

Ag⁺ ion complexation properties of *N*-phenylpolythiazaalkane derivatives: synthesis, crystallography, ¹H NMR spectroscopy, potentiometry and metal ion recognition properties

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A series of *N*-phenylpolythiazaalkane derivatives; the cyclic derivatives 4-phenyl-1-thia-4-azacyclohexane **1**, 7-phenyl-1,4-dithia-7-azacyclononane **2**, 10-phenyl-1,4,7-trithia-10-azacyclododecane **3** and 13-phenyl-1,4,7,10-tetrathia-13-azacyclopentadecane **4** and acyclic derivatives 6-phenyl-3,9-dithia-6-azaundecane **5** and 9-phenyl-3,6,12,15-tetrathia-9-azaheptadecane **6**, have been studied towards complexation with Ag⁺ ion. Single crystals of two Ag(I) complexes, [Ag(**2**)₂][CF₃SO₃] and [Ag(**4**)][CF₃SO₃] were prepared and their structures were determined in the crystalline state by X-ray diffraction. In [Ag(**2**)₂][CF₃SO₃], two bidentate **2** ligands, in which two sulfur atoms act as coordination sites, sandwich Ag(I) to give a four-coordinate complex in near tetrahedral geometry. In [Ag(**4**)], Ag(I) enters into a cavity composed of four sulfur atoms to give a distorted tetrahedral geometry. The changes of the chemical shifts in ¹H NMR spectroscopy by the addition of CF₃SO₃Ag indicate that **1** and **2** exhibit small downfield shifts only for the protons of the thioether moiety, while **3**, **4**, **5** and **6** show drastic shifts for all protons. Ag⁺ ion complexation with *N*-phenylpolythiazaalkane and polythiaalkane derivatives, which were used for comparison, was studied in acetonitrile solution by potentiometry. Results show that the complex stability is governed primarily by the number of sulfur donor atoms, and the nitrogen atom of the *N*-phenylpolythiazaalkane derivatives scarcely contributes to the stability of the complexes. The extraction of transition metal ions with *N*-phenylpolythiazaalkane derivatives was examined and very high Ag⁺ ion selectivity was observed for most of them. The extraction equilibria of the Ag(I) complexes of *N*-phenylpolythiazaalkane derivatives were studied and the extraction constants of the extracted complexes determined. Results indicate that the extractability of 1 : 1 complexes depends on their stability. In liquid membrane transport, all *N*-phenylpolythiazaalkane derivatives exhibited Ag⁺ ion selective transportability and the order for the Ag⁺ ion transport rate was **5** > **2** ≈ **3** > **4** ≈ **6** ≫ **1**.

Crown and azacrown ethers have been studied widely as hosts to recognize specific guest ions.^{1–12} The functional ability of the crown compounds is generally based on the cavity size of a ring, the molecular structure, the number of donor atoms, and the nature of donor atoms. Thiocrown ethers incorporating only sulfur atoms have been widely investigated as extracting reagents^{13–26} for soft metal ions. The crystal and molecular structures of some Ag(I) complexes with thiocrown ethers have been discussed using X-ray diffraction method.^{27–35} There were a few studies, however, concerning the metal ion complexabilities and selectivities for polythiazaalkane derivatives^{36–42} containing both sulfur and nitrogen atoms as donor atoms on the crown rings. Especially, *N*-phenylpolythiazaalkane derivatives are important for application as coordination moieties for chromogenic reagents,^{43–46} prepared by combining *N*-phenylmonoazacrown ethers with organic dyes.^{47–49}

In this study, we describe the correlation between Ag(I) complexation behavior and molecular structures for a series of macrocyclic *N*-phenylpolythiazaalkane derivatives, **1**, **2**, **3** and **4**, and acyclic derivatives, **5** and **6** (Fig. 1) from the following points of view: (1) X-ray structural analysis for the complexes [Ag(**2**)₂][CF₃SO₃] and [Ag(**4**)][CF₃SO₃]; (2) conformational analysis for Ag(I) complexes containing polythiazaalkane moieties by ¹H NMR titration measurement; (3) stability constants for the Ag(I) complexes; (4) metal ion recognition properties on solvent extraction and Ag(I) extraction equilibria; (5) bulk liquid membrane transport of Ag⁺ ion.

Results and discussion

Syntheses

Cyclic *N*-phenylpolythiazaalkane derivatives, **2** and **4**, and acyclic derivatives, **5** and **6**, were synthesized by methods described previously.^{42,44} Compound **1** was synthesized by the cyclization reaction of *N,N*-bis(*p*-tosylsulfonyloxyethyl)aniline with Na₂S and was obtained in moderate yield.

Compound **3** was synthesized by the cyclization reaction of 3-thiopentane-1,5-dithiol with *N,N*-bis(2-iodoethyl)aniline in the presence of Cs₂CO₃ as base in DMF. Cyclization reaction using Cs₂CO₃ is known to be superior in terms of the yield of macrocyclic compound to the reaction using sodium ethoxide as a base,⁵⁰ although sodium ethoxide has been used as a base for synthesis of alkyl sulfides by the reaction of thiol with halides.^{51,52} This reaction gave **3** in good yield; no compound formed by the 2:2 cyclization reaction of the reactants was isolated.

X-Ray structure of complexes [Ag(**2**)₂][CF₃SO₃] and [Ag(**4**)]-[CF₃SO₃]

A colorless crystal of complex [Ag(**2**)₂][CF₃SO₃] was grown by vapor diffusion of acetonitrile from a solution containing CF₃SO₃Ag and **2** in a mole ratio of 1 : 2. Fig. 2 shows the structure of [Ag(**2**)₂][CF₃SO₃]. Selected bond lengths and angles are listed in Table 1. The averages of Ag–S bond distances and

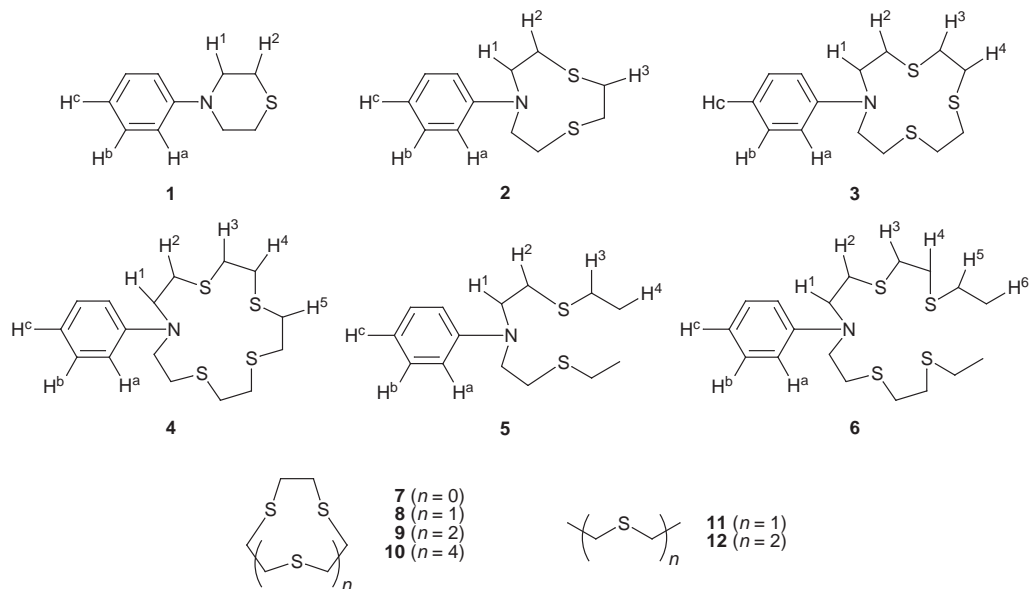


Fig. 1 Structural formulae of *N*-phenylpolythiazaalkane derivatives used here.

