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Synthesis and ligand properties of thianthrenophane

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Thianthrenophane **1** has a cavity which offers enough room to potentially enable endohedral coordination to small ions or molecules. For the complexation of silver(I) perchlorate the complex stability constants of **1** $\log K_1 = 5.45 \pm 0.13$ and of thianthrene $\log K_2 = 9.16 \pm 0.10$ were determined by UV/Vis titration. Single competition transport experiments with ten metal salts demonstrate a very high selectivity of **1** as a carrier for silver(I) and a distinctly higher transport rate compared to carriers such as thianthrene and 1,4,8,11-tetrathiacyclotetradecane (14-ane-S_4). Although the X-ray crystal structure analysis of the polymeric [Ag(**1**)]ClO_4·(dioxane)$_7$ complex shows an exohedral coordination to silver(I) we suggest that the formation of an endohedral [Ag(**1**)]$^+$ complex is the explanation for the unusual carrier selectivity of silver(I) by **1** in bulk liquid membrane.

Introduction

Over the past years the focus in cyclophane chemistry has changed from pure electronic and structural properties to the investigation of the function and application of cyclophanes.[1–7] In particular, the host–guest chemistry,[8] the use of cyclophanes as ligands in metal clusters,[9] as chiral auxiliaries in asymmetric synthesis,[10,11] for chemical vapor deposition polymerisation[12] and polymeric transition-metal cyclophane complexes[13] are of recent interest.

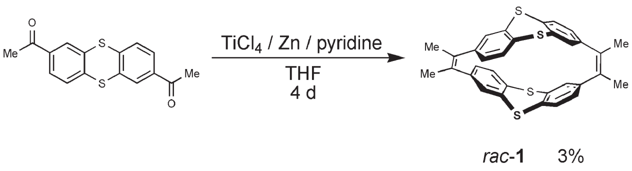
Cyclophanes containing heterocycles, *e.g.* [2.2]-(2,5)-furanophane[14] and [2.2]-(2,5)-thiophenophane[15] as well as annelated cyclophanes such as [2.2]-(2,6)-naphthalenophane[16] and [2.2]-(9,10)-anthracenophane,[17] have been described in the literature. The most well-known cyclophanes containing sulfur are thia-bridged cyclophanes.[5] The possibility of sulfur atoms to coordinate to soft metal ions has allready been demonstrated for 2,11-dithia[3.3]paracyclophane which yields polymeric structures with silver(I) and copper(I).[13] Thianthrene has also been used as a ligand for transition metals such as silver,[18,19] palladium,[18] platinum[18] and mercury.[18] Therefore, we designed a cyclophane (**1**) that is built up from two thianthrene units and which might have enough room between the butterfly-like thianthrene moieties to accommodate small ions or molecules. This thianthrenophane should be able to offer both exohedral sulfur coordination sites to soft metal ions and endohedral π-face coordination.

In the present study we will probe the ligand properties of this new thianthrenophane to silver(I) ions by UV/Vis titration experiments as well as by testing the transport capabilities through liquid membranes in comparison with other soft metal ions and in comparison with the thianthrene parent compound and 1,4,8,11-tetrathiacyclotetradecane (14-ane-S4). In addition we will present the X-ray crystal structure determination of a polymeric [Ag(**1**)]ClO_4·(dioxane)$_7$ complex.

Results and discussion

Synthesis and crystal structure of 1

Cyclophane **1** was synthesised by McMurry coupling using high-dilution technique analogous to Yamato *et al.*[20,21] (Scheme 1). The starting material for the McMurry cyclisation, 2,7-diacetylthianthrene, can be obtained by Friedel–Crafts acylation of thianthrene with two equivalents of acetyl chloride in high quantities,[22] which is necessary because the yield in the subsequent cyclisation reaction was very low. Nevertheless, thanks to the easy availability of 2,7-diacetylthianthrene we were able to synthesise several hundred milligrams of **1**.



Scheme 1 Synthesis of thianthrenophane **1**.

Because thianthrenophane **1** has two stereogenic planes three possible stereoisomers exist. One isomer is the achiral *meso*-form with C_{2h} symmertry and the others represent a pair of enantiomers with D_2 symmetry (Fig. 1).

