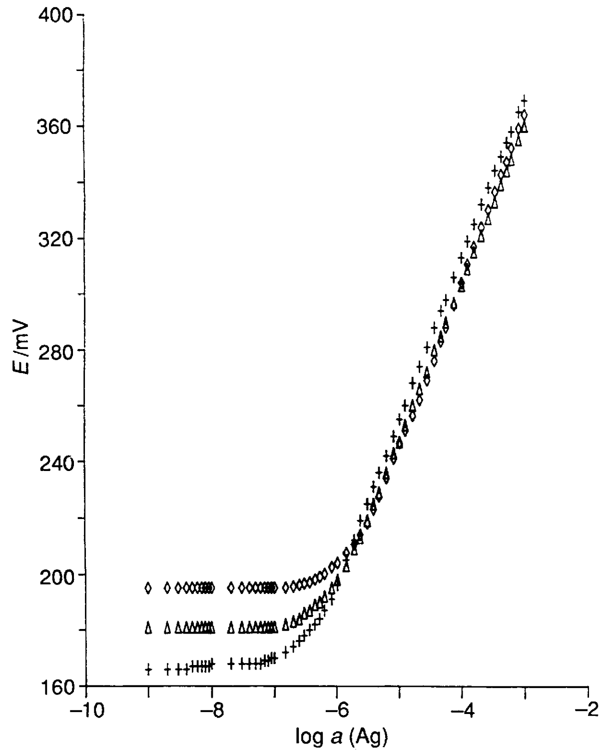


Fig. 1 Electrode responses for Ag^+-selective electrodes based on the dithiamacrocycles synthesised: L^1 (+), L^2 (◇) and L^3 (△)

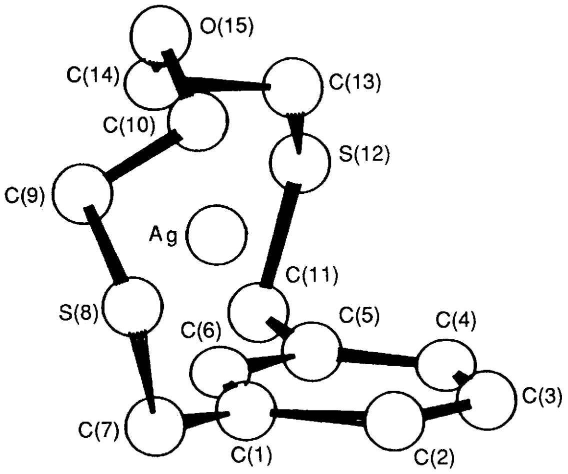


Fig. 2 Schematic drawing of the molecular structure of $[AgL]^+$ (X-ray diffraction data) which is similar to that proposed for macrocycles L^1–L^3 and their silver(I) complexes. For L, C(6) is a pyridine N atom

membrane was 0.3 mm. The conductive material (graphite-loaded epoxy resin) used as the solid internal contact of the membrane electrode has been described previously.[6,7] The electrode was usually conditioned before use by soaking for 24 h in a 10^{-3} mol dm^{-3} $AgNO_3$ solution.

Electromotive Force Measurements.—The response characteristics, response time of the constructed membrane electrodes and the selectivity coefficients $K^{pot}_{A/B}$ (fixed interference method)[8] were determined by the reported standard methods. For measuring the membrane potentials the following electrochemical cell was used: solid internal contact|sensor membrane|working solution|reference electrode. The e.m.f. was measured relative to a Ag–AgCl double-junction reference electrode (Orion 90-02-00) with the outer chamber filled with 10^{-1} mol dm^{-3} potassium nitrate solution. A Crison (Barcelona) digital potentiometer (±0.1 mV) was used. All measurements were carried out at 25 ± 0.1 °C.

Results and Discussion

Synthesis.—Three benzene derivatives, polythiamacrocycles L^1–L^3, were synthesised for the first time and tested as sensors for Ag^+ in ion-selective membrane electrodes. All were prepared by reaction of α,α′-dichloro-*m*-xylene with different disulphide derivatives under high dilution conditions.

Ion Selectivities.—Electrode responses for Ag^+-selective electrodes based on the dithiamacrocycles synthesised are shown in Fig. 1. Electrode characteristics and selectivity coefficients for Ag^+ with respect to other cations are summarized in Tables 1 and 2, respectively. All of these electrodes are highly Ag^+ selective. Mercury(II) interferes with the electrode response the most seriously, but the corresponding selectivity coefficient for Ag^+ with respect to Hg^{2+} is still in the range 2.3×10^{-3}–8.0×10^{-3}. An excellent Nernstian response (slope range 56–59 mV per decade) to the silver activity change occurs in the range 10^{-7}–10^{-2} mol dm^{-3}. The good 'molecular recognition' exhibited by these macrocyclic molecules towards the Ag^+ ion can be attributed to different factors.