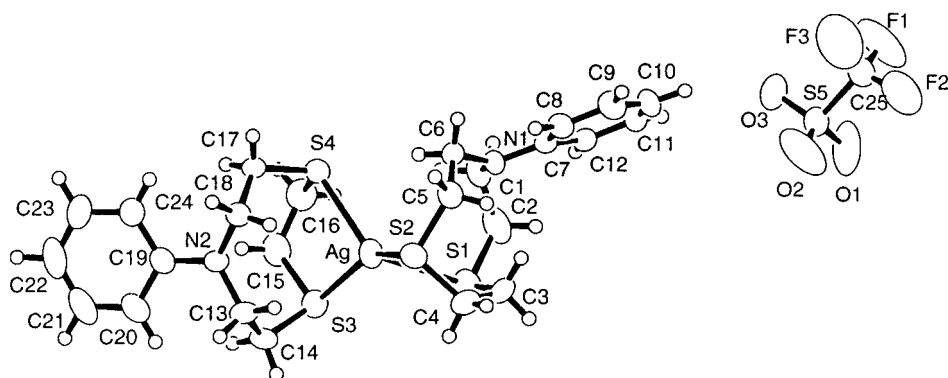


Fig. 2 Single-crystal X-ray structure of $[\text{Ag}(\mathbf{2})_2][\text{CF}_3\text{SO}_3]$ with atom numbering scheme adopted.

Table 1 Selected bond lengths (Å) and angles (°) for $[\text{Ag}(\mathbf{2})_2][\text{CF}_3\text{SO}_3]$

Ag–S(1)	2.684(2)	Ag–S(4)	2.577(2)
Ag–S(2)	2.500(2)	N(1)–C(1)	1.450(7)
Ag–S(3)	2.562(2)	N(2)–C(19)	1.400(7)
S(1)–Ag–S(2)	83.75(6)	C(1)–N(1)–C(6)	118.8(5)
S(1)–Ag–S(3)	98.14(5)	C(1)–N(1)–C(7)	118.5(5)
S(1)–Ag–S(4)	127.12(6)	C(6)–N(1)–C(7)	118.5(5)
S(2)–Ag–S(3)	146.72(6)	C(13)–N(2)–C(18)	118.2(5)
S(2)–Ag–S(4)	120.81(6)	C(13)–N(2)–C(19)	119.4(5)
S(3)–Ag–S(4)	84.49(5)	C(18)–N(2)–C(19)	119.1(5)

Table 2 Selected bond lengths (Å) and angles (°) for $[\text{Ag}(\mathbf{4})][\text{CF}_3\text{SO}_3]$

Ag–S(1)	2.444(2)	Ag–S(4)	2.540(2)
Ag–S(2)	2.827(2)	N–C(11)	1.441(9)
Ag–S(3)	2.607(2)		
S(1)–Ag–S(2)	84.54(6)	S(3)–Ag–S(4)	85.80(6)
S(1)–Ag–S(3)	136.66(7)	C(1)–N–C(10)	112.0(6)
S(1)–Ag–S(4)	137.18(7)	C(1)–N–C(11)	116.8(6)
S(2)–Ag–S(3)	79.85(6)	C(10)–N–C(11)	111.7(6)
S(2)–Ag–S(4)	101.98(6)		

chelating S–Ag–S angles are 2.58 Å and 84.12°, respectively. The Ag–N distances are 3.863(8) and 3.884(0) Å and the nitrogen atoms are located appreciably away from Ag(I). The Ag(I) is sandwiched between two **2** ligands and coordinated in an *exo-exo* form by two pairs of two sulfur atoms of each ligand and the coordination geometry is close to tetrahedral. The S–Ag–S angles are similar to those found for the following complexes: 84.4° (average) for tetrahedral $[\text{Ag}(\mathbf{8})\text{Cl}]$;²⁷ 82.1° for square pyramidal $[\text{Ag}_2\text{L}_2]^{2+}$ (L = 1,4,7,10,13-pentathiacyclopentadecane);²⁸ 77.43 and 80.35° for octahedral $[\text{Ag}(\mathbf{10})]^+$;²⁹ 80.9° for octahedral $[\text{Ag}(\mathbf{8})_2]^+$.²⁷ The torsion angles of the N(1)–C(7) axis to all C–N–C–C bonds and the surrounding bond angles of nitrogen atoms indicate that the $\text{C}_{\text{Ar}}\text{--N}(\text{C}_{\text{R}})_2$ unit has planar NC_3 geometry (mean valence angle for $\text{N}_{\text{sp}^2} \geq 117.5^\circ$).⁵³ Thus C(1) and C(6) lie nearly in the phenyl plane, the methylene hydrogens being located somewhat away from the phenyl

moiety. The N(1)–C(7) and N(2)–C(19) bond lengths are slightly longer compared with planar $\text{C}_{\text{Ar}}\text{--N}_{\text{sp}^2}$ (1.371 Å).⁵³

Similarly to $[\text{Ag}(\mathbf{2})_2][\text{CF}_3\text{SO}_3]$, colorless crystals of complex $[\text{Ag}(\mathbf{4})][\text{CF}_3\text{SO}_3]$ were obtained from a $\text{CF}_3\text{SO}_3\text{Ag}$ solution containing an equimolar amount of **4**. Fig. 3 shows the structure of $[\text{Ag}(\mathbf{4})][\text{CF}_3\text{SO}_3]$ and selected bond lengths and angles are listed in Table 2. Ag(I) lies in a cavity composed of four sulfur atoms to give a four-coordinate distorted tetrahedral complex. The average S–Ag–S bond angles of three-connected five-membered ethylene rings, *i.e.*, S(1)–Ag–S(2), S(2)–Ag–S(3) and S(3)–Ag–S(4), is 83.4°. The resulting large S(1)–Ag–S(4) bond angle [136.66(7)°] makes it advantageous for Ag(I) to interact electrostatically with the nitrogen atom on the opposite side. The Ag–S(1) (2.444 Å) and Ag–S(4) (2.540 Å) bond distances are shorter than Ag–S(2) and Ag–S(3) and similar to those of Ag(I) complexes of *exo* and/or polymeric conformation.^{54–56} The Ag–N distance [3.234(4) Å] is shorter than the sum of the van

