Synthesis of diazahexathia-24-crown-8 derivatives and structures of Ag+ complexes†

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Diazahexathia-24-crown-8 (**2**) has been isolated from the reaction mixture during the preparation of monoazatrithia-12-crown-4 (**1**). When *N*-Boc protected bis(2-chloroethyl)amine was employed as a starting material, *N*-Boc protected monoazatrithia-12-crown-4 (**3**) and *N*-Boc protected diazahexathia-24-crown-4 (**4**) were separated easily. Double-armed diazahexathia-24-crown-8 having two 3′,5′-dichlorobenzyl groups (**5a**) or two 2-phenylethyl groups (**5b**) were also prepared using reductive amination. The stoichiometry and detailed structures of the Ag+ complexes with **5a** and **5b** were investigated by ^{1}H NMR titration experiments and X-ray crystallography.
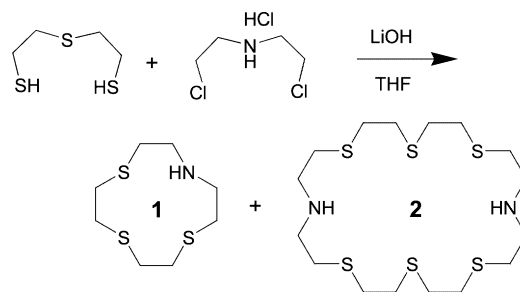
Introduction

Sulfur containing macrocyclic ligands are strong binding agents for transition metal ions. Many kinds of azathiacrown ethers have been prepared, and detailed complexation properties and structures of their complexes have been reported.[1] We have reported the syntheses of 4-hydroxybenzyl- and pyridylmethyl-armed azacrown ethers and cyclams in order to develop new armed-macrocyclic ligands capable of forming supramolecules with metal cations.[2] It will be possible to extend the chemistry of armed-azacrown ethers, when sulfur-containing macrocyclic ligands are used instead of the azacrown ethers. We decided to make the armed-azathiacrown ethers, and monoazatrithia-12-crown-4 ether (**1**) is required as a starting material for the new armed-thiacrown ethers. Ligand **1** was prepared as described.[1c] During this procedure, we also obtained diazahexathia-24-crown-8 ether (**2**) which has not been previously reported. Here, we report the preparation of ligand **2** and double-armed diazahexathia-24-crown-8 ethers (**5a** and **5b**), and the structures of Ag+ complexes with the new macrocyclic ligands.

Result and discussion

Synthesis of diazahexathia-24-crown-8 and double-armed diazahexathia-24-crown-8 ethers

According to the paper described by Tanaka *et al.*,[1c] bis(2-chloroethyl)amine hydrochloride was reacted with bis(2-mercaptoethyl)sulfide in the presence of LiOH in absolute THF to give two products (Scheme 1). The two products could not be separated by column chromatography (silica-gel and alumina) nor gel-

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of **3**, **4**, **5a** and **5b**; FAB-MS for AgOTf complexes with **5a** and **5b**; an ORTEP diagram of **3** (*N*-Boc-protected monoazatrithia-12-crown-4). See DOI: 10.1039/b513293b

Scheme 1

permeation (sephadex LH-20) chromatography. Recrystallization from heptane was a much better separatoin method giving three fractions, ligand **1** (4.8%), a mixture of **1** and **2** (21.6% estimated as **1**), and **2** (1.8%).

