Syntheses of a series of S_6 thioether cages and their coordination chemistry with Ag^+†

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The syntheses of four S_6-cages with different cavity sizes are described. In regard of potential applications for radioimmunotherapy with ^{111}Ag, their coordination behaviour towards Ag(I) was evaluated by studies of their reactivity in solution and of their crystal structures. All cages reacted differently with Ag(I). Whereas S_6-cages based on 3,8,12,17,20,25-hexathiabicyclo[8.8.8]-hexacosane (**14**) and on 5,9,17,21,28,31-hexathiabicyclo[11.11.11]pentatriacontane (**18**) showed only external Ag(I) coordination, successive adaptation of the cage size, yielded ligand **24**, based on 4,7,13,21,24,25-hexathiabicyclo[8.8.8]hexacosane, which gave a complex with internal-peripheral Ag(I) binding.

Introduction

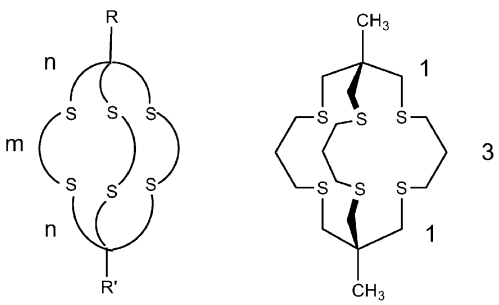
Targeted radiotherapy is a very important strategy for the treatment of severe diseases such as various types of cancer.[1] Among the different radionuclides of potential use in radiotherapy, the radiation properties (half life time, type and energy of decay) of the radioisotope ^{111}Ag make it especially interesting for applications in radiotherapy.[2,3] Large amounts of high specific activity ^{111}Ag can be prepared by the neutron irradiation of Pd^0 and subsequent separation of ^{111}Ag by liquid–liquid extraction. If isotope enriched palladium is irradiated, essentially no carrier added ^{111}Ag can be received, in the case of natural palladium, ^{111}Ag contains ^{109}Ag as carrier.[4] The applicability of ^{111}Ag in nuclear medicine, however, relies to a large extent on the possibility to immobilize the labile Ag^+ ion by binding it to a potent ligand, so that transmetallation in the organism cannot take place. Several approaches have been described in the literature.[5–11] So Mäcke *et al.*[8] have presented a macrocycle derived from tetraazatetrathiacyclen, which up to now has the highest known stability constant for Ag^+, but apparently still not high enough to prevent transmetallation under physiological conditions. We also have developed open chain and cage ligands based on a NS_3 donor set to bind Ag^+, but were not able to encapsulate the metal ion into the cages.[9] The reason for it is probably due to the fact that the NS_3 cages are too small to allow incorporation of the Ag^+.

Whereas most Ag^+ complexes exhibit a tetrahedral coordination sphere, hexadentate chelators seem to be an alternative.[10] This was shown by Schröder *et al.*[11] who were able to encapsulate the Ag^+ with a S_6-thioethercrown ligand. Our efforts to use S_6-macrocycles, however, gave mainly tetradentate complexes of Ag^+.[2] To improve this we present now a series of S_6-cages with varying cage sizes together with the crystal structures of their Ag^+ complexes. We designed a series of macrobicyclic ligands, abbreviated in the following as *R,R′*-[nmn-S_6] (Scheme 1) which combine the advantages of thioether donors with the stabilising chelate effect of cage compounds. Related cages and their Co(II) and Co(III) coordination compounds have been presented elsewhere.[12] The synthetic methodology follows an adaptation of the cyclisation protocol, using Cs_2CO_3 as a base for high dilution reactions in DMF.[13]

Results and discussion

Syntheses and structures

The preparation of CH_3,CH_3-[131-S_6] (**9**), based on the 3,7,11,15,18,22-hexathiabicyclo[7.7.7]tricosane framework, has been described by Osvath and Sargeson.[12] Thereby 1,1,1-tris-(*para*-benzylsulfonylethyl)ethane was reacted with



Scheme 1 Basic structure of the S_6-cages, abbreviated as *R,R′*-[nmn-S_6] (left) and as an example CH_3, CH_3-[131-S_6] (right).

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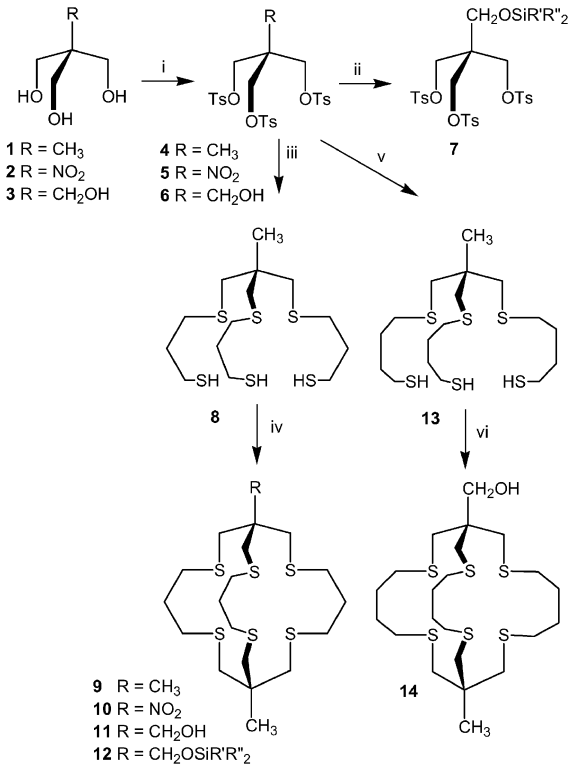
† Electronic supplementary information (ESI) available: bond lengths and angles of **9**, **11**, [Ag(**14**)(tosylate)], [Ag(**24**)(triflate)], and [Ag(**18**)(triflate)]. See DOI: 10.1039/b606510b



Scheme 2 Synthesis of the cages **9**–**12** and **14**: (i) TsCl in pyridine; (ii) *tert*-butyldimethyl-silyl chloride, imidazole in DMF; (iii) HS–$(CH_2)_3$–SH, EtONa in EtOH; (iv) **4**–**7**, Cs_2CO_3 in DMF; (v) HS–$(CH_2)_4$–SH, EtONa in EtOH; (vi) **6**, Cs_2CO_3 in DMF.

3-mercaptopropionic acid in EtOH in the presence of sodium to give the triester, which was reduced with $LiAlH_4$ to the triol. The triol was then converted to the trichloride with $SOCl_2$, which was doubly cyclised with an excess of 1,1,1-tris(mercaptomethyl)ethane in the presence of Cs_2CO_3 in DMF. The purification of the cage was achieved through chromatography of the corresponding Co(III) complex, whereas the free ligand could not be isolated.

Since we are particularly interested in the free ligands, we decided to use a different approach as shown in Scheme 2. The synthetic strategy as outlined for cage **9** is the same for all the cages described below. The caps **4**–**6** were prepared by tosylation of 1,1,1-tris(hydroxymethyl)ethane (**1**), tris(hydroxymethyl)nitromethane (**2**) and pentaerythrite (**3**) with tosyl chloride in pyridine. It is essential to have additional functionalities "R" attached to the carbon-bridge-head in the caps, since such bifunctional ligands should be attached in a later step to targeting molecules such as peptides or antibodies. The tritosylates **4** and **5** could be purified by crystallization. Compound **6** was purified by column chromatography to separate the desired product from the di- and tetratosylated derivatives. The tritosylate **6** was also reacted with *tert*-butyldimethylsilyl chloride and imidazole in DMF[14] to give the hydroxy-protected product **7**.