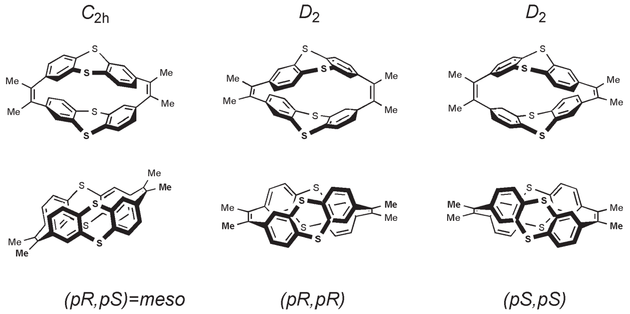


Fig. 1 Possible isomers of thianthrenophane **1**.

The IR-spectrum of 2,7-diacetylthianthrene shows a very intense carbonyl band at 1683 cm^{-1} which is replaced by a strong band due to the C=C double bond stretching at 1736 cm^{-1} in **1**. The ^{1}H-NMR of our product **1** shows only one set of signals indicating that a single isomer was formed, either the *meso*-form or a racemic mixture of the two enatiomers (see Fig. 1). An X-ray crystal structure analysis of **1** (Fig. 2) indeed demonstrates that the cyclophane crystallises as a conglomerate of the two D_2 enantiomers.

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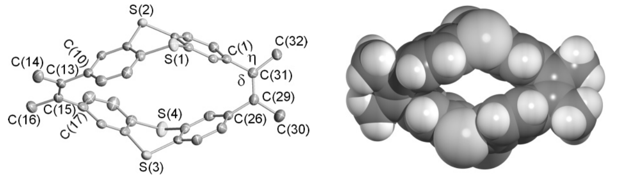


Fig. 2 Solid state structure of the asymmetric unit (50% probability level) and space filling model of thianthrenophane **1**.

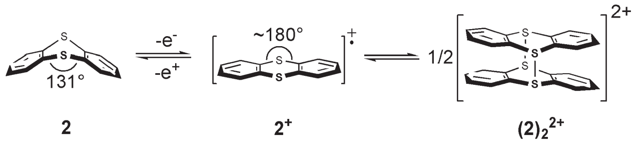
The crystal structure analysis reveals a crossed orientation of the two thianthrene units with an angle of 42.7° between the S(1)–S(2) and S(3)–S(4) axes. As a consequence of the twisted thianthrene units the two ethene bridges are also not arranged parallel but are crossed with an angle of 58.0° between the C(13)–C(15) and C(31)–C(29) axes. The ethene bridges of **1** show distinct deviation from planarity with torsion angles of 7.7° between the C(10)–C(13)–C(14) plane and the C(17)–C(15)–C(16) plane and of 2.7° between the C(1)–C(31)–C(32) plane and the C(26)–C(29)–C(30) plane. These distortions are similar to the one in (*Z*)-2,3-diphenyl-2-butene (3.9°) which is assumed to be strainless.[23]

The bond lengths and angles as well as the butterfly structure of the thianthrene rings in **1** are similar to common thianthrenes.[24–26] The folded structure of each thianthrene subunit has an interplanar angle of 129.3 and 129.9°, respectively, which is also comparable to the corresponding angle of known thianthrene structures.[24–26] Nevertheless, the cyclophane **1** is a somewhat strained molecule with the following structural characteristics: (a) all planes of the folded thianthrene units show a slight deviation out of planarity; (b) the mean bond angle $\delta = 119.5°$ of the (*Z*)-stilbene units in **1** is smaller than $\delta = 122.8°$[23] of (*Z*)-2,3-diphenyl-2-butene; and (c) the average angle $\eta = 124.7°$ is enlarged compared with $\eta = 114.6°$[23] of (*Z*)-2,3-diphenyl-2-butene.

The size of the cavity of cage compound **1** is limited by the distance from the centroid between S(1) and S(2) to the centroid between S(3) and S(4) which is 5.95 Å. Subtraction of the van-der-Waals radii of two sulfur atoms (3.60 Å)[27] yields a distance of 2.35 Å. Thus, thianthrenophane **1** should provide enough room between both thianthrene units in order to serve as a host for small metal ions such as Ag^+ ($r = 1.15$ Å, see space filling model, Fig. 2).