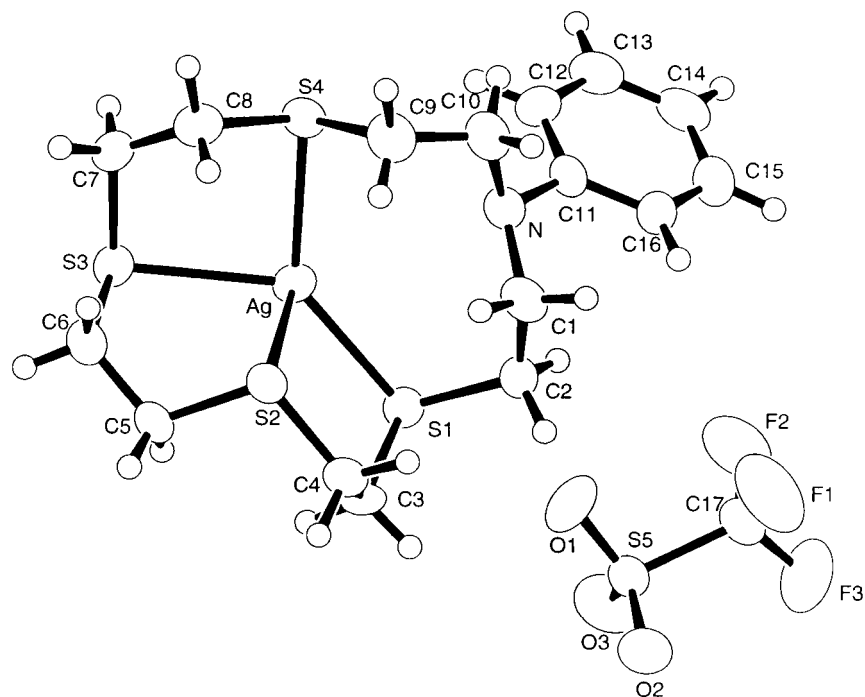


Fig. 3 Single-crystal X-ray structure of $[\text{Ag}(4)][\text{CF}_3\text{SO}_3]$ with atom numbering scheme adopted.

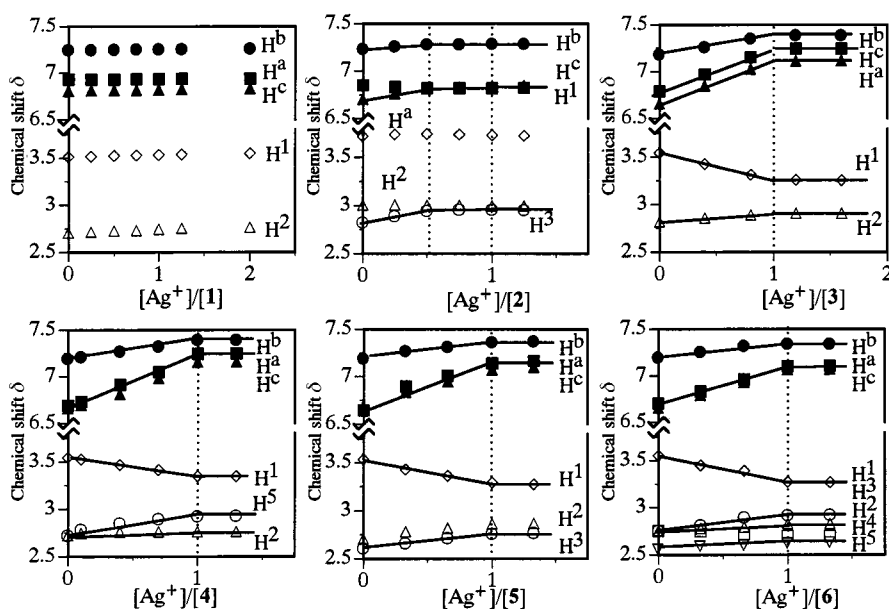


Fig. 4 The changes in ^1H NMR chemical shifts for the typical protons of *N*-phenylpolythiaalkane derivatives by titration of $\text{CF}_3\text{SO}_3\text{Ag}$ in CD_3CN . Each symbol in the plots refers to the assignment of the protons indicated in Fig. 1.

der Waals radii (3.5 \AA)⁵⁷ of the atoms. This fact indicates that there is an interaction between the $\text{Ag}(\text{i})$ and the nitrogen atom, as supported by ^1H NMR studies (*vide infra*). The torsion angles of the $\text{N}-\text{C}(11)$ axis to all $\text{C}-\text{N}-\text{C}-\text{C}$ bonds and the surrounding bond angles of nitrogen atoms indicate that the $\text{C}_{\text{Ar}}-\text{N}(\text{C}_{\text{R}})_2$ unit has tetrahedral NC_3 geometry, with valence angles for N_{sp^3} of $108-114^\circ$.⁵³ The $\text{N}-\text{C}(10)$ bond makes an angle of *ca.* 70° relative to the phenyl plane, in which the $\text{C}(10)$ methylene hydrogens are fairly close to the phenyl moiety owing to the tetrahedral NC_3 geometry. The $\text{N}-\text{C}(11)$ bond length is longer than those of planar $\text{C}_{\text{Ar}}-\text{N}_{\text{sp}^2}$ and pyramidal $\text{C}_{\text{Ar}}-\text{N}_{\text{sp}^3}$ (1.426 \AA),⁵³ but fairly short compared to $\text{C}_{\text{Ar}}-\text{N}^+-\text{C}_3$ (1.465 \AA).⁵³

$\text{Ag}(\text{i})$ -induced changes in ^1H NMR chemical shifts

Ag^+ ion binding behavior was examined by ^1H NMR spectroscopy in CD_3CN . The ^1H NMR spectral changes upon addition

of $\text{CF}_3\text{SO}_3\text{Ag}$ to each *N*-phenylpolythiaalkane solution revealed that the formation and the dissociation of $\text{Ag}(\text{i})$ complexes were fast. Plots of the $\text{Ag}(\text{i})$ -induced ^1H NMR chemical shifts of protons of *N*-phenylpolythiaalkane derivatives vs. the molar ratio $\text{CF}_3\text{SO}_3\text{Ag}:\text{ligand}$ ($\equiv a_{\text{L}}$) for $7 \times 10^{-3} \text{ mol dm}^{-3}$ ligand solutions are shown in Fig. 4. The addition of $\text{CF}_3\text{SO}_3\text{Ag}$ to a solution containing **1** causes gradually and continuously downfield shifts of all the proton signals even at $a_{\text{L}} \geq 1$ because of the low Ag^+ ion complexability. The binding behavior of cyclic analog, **2**, containing two sulfur atoms differs from those of the other analogs. The plot for **2** displays two break points at $a_{\text{L}} = 0.5$ and 1.0 . This fact indicates that **2** forms a 1:2 [$\text{Ag}(\text{i})$:ligand] complex below $a_{\text{L}} = 0.5$ and then a 1:1 complex at $a_{\text{L}} \geq 0.5$. For the other analogs, only one break point for each proton signal is observed clearly at $a_{\text{L}} = 1$, and demonstrates that Ag^+ ion forms predominantly 1:1 complexes under the experimental conditions.