The next step (iii) consisted in the alkylation of cap **4** with 1,3-propanedithiol, used in a 15-fold excess to prevent intramolecular dialkylation, in EtOH and in the presence of sodium ethylate as base to give the building block **8**. Compound **8** was

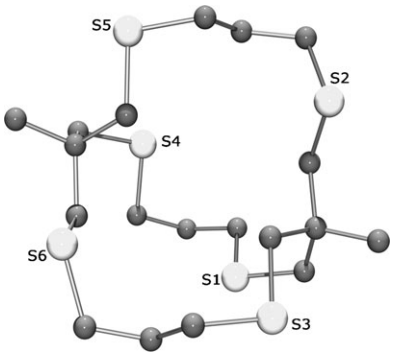


Fig. 1 Structure of **9** with the *exo* orientation of the lone pairs of the thioether sulfur atoms. Details about bond lengths and angles are contained in Table S1 of the ESI†.

then reacted (iv) with the caps **4**–**7** under high dilution conditions and in the presence of Cs_2CO_3 in DMF to give the bicyclic ligands **9**–**12** with yields between 10 and 22%. Compound **12** was also converted into **11** by deprotection with tetrabutylammonium fluoride. From a comparison of the yields of the cyclisation reaction with **6** (22%) and **7** (15%) it is obvious that protection of the alcoholic function with a silyl group results in a lower yield as compared to the reaction without the protecting group. At a first glance this is unexpected since an unprotected OH group can potentially crosslink, however, the sterical bulk of the protecting group probably hinders the approach of the S_6 building blocks and increases the rate of crosslink, thus, the formation of side products.

To obtain more detailed information about the conformation of the S_6-cages we grew crystals and solved the structures of **9** and **11**. In the free ligand **9** all non-bonding electron pairs of the thioether sulfurs are in *exo* orientation (Fig. 1). Six of the C–C–S–C torsion angles are in the range of 69° to 95°. The conformation of the other bonds is nearly antiperiplanar.

In **11**, the non-bonding electron pairs are also in the *exo* conformation and five of the torsion angles are in the range of 73° to 95° (Fig. 2).

A close comparison of the two structures shows that they are nearly superimposable. Therefore we expect that the coordination reactions of the two ligands with Ag^+ will be

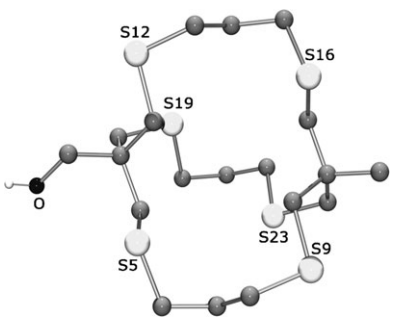


Fig. 2 Structure of **11** (one of two independent molecules is shown). Details about bond lengths and angles are contained in Table S2 of the ESI†.

similar and that the hydroxo group will not influence the binding of the metal ion. The structure of the free ligand implies that metal coordination into the cavity of the S_6-cages requires substantial rearrangement of the cage conformation. From the *exo* conformation the sulfur donors must change to an *endo* conformation, which will require a high activation energy. The reaction of Ag^+ salts with the cage ligands **9–11** resulted in complexes from which no crystals suitable for an X-ray diffraction analysis could be obtained. Consequently, other physical chemical methods were used for their structural characterization. In the ESI-MS spectrum the signal for M^+ of $[Ag(\mathbf{11})]^+$ can be detected implying the formation of a 1 : 1 complex in solution. The very low solubility of the Ag^+ complexes with all cages **9–11** points towards the formation of polymers in the solid state. The ^{1}H-NMR spectrum of $[Ag(\mathbf{11})][BF_4]$ in d_6-DMSO is very similar to that of the free ligand with low field shifts <0.1 ppm. This indicates exocyclic Ag^+ coordination and rapid exchange between the six sulfur atoms taking place. Taking these analytical data all together and considering the especially unfavourable structure of the free ligands we conclude that the cages are either to small or the activation energy for the conformation change is too high to encapsulate the metal ion.

More flexible cages with butylene [141-S_6] instead of propylene [131-S_6] bridges should decrease the energy barrier required for turning the *exo* sulfur lone pairs into *endo* conformation and increase at the same time the cavity size. Correspondingly, the synthesis of *R*,*R*′-[141-S_6] **14**, based on the 3,8,12,17,20,25-hexathiabicyclo[8.8.8]hexacosane framework, follows exactly the same strategy as that for **11** (Scheme 2). With 1,4-butanedithiol instead of 1,3-propenedithiol **13** was obtained. After cyclisation with **6**, the new cage CH_3,CH_2OH-[141-S_6] **14** was obtained in 29% yield. The reaction of **14** with Ag[BF_4], Ag[F_3CSO_3] or Ag[$O_3SC_7H_7$] gave the corresponding complex $[Ag(\mathbf{14})]^+$ as confirmed by ES-MS measurements. Again the ^{1}H-NMR spectrum of the complex is highly symmetrical and indicates either a rapid exchange of the metal ion outside the ligand or inclusion in the cage. Crystals suitable for X-ray structure analysis could be grown and the structure was elucidated. The structure of $[Ag(\mathbf{14})][O_3SC_7H_7]$ clearly shows that Ag^+ is not encapsulated in the cavity of cage **14** as implied by the ESI-MS measurements but is coordinated "*exo*" by three thioether sulfur donors from three different cages. The fourth position of the distorted tetrahedron is occupied by an oxygen of the tosylate counter-ion (Fig. 3).

The Ag–S bond lengths are in the expected range between 2.511 and 2.563 Å and the Ag–O bond is 2.44 Å. The angles around the Ag^+ ion are in the range 94° to 127°. Since the Ag^+ ion is connected by three cages and these cages again connect to further Ag(I) cations, a polymeric structure must result. This feature will be shown schematically and compared to the other complexes later in the general discussion.

Since increasing the number of carbons and, thus, the bridge lengths between two vicinal sulfur atoms, did not allow incorporating the Ag^+, the remaining structural elements which can be varied are the methylene groups connected to the bridgehead carbon. Introduction of ethylene or propylene chains will again increase the cavity size and render the cage