Redox properties of 1

Although the thianthrene radical cation $\mathbf{2}^+$ is widely used as a one-electron oxidant the electrochemistry of thianthrene itself is complicated. The one-electron oxidation of thianthrene under superdry conditions is followed by a planarisation of the ring system (the butterfly angle of **2** in the gas phase is 131°[28] and 128°[26] in the solid state and the butterfly angle of $\mathbf{2}^+AlCl_4^-$ is 174°[29] in the solid state) and a dimerisation *via* the sulfur atoms to give $(\mathbf{2})_2^{2+}$ in polar solvents such as MeCN (see Scheme 2).[30]



Scheme 2 Oxidation of thianthrene **2** and reversible dimerisation of the monoradical cation.

The redox behaviour of thianthrenophane **1** was investigated by cyclic voltammetry (CV) in butyronitrile. At a high scan rate ($v > 5000$ mV s^{-1}) the cyclic voltammogram shows two chemically reversible oxidation signals (Fig. 3).

Digital simulation of the CV (with DigiSim)[31] yields a peak potential difference ΔE of 126 mV between the two oxidation signals with $E_{1/2}(\text{I}) = 872$ mV and $E_{1/2}(\text{II}) = 998$ mV *versus* ferrocene as the internal reference.

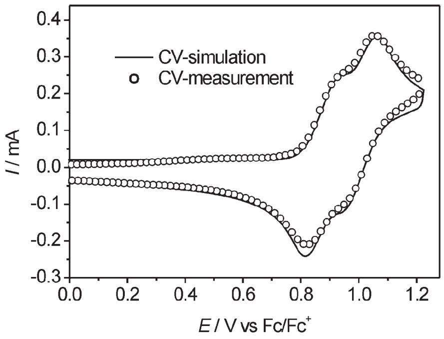


Fig. 3 Cyclic voltammogram of thianthrenophane **1** in PrCN/0.1 M TBAH ($v = 5000$ mV s^{-1}).

The oxidation of **1** is chemically reversible at high scan rates only. At lower scan rates chemical follow up reactions take place and the back reduction signal almost disapears. We suppose that the generated radical cations of **1** are unstable due to the existence of strained double bonds which may lead to irreversible oligomerization reactions. But as mentioned above, CV of thianthrene itself reveals two reversible oxidation signals only in the case of aprotic solvents under superdry conditions. Although our CV experiments were carried out under Ar inert gas with rigorously dried solvents we cannot exclude that traces of water are present which might lead to the irreversible formation of sulfoxides as final products.[32]

Stability constants for the complexation of silver(I) with thianthrenophane 1 and thianthrene 2

In order to probe the ligand properties of thianthrenophane **1** to soft metal ions we measured the complex formation constant of the appropriate silver complex in comparision with that of thianthrene **2**.

The complex stability constants *K* were determined by UV/Vis titration experiments with thianthrenophane **1** (K_1) and thianthrene **2** (K_2) as ligands in silver(I) complexes. In both cases we used a solution of the ligand in CH_2Cl_2 which was titrated by a silver(I) perchlorate solution in MeCN–CH_2Cl_2 1 : 9. The UV/Vis spectra obtained were analysed by global least squares data fitting by the Levenberg–Marquardt method using SPECFIT/32™ software.[33] The 'singular value decomposition' (SVD) analysis of the experimental absorbance data for both ligands shows that only two spectroscopically distinguishable species are present, *i.e.* the free ligand and one complex are in equilibrium. The compositions of the complexes were determined by Job's method.[34] The resulting Job-plots indicate that thianthrenophane forms a 1 : 1 complex $[Ag(\mathbf{1})]ClO_4$ with silver(I) while a 1 : 2 aggregate $[Ag(\mathbf{2})_2]ClO_4$ is formed in the case of thianthrene.