The extents of the changes in ^1H NMR chemical shift (ppm)

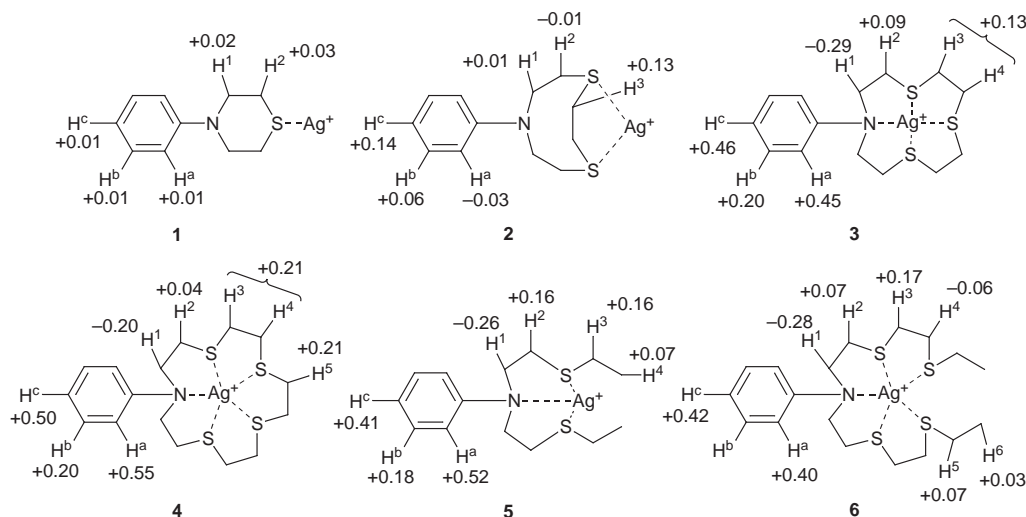


Fig. 5 Ag^+ induced changes in ^1H NMR chemical shifts and assumed structures of the $\text{Ag}(\text{I})$ complex for *N*-phenylpolythiazaalkane derivatives. A plus sign (+) and a minus sign (-) denote shifts of proton signals to lower and higher magnetic fields, respectively.

induced by the addition of equimolar $\text{CF}_3\text{SO}_3\text{Ag}$ are illustrated schematically in the structural formulae of $\text{Ag}(\text{I})$ complexes (Fig. 5). The $\text{Ag}(\text{I})$ -induced changes in chemical shift for the protons of *N*-phenylpolythiazaalkane derivatives are conveniently divided into three groups: downfield shifts for the protons of thioether moiety, downfield shifts for the phenyl protons, and upfield shifts for the protons of the dialkylamine moiety. First, when Ag^+ ion interacts tightly with sulfur atom(s), the bound $\text{Ag}(\text{I})$ withdraws electron density from the protons on the sulfide moiety to cause downfield shifts of the chemical shifts. Secondly, the decrease in the π -electron density of the phenyl group is induced by electrostatic interaction between the nitrogen atom and the $\text{Ag}(\text{I})$ coordinated to sulfur atoms, resulting in downfield shifts for the phenyl protons. Thirdly, as already discussed by Alfimov *et al.*,⁵⁸ the increase in electron density on the nitrogen atom is induced by the electrostatic interaction with $\text{Ag}(\text{I})$, while the electron densities of the neighboring methylene protons of the nitrogen atom are decreased by the electron withdrawing phenyl group when the ionophores bearing a benzothiazole moiety are in the free form. The ring-current effects of the adjacent aromatic group on the methylene protons (H^1), caused by conformational change due to the complexation with Ag^+ ion, may also cause an up-field shift.⁵⁸

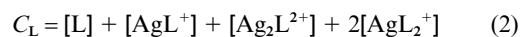
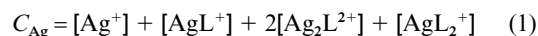
For cyclic analogs, **1** and **2**, with a small crown ring, changes in chemical shift are observed only for methylene protons of the sulfide moiety and the downfield shifts of the phenyl protons are slight. As mentioned above, $\text{Ag}(\text{I})$ coordinated to **2** in an *exo-exo* form is distinct from the nitrogen atom, and the electrostatic interaction between the nitrogen atom and the $\text{Ag}(\text{I})$ coordinated to sulfur atom(s) is very weak. Downfield shifts of phenyl protons by the addition of equimolar $\text{CF}_3\text{SO}_3\text{Ag}$ were observed for ligands **3–6**. This indicates that the $\text{Ag}(\text{I})$ coordinated to sulfur atoms interacts electrostatically with the nitrogen atom of the polythiazaalkane moiety. The extents of downfield shifts of the phenyl protons of the ligands are similar to each other. A macrochelate ring S-C-C-N-C-C-S with $\text{Ag}(\text{I})$ is formed as seen in the X-ray structure of $[\text{Ag}(\mathbf{4})][\text{CF}_3\text{SO}_3]$, thus ligands **3–6** probably adopt a similar conformational arrangement.

A relationship between the π -electron density in the aromatic rings and the chemical shift of the proton, $\Delta\sigma = 9.54\Delta\rho$, was observed,⁵⁹ where $\Delta\sigma$ and $\Delta\rho$ are the changes in the shielding constant and the π -electron density, respectively, relative to benzene. The percentage decrease in electron density of the phenyl moiety upon Ag^+ ion complexation are estimated to be 18, 21, 19 and 16% of an electronic charge for **3**, **4**, **5** and **6**, respectively. The changes of the chemical shifts of phenyl pro-

tons, H^a , H^b and H^c , reveal dramatic *ortho-para* directing effects when the $\text{Ag}(\text{I})$ complexes are formed. This result also demonstrates that the nitrogen atom also interacts with $\text{Ag}(\text{I})$ in solution.

Potentiometry

The stability constants of *N*-phenylpolythiazaalkane derivatives (**L**) with Ag^+ ion were determined using acetonitrile as a solvent by potentiometric titration. The stoichiometric relationships are given by equations (1) and (2) and the succes-



sive stability constants of the $\text{Ag}(\text{I})$ complexes are defined as $K_{\text{AgL}} = [\text{AgL}^+]/([\text{Ag}^+][\text{L}])$, $K_{\text{Ag}_2\text{L}} = [\text{Ag}_2\text{L}^{2+}]/([\text{AgL}^+][\text{Ag}^+])$ and $K_{\text{AgL}_2} = [\text{AgL}_2^+]/([\text{AgL}^+][\text{L}])$.

Constants giving a minimum weighted sum of the squares of the deviations in pAg in equation (3)⁶⁰ where $w = 1/(\text{pAg}_{i+1} -$

$$U = \sum w(\text{pAg}_{\text{obs}} - \text{pAg}_{\text{cal}})^2 \quad (3)$$

$\text{pAg}_{i-1})^2$, were calculated by non-linear regression. The standard deviation in pAg units was evaluated from a titration of 25–35 data points by the use of the following equation: $\sigma_{\text{fit}} = (U/\Sigma w)^{1/2}$. The formation of higher *N*-phenylpolythiazaalkane complexes such as AgL_3 and AgL_4 or dimer complexes such as Ag_2L_2 was not observed under the experimental conditions used here. The stability constants of $\text{Ag}(\text{I})$ -polythiaalkane complexes were also determined for comparison. The results for *N*-phenylpolythiazaalkane complexes together with those for polythiaalkane complexes are listed in Table 3.