Fig. 1 shows ^{1}H NMR spectra for the ring protons of ligands **1**, **2** and a mixture of **1** and **2**. As shown in Fig. 1, the proton signals for the hydrogen atoms on carbons next to the S and N atoms for **1** and **2** are easily distinguished. In ligand **1** (Fig. 1a), the proton signals for the hydrogen atoms on carbons next to the S and N atoms appeared as a multiplet at 2.95–2.87 ppm and a triplet at 2.75 ppm. On the other hand, since the 24-membered ring is
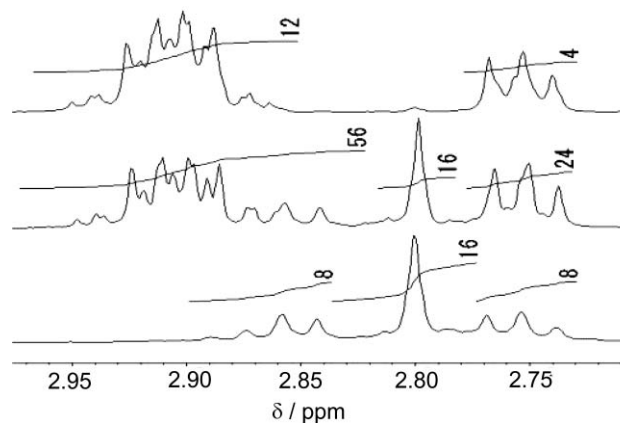

Fig. 1 ^{1}H NMR spectra of **1** (a), a mixture of **1** and **2** (b), and **2** (c) in CDCl$_3$.

more flexible than a 12-membered ring, ligand **2** gave more simple signals as shown in Fig. 1c. Signals for the methylene protons between the S and N atoms appeared at 2.86 and 2.75 ppm as two triplets, and signals for the methylene protons next to the S atoms appeared at 2.80 ppm as a singlet. From these ^{1}H NMR spectral data, the ratio of ligand **1** to ligand **2** in the mixture (Fig. 1b) was calculated to be 4 : 1.

Because the separation of ligands **1** and **2** is not efficient in the method described above, *tert*-butyloxycarbonyl-(Boc-) protected bis(2-chloroethyl)amine[1a] was used for the cyclization (Scheme 2). *N*-Boc-protected bis(2-chloroethyl)amine was treated with bis(2-mercaptoethyl)sulfide under the same conditions. In this reaction, *N*-Boc-protected monoazatrithia-12-crown-4 (**3**) and *N*,*N'*-diBoc-protected diazahexathia-24-crown-8 (**4**) were separated by silica-gel column chromatography and isolated in 16 and 6.5% yields, respectively. Edema *et al.* reported that octathia-24-crown-8 was prepared in a 74% yield using $CsCO_3$ as a template in DMF solution.[3] In order to increase the yield of ligand **4**, $CsCO_3$ was employed as a template in DMF solution under high-dilution conditions. However, in this case, ligand **3** was obtained in 4% yield and ligand **4** was not obtained at all. Deprotection of the Boc groups of **4** was carried out using CF_3COOH in dichloromethane to give **2** in 85% yield.
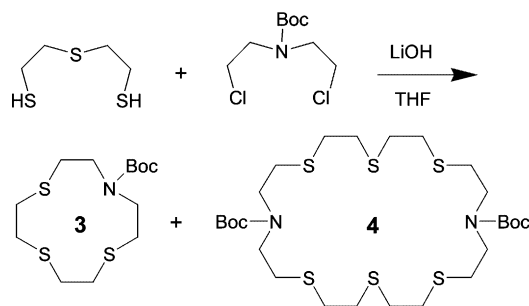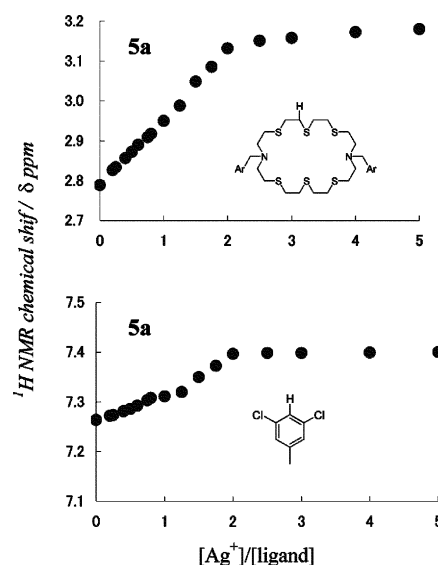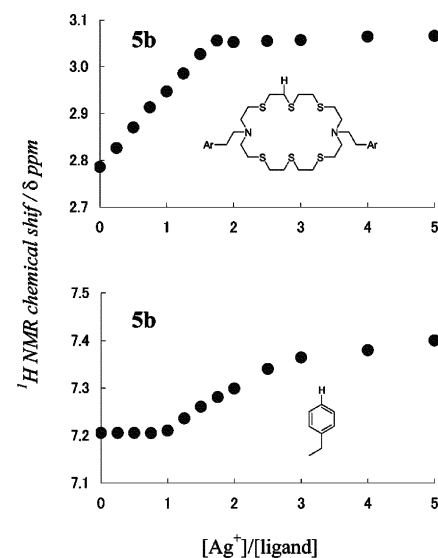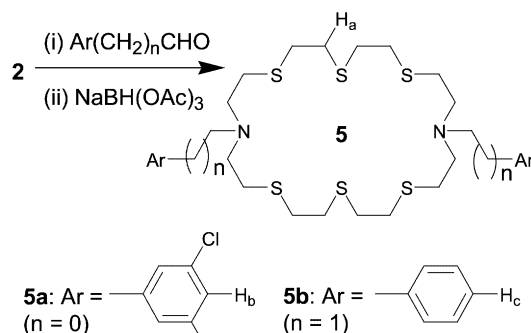
Scheme 2