We obtained $\log K_1 = 5.45 \pm 0.13$ and $\log K_2 = 9.16 \pm 0.10$ by the global analysis fits. If one assumes that the complexation of silver with the first and the second thianthrene ligand has the same heat of formation the complex stability constant of a hypothetical 1 : 1 $[Ag(\mathbf{2})]^+$ complex will be $\log K_2/2 = 4.58$ which is somewhat smaller than $\log K_1$. This discrepancy indicates a different type of Ag^+ complexation by thianthrene and by the cyclophane **1**.

The UV/Vis spectra of **1** and of **2** are given in Fig. 4. Both compounds show a distinct absorption maximum at *ca.* 260 nm which is comparable in molar absorptivity if a factor of two is applied for **2**. At $\lambda > 280$ nm there is a broad and less intense shoulder for both compounds. The main difference of both spectra is that the bands in **1** are much broader and less resolved. This broadening might be due to exciton coupling[35–37] of the two thianthrene subunits in **1**.

Upon silver ion complexation the spectra of **1** and of **2** retain their shape but the molar absorbtivity at the peak maximum decrases significantly and the spectral features become somewhat broader.

Table 1 Transport rates J^a (10^{-8} mol m^{-2} s^{-1}) for three carrier molecules

	Source phase concentration/10^{-3} M	**1** (10^{-3} M)	**2** (2×10^{-3} M)	14-ane-S_4 (10^{-3} M)
Pb^{2+}	172	0.02	0.01	0.01
Zn^{2+}	158	0.01	0.05	0.05
Al^{3+}	151	—^{b}	—	—
Ca^{2+}	95	—	0.61	0.61
K^+	153	—	—	—
Mg^{2+}	127	—	—	—
Na^+	146	—	—	—
Cd^{2+}	161	0.02	—	0.003
Ag^+	166	37.53	8.93	1.51
Hg^{2+}	150	2.85	1.58	0.33

[a] Calculated from $J = cVt^{-1}A^{-1}$, with c = concentration of receiving phase after time t = 120 h, V = 5.0 ml (volume of receiving phase) and $A = 7.09 \times 10^{-5}$ m^2 (effective exchange area).[42] [b] All missing data lie below the detection limit of the used device.

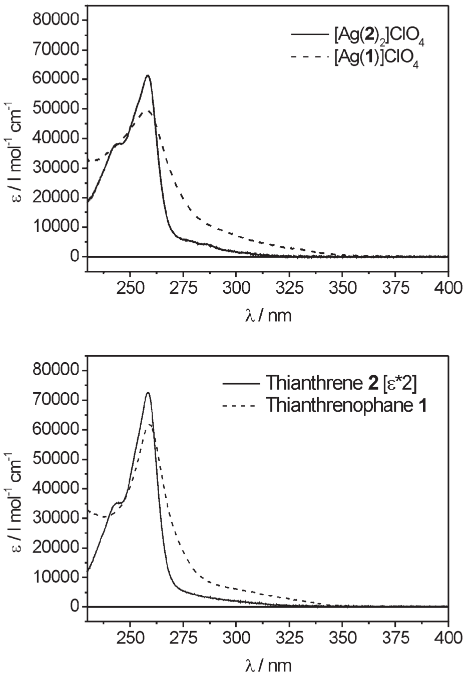


Fig. 4 UV/Vis spectra of the ligands (**1** and **2**) and their silver(I) complexes [Ag(**1**)]ClO_4 and [Ag(**2**)$_2$]ClO_4 in CH_2Cl_2 after deconvolution by global analysis.

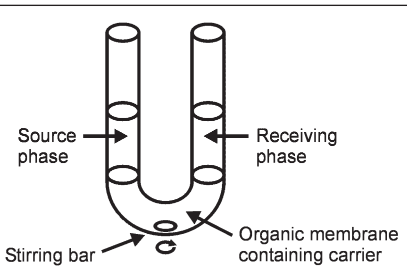
The 1 : 1 stoichiometry of [Ag(**1**)]ClO_4 and the distinct difference between logK_1 and logK_2/2 suggests an endohedral coordination of Ag^+ by **1**, whereas the 1 : 2 stoichiometry of [Ag(**2**)$_2$]ClO_4 suggests a coordination of Ag^+ by the sulfur atoms on the convex side of thianthrene.