It is seen from Table 3 that **6** forms the most stable 1:1 complex among *N*-phenylpolythiazaalkane derivatives and the order of complexability for Ag^+ ion is **6** > **3** \approx **4** > **2** \approx **5** > **1**. The value of $\log K_{\text{AgL}}$ for **2** is about twice that for monodentate ligand **11**, since **2** acts as a bidentate ligand upon complexation with Ag^+ ion. The stabilities of $\text{Ag}(\text{I})$ complexes of polythiaalkane derivatives have a similar magnitude to those of polythiazaalkane derivatives. Logarithmic values of K_{AgL} were plotted against the number of sulfur atoms of the ligands in Fig. 6 and illustrates that the stability of the complex is primarily dependent on the number of sulfur atoms of the complexing parts rather than the structure of the ligand. By contrast, the crystal X-ray diffraction data showed a macrochelate ring of the $\text{Ag}(\text{I})$ complex of **4** and the $\text{Ag}(\text{I})$ -induced changes were

Table 3 Stability constants of Ag(I) complexes in acetonitrile^a

Ligand	log K_{AgL}	log K_{Ag_2L}	log K_{AgL_2}	σ_{fit}^b
1	1.71		1.3	0.0055(25)
2	3.70		3.0	0.0043(35)
3	5.92	1.2	1.7	0.0872(20)
4	5.67		2.4	0.0068(20)
5	3.59			0.0078(25)
6	6.47	2.2	1.5	0.0257(22)
7	1.82	1.6	1.5	0.0049(21)
8	5.69		2.7	0.0155(20)
9	6.09		2.4	0.0096(29)
10	8.03	1.5		0.0065(20)
11	2.20		1.3	0.0194(23)
12	3.38	0.7	3.2	0.0114(20)

^a [TMAP] = 0.1 mol dm⁻³, at 25 °C. ^b Number of data points is given in parentheses.

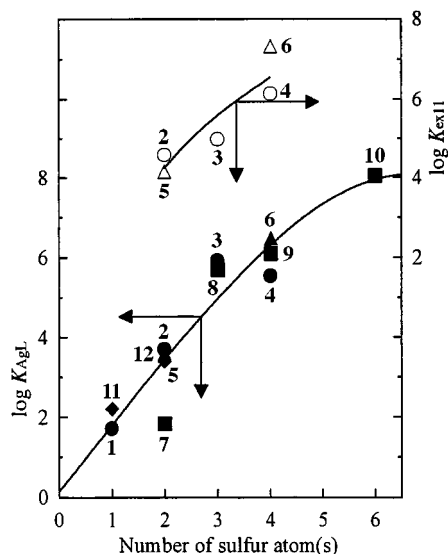


Fig. 6 Plots of log K_{AgL} and log K_{ex11} vs. number of sulfur atom(s) on the polythiazaalkane moiety. Closed and open symbols in plots represent the stability and the extraction constants, respectively.

observed by ¹H NMR measurement. The tendency of the stability constants shows that such an interaction between complexed Ag(I) and nitrogen, however, is too weak to affect the stability constant of the Ag(I) complex with *N*-phenylpolythiazaalkane derivatives.

In the crystal of [Ag(4)][CF₃SO₃], Ag(I) is included in three linked five-membered chelate rings, in which the Ag–S(1) and Ag–S(4) distances are much shorter than Ag–S(2) and Ag–S(3). The strain of three linked chelate rings for [Ag(4)][CF₃SO₃] seems to be larger than that for [Ag(2)₂][CF₃SO₃] and should be why the value of K_{AgL} of the [Ag(4)]⁺ complex is smaller than that of the overall stability constant of [Ag(2)₂]⁺ (log β₂ = 6.7) without taking into account a chelate effect. Further, the stability of [Ag(4)]⁺ is lower than that of [Ag(6)]⁺ (log K_{AgL} = 6.47) being similar to the overall stability constant of [Ag(2)₂]⁺. The result demonstrates that the strain of three linked chelate rings and the rigidity of the ring structure reduces the stability of the Ag(I) complex with 4.

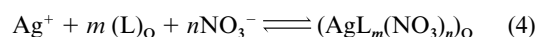
Solvent extraction behavior

The distribution of *N*-phenylpolythiazaalkane derivatives in aqueous acidic solution–1,2-dichloroethane was examined. The distribution of *N*-phenylpolythiazaalkane derivatives into the aqueous phase increased gradually with an increase in the concentration of nitric acid due to the protonation of a nitrogen atom to form the cationic HL⁺ species. The relationship between the percentage for each *N*-phenylpolythiazaalkane derivative in the organic phase and log [HNO₃] in the aqueous

phase indicates that all ligands except for 1 were entirely distributed in the organic phase in the range of log [HNO₃] ≤ 0.5.

The metal ion recognition properties for *N*-phenylpolythiazaalkane derivatives were examined by solvent extraction. The metal ion complex is extracted with a counter anion as an ion-pair complex from the aqueous phase when the *N*-phenylpolythiazaalkane derivative used is a neutral ligand. Therefore, nitrate ion was used as a counter anion to estimate the Ag⁺ ion extractability and the extraction equilibrium constants for the ion-pair complexes. The results of solvent extraction of transition metal ions with *N*-phenylpolythiazaalkane derivatives are summarized in Table 4. No extraction of any divalent transition metal ions, even Hg²⁺ which is well known to have a high affinity for thiacycrown ethers,^{14–19} was observed for all *N*-phenylpolythiazaalkane derivatives under the conditions used here. It is noteworthy that *N*-phenylpolythiazaalkane derivatives except for 1 exhibited a remarkably high Ag⁺ ion selectivity. The extractabilities of macrocyclic derivatives for Ag⁺ ion increased with the increase of the number of sulfur atoms in the ligand, and the order of the extractabilities is 4 > 3 > 2 ≫ 1; 1 showed no extractability for any metal ions, even for Ag⁺ ion, while 4 exhibited the highest Ag⁺ ion extractability (>95%). For acyclic derivatives, the extractability of 6 for Ag⁺ ion is much higher than that of 5.

The effect of pH change on Ag⁺ ion extraction percentage, *E*(%), for each *N*-phenylpolythiazaalkane derivative was examined under the conditions detailed in Table 4, and no change of the value of *E*(%) was observed in the range pH 1–7. This fact suggests that no cationic HL⁺ species forms in the aqueous phase under such conditions. The extraction equilibria of the complexes were examined by changing the concentrations of nitrate ion and ligand. If the composition of the extracted species is assumed to be 1 : *m* : *n* for Ag(I) : ligand : NO₃⁻, the extraction equilibrium and the constant, K_{ex} , are defined by equations (4) and (5) and the distribution ratio, D_{Ag} , of Ag⁺ ion



$$K_{ex} = [AgL_m(NO_3)_n]_O / [Ag^+][L]_O^m [NO_3^-]_O^n \quad (5)$$

is given by equation (6) where the subscript ‘O’ refers to con-

$$D_{Ag} = \frac{[AgL_m(NO_3)_n]_O}{[AgL_m(NO_3)_n] + [AgL_m^+] + [Ag^+]} \quad (6)$$

centration in the organic phase. If the concentrations of AgL_{*m*}(NO₃)_{*n*} and AgL_{*m*} complexes are much lower than that of Ag⁺ ion in the aqueous phase, the denominator of equation (6) can be expressed by [Ag⁺]. If [L]_O ≫ [AgL_{*m*}(NO₃)_{*n*}]_O, the logarithmic form of equation (5) is rewritten by the substitution of equation (6) as equation (7).