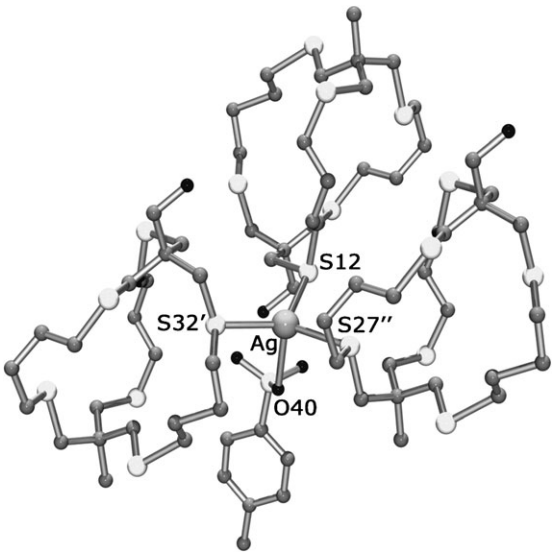


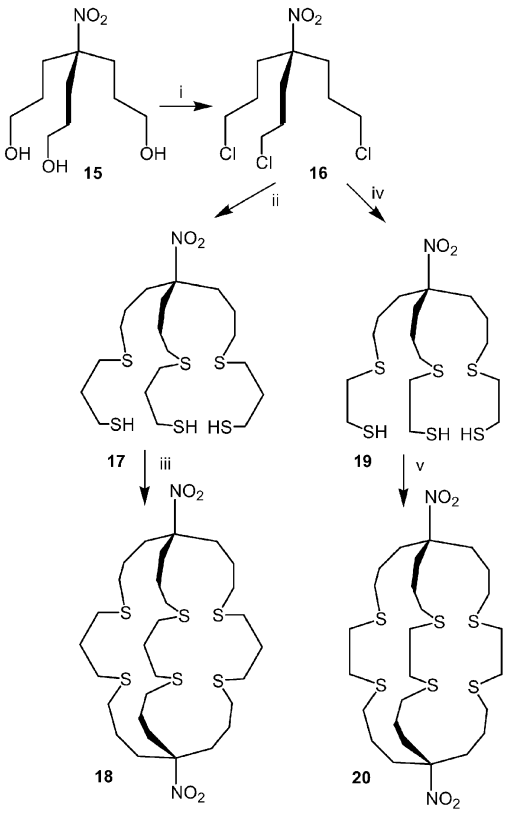
Fig. 3 Structure of the complex cation of [Ag(**14**)]tosylate. Selected bond lengths and angles: Ag–S12 2.563(4), Ag–O40 2.438(8), Ag–S32′2.511(4), Ag–S27″2.552(4) Å; S12–Ag–O40 106.3(2), S12–Ag–S32′ 122.64(13), S12–Ag–S27″ 104.07(13)° (Symmetry operations: (′) 1−*x*, −*y*, −*z*; (″) −*x*, −*y*, −*z*).

conformationally more flexible. Accordingly, the cage NO_2,NO_2-[333-S_6] **18**, based on the 5,9,17,21,28,32-hexathiabicyclo-[11.11.11]pentatriacontane framework, was prepared by reacting tris-(3-hydroxypropyl)nitromethane (**15**) with $SOCl_2$ to afford building block **16**, which was then converted to the corresponding trithiol **17** with an excess of 1,3-propanedithiol. The cage **18** was obtained by cyclisation of **16** with **17** under high dilution condition in the presence of Cs_2CO_3 in 42% yield (Scheme 3).

The Ag^+ complex $[Ag(\mathbf{18})]^+$ was formed by reacting the ligand with different Ag^+ salts in acetonitrile, THF or methanol. ESI-MS gave the mass of a 1 : 1 complex as has been shown before with $[Ag(\mathbf{14})]^+$. Since ESI-MS does only give the molecular composition of these complexes and only X-ray structure data will show whether Ag^+ is really encapsulated in the cage. Single crystals of $[Ag(\mathbf{18})][O_3SCF_3]$ were grown from acetonitrile–diethyl ether. The structure of the complex is shown in Fig. 4.

Each ligand molecule **18** is now connected to two Ag^+ ions, inducing the formation of strings. The coordination geometry around the Ag^+ cation is distorted tetrahedral. Two coordination sites are occupied by two thioether groups from two different chains between the bridgehead carbons of the same ligand, the other two by one thioether group stemming from a second ligand molecule and by the oxygen of the triflate ion. Thus, all thioether sulfurs of one ligand are engaged in coordination to two silver cations. Ag–S bond lengths are in the normal range 2.48 to 2.62 Å, the longest being the one to the second ligand molecule. The angles around Ag^+ are between 95.38° and 129.8°. The structure of the crystals can be described by polymeric chains (see general discussion).

The synthesis of NO_2,NO_2-[323-S_6] (**20**), based on the 5,8,16,19,26,29-hexathiabicyclo-[10.10.10]dotriacontane framework, was accomplished in analogy to **18** but using



Scheme 3 Synthesis of the cages **18** and **20**: (i) SO_2Cl; (ii) $HS–(CH_2)_3–SH$, EtONa in EtOH; (iii) **16**, Cs_2CO_3 in DMF; (iv) $HS(CH_2)_2–SH$, EtONa in EtOH; (v) **16**, Cs_2CO_3 in DMF.

1,2-ethanedithiol as bridging component (Scheme 3). The Ag^+ complexes were prepared in acetonitrile or EtOH–THF. The previously described complexes $[Ag(\mathbf{14})]^+$ and $[Ag(\mathbf{18})]^+$ did not move on TL chromatography, obviously because of their polymeric structure. In contrast, the complex $[Ag(\mathbf{20})]^+$ gave chromatograms with several distinct spots which changed in intensity with time. The dynamic equilibrium between several species did not allow the isolation of a pure compound with chromatographic methods but implied the presence of molecular species. The dynamic equilibrium points towards a low stability probably due to a too large cage. This observation implied the possibility of encapsulating Ag^+ with a smaller ligand than **20** but a larger or more flexible one than **9**. A synthetically achievable combination is an ethylene spacers for the bridgehead carbons and between the thioether donors. The synthesis of the underivatised cage [222-S_6] (**24**) 4,7,13,16,21,24-hexathiabicyclo[8.8.8]hexacosane was performed according to Scheme 4 with the building block **23** and applying the same methodological strategy as for the other ligands.

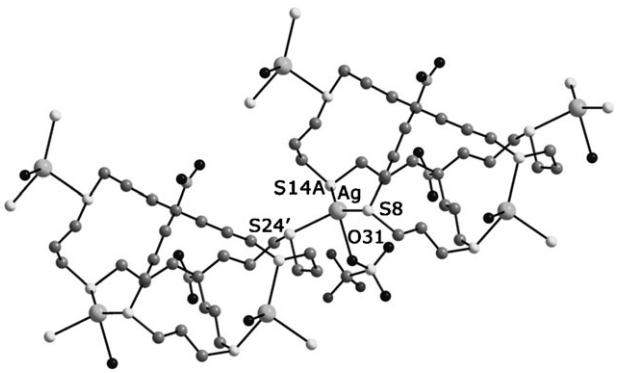
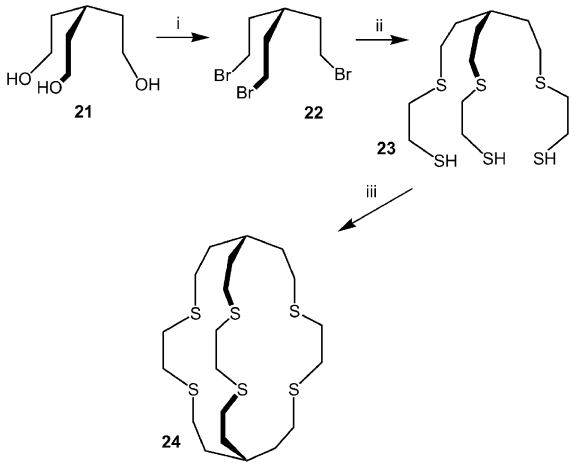


Fig. 4 Structure of the complex cation of [Ag(**18**)]triflate. Sulfur atom S14 is disordered over two sites. S14A represents the major site with occupancy of 0.915 and S14B with 0.085 occupancy. The minor site is not shown for clarity. Selected bond lengths: Ag–O31 2.526(4), Ag–S8 2.5164(15), Ag–S14A 2.5090(16), Ag–S24′ 2.6231(15). (Symmetry operation: $-x + 1/2, y - 1/2, -z + 1/2$).