Transport properties of 1 as a carrier in liquid membranes

In order to further elucidate the complex formation of thianthrenophane **1** as well as its application in ion transport processes in liquid membranes we carried out single competition transport experiments with ten metal salts.[38–40]

Thianthrenophane **1** was used as the carrier in comparison with thianthrene **2** and 14-ane-S_4. Bulk liquid membranes as they were used in our case were comprised of an aqueous source phase and a receiving phase separated by a CH_2Cl_2 phase as the membrane (Scheme 3).[41]

The aqueous source phase contained nine nitrate salts and mercury acetate at concentrations given in Table 1. The receiving phase was analysed by AAS for Ca^{2+}, K^+, Mg^{2+}, $Na^+$and Hg^{2+}, and all remaining metals by ICP-OES after 120 h to determine the transport rates J for each metal ion (Table 1).



Scheme 3 Bulk liquid membrane cell with a source phase and a receiving phase separated by an organic membrane phase.

Under the contitions employed **1** transports silver(I) with a much higher rate and selectivity than thianthrene **2** does. The ion flux of silver(I) was about 13 times higher than that of mercury(II) and more than a thousand times higher than that of cadmium(II), zinc(II) and lead(II) for **1**. For thianthrene **2** as the carrier which was used in the same equivalent concentration per sulfur atoms (Table 1) the transport is also selective for silver(I) but the selectivity is lower than for the cyclophane **1**. In the case of thianthrene, silver(I) was transported only about five times faster than mercury(II). Furthermore, the transport rate of silver(I) is four times higher for cyclophane **1** compared to the thianthrene.

Macrocyclic polythioethers such as 14-ane-S_4 are extraction reagents which are known to be selective for soft metal ions such as silver(I).[43] In fact the selectivity for the silver(I) transport of 14-ane-S_4 at the same carrier concentration as for cyclophane **1** is similar to that of thianthrene although the ion fluxes for 14-ane-S_4 are distinctly smaller than those of thianthrene and **1**.

According to a simplified equation reported by Reusch and Cussler[44] the transport rate J_M depends on the diffusion coefficient of the carrier–metal complex D, the complex formation constant for the carrier–metal complex K, and a partition coefficient k for the metal ion partitioning between the aqueous and membrane phases, the cation concentration in the source phase C_M, and the carrier concentration C_C as well as the transport length l: $J_M = D \cdot k \cdot K \cdot C_M{}^2 \cdot C_C/l$. However, in practice a decrease of J_M for higher complexation constants was observed experimentally and described theoretically by Lamb *et al.*[45] Without additional information about the above-mentioned quantities it is impossible to give definite conclusions about the transport rate and selectivity of the three carriers. Tentatively, we explain both the high selectivity of the silver(I) transport by thianthrenophane **1** and the high transport rate by the formation of an endohedral [Ag(**1**)]$^+$ complex. Because of the smaller size this endohedral [Ag(**1**)]$^+$ complex should have a higher diffusion coefficient than [Ag(**2**)$_2$]$^+$. The formation of an endohedral [Ag(**1**)]$^+$ complex is also supported by the analysis of the UV titration which suggests a 1 : 1 carrier–metal ratio and a complex stability constant which would be unlikely for an exohedral complex formation.

Crystal structure of [Ag(1)]ClO_4·(dioxane)$_7$

Reaction of **1** with one equivalent of silver(I) perchlorate in THF affords a colourless solid which was recrystallised from dioxane to obtain colourless needles of complex [Ag(**1**)]ClO_4·(dioxane)$_7$. The X-ray structure analysis reveals a coordination polymer of silver(I) and thianthrenophane **1** in which thianthrenophane acts as a pure S ligand to Ag^+ (see Fig. 5). This contrasts the structure of many other cyclophane–Ag^+ complexes where silver(I) sits endohedrally in the cage coordinated by the arene π-systems.[9,46]