Blake *et al.* reported that the Ag^+ complexes with octathia-24-crown-8 ([24]aneS$_8$) and octathia-28-crown-8 ([28]aneS$_8$) form a coordination polymer and a discrete 2 : 1 (Ag^+ : ligand) complex, respectively.[4] If side arms, which can cover the Ag^+ ions incorporated in the macrocyclic moiety, are introduced to the N atoms of ligand **2**, it is expected that polymerization such as that of the Ag^+–[24]aneS$_8$ system might be prevented and a discrete 2 : 1 (Ag^+ : ligand) complex would be formed. Therefore, double-armed diazahexathia-24-crown-4 having 3,5-dichlorobenzyl groups (**5a**) or 2-phenylethyl groups (**5b**), which are longer side-arms than **5a**, were prepared by the reductive amination of **4** with 3,5-dichlorobenzaldehyde and 2-phenylethanal, respectively.

Ag$^+$ ion induced ^{1}H NMR experiments

In order to investigate the molecular structure of the Ag^+ complexes of **5a** and **5b** in solution, ^{1}H NMR titration experiments were carried out in a mixture of CD_2Cl_2 and CD_3OD (1 : 1). Fig. 2 and 3 show the Ag^+ induced ^{1}H NMR chemical shift changes of the ring protons next to the S atoms (H$_a$ in Scheme 3) and the 4-protons of the aromatic side-arms (H$_b$ in Scheme 3). In both cases, the ring protons (H$_a$) have an inflection point at $[Ag^+]/[\text{ligand}] = 2.0$. Interestingly, the 4-proton of the aromatic

Fig. 2 ^{1}H NMR chemical shift change of **5a**.

Fig. 3 ^{1}H NMR chemical shift change of **5b**.

5a: Ar = (3,5-dichlorophenyl) —H$_b$
(n = 0)

5b: Ar = (phenyl) —H$_c$
(n = 1)

Scheme 3

ring in **5b** shows an unusual curve; the signal does not change till 1 : 1 ($[Ag^+]/[\text{ligand}]$), and then shows a gradual change, though the 4-proton (H$_b$) of the aromatic ring of **5a** has a distinct inflection point at $[Ag^+]/[\text{ligand}] = 2.0$. These titration experiments suggested

that (i) the stoichiometry of the interaction of Ag⁺ and both double-armed diazahexathia-24-crown-8 derivatives is 2 : 1 in CD$_2$Cl$_2$/CD$_3$OD solution, and (ii) the aromatic side-arms in **5b** may have a very weak interaction in solution.