Scheme 4 Synthesis of the cage **24**: (i) PBr_3–HBr; (ii) $HS(CH_2)_2SH$, EtONa in EtOH; (iii) **22**, Cs_2CO_3 in DMF.

Building blocks for a combination of spacer lengths as required for **24** are not commercially available. Bromination of **21** with HBr–PBr_3 gave the corresponding tribromide **22** and reaction in the usual way with an excess of 1,2-ethanedithiol gave the trithiol **23**. Compound **23** was then cyclised with **22** under high dilution condition in the presence of Cs_2CO_3 in DMF to give the final product **24** in 20% yield.

The reaction of cage **24** with different Ag(I) salts in acetonitrile or EtOH–THF and gave a 1 : 1 complex after 6 h at 50 °C as indicated by ESI-MS. The complex $[Ag(\mathbf{24})][O_3SCF_3]$ could be crystallized from acetonitrile and single crystals were grown by slow diffusion of diethyl ether through the vapour phase. The overall structure of this complex gives again a different picture. The Ag^+ ion is now coordinated by four sulfur atoms from one single ligand and by one sulfur from a second ligand molecule (Fig. 5). This time, the counter-ion does not participate in coordination to Ag^+.

Three out of the five Ag–S bonds are relatively short (2.51–2.68 Å) and two are longer (2.80–2.96 Å). The structure consists of polymeric chains. Still, Ag^+ is not in the cavity of the cage but bound by four sulfurs from the same ligand on one face of the cage. In the ^{1}H-NMR of the Ag^+ complex the signals are shifted up to 0.23 ppm to lower field as compared to the signals of the free ligand. The complexation of **24** with ^{111}Ag(I) was studied by TL chromatography. After 30 min in acetonitrile at 50 °C the TL chromatogram showed one single peak with $R_f = 0.45$. No free ^{111}Ag(I) could be observed after

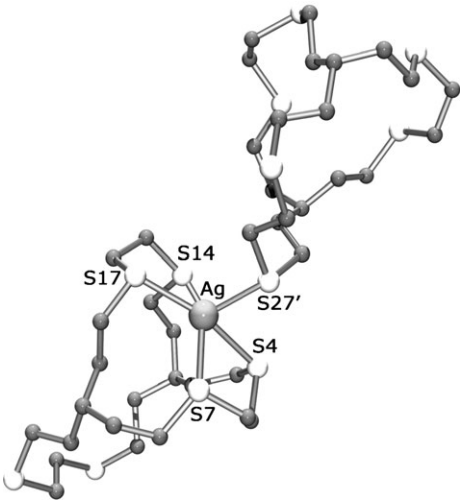


Fig. 5 Structure of the complex cation of [Ag(**24**)]triflate. Selected bond lengths and angles: Ag–S4 2.603(3), Ag–S7 2.800(3), Ag–S14 2.967(3), Ag–S17 2.516(3), Ag–S27′ 2.687(3) Å; S4–Ag–S7 81.21(10), S4–Ag–S14 91.61(10), S4–Ag–S17 163.37(10), S4–Ag–S27′ 88.36(9), S7–Ag–S14 150.18(9), S7–Ag–S17 98.39(10), S7–Ag–S27′ 88.43(8), S14–Ag–S17 80.48(11), S14–Ag–S27′ 120.45(9), S17–Ag–S27′ 108.26(9) (Symmetry operation: $-x + 3/2, -y, z + 1/2$).

this reaction time. The complex with ^{111}Ag(I) formed in this way is stable in PBS (phosphate buffered saline, pH 7.6) and only little decomposition was observed. According to TLC, the half-life time of this complex is about 20 days.

General structural considerations

To better understand the complexation properties of the S_6-cages prepared herein and to better predict a cage structure able to encapsulate Ag^+, simple molecular modelling was used in addition to the X-ray diffraction studies. Since the length of the bridges connecting the sulfur atoms and the size of the caps can be varied to optimize the conformation and flexibility of the free ligand as well as the size of its cavity, we have studied these two factors in more detail.

The structures of two derivatives of the basic cage framework [131-S_6] (**9** and **11**) clearly show that the free ligands have a very unfavourable conformation with the free electron pairs of all sulfurs being present in the *exo* position. We therefore moved to caps with longer bridges such as [141-S_6] (**14**). Molecular modelling with Hyperchem[15] indicates that the more flexible chains with four carbon atoms now allow a conformation with three of the sulfur atoms having their free electron pairs *endo*, and three *exo*, which in a way is a better preorganisation than in [131-S_6]. In the calculated structure there are only two close contacts, which are smaller than the sum of van der Waals radii by only 0.074 Å (S–C-contact) and 0.087 Å (S–S contact). Dreiding models and molecular modelling showed that in this ligand the conformation changes necessary to move all electron pairs of six sulfur atoms in the *endo* position implied rotations, which are hindered by interactions between the hydrogen atoms of the caps.

Consequently, we looked at cages with larger caps having two ([222-S_6] as in **24**, or [232-S_6] as in **20**)) or three ([232-S_6] as in **18**) carbon atoms. In the free ligand [232-S_6] all bond lengths and angles are close to their optimal values. The electron pairs of the sulfurs are *exo* or half *exo* positioned. The stick model clearly shows a higher flexibility for [232-S_6] than for [131-S_6] and no steric hindrance in the rotations. The calculated structure of [333-S_6] is very similar to that of [232-S_6] with only one close contact between the sulfur atoms (sum of the van der Waals radii 3.482 Å, *versus* contact 3.438 Å).

Because of the structural complexity of cages with six thioether sulfurs, a prediction for the "best" ligand seems very difficult. On one side thermodynamic aspects such as preorganization of the ligand and size of the cavity to bind Ag^+ are relevant. On the other side, kinetic aspects also seem very important, since Ag^+ first binds to an *exo* electron pair of a sulfur atom then has to move inside the cavity by rotation. This is only possible if the energy barrier for the rotation is not too large, which can be achieved by a higher flexibility of the ligand, which, however, implies that the chelate ring size is also modified and thus the thermodynamic stability is changed. Molecular modelling is helpful, but the dynamic required for inclusion is difficult to predict and calculate. Thus, we prepared a series of S_6-cages to test in an experimental way the consequences of structural changes. The systematic structural modifications of the S_6-cages have given a series of Ag^+ complexes which are all polymeric in the solid state with the metal ion outside of the cage. However, on going from the [141-S_6] cage (**14**) to [222-S_6] cage (**24**) we observe a systematic change in the coordination chemistry. With **14**, a cage with a small cap, the Ag^+ is coordinated in an monodentate way to three different macrocycles and the counter ion resulting in a band structure (Fig. 6). Going to cages with larger caps we