The complex shows a one-dimensional polymeric structure where each silver ion is coordinated by two ligands. Regarding the [Ag(**1**)$_2$] substructure the metal ion is coordinated by two sulfur atoms of each bidentate ligand part. The bond angles S(1′)–Ag(1)–S(2′) and S(3)–Ag(1)–S(4) are 68° and the mean Ag–S bond length is 2.81 Å. These values are comparable to the S–Ag–S bond angle of 70.9° and Ag–S bond lengths of 2.63 and 2.79 Å in the dinuclear [Ag_2(thianthrene)$_2ClO_4$)$_2$] complex described by Munakata *et al.*[19] In contrast to the structure of [Ag(**1**)]ClO_4·(dioxane)$_7$ this dimeric thianthrene complex not

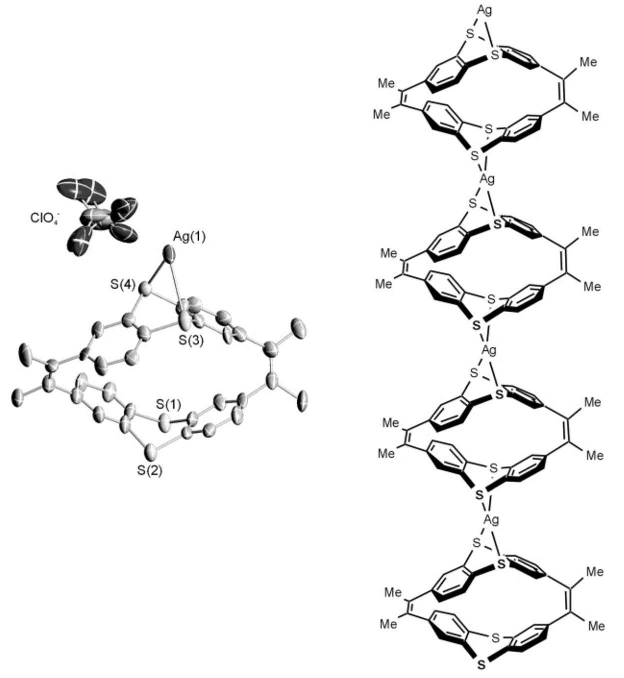


Fig. 5 Solid state structure (50% probability level) of the asymmetric unit and polymeric representation of $[Ag(\mathbf{1})]ClO_4 \cdot (dioxane)_7$ (the solvent molecules and hydrogen atoms are omitted).

only shows the coordination of sulfur atoms to silver(I) but also a complexation by the π-system of phenylene rings to silver(I). Owing to the complexation the interplanar angles of the folded thianthrene units of our ligand show a narrowing from 129.3 and 129.9° (**1**) to 121.8 and 122.0°, respectively. Thus the distance from the centroid between S(1) and S(2) to the centroid between S(3) and S(4) is enlarged to 6.32 Å. After subtraction of the van-der-Waals radius of two sulfur atoms the size of the cavity is specified by the resulting distance of 2.72 Å. The twist angles of the uncoordinated cyclophane **1** mentioned above are comparable to the ligand structure in the $[Ag(\mathbf{1})]ClO_4 \cdot (dioxane)_7$ complex. Although the solid state structure of $[Ag(\mathbf{1})]ClO_4 \cdot (dioxane)_7$ is polymeric it is unlikely that fragments of this structure constitute the entities present in solution. In fact $[Ag(\mathbf{1})]ClO_4 \cdot (dioxane)_7$ is insoluble in moderately polar solvents such as CH_2Cl_2 or THF and can only be dissolved upon addition of, for example, MeCN from which silver-free **1** could be isolated.

Conclusion

In this study we have shown that $[Ag(\mathbf{1})]^+$ forms a 1 : 1 complex in CH_2Cl_2 solution with a stability constant of 5.45 ± 0.13. Competitive membrane phase transport experiments with ten metal salts and two alternative carriers (thianthrene and 14-ane-S_4) demonstrate the high selectivity of **1** as a carrier for silver(I) compared to, for example, Hg^{2+} as well as its distinctly higher transport rates compared to the other carriers. We suggest an endohedral $[Ag(\mathbf{1})]^+$ complex to be the active unit in the transport experiments at very low concentrations while $[Ag(\mathbf{1})]^+$ forms a polymeric exohedral coordination structure in the solid state.