Crystal structures of Ag⁺ complexes of 5a and 5b

The detailed structures of the Ag⁺ complexes of **5a** and **5b** have been determined by X-ray analysis at 90 K (Fig. 4 and 5, and Tables 1 and 2). These Ag⁺ complexes form 2 : 1 (Ag⁺:ligands) complexes as expected, and the Ag⁺ ions are placed in the cavity of the 24-membered ring in a very distorted trigonal-bipyramidal environment. In both complexes, three equatorial coordination sites and one axial position is taken up by three S atoms (Ag1–S; 2.4598(4)–2.5849(4) Å for **5a** and 2.4881(6)–2.5530(6) Å for **5b**) and an N atom (Ag1–N1; 2.5605(13) Å for **5a** and 2.5921(19) Å for **5b**), respectively. The second axial position of the trigonal-bipyramid is blocked by the Cl atoms in the side-arms (Ag1–Cl1 3.616 Å) in **5a**, while an S atom in the nearest-neighbor molecule coordinates to the second axial position (Ag1–S3** 3.009 Å) in **5b**.
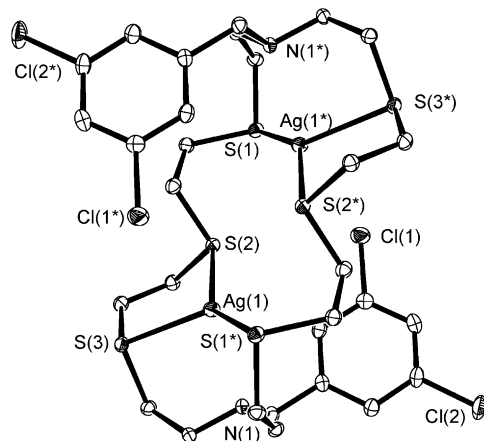

Fig. 4 Crystal structure of AgOTf complex of **5a**. Hydrogen atoms and non-coordinating anions are omitted. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 5 Crystal structure of AgOTf complex of **5b**. Hydrogen atoms and non-coordinating anions are omitted. Displacement ellipsoids are drawn at the 50% probability level.
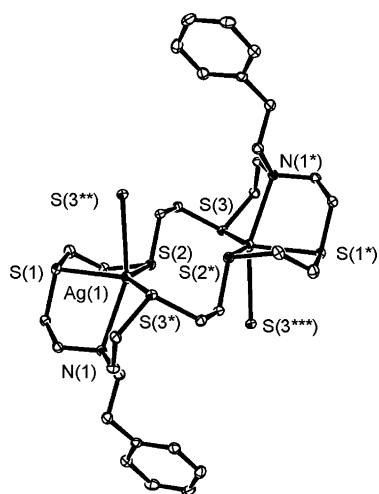
Table 1 Selected bond lengths (Å) and bond angles (°) of AgOTf complex of **5a**

Ag(1)–S(1*)	2.4598(4)	Ag(1)–N(1)	2.5605(13)
Ag(1)–S(2)	2.4927(4)	Ag(1)–Cl(1)	3.616
Ag(1)–S(3)	2.5849(4)	Ag(1)–Ag(1*)	4.591
S(1*)–Ag(1)–S(2)	144.798(14)	S(1*)–Ag(1)–S(3)	127.864(13)
S(1*)–Ag(1)–N(1)	81.82(3)	S(2)–Ag(1)–S(3)	86.336(13)
S(2)–Ag(1)–N(1)	115.30(3)	N(1)–Ag(1)–S(3)	81.79(3)

Symmetry transformations used to generate equivalent atoms: * −x, −y + 1, −z.

Table 2 Selected bond lengths (Å) and bond angles (°) of AgOTf complex of **5b**

Ag(1)–S(3*)	2.4881(6)	Ag(1)–N(1)	2. 5921(19)
Ag(1)–S(2)	2.5112(6)	Ag(1)–S(3*)	3.009
Ag(1)–S(1)	2.5530(6)	Ag(1)–Ag(1*)	4.706
S(3*)–Ag(1)–S(2)	142.241(19)	S(3*)–Ag(1)–S(1)	129.035(19)
S(3*)–Ag(1)–N(1)	80.60(4)	S(2)–Ag(1)–S(1)	88.695(18)
S(2)–Ag(1)–N(1)	108.96(4)	N(1)–Ag(1)–S(1)	79.66(4)

Symmetry transformations used to generate equivalent atoms: * −x + 2, −y, −z.