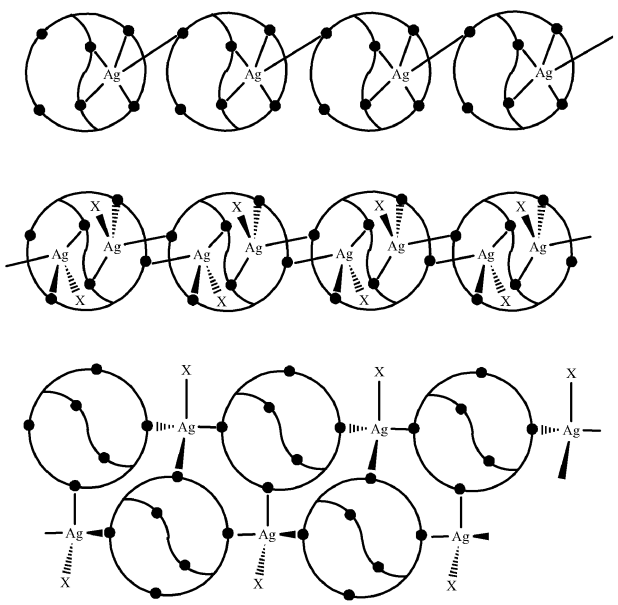


Fig. 6 Schematic view of the coordination modes of several S_6-cages. Black dots represent thioether sulfur atoms and X the counter ions. Top: [Ag(**24**)]triflate; Middle: [Ag(**18**)]triflate; Bottom: [Ag(**14**)] tosylate.

observe a higher tendency to bind Ag(I) by more sulfur atoms from the same ligand. Hence, the Ag^+ complex of NO_2,NO_2-[333-S_6] cage (**18**) produces a polymer in which each metal ion is bound by two sulfur atoms of one ligand, a sulfur of a second cage and the counter ion. Finally, in [222-S_6] cage (**24**) Ag^+ forms a complex in which four sulfurs of the same ligand and one of a neighbouring cage are bound. In this last case, Ag^+ is sitting on one of the faces of the cage, but still exposed to solvent or other ligands. The coordination of Ag^+ can be considered as an intermediate before full inclusion, it was however not possible to push the cation into the cage, even under strong thermal conditions or with the aid of microwave heating.

Conclusions

Although simple molecular modelling studies confirm from a thermodynamic point of view that the size of the cages would allow accommodation of Ag^+ in their cavities with a reasonable complex geometry, the kinetics of the formation seems to be the main obstacle. Once the Ag^+ is bound by one of the sulfur donors a high-energy barrier for the rotation necessary to bring the metal ion from the *exo* to the *endo* position prevents the encapsulation. Probably a subtle balance between thermodynamic and kinetic properties of the ligands is needed to finally bring the Ag^+ in the cage.

Experimental

General remarks

All starting materials were purchased either from Fluka or Aldrich and used without further purification. All reactions were carried out under an inert atmosphere (N_2). NMR spectra were recorded on a Varian Gemini 2000, 300 MHz at room temperature and referred to the residual solvent signal. IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. MS spectra and elemental analysis were performed by the analytical service of the ETH Zürich. Melting points were measured with a Büchi 510 and are uncorrected. Compounds **15**[7] and **21**[10] have been prepared as described elsewhere.

Syntheses

1,1,1-Tris(*para*-tolylsulfonylmethyl)ethane (4). At 0 °C a solution of *para*-toluenesulfochloride (47.6 g, 250 mmol) in absolute pyridine (90 ml) was added to a suspension of 1,1,1-tris(hydroxymethyl)ethane **1** (10 g, 83 mmol) in absolute pyridine (70 ml) over 2 h. The reaction mixture was stirred at rt overnight and hydrolysed by adding ice. The product was extracted with CH_2Cl_2 and the organic phase successively washed with 1M HCl, brine and water. After drying over Na_2SO_4 the solvent was evaporated. Recrystallisation from methanol yielded a white solid. Yield 33.8 g (70%). Mp 107–109 °C. (Found: C, 53.34; H, 5.20, O, 24.51, S, 16.70% $C_{26}H_{30}O_9S_3$ (M 582.72) requires: C, 53.59; H, 5.19; O, 24.71; S, 16.51%; IR (KBr, cm^{-1}): 1600 (m), 1358 (m), 1178 (s), 1096 (w), 1006 (m), 986 (w), 962 (m), 868 (w), 838 (m), 814 (m), 668 (m), 600 (w), 558 (m) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3 H), 2.47 (s, 9 H), 3.77 (s, 6 H), 7.36 (d, J = 8.3 Hz, 6 H), 7.71 (d, J = 8.3 Hz, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 16.0, 21.5, 39.4, 69.8, 128.0, 130.2, 132.1, 145.5. FAB-MS: m/z 583.0 (100%).

Tris(*para*-tolylsulfonylmethyl)nitromethane (5). The compound was prepared in analogy to **4** starting from **2** and crystallized from methanol–dichloromethane with a yield of 57%. Mp. 119–121 °C. (Found: C, 49.01; H, 4.40; N, 2.35; O, 28.43, S, 15.85%, $C_{25}H_{27}NO_{11}S_3$ (M 613.67) requires: C, 48.93; H, 4.43; N, 2.28; O, 28.68; S, 15.68%; IR (KBr, cm^{-1}): 2928 (w), 1598 (s), 1566 (s), 1494 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 9 H), 4.29 (s, 6 H), 7.38 (d, J = 8.4 Hz, 6 H), 7.72 (d, J = 8.4 Hz, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.7, 64.3, 87.2, 128.15, 130.3, 131.0, 146.1. FAB-MS: 614.1 (64.75%).

Pentaerythrite-tris(*para*-tolylsulfonate) (6). The compound was prepared in analogy to **4** starting from **3**. Chromatography on silica with ethyl acetate–hexane (1 : 1) yielded a white solid. (43%). Mp. 103–105 °C. (Found C, 51.99; H, 5.00; O, 26.58; S, 16.26%, $C_{26}H_{30}O_{10}S_3$ (M 598.7) requires C, 52.16; H, 5.05; O, 26.72; S, 16.07%). IR (KBr, cm^{-1}): 3542 (m), 2980 (w), 1598 (m), 1358 (s), 1192 (s), 1174 (s), 1096 (m), 1064 (m), 1020 (m), 990 (s), 968 (s), 864 (s), 848 (s), 834 (s), 810 (s), 670 (s), 628 (m), 556 (s). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.02 (t, J = 6.2 Hz, 1 H), 2.47 (s, 9 H), 3.52 (d, J = 6.2 Hz, 2 H), 3.92 (s, 6 H), 7.37 (d, J = 8.6 Hz, 6 H), 7.72 (d, J = 8.6 Hz, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.6, 44.7, 59.3, 66.6, 128.0, 130.2, 131.9, 145.6. FAB-MS: m/z 599.2 (66.78%).

Pentaerythrite-(*tert*-butyl-dimethylsilylether)-tris(*para*-toylsulfonate) (7). A solution of **6** (3.80 g, 6.3 mmol) imidazole (0.48 g, 7.0 mmol) and *tert*-butyl-dimethylchlorosilane (1.05 g, 7.0 mmol) in DMF (5 ml) was stirred under N_2 for 24 h at rt. The solvent was evaporated and the residue taken up in CH_2Cl_2 and washed with phosphate buffer (1M, pH = 7.4). After drying the organic phase was evaporated and the residue chromatographed on silica (ethylacetate : iso-hexane = 1 : 2) to give a white product, which was dried at 90 °C in high vacuum. Yield: 81% (3.64 g). Mp. 76–78 °C. (Found C, 54.05; H, 6.15; S, 13.62%, $C_{32}H_{44}O_{10}SiS_3$ (M 712.96) requires: C, 53.91; H, 6.22; S, 13.49%). IR (KBr, cm^{-1}): 2950 (m), 1598 (m), 1472 (m), 1358 (s). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = −0.07 (s, 6) 0.73 (s, 9 H), 2.47 (s, 9 H), 3.41 (s, 2 H), 3.85 (s, 6 H), 7.36 (d, J = 8.5 Hz, 6 H), 7.72 (d, J = 8.5 Hz, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = −6.7, 17.8, 21.5, 25.5, 44.4, 59.4, 66.5, 128.0, 130.1, 132.0, 145.4. FAB-MS: m/z 713.2 (23.43%).