Experimental

rac-1,4(2,7)-Bisthianthrenediyl-2,3,5,6-tetramethylcyclohexanophane-2,5-diene (1)

Titanium tetrachloride (23.8 g, 13.8 ml, 125 mmol) was added slowly to 500 ml of dry THF at 0 °C under a nitrogen atmosphere. After warming up to room temperature zinc dust (18.0 g, 275 mmol) was added in small portions. The yellow suspension changed colour from green to purple and finally to black. A solution of 2,7-diacetylthianthrene (2.71 g, 9.00 mmol) in 250 ml dry THF and dry pyridine (22.5 ml, 200 mmol) was added to the black mixture of the McMurry reagent within four days under continuous reflux and stirring (with a 250 ml funnel-constant-addition with glass needle valve from Normag®). After an additional 12 h of reflux the reaction mixture was cooled to room temperature and hydrolysed with 200 ml of 10% aqueous potassium carbonate solution. Most of the solvent was distilled off (*ca.* 500–600 ml) and CH_2Cl_2 (250 ml) was added to the suspension. The black precipitate was filtered off, hydrolysed with hydrochloric acid (400 ml, 2 M) and the insoluble solid was filtered off. This solid was extracted with CH_2Cl_2 (100 ml). Each of the aqueous phases was extracted with CH_2Cl_2 (200 ml). The combined organic phases were washed twice with water (200 ml), dried over sodium sulfate and concentrated. The residue was purified by flash-chromatography over silica gel with petroleum–CH_2Cl_2 6 : 1 as the eluent to give the crude product **1**. This was recrystallised twice from EtOAc–CH_2Cl_2 1 : 9 to yield colourless crystals (135 mg, 3%). Mp 263 °C (from EtOAc–CH_2Cl_2 1 : 9); δ_H(250.13 MHz; $CDCl_3$) 7.19 (4 H, d, J = 7.93 Hz, Ar 4-H, 9-H), 6.97 (4 H, dd, J 7.93 and 1.83 Hz, Ar 3-H, 8-H), 6.55 (4 H, d, J 1.53 Hz, Ar 1-H, 6-H), 2.09 (12 H, s, CH_3); δ_H(62.90 MHz; $CDCl_3$) 144.6, 134.5, 134.5, 134.3, 130.8, 127.5, 127.4, 19.9 (CH_3); ν_{max}/cm^{-1} 1736s (C=C), 1448vs, 1376s, 1234s, 881s, 821vs, 728m; m/z (EI) 536.0763 (M^+, 100%. $C_{32}H_{24}S_4$ requires 536.0761), 268 (M^{2+}, 23%).

$[Ag(\mathbf{1})]ClO_4 \cdot (dioxane)_7$

Silver(I) perchlorate (31.5 mg, 140 μmol) in THF (1 ml) was added to a solution of **1** (75.0 mg, 140 μmol) in THF (12 ml). The mixture was stirred for 20 min at room temperature. The colourless precipitate was filtered off, washed with THF and dried under vacuum to yield the crude product (156 mg). The product was recrystallised from dioxane to give colourless needles.

Cyclic voltammetry

The electrochemical experiments were performed in superdry, argon-saturated PrCN with 0.1 M tetrabutylammoniumhexafluorophosphate (TBAH) as supporting electrolyte and 0.002 M substrate using a conventional three-electrode set-up with a platinum disk electrode (0.12 cm^2). The solution was dried *in situ* by the addition of activated (at 300 °C and 10^{-3} mbar) aluminium oxide. The potentials are referenced against ferrocene (Fc/Fc^+). Digital fits of the experimental cyclic voltammograms were done with DigiSim.[31]

UV/Vis titration

The complexation of silver(I) with ligands **1** and **2** was done by the stepwise addition of a 0.006 M silver(I) perchlorate solution with a microliter syringe into a 10^{-5} M solution of **1** or **2**, respectively, in 1 : 9 MeCN–CH_2Cl_2 in a UV quartz cell. The spectra obtained were analysed by global analysis using the SPECFIT/32™ software.[33] Taking into account that silver(I) forms $[Ag(MeCN)_4]ClO_4$[47] with MeCN we determined a value of 5.19 ± 0.25 for $\log K([Ag(\mathbf{1})]ClO_4)$ and 9.04 ± 0.14 for $\log K([Ag(\mathbf{2})_2]ClO_4)$ which are marginally lower than the values mentioned above which were obtained without consideration of MeCN complexation.