The data show that the longer side-arms of **5b** do not participate in coordination in the solid state. These results support the ¹H NMR titration experiments. The Ag(1)–Ag(1*) distances are 4.591 and 4.706 Å in **5a** and **5b**, respectively. Therefore there are no interactions between the Ag⁺ ions incorporated in the macrocyclic moieties.

Conclusions

Diazahexathia-24-crown-8 (**2**) was isolated as a by-product of the synthesis of azathia-12-crown-4. When *N*-Boc-protected bis(2-chloroethyl)amine is employed as a starting material, 12-membered crown ether (**3**) and 24-membered crown ether (**4**) were completely separated by column chromatography. Double-armed diazahexathia-24-crown-8 derivatives (**5a** and **5b**) were also prepared. Structures of the Ag⁺ complexes with **5a** and **5b** in solution and solid state were investigated by ¹H NMR and X-ray analysis. From these studies, it was found that **5a** and **5b** form 2 : 1 complexes with Ag⁺, and 3,5-dichlorobenzyl side-arms can block the Ag⁺ ion incorporated in the cavity, though the longer phenylethyl side-arms do not. Preparation of armed-monoazatrithia-12-crown-4 derivatives and the structures of their metal complexes will be published elsewhere.

Experimental

All melting points were obtained with a Mel-Temp capillary apparatus and are not corrected. ¹H NMR spectra were measured on a JEOL ECP400 spectrometer. FAB-MS spectra were recorded using a JEOL MS-600H spectrometer. Absolute THF was purchased from Kanto Chemical Co. Other starting materials were used as purchased.

Reaction of bis(2-chloroethyl)amine with bis(2-mercaptoethyl)sulfide

A mixture of bis(2-chloroethyl)amine hydrochloride[1a] (1.00 g, 5.60 mmol), bis(2-mercaptoethyl)slufide (0.86 g, 5.60 mmol) and lithium hydroxide monohydrate (1.38 g, 33.6 mmol) in THF (450 mL) was refluxed under a nitrogen atmosphere for 7 days. The reaction mixture was filtered and then concentrated *in vacuo*. The residue was extracted with chloroform twice and the extractant was washed with water. After drying over anhydrous sodium sulfate, the solvent was removed. The crude product was recrystallized from hexane and then heptane to give **1** (4.8%, 0.060 g), a 2 : 1 mixture of **1** and **2** (21.6%, 0.268 g estimated as **1**), and **2** (1.8%, 0.022 g).

Ligand 1. Mp 82.0–83.0 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 2.97–2.82 (m, 12H), 2.75 (t, $J = 5.5$ Hz, 4H), 1.60 (s, 1H); m/z (*m*-NBA as a matrix) 224 ([M + 1]$^+$, 100%).

Ligand 2. Mp. 83.5–84.0 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 2.86 (t, $J = 6.1$ Hz, 8H), 2.8 (s, 16H), 2.75 (t, $J = 6.1$ Hz, 8H), 1.58 (s, 1H); m/z (*m*-NBA as a matrix) 447 ([M + 1]$^+$, 100%); found: C, 43.01; H, 7.67; N, 6.27. C$_{16}$H$_{34}$N$_2$S$_6$ requires C, 43.32, H, 7.38, N, 6.23%.

Reaction of N-Boc-bis(2-chloroethyl)amine with 2-mercaptethylsulfide

N-Boc-bis(2-chloroethyl)amine (1.74 g, 7.22 mmol), bis(2-mercaptoethyl)sulfide (1.01 g, 6.50 mmol) and lithium hydroxide (1.82 g, 43.4 mmol) in THF (400 mL) was refluxed under a nitrogen atmosphere for 7 days. The reaction mixture was purified by column chromatography on silica-gel (gradient elution method: ethylacetate–hexane = 1 : 20, 1 : 5, and then 1 : 4) to give *N*-Boc-protected macrocycles **3** and **4** in 16% (0.338 g) and 6.5% (0.138 g) yields, respectively.