1,1,1-Tris(5-mercapto-2-thiapentanyl)ethane (8). To a solution of sodium (2.6 g, 113 mmol) in abs. ethanol (200 ml), 1,3-propanedithiol (55.7 g, 0.515 mol) was added at 60 °C. To this, **4** (20 g, 34 mmol) was added in small portions over 7 h. The reaction mixture was heated overnight and after cooling, acidified with 1M HCl. Solvents were evaporated and the residue dissolved in CH_2Cl_2. The organic phase was washed with brine and dried over Na_2SO_4. The mixture was chromatographed on silica (CH_2Cl_2 : hexane = 2 : 1) and the compound was isolated as a colourless oil. Yield 8.3 g (62%). (Found C, 42.98; H, 7.72; S, 49.32%, $C_{14}H_{30}S_6$ (M 390.75) requires:

C, 43.03; H, 7.74; S, 49.23%). IR (KBr, cm^{-1}): 2956 (s), 2908 (s), 2548 (m), 1424 (s), 1370 (m), 1344 (m), 1296 (s), 1252 (s), 1204 (m), 866 (m), 754 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 3 H), 1.36 (t, J = 8 Hz, 3 H), 1.85 (tt, J = 7 Hz, 6 H), 2.57–2.65 (m, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.2, 23.8, 32.1, 33.4, 40.3, 41.5. EI-MS: m/z 390.0 (11.3%).

1,9-Dimethyl-3,7,11,15,18,22-hexathiabicyclo[7.7.7]tricosane (9). Caesium carbonate (2.84 g, 8.7 mmol) was suspended in dry DMF (270 ml) under nitrogen. **4** (2.98 g, 5.12 mmol) and **8** (2 g, 5.12 mmol) each dissolved in dry DMF (320 ml) were added at the same time dropwise under stirring over 72 hours at 60 °C in a nitrogen atmosphere. After complete addition the reaction mixture was stirred for an additional day. The solvent was removed in vacuum and the remaining solid was extracted several times with dichloromethane. Evaporation of the solvent gave a brownish semisolid. Column chromatography over silica with dichloromethane as eluent yielded the product as a white, crystalline solid. Yield 0.24 g (10%). Mp. 104–105 °C. (Found C, 49.96; H, 7.76; S, 42.22%, $C_{19}H_{36}S_6$ (M 456.85) requires: C, 49.95; H, 7.94; S, 42.11%). IR (KBr, cm^{-1}): 2912 (s), 1430 (m), 1254 (m), 844 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 6 H), 1.99 (q, J = 6.6 Hz, 6 H), 2.75 (t, J = 6.6 Hz, 12 H), 2.87 (s, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.1, 28.4, 21.6, 40.8, 42.2. EI-MS: m/z 456.1 (23.34%).

1-Nitro-9-methyl-3,7,11,15,18,22-hexathiabicyclo[7.7.7]tricosane (10). The compound was prepared from **5** and **8** in analogy to the cage **9**. The purification was achieved by column chromatography on silica with dichloromethane : iso-hexane = 8 : 1. Yield 12%. Mp. 117–119 °C. (Found C, 44.40; H, 6.95; N, 2.90; O, 6.45; S, 39.31%, $C_{18}H_{33}NO_2S_6$ (M 487.82) requires C, 44.32; H, 6.82; N, 2.87; O, 6.56; S, 39.44%). IR (KBr, cm^{-1}): 2908 (m), 1538 (s), 1406 (m), 1374 (w), 1344 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 3 H), 2.02 (tt, J_{AB} = J_{BC} 6.7 Hz, 6 H), 2.74 (t, J = 6.7 Hz, 6 H), 2.83 (s, 6 H), 3.43 (s, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.9, 28.4, 31.7, 32.3, 38.3, 40.7, 42.1, 95.6. EI-MS: m/z 487.0 (33.43%), 441.1 (33.29%, M-NO_2).

1-Hydroxymethyl-9-methyl-3,7,11,15,18,22-hexathiabicyclo[7.7.7]tricosane (11). The compound was prepared from **8** and **6** in analogy to **9**. Purification was achieved by column chromatography over silica with dichloromethane : acetonitrile = 9 : 1 as eluent. Yield 22%. Mp. 164 °C. (Found C, 48.11; H, 7.61; O, 3.67; S, 40.76%, $C_{19}H_{36}OS_6$ (M 472.85) requires: C, 48.26; H, 7.67; O, 3.38; S, 40.69%). IR (KBr, cm^{-1}): 3448 (w), 2950 (m), 2912 (s), 1448 (m), 1430 (m), 1400 (m), 1290 (m), 1254 (m), 1188 (w), 844 (w), 742 (w). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 3 H), 2.00 (tt, J = 6.6 Hz, 6 H), 2.76 (t, J = 6.6 Hz, 12 H), 2.88 (s, 6 H), 2.98 (s, 6 H), 3.65 (s, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.1, 28.2, 31.5, 31.7, 38.3, 40.9, 42.4, 45.6, 68.0. EI-MS: m/z 472.2 (100%).

1-(*tert*-Butyl-dimethylsilyloxymethyl)-9-methyl-3,7,11,15,18,22-hexathia[7.7.7]tricosane (12). The compound was prepared in analogy to **9** starting from **7** and **8**. Purification was achieved by column chromatography on silica with CH_2Cl_2 as eluent. Yield 15%. Mp 78–81 °C. (Found C, 51.05; H, 8.33; S, 32.68%, $C_{25}H_{50}OSiS_6$ (M 587.12) requires C, 51.14; H, 8.58; S, 32.77%). IR (KBr, cm^{-1}): 2952 (s), 2924 (s), 2854 (m), 1464 (m), 1414 (m), 1250 (m), 1092 (s) 844 (w), 742 (w). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 6H), 0.89 (s, 9 H), 1.09 (s, 3 H), 1.99 (t, J = 6.6 Hz, 6 H), 2.73 (t, J = 6.6 Hz, 6 H), 2.73 (t, J = 6.6 Hz, 6 H), 2.87 (s, 6 H), 2.92 (s, 6 H), 3.57 (s, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = −5.71, 18.11,, 24.1, 25.8, 28.4, , 31.6, 31.8, 38.0, 40.7, 42.1, 45.9, 66.8. FAB-MS: m/z 587.3 (100%).