$$\log D_{Ag} = \log K_{ex} + m \log [L]_O + n \log [NO_3^-] \quad (7)$$

Plots of log D_{Ag} vs. log [NO₃⁻] gave straight lines with a slope of unity for all ligands. The plots of log $D_{Ag} - \log [NO_3^-]$ vs. log [L]_O for the *N*-phenylpolythiazaalkane derivatives 3–6 also give straight lines with a slope of unity as shown in Fig. 7. The results demonstrate that the ion-pair complexes AgL(NO₃) can be extracted into the organic phase. On the other hand, the plot for 1 gives a straight line with a slope of two, indicating that the extractive species is AgL₂(NO₃). For the plot for 2, the slope of the straight line is shifted from one to two around –log [L]_O = 3. The extractive species, therefore, changes from AgL(NO₃) to Ag(L)₂(NO₃) above log [L]_O = –3. The values of the extraction equilibrium constants, K_{ex} , are summarized in Table 5. It is clear that the order of K_{ex} for the 1 : 1 : 1 complexes, AgL(NO₃), is 6 > 4 > 3 > 2 > 5 ≫ 1. Both upward curves of the plots of log K_{AgL} and log K_{ex11} vs. the number of sulfur atoms are similar to

Table 4 Metal ion extraction^a

Ligand	Extraction quantity ^b (%)									
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Pb(II)	Cd(II)	Ag(I)	Hg(II)
1	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	40	0
3	0	0	0	0	0	0	0	0	62	0
4	0	0	0	0	0	0	0	0	95	0
5	0	0	0	0	0	0	0	0	17	0
6	0	0	0	0	0	0	0	0	>99	0

^a Organic phase: [ligand] = 2×10^{-4} mol dm⁻³ in 1,2-dichloroethane; aqueous phase: [metal ion] = 5×10^{-5} mol dm⁻³, [KNO₃] = 0.1 mol dm⁻³, pH 1.5. ^b Evaluated from the metal ion concentration in the aqueous phase.

Table 5 Extraction constants for Ag(I) complexes^a

Ligand	log K_{ex11} ^b	log K_{ex12} ^c
1		3.33 ± 0.12
2	4.57 ± 0.07	7.83 ± 0.08
3	4.98 ± 0.04	
4	6.14 ± 0.03	
5	4.04 ± 0.05	
6	7.31 ± 0.02	

^a 1,2-Dichloroethane–water biphasic system. ^b $K_{\text{ex11}} = [\text{AgL}(\text{NO}_3)]_{\text{O}} / [\text{Ag}^+]_{\text{O}}[\text{L}]_{\text{O}}[\text{NO}_3^-]_{\text{O}}$. ^c $K_{\text{ex12}} = [\text{AgL}_2(\text{NO}_3)]_{\text{O}} / [\text{Ag}^+]_{\text{O}}[\text{L}]_{\text{O}}^2[\text{NO}_3^-]_{\text{O}}$.

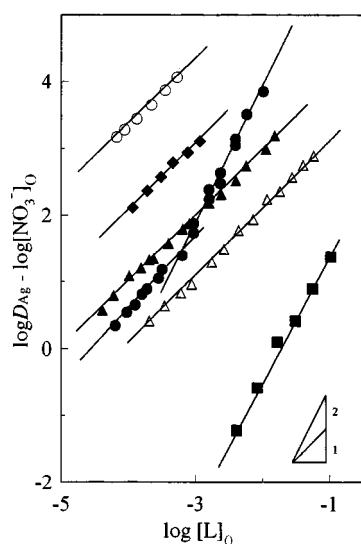


Fig. 7 Plots of $\log D_{\text{Ag}} - \log [\text{NO}_3^-]_{\text{O}}$ vs. $\log [\text{L}]$. Aqueous phase: $[\text{Ag}^+] = 1 \times 10^{-5}$ mol dm⁻³ at pH = 5.4. 1, (■); 2, (●); 3, (▲); 4, (◆); 5, (△); 6, (○).

each other as shown in Fig. 6. Plots of $\log K_{\text{ex11}}$ vs. $\log K_{\text{AgL}}$ give a straight line with a slope of unity. The result suggests that the extractability of the *N*-phenylpolythiazaalkane derivatives for Ag⁺ ion is mainly dependent on the stability of the complex.

Liquid membrane transport

The Ag⁺ ion transportabilities of *N*-phenylpolythiazaalkane derivatives as neutral carriers were examined in a bulk transport system using a liquid membrane. A source phase and a receiving phase were simultaneously in contact with a liquid membrane phase composed of a 1,2-dichloroethane solution of the ligand. In this study, Ag⁺ ion is transported as a ternary Ag(I) complex through the membrane phase. The transport system used here undergoes a symport process, the motive force being the diffusion of the Ag(I) complex through the liquid membrane. The transport behavior of Ag⁺ ion through the liquid membranes containing *N*-phenylpolythiazaalkane derivatives is shown in Fig. 8. All of the compounds exhibited transportability for Ag⁺ ion and the amount of Ag⁺ ion transported to

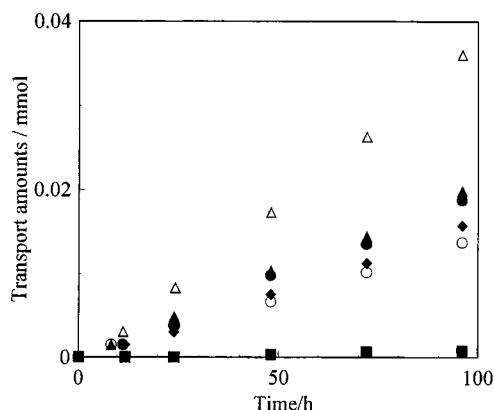


Fig. 8 Time-dependent profiles of silver ion membrane transport. The source phase (15 mL): $[\text{AgNO}_3] = 5 \times 10^{-3}$ mol dm⁻³ (15 mL) and $[\text{H}_2\text{SO}_4] = 0.01$ mol dm⁻³; the receiving phase (15 mL): $[\text{H}_2\text{SO}_4] = 0.01$ mol dm⁻³; liquid membrane phase (15 mL): [ligand] = 2.5×10^{-4} mol dm⁻³ in 1,2-dichloroethane. 1, (■); 2, (●); 3, (▲); 4, (◆); 5, (△); 6, (○).