(*a*) *Structural factors.* Presently we do not know the molecular structure of these macrocycles, but in a recent paper we have reported the molecular structure of a very similar molecule[1] solved by X-ray diffraction methods. 6-Oxa-3,9-dithia-15-aza-bicyclo[9.3.1]pentadeca-1(15),11,13-triene (L) is very similar to L^1, containing a pyridine moiety instead of a benzene group. As a working hypothesis we can assume a similar molecular structure for both molecules. The same would be true for the macrocycles L^2 and L^3.

Fig. 2 shows a schematic drawing of the molecular structure of $[AgL]^+$ and that proposed for the silver complexes of macrocycles L^1–L^3 is similar. This molecule exhibits a non-planar conformation. The pyridine ring and atoms C(7) and C(11) lie in a plane, the average deviation from this plane being only 0.017 Å. Atoms C(7), C(11), S(8) and S(12) also lie in a plane, but the angle between these two planes is 88.1°, the aliphatic chain being folded over the aromatic ring. The S(8)$\cdots$S(12) distance is 6.52 Å, so there is space enough to allocate a Ag^+ ion [covalent radius for sulphur atom, 1.127 Å; ionic radius for Ag^+, 1.29 Å (ref. 9)]. In this model the Ag^+ ion would be in an advantageous linear co-ordination environment of sulphur (thioether) atoms. The repulsions due to the hydrogen atom attached to the aromatic carbon atom C(6) are expected to be minimized due to the non-planar conformation of the molecule. This should at least be correct for small cations such as Ag^+.

(*b*) *Chemical co-ordination factors.* It is well known that the Ag^+ ion (d^{10}) exhibits strong affinity towards sulphur-derived ligands and shows a remarkable preference for linear co-ordination.

To explain the silver selectivity of the membrane electrodes based on the macrocycles synthesised it is essential to take into account all these effects. It is not a matter of the size of the macrocyclic cavity, because there is enough space to allocate any of the metal ions tested in this study. In addition, the flexibility of the twisted aliphatic chain could conform to the required ion size, as we have already shown for the copper(II) complex of compound L. This is trigonal bipyramidal with a S$\cdots$S distance considerably shorter than that found in the free ligand.[1] The mono- or di-valent metal ions tested in the present study (Table 2) have larger ionic radii than that of Ag^+ (Tl^+, 1.64; K^+, 1.52; Pb^{2+}, 1.33; Sr^{2+}, 1.32 Å) or smaller [Na^+, 1.16; Hg^{2+}, 1.16; Ca^{2+}, 1.14; Cd^{2+}, 1.09; Zn^{2+}, 0.88; Cu^{2+}, 0.87; Mg^{2+}, 0.86; Co^{2+}, 0.84; Ni^{2+}, 0.83 Å (ref. 9)] but they do not show a strong sulphur (thioether) affinity or linear co-ordination preference, except for Hg^{2+}. Only Hg^{2+} exhibits a comparable size and chemical characteristics to those of Ag^+. The better selectivity of these sensors for Ag^+ compared with Hg^{2+} ($K^{pot}_{A/B} \approx 10^{-3}$) could be attributed to electronic factors or mobility problems inside the membrane. Presently, the reason is not completely clear. The Hg^{2+} gives the most severe interference for the membrane electrodes based on these polythiamacrocycles.

The effect of the pH on these ion-selective electrodes was also studied. All show no significant changes in potential in the range $2.5 < pH < 8.5$ (Table 1). The response time is excellent for the three membrane electrodes studied. The electrode based on the macrocycle L^2 exhibits the worst time response. This behaviour could be attributed to the presence of three sulphur atoms as co-ordinating sites in the macrocyclic cavity, making the corresponding complex of Ag^+ slightly more stable than those of L^1 or L^3, which results in a difficulty in exchanging the Ag^+ of the complex in the pvc membrane with the Ag^+ in the test solution. The lifetime for all of electrodes is also very good.

The selectivities of the silver-selective electrodes were investigated by the mixed interference method. Table 2 reports the corresponding $K^{pot}_{A/B}$ values for the metal ions tested. This table shows the better behaviour of the L^3-based membrane electrode with respect to the other electrodes for all of the metal ions tested, except for Zn^{2+}, Ni^{2+}, Tl^+ and Co^{2+}, however the differences between the three electrodes are not significant. Only Hg^{2+} provides any interference, however the corresponding selectivity coefficients are good enough to assure technical applications of all of them.

Presently it is not possible to rationalize the observed trends in these potential coefficients. We have attempted to correlate the found experimental values with the ionic radii of the corresponding metal ions, but no significant correlation has been obtained in any case.

It can be concluded that all the silver ion-selective membrane electrodes based on macrocycles L^1–L^3 exhibit good sensitivities, detection limits, reproducibilities and selectivities.

Acknowledgements

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