1,1,1-Tris(6-mercapto-2-thiahexanyl)-ethane (13). The compound was prepared from 1,4-butanedithiole and **4** in analogy to **8**. The residue after evaporation of the solvent was subjected to column chromatography on silica (CH_2Cl_2 : hexane = 2 : 1). Yield 60%. Found C, 47.20; H, 8.42%, $C_{17}H_{36}S_6$ (M 432.83) requires: C, 47.17; H, 8.38%). IR (KBr, cm^{-1}): 2928 (s), 2848 (m), 2548 (w), 1450 (m), 1370 (m), 1280 (m), 1244 (m), 1202 (w), 860 (w), 738 (w). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 3 H), 1.35 (t, J = 7.9 Hz, 3 H), 1.67–1.71 (m, 12 H), 2.49–2.56 (m, 12 H), 2.63 (s, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.7, 24.1, 28.3, 33.3, 32.8, 40.3, 41.6. FAB-MS: m/z 432.0 (100%).

1-Hydroxymethyl-10-methyl-3,8,12,17,20,25-hexathiabicyclo[8.8.8]hexacosane (14). The compound was prepared starting from **13** and **6** in analogy to **9**. Column chromatography over silica with dichloromethane : acetonitrile = 9 : 1 as eluent gave the product as a white, crystalline solid. Yield 29%. M.p.: 80–82 °C. (Found C, 51.47; H, 8.26; O, 3.29; S, 37.11%, $C_{22}H_{42}OS_6$ (M 514.93) requires C, 51.31; H, 8.22; O, 3.11; S, 37.36%). IR (KBr, cm^{-1}): 3438 (m, br), 2914 (s), 2848 (m), 1420 (m), 1372 (w), 1280 (m), 1240 (m), 1052 (m), 858 (w), 750 (w). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 3 H), 1.78–1.83 (m, 12 H), 2.60–2.65 (m, 12 H), 2.77 (s, 6 H), 2.87 (s, 6 H), 3.67 (s, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.7, 27.0, 27.2, 32.9, 32.9, 37.4, 40.0, 41.4, 44.2, 68.0. FAB-MS: m/z (%) = 514.2 (69.46%).

Tris(3-chloropropanyl)nitromethane (16). A mixture of tris(3-hydroxypropanyl)nitromethane **15** (10 g, 43 mmol) and thionyl chloride (16 ml, 216 mmol) was stirred at rt for one hour. Excess thionyl chloride was evaporated and the mixture chromatographed on silica with CH_2Cl_2 as eluent. The product was isolated as a yellow oil. Yield 10.7 g (86%). (Found C, 41.59; H, 6.26; N, 4.64; O, 11.20%, $C_{10}H_{18}Cl_3NO_2$ (M 290.62) requires: C, 41.33; H, 6.24; N, 4.82; O, 11.01%). IR (KBr, cm^{-1}): 2964 (s), 2872 (m), 1537 (s), 1448 (m), 1354 (m), 1316 (m), 1116 (w), 842 (w), 782 (w), 732 (w), 652 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.66–1.75 (m, 6 H), 2.06–2.12 (m, 6 H), 3.56 (t, J = 6.1 Hz, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 26.5, 32.8, 44.2, 93.0. EI-MS: m/z 243.0 (12.35%).

Tris(7-mercapto-4-thiaheptanyl)nitromethane (17). The compound was prepared starting from **16** and 1,3-propanedithiole in analogy to **8**. The residue was subjected to column chromatography on silica (CH_2Cl_2 : hexane = 3 : 1). The compound was isolated as a colourless oil. Yield 53%. (Found C, 45.07; H, 7.74; N, 2.67; O, 6.17; S 38.25%, $C_{19}H_{39}NO_2S_6$

(M 505.88) requires: C, 45.11; H, 7.77; N, 2.77; O, 6.32; S, 38.03%). IR (KBr, cm^{-1}): 2928 (s), 2548 (m), 1531 (s), 1452 (m), 1352 (m), 1298 (m), 1260 (m), 842 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.37 (t, J = 8 Hz, 3 H), 1.44–1.54 (m, 6 H), 1.81–1.90 (tt, J = 7 Hz, 6 H), 1.98–2.04 (m, 6 H), 2.51 (t, J = 7 Hz, 6 H), 2.58–2.66 (m, 12 H). ^{13}C- NMR (75 MHz, $CDCl_3$): δ = 23.2, 23.5, 30.3, 31.7, 33.1, 34.4, 93.8. EI-MS: m/z 505.10 (0.8%).

1,13-Dinitro-5,9,17,21,28,32-hexathiabicyclo[11.11.11]pentatriacontane (18). The compound was prepared starting from **17** and **16** in analogy to **9**. Column chromatography over silica with CH_2Cl_2 as eluent yielded the product as a white, crystalline solid. Yield 42%. Mp 75–78 °C. (Found C, 50.66; H, 7.76; N 4.13; O, 9.26; S, 28.21%, $C_{29}H_{54}N_2O_4S_6$ (M 687.12) requires: C, 50.69; H, 7.92; N, 4.08; O, 9.31; S, 28.00%). IR (KBr, cm^{-1}): 3448 (w, br), 2914 (m), 1534 (s), 1450 (m), 1350 (w), 1280 (w), 834 (w), 792 (w). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.57–1.64 (m, 12 H), 1.82–1.91 (m, 6 H), 2.05–2.16 (m, 12 H), 2.50–2.71 (m, 24 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.5, 23.7, 24.3, 29.0, 29.1, 30.2, 30.8, 31.0, 31.2, 32.0, 32.3, 34.5, 34.6, 34.9, 93.7. EI-MS: m/z 686.2 (17.37%).

Tris(6-mercapto-4-thiahexanyl)nitromethane (19). The compound was prepared from 1,2-ethanedithiole and **16** in analogy to **8**. The residue was subjected to gradient column chromatography on silica (CH_2Cl_2 : hexane from 1 : 1 to 1 : 0). The compound was isolated as a colourless oil. Yield 63%. IR (KBr, cm^{-1}): 2922 (s), 2542 (m), 1532 (s), 1452 (s), 1426 (s), 1352 (s), 1268 (s), 1268 (s), 1208 (s), 1140 (m), 964 (m), 842 (m), 696 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.54–1.46 (m, 6 H), 1.79–1.75 (m, 3 H), 2.03–1.97 (m, 6 H), 2.56–2.51 (m, 6 H), 2.78–2.68 (m, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.6, 24.5, 31.6, 34.3, 36.1, 93.6. FAB-MS: m/z 463.3 (9%).

1,12-Dinitro-5,8,16,19,26,29-hexathiabicyclo[10.10.10]dotriacontane (20). The compound was prepared starting from **16** and **19** in analogy to **9**. Column chromatography over silica with CH_2Cl_2 as eluent yielded the product as a colourless oil that solidified upon standing. Yield 17%. IR (KBr, cm^{-1}): 2926 (m), 1534 (s), 1452 (m), 1350 (m) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.56–1.65 (m, 12 H), 2.08–2.14 (m, 12 H), 2.52–2.66 (m, 12 H), 2.72–2.82 (m, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 23.4, 24.2, 24.5, 31.8, 32.0, 32.4, 32.6, 32.7, 34.5, 35.0, 93.6. FAB-MS: m/z = 645.0 (8%).