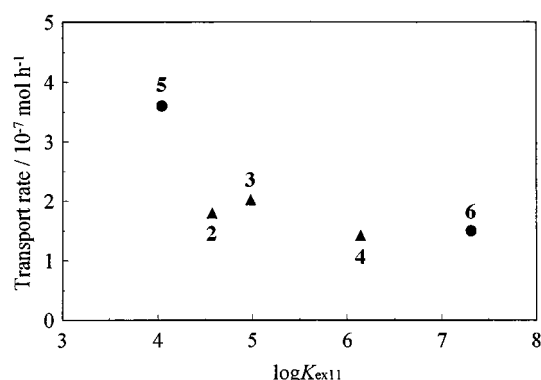


Fig. 9 Plots of transport rate vs. $\log K_{\text{ex11}}$. Triangle and circle symbols in plots mean cyclic and acyclic polythiazaalkane derivatives, respectively.

the receiving phase increased almost linearly for each ligand with running time. The transport rates for the ligands were calculated from Fig. 8. The transportability of Ag⁺ ion decreased in the order: 5 (3.6 ± 0.09) > 2 (1.8 ± 0.09) ≈ 3 (2.0 ± 0.04) > 4 (1.4 ± 0.10) ≈ 6 (1.5 ± 0.04) ≫ 1 (0.08 ± 0.008), where the values in parentheses are the Ag⁺ ion transport rates (10⁻⁷ mol h⁻¹). An approximately negative correlation between the transport rates for Ag⁺ ion and the values of $\log K_{\text{ex11}}$ for the *N*-phenylpolythiazaalkane derivatives, except for 1, was observed as shown in Fig. 9. Compound 1 exhibited much lower Ag⁺ ion transportability due to the extremely low Ag⁺ ion extractability. In the Ag⁺ ion transport system, the high Ag⁺ ion extractability is advantageous for the extraction of Ag⁺ ion into the membrane phase, although it is disadvantageous for the release of Ag⁺ ion from the membrane phase to the receiving phase. The balance of both processes is the most important factor governing the transportability. The release process seems, especially, to

be the rate-determining step for the Ag⁺ ion transport in this system and is the reason why **5**, which has much lower Ag⁺ ion extractability than **6**, exhibited the best Ag⁺ ion transport-ability.

The membrane transport values for other metal ions such as Cu²⁺ and Hg²⁺ were also examined under similar experimental conditions. No metal ion transport was, however, observed because these metal ions could not be extracted from the source phase to the liquid membrane. These results are compatible with those of the solvent extraction experiments of the same transition metal ions.

Experimental

Materials

N-Phenylpolythiazaalkane derivatives **2**, **4**, **5** and **6** were prepared as described previously.^{42,44} The reagents used here were of analytical grade and the other chemicals were of guaranteed-reagent grade. All of the organic solvents were purified in the usual way. Water was doubly distilled.

Instrumentation

Melting points were determined with a YANACO melting point apparatus and were uncorrected. Mass spectra were measured with a JEOL JMS-DX303 instrument. The routine ¹H NMR measurements were carried out with a Hitachi R-90 spectrometer with CDCl₃ solutions containing tetramethylsilane as an internal standard. The specific ¹H NMR measurements such as CF₃SO₃Ag titrations were carried out with a Varian XL-200 spectrometer. The pH and pAg measurements were made at 25.0 ± 0.5 °C using a TOA pH Meter HM-30S equipped with a TOA GST-5311C glass electrode and a Ag wire electrode, respectively. Electronic spectra were obtained on a Hitachi 150-20 spectrophotometer with 1 cm quartz cells. Extractions were carried out in a thermostatted chamber (25.0 ± 0.2 °C) with a TAITEC personal-10 incubator. The concentrations of metal ions in aqueous solutions were determined by a SEIKO SAS/727 atomic absorption spectrophotometer.

Synthesis

4-Phenyl-1-thia-4-azacyclohexane 1. The tosylation of *N,N*-bis(2-hydroxyethyl)aniline with *p*-tolylsulfonyl chloride in the presence of NaOH in water–THF solution gave *N,N*-bis(2-*p*-tolylsulfonyloxyethyl)aniline. An acetone–water (1 : 1) solution (300 mL) of *N,N*-bis(2-*p*-tolylsulfonyloxyethyl)aniline (24.5 g, 0.05 mol) and Na₂S (12.0 g, 0.05 mol) was stirred at reflux temperature for 2 h. After reaction, the mixture was concentrated and then 100 mL of water added. The solution was then extracted with CHCl₃ (100 mL × 3) and the combined extract dried over MgSO₄ and the solvent evaporated *in vacuo*. The residue was subjected to column chromatography (silica gel; eluent, benzene–CHCl₃) to give **1** as a white solid. Yield: 6.84 g (76%). Mp 31–32 °C. ¹H NMR (CDCl₃): δ 2.68–2.80 (m, 4 H, SCH₂), 3.48–3.59 (m, 4 H, NCH₂) and 6.85–7.35 (m, 5 H, ArH). EI mass spectrum: *m/z* 179 (M⁺) (Found: C, 66.73; H, 7.27; N, 7.73. C₁₀H₁₉NS requires C, 67.00; H, 7.31; N, 7.81%).

10-Phenyl-1,4,7-trithia-10-azacyclododecane 3. Iodination of *N,N*-bis(2-*p*-tolylsulfonyloxyethyl)aniline with NaI in acetone solution gave *N,N*-bis(2-iodoethyl)aniline. To dry DMF (500 mL) was added Cs₂CO₃ (4.24 g, 0.011 mol) and the solution stirred at 60 °C under a nitrogen atmosphere then a dry DMF solution (100 mL) containing 3-thiopentane-1,5-dithiol (1.54 g, 0.01 mol) and *N,N*-bis(2-iodoethyl)aniline (4.00 g, 0.01 mol) was added dropwise over 24 h. After the addition was complete, the mixture was stirred at 60 °C for 24 h. After the reaction, the mixture was concentrated, and then 200 mL of water was

Table 6 Crystal data for [Ag(2)₂][CF₃SO₃] and [Ag(4)][CF₃SO₃]

Compound	[Ag(2) ₂][CF ₃ SO ₃]	[Ag(4)][CF ₃ SO ₃]
Formula	AgF ₃ N ₂ O ₃ S ₅ C ₂₅ H ₃₄	AgF ₃ NO ₃ S ₅ C ₁₇ H ₂₅
<i>M</i>	735.72	616.55
Crystal size/mm	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.1
System, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> /Å	11.346(9)	10.991(2)
<i>b</i> /Å	12.017(2)	12.252(2)
<i>c</i> /Å	13.398(7)	9.264(1)
<i>α</i> /°	62.71(4)	106.55(1)
<i>β</i> /°	69.77(0)	103.30(1)
<i>γ</i> /°	78.04(2)	90.62(2)
<i>U</i> /Å ³	1520.9(1)	1159.8(4)
<i>Z</i>	2	2
<i>D</i> _c /g cm ⁻³	1.606	1.765
<i>F</i> (000)	752.00	624.00
<i>μ</i> (Mo–Kα)/cm ⁻¹	10.53	13.60
2 θ _{max} /°	52.6	51.4
No. of reflections measured	6455	3983
No. of variables	352	271
<i>R</i> , <i>R</i> _w ^a	0.051, 0.058	0.064, 0.084

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 4F_o^2 / \sigma^2(F_o)^2$.

added. The solution was extracted with CHCl₃ (100 mL × 4) and the combined extract washed twice with water, a 20% Na₂S₂O₃ aqueous solution and water. The extract was dried over MgSO₄ and the CHCl₃ was evaporated *in vacuo*. The residue was purified by column chromatography (silica gel; eluent, hexane–benzene) to give **3** as a white solid. Yield: 1.57 g (52%). Mp 176–177 °C. ¹H NMR (CDCl₃): δ 2.73–2.90 (m, 12 H, SCH₂), 3.56 (t, 4 H, NCH₂), 6.70–7.25 (m, 5 H, ArH). EI mass spectrum: *m/z* 299 (M⁺) (Found: C, 55.84; H, 6.93; N, 4.75. C₁₄H₂₁NS₃ requires C, 56.14; H, 7.07; N, 4.68%).