Macrocycle 3. Mp (decomp.) > 141 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 3.46 (s, 4H), 2.74–2.79 (m, 12H), 1.45 (s, 9H); m/z (*m*-NBA as a matrix) 324 ([M + 1]$^+$, 50%); Found: C, 48.13; H, 7.59; N, 3.79. C$_{13}$H$_{25}$NO$_2$S$_3$ requires C, 48.26; H, 7.79; N, 4.33%.

Macrocycle 4. Mp (decomp.) > 95 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 3.43 (s, 8H), 2.70–2.86 (m, 24H), 1.46 (s, 18H); m/z (*m*-NBA as a matrix) 647 ([M + 1]$^+$, 5%); Found: C, 47.75; H, 7.51; N, 3.46. C$_{26}$H$_{50}$N$_2$O$_4$S$_6$H$_2$O requres C, 47.60; H, 7.84; N, 4.27%. The combustion analysis for **3** and **4** have been carried out twice for different batches of product, and all analytical data were almost the same. The observed contents of nitrogen in the *N*-Boc-protected azathiacrown ethers were less than the calculated values, because these compounds are not stable. Combustion analysis was not carried out for *N*-Boc protected monoazatetrathia-16-crown-6 in the previous paper.[4]

Removing the Boc groups from 3 and 4

N-Boc-protected azathiacrown ethers, **3** (0.104 mmol) or **4** (0.212 mmol), were dissolved in 40%-CF$_3$COOH in dichloromethane (50 mL). After the mixture was stirred at room temperature for 10 min and the solvent was removed *in vacuo*, methanol (30 mL) was added to the residue and evaporated. The procedure was repeated twice. To the residual oils, chloroform (50 mL) was added and the organic layer was washed with saturated aqueous NaHCO$_3$ solution and water. The chloroform layer was dried over Na$_2$SO$_4$ and concentrated to give **1** (88%, 0.021 g) or **2** (84%, 0.089 g).

N,N′-Bis(3′,5′-dichlorobenzyl)diazahexathia-24-crown-8 (5a)

After a mixture of 3,5-dichlorobenzaldehyde (0.260 g, 1.50 mmol) and **2** (0.219 g, 0.50 mmol) in dry 1,2-dichloroethane (10 mL) was stirred at room temperature for 1 day under a nitrogen atmosphere, triacetoxysodium borohydride (0.424 g, 2.00 mmol) and 1,2-dichloroethane (10 mL) were added and the mixture was stirred at room temperature for 3 days. Saturated aqueous Na$_2$CO$_3$ was added and the aqueous layer was extracted with chloroform (3 × 20 mL). The combined organic layers were washed with water, dried over Na$_2$SO$_4$, and concentrated. The residual oil was recrystallized from chloroform–acetonitrile to give **5a** in 52% (0.199 g). Mp 129.5–130.0 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 7.31 (d, $J = 1.70$ Hz, 4H), 7.26 (t, $J = 1.70$ Hz, 2H), 3.59 (s, 4H), 2.85–2.76 (m, 16H), 2.76–2.65 (m, 16H); m/z (*m*-NBA as a matrix): 765 ([M + 1]$^+$, 20%). Found: C, 46.97; H, 5.81; N, 3.23. C$_{30}$H$_{42}$N$_2$S$_6$Cl$_4$ requires C, 47.11; H, 5.53; N, 3.66%.

N,N′-Bis(2′-phenylethyl)diazahexathia-24-crown-8 (5b)

The preparation procedure was the same as that used for **5a**. Yield 55% (0.180 g); mp 67.0–68.0 °C; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 7.31–7.16 (m, 10H), 2.84–2.71 (m, 32H), 2.64 (t, $J = 6.8$ Hz, 8H); m/z (F*m*-NBA as a matrix) 655 ([M + 1]$^+$, 100%). Found: C, 58.44; H, 7.48; N, 4.11. C$_{32}$H$_{50}$N$_2$S$_6$ requires C, 58.66; H, 7.69; N, 4.28%.