1,5-Dibromo-3-(2-bromoethyl)pentane (22). To ice cooled 3-(2-hydroxyethyl)pentane-1,5-diol (**21**) (4.7 g, 31.7 mmol) PBr_3 (106.6 g, 37 ml) was slowly added. Then HBr (47%, 8 ml) was added to the mixture, which was stirred for 1 h at 0 °C, then 2 h at rt and finally 12 h at 100 °C. The mixture was diluted with water (300 ml) and neutralized with $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2. The organic phase was washed with water, dried with Na_2SO_4 and evaporated to dryness. The yellow oil was dried in high vacuum at 80 °C, whereby the nearly pure product was obtained. Yield 84% (9.03 g, 26.8 ml). IR (KBr, cm^{-1}): 2966 (s), 2932 (s), 1654 (m), 1560 (m), 1448 (s), 1260 (s), 1228 (s). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.89 (m, 7 H), 3.41 (t, J = 7.0, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 30.3, 34.7, 36.1. EI-MS: m/z 256.9 (58% M^+ − Br).

6-(5-Mercapto-3-thiapentanyl)-1,11-dimercapto-3,9-dithiaundecane (23). The compound was prepared from 1,2-ethanedithiol and **22** in analogy to **8**. The raw product was subjected to gradient column chromatography on silica (CH_2Cl_2 : hexane from 1 : 1 to 3 : 1). The compound was isolated as colourless oil. Yield 27%. IR (KBr, cm^{-1}): 3446 (w, br), 2916 (s), 2850 (m), 2538 (w), 1684 (w), 1654 (w), 1560 (w), 1424 (m), 1268 (m), 1208 (m), 1138 (m), 964 (w), 692 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.54–1.61 (m, 6 H), 1.68–1.78 (m, 4 H), 2.55 (t, J = 7.7 Hz, 6 H), 2.71–2.77 (m, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.7, 29.4, 33.1, 35.7, 36.3.

4,7,13,16,21,24-Hexathiabicyclo[8.8.8]hexacosane (24). The compound was prepared starting from **22** and **23** in analogy to **9**. Column chromatography over silica with CH_2Cl_2 as eluent yielded the product as a white, crystalline solid. Yield 20%. IR (KBr, cm^{-1}): 3446 (m, br), 2924 (s), 1684 (m), 1654 (m), 1636 (m), 1560 (m), 1436 (m), 1194 (m). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.55–1.78 (m, 14 H), 2.57–2.72 (m, 12 H), 2.79 (s, 6 H), 2.83 (s, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 27.5, 29.0, 30.1, 30.5, 30.7, 32.0, 32.1, 33.6, 33.8, 34.3, 35.0, 36.0, 37.6.

Table 1 Crystal data and structural refinement for the cages **9** and **11**

	9	**11**
Formula	$C_{19}H_{36}S_6$	$C_{19}H_{36}OS_6$
MW	456.84	472.84
Temperature/K	208(2)	293(2)
Wavelength/Å	1.54184	1.54184
Crystal	Monoclinic	Monoclinic
Space group	Cc	$P2(1)/c$
A/Å	9.432(1)	18.186(4)
b/Å	27.584(2)	26.587(4))
c/Å	9.901(1)	10.255(2)
α (°)	90	90
β (°)	114.26(1)	101.16(1)
γ (°)	90	90
Volume/Å^3	2348.5(4)	4864(1)
Z	4	8
Density calc./mg m^{-3}	1.292	1.291
Abs. coefficient/mm^{-1}	5.374	5.239
F(000)	984	2032
Crystal size/mm	0.15 × 0.15 × 0.15	0.30 × 0.20 × 0.15
Theta range/°	5.39–64.00	5.23–65.00
Index ranges	$-10 <= h <= 10$, $-2 <= k <= 32$, $-11 <= l <= 11$	$-21 <= h <= 21$, $-31 <= k <= 0$, $-1 <= l <= 12$
Reflections collected	4265	9737
Independent reflections	3831	8238
Absorption correction	None	psi scan
T_{max}/T_{min}	—	0.9000/0.5877
Refinement method	Full matrix	Full matrix
Goodness on F^2	0.931	0.997
Final R indices [$>I > 2$ sigma(I)]	0.0754/0.1989	0.0552/0.1378
R indices (all data)	0.0957/0.2235	0.0899/0.1604
Largest diff. peak and hole	0.428/–0.433	0.754/–0.331

Table 2 Crystal data and structural refinement for [Ag(**14**)]tosylate, [Ag(**24**)]triflate and [Ag(**18**)]triflate · $2CH_3CN$

	[Ag(**14**)]tosylate	[Ag(**24**)]triflate	[Ag(**18**)]triflate · $2CH_3CN$
Formula	$C_{29}H_{49}AgO_4S_7$	$C_{21}H_{38}AgF_3O_3S_7$	$C_{35}H_{60}Ag_2F_6O_{10}N_4S_8$
MW	793.97	727.80	1283.09
Temperature/K	208(2)	208(2)	208(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$C2/c$
A/Å	10.707(4)	10.3960(10)	21.614(8)
b/Å	17.737(4)	15.421(2)	13.491(2)
c/Å	19.081(8)	18.421(1)	18.364(8)
α/°	90	90	90
β/°	103.61(2)	90	109.70(2)
γ/°	90	90	90
Volume/Å^{-3}	3522(2)	2953.2(9)	5041(3)
Z	4	4	4
Density calc./mg m^{-3}	1.497	1.637	1.691
Abs. coefficient/mm^{-1}	1.020	1.219	1.185
F(000)	1656	1496	2616
Crystal size/mm^3	0.15 × 0.15 × 0.10	0.40 × 0.30 × 0.15	0.20 × 0.15 × 0.15
Theta range/°	3.02–24	3.24–26.49	3.02–26.96
Index ranges	$-1 <= h <= 12$, $0 <= k <= 20$, $-21 <= l <= 21$,	$0 <= h <= 13$, $0 <= k <= 19$, $-23 <= l <= 23$,	$-27 <= h <= 16$, $-15 <= k <= 17$, $-22 <= l <= 23$
Reflections collected	6398	6656	12148
Independent reflections	5419	6098	5466
Absorption correction	Difabs	Psi scan	Psi scan
T_{max}/T_{min}	1.000/0.8721	0.9552/0.9050	0.87360/0.75096
Refinement method	Full matrix	Full matrix	Full matrix
GoF	0.956	1.029	1.005
Final R indices [$I > 2\sigma(I)$]	0.0776/0.0755	0.0675/0.1353	0.0476/0.1055
R indices (all data)	0.3303/0.1173	0.1410/0.1668	0.1007/0.1235
Largest diff. peak and hole	0.534/–0.970	0.823/–0.759	1.488/–0.627

X-ray crystallographic study

X-ray crystal structure analyses were performed on CAD-4 Enraf Nonius diffractometers with Cu Kα (λ = 1.54184 Å) (compounds **9** and **11**) and Mo Kα radiation (λ = 0.71073 Å) ([Ag(**14**)]tosylate, [Ag(**24**)]triflate and [Ag(**18**)]triflate).

All structures were solved by direct methods using the program SHELXS-97 and refined using the program SHELXL-97.[16] The refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms except of two restrained C atoms in the structure of [Ag(**14**)]-tosylate. Hydrogen atom positions were included at idealized positions and treated by the 'riding model' option of SHELXL-97. Some disorder positions were considered in the refinement of the structures of compound **11** and [Ag(**18**)]triflate · $2CH_3CN$. More details about crystal data and the structure refinements are contained in Table 1 and Table 2.‡

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‡ CCDC reference numbers 292370–292372 and 633283 and 633284. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606510b

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