Membrane transport experiments

The nitric acid and all metal salts have been used in pro analysis quality without further purification. Thianthrene was purchased from Fluka and 1,4,8,11-tetrathiacyclotetradecane from Aldrich, both were used without further purification. In order to obtain reliable results an identical experimental set-up consiting of a horseshoe bend standard glass tube with an identical source phase (metal salts in 5 ml 10% aqueous nitric acid) and receiving phase (5 ml pure 10% aqueous nitric acid) separated by the CH_2Cl_2 membrane (5 ml) and stirring bar (50 rpm) was used for all experiments. The period of transportation was 120 h and the effective exchange area was 7.09 × 10^{-5} m^2 in all cases. For the quantitative determinations of Ca^{2+}, K^+, Mg^{2+} and Na^+ a Unicam Solar 939 atomic absorption spectrometer was used. The content of Hg^{2+} was measured with a Seefelder Hg-254 NE analyser. The concentrations of all remaining metal salts were measured with a Spectroflame ICP-OES.

X-Ray measurement of 1 and of [Ag(1)]ClO_4·(dioxane)$_7$

All data were collected from shock-cooled crystals on a Bruker Smart Apex D8 3 circle diffractometer (graphite-monochromated Mo-Kα radiation, $\lambda = 71.073$ pm) equipped with a low temperature device at 173(2) K.[48] An empirical absorption correction was employed for structure **1**.[49] Structures **1** and [Ag(**1**)]ClO_4·(dioxane)$_7$ were solved by direct methods (SHELXS-97[50]) and refined by full-matrix least squares procedure against F^2 (SHELXL-97[51]). R values: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$. **1**: $C_{32}H_{24}S_4$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 1183.13(10)$, $b = 1478.32(13)$, $c = 1595.19(14)$ pm, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$, $V = 2.7901(4)$ nm^3, $\rho_c = 1.278$ Mg m^{-3}, 27669 reflections measured, 5746 unique, R_1 $[I > 2\sigma(I)] = 0.0546$, wR_2 (all data) = 0.1200, $g_1 = 0.0397$, $g_2 = 1.7844$ for 329 parameters. The Flack parameter refined to 0.10(8), therefore the absolute structure was determined correctly. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically. [Ag(**1**)]ClO_4·(dioxane)$_7$: $C_{30}H_{40}Ag_{0.5}Cl_{0.5}O_9S_2$, monoclinic, space group $P2_1/c$,[52] $Z = 8$, $a = 2875.0(5)$, $b = 1096.8(2)$, $c = 2056.2(4)$ pm, $\alpha = 90.00$, $\beta = 90.104(5)$, $\gamma = 90.00°$, $V = 6.48(1)$ nm^3, $\rho_c = 1.394$ M g m^{-3}, 16989 reflections measured, 6242 unique, R_1 $[I > 2\sigma(I)] = 0.0962$, wR_2 (all data) = 0.1895, $g_1 = 0.0843$, $g_2 = 0.0000$ for 622 parameters and 669 restraints. Owing to the unsatisfying crystal quality (three of the seven dioxane molecules were disordered as well as the ClO_4^- anion) and the resulting decay of intensities at higher scattering angles the data had to be cut at the $d = 1.0$ Å resolution limit. All non-hydrogen atoms were refined anisotropically with the exception of the dioxane molecules. The hydrogen atoms were refined isotropically. The disordered molecules were refined with different occupation factors. All disordered fragments were refined with SAME- and SADI-restraints implemented in SHELXL.

CCDC reference numbers 238344 (**1**) and 238345 {[Ag(**1**)]ClO_4·(dioxane)$_7$}.

See http://www.rsc.org/suppdata/ob/b4/b407048h/ for crystallographic data in .cif or other electronic format.

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