[Ag(2)₂][CF₃SO₃]. Compound **2** (23.9 mg, 0.1 mmol) was dissolved in 10 mL acetonitrile solution containing 0.05 mmol CF₃SO₃Ag. The acetonitrile solution was stored in the dark and the solvent was removed by slow diffusion at room temperature and the residue was used for X-ray structure analysis. Yield: 64.7 mg (88%). Mp 185–186 °C. ¹H NMR (CD₃CN): δ 2.94 (s, 4 H, SCH₂), 2.98–3.02 (m, 4 H, SCH₂), 3.71–3.76 (m, 4 H, NCH₂), 6.78–7.31 (m, 5 H, ArH) (Found: C, 40.85; H, 4.73; N, 3.78. C₂₅H₃₄AgF₃N₂O₃S₅ requires C, 40.81; H, 4.66; N, 3.81%).

[Ag(4)][CF₃SO₃]. Compound **4** (35.9 mg, 0.1 mmol) was dissolved in 10 mL acetonitrile solution containing 0.1 mmol CF₃SO₃Ag. The acetonitrile solution was stored in the dark and the solvent was removed by slow diffusion at room temperature and the residue was used for X-ray structure analysis. Yield: 56.2 mg (91%). Mp 198–199 °C. ¹H NMR (CD₃CN): δ 2.72–3.05 (m, 16 H, SCH₂), 3.31–3.36 (m, 4 H, NCH₂), 7.14–7.42 (m, 5 H, ArH) (Found: C, 33.14; H, 4.13; N, 2.23. C₁₇H₂₅AgF₃NO₃S₅ requires C, 33.12; H, 4.09; N, 2.27%).

X-Ray structure determinations

Crystallographic data for complexes, [Ag(2)₂][CF₃SO₃] and [Ag(4)][CF₃SO₃], are listed in Table 6. Each crystal was mounted in a glass capillary. X-Ray diffraction measurements were made at room temperature with graphite monochromated Mo–Kα radiation on an Enraf-Nonius CAD4-EXPRESS four-circle diffractometer for [Ag(2)₂][CF₃SO₃] and a Rigaku R-Axis IV imaging plate areas detector for [Ag(4)][CF₃SO₃]. Cell dimensions for both crystals were determined from the setting angle values of 25 centered reflections with the CAD 4 diffractometer. Intensity data were corrected for Lorentz and polarization effects.

All structures were solved by heavy atom methods, and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations.

Scattering factors and anomalous dispersion terms were taken from ref. 61. All hydrogen atoms were included for refinements, in which their positions were located from different Fourier maps. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.⁶²

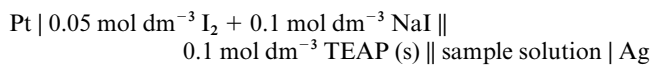
CCDC reference number 186/1227.

¹H NMR titration measurements

The ¹H NMR titrations were performed in CD₃CN and were recorded on Varian XL-200 spectrometer. The CD₃CN contained 7×10^{-3} mol dm⁻³ ligand and variable amounts of CF₃SO₃Ag and the resulting chemical shifts were reported relative to the signal of tetramethylsilane (TMS) at 0 ppm.

Potentiometric measurements

The stability constants for Ag(I) complexes of *N*-phenylpolythiazaalkane and polythiaalkane derivatives were determined by potentiometric titration. All measurements were performed in acetonitrile solution containing 0.1 mol dm⁻³ tetraethylammonium perchlorate (TEAP) at 25.0 ± 0.2 °C. Two titrations were performed to determine the stability constants. First, a solution of 1–20 mmol dm⁻³ silver perchlorate was titrated with 1–20 mmol dm⁻³ of a *N*-phenylpolythiazaalkane derivative. The Ag indicator electrode was calibrated by silver perchlorate solution without addition of titrant (titration ratio = 0). Secondary titration of 1–20 mmol dm⁻³ of a *N*-phenylpolythiazaalkane derivative with 1–20 mmol dm⁻³ silver perchlorate was done on the basis of the preliminary calibration using the solutions of a known concentration of silver perchlorate. The equilibrium concentration of Ag⁺ ion was evaluated as the negative logarithms value, pAg, from the electromotive force of the following electrochemical cell:



A titration curve was obtained as a plot of pAg vs. titration ratio.

Solvent extraction

In solvent extraction using *N*-phenylpolythiazaalkane derivatives, equal amounts (10 mL) of water and 1,2-dichloroethane were placed in a 50 mL stoppered centrifuge tube, and shaken for 10 min at 200 strokes min⁻¹. For the measurement of the distribution ratio of *N*-phenylpolythiazaalkane derivative, an aqueous solution containing nitric acid was shaken with a 1,2-dichloroethane solution containing a *N*-phenylpolythiazaalkane derivative at a concentration of 2×10^{-4} mol dm⁻³. The ligand concentration in the organic phase was estimated by absorption spectroscopy. In solvent extraction of metal ions, nitrate ion was chosen as the counter anion for the metal complex of the *N*-phenylpolythiazaalkane derivative. Extraction experiments for a comparison of the metal ion extractabilities were carried out as follows: An aqueous solution containing 5×10^{-5} mol dm⁻³ metal nitrate and 0.1 mol dm⁻³ potassium nitrate and a 1,2-dichloroethane solution containing 2×10^{-4} mol dm⁻³ *N*-phenylpolythiazaalkane derivative was placed in a stoppered centrifuge tube. After shaking and then allowing the mixture to stand, the Ag⁺ ion concentration in the aqueous phase was determined by atomic absorption spectrometry. Distribution equilibria of the complexes of Ag(I)–*N*-phenylpolythiazaalkane–nitrate ion were examined as follows: The ionic strength of an aqueous solution containing 1×10^{-5} mol dm⁻³ silver nitrate was adjusted to 0.1 M using potassium nitrate and sulfate. The aqueous solution was shaken with 1,2-dichloroethane solution containing a known quantity of *N*-phenylpolythiazaalkane derivative. The silver ion concentration in the aqueous phase was measured by atomic absorp-

tion spectrometry, and the silver ion concentration in the organic phase was calculated from the amount of silver ion in the aqueous phase.

Transport through a liquid membrane

An apparatus (a dual cylindrical cell) for transport experiments across a liquid membrane was described as reported previously.⁴⁵ Both the inner aqueous source phase (15 mL) containing 5×10^{-3} mol dm⁻³ metal nitrate and 1×10^{-2} mol dm⁻³ H₂SO₄ and the outer receiving phase (15 mL) containing 1×10^{-2} mol dm⁻³ H₂SO₄ were in contact with the liquid membrane phase (15 mL) of neutral ligand in 2.5×10^{-4} mol dm⁻³ in 1,2-dichloroethane. The three phases in the transport cell were agitated carefully by a stirring bar at 200 r.p.m. on the bottom of the cell at 25.0 ± 0.2 °C. An aliquot of aqueous solution was taken from both the source and the receiving phases at regular time intervals to be subjected to atomic absorption spectrometry.

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