Preparation of AgOTf complexes

AgOTf (0.03 mmol) in acetonitrile (1 mL) was treated with host (0.01 mmol) in acetonitrile (1 mL). After the solvent had evaporated, the crystals were obtained to give the AgOTf complex quantitatively.

AgOTf complex of 5a. Mp (decomp.) 150.0–150.6 °C; Found. C, 29.91; H, 3.36; N, 2.21. C$_{32}$H$_{42}$N$_2$F$_6$O$_6$S$_8$Cl$_4$Ag$_2$ requires C, 30.06; H, 3.31; N, 2.19%; m/z (*m*-NBA as a matrix) 1279 ([M + 2Ag + 2OTf]$^+$), 1128 ([M + 2Ag + OTf]$^+$), 1021 ([M + Ag + OTf]$^+$), 978 ([M + 2Ag]$^+$), 871 ([M + Ag]$^+$).

AgOTf complex of 5b. Mp (decomp.) 140.0–144.0 °C; Found. C, 34.85; H, 4.61; N, 2.26. C$_{34}$H$_{50}$N$_2$F$_6$O$_6$S$_8$Ag$_2$ requires C, 34.93; H, 4.31; N, 2.40%; m/z (*m*-NBA as a matrix) 1276 ([M + 3Ag + 2OTf]$^+$), 1019 ([M + 2Ag + OTf]$^+$), 869 ([M + 2Ag]$^+$), 763 ([M + Ag]$^+$).

¹H NMR titration experiments

Titration experiments were carried out by addition of 0.1–5.0 equivalents of AgOTf in a mixture of CD$_2$Cl$_2$–CD$_3$OD (1 : 1) (0.002 mmol µL^{-1}) to **5a** or **5b** in a mixture of CD$_2$Cl$_2$–C$_3$OD (1 : 1) (0.02 mmol per 0.65 mL) at 298 K.

X-Ray structure determination

The crystals of the AgOTf complexes of **5a** and **5b** were mounted on the top of a glass fiber, and the data collections were carried out on Bruker SMART CCD area diffractometer at 90 K. Data

Table 3 Crystal data and structural determination details

Compound	**5a**-AgOTf	**5b**-AgOTf	**3**
Formula	$C_{32}H_{42}Ag_2Cl_4F_6N_2O_6S_8$	$C_{34}H_{50}Ag_2F_6N_2O_6S_8$	$C_{13}H_{25}NO_2S_3$
M	1278.70	1168.98	323.52
T/K	90	90	90
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
$a/Å$	8.4064(5)	6.4971(3)	21.1574(13)
$b/Å$	10.4171(6)	17.1739(9)	8.5512(6)
$c/Å$	13.9910(8)	19.2924(10)	9.2467(6)
$\alpha/°$	70.3250(19)		
$\beta/°$	81.8880(10)	90.8450(10)	98.9910(10)
$\gamma/°$	13.9910(8)		
$U/Å^3$	1129.33(11)	2152.42(19)	1652.37(19)
Z	1	2	4
$D_c/\text{g cm}^{-3}$	1.880	1.804	1.300
μ/mm^{-1}	1.543	1.370	0.447
Reflections collected	8419	15693	12033
Unique reflections, R_{int}	5518, 0.0118	5327, 0.0409	4115, 0.0272
Absorption correction	SADABS	SADABS	SADABS
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0216$, $wR_2 = 0.0574$	$R_1 = 0.0274$, $wR_2 = 0.0615$	$R_1 = 0.0369$, $wR_2 = 0.0937$
R indices (all data)	$R_1 = 0.0231$, $wR_2 = 0.0581$	$R_1 = 0.0402$, $wR_2 = 0.0667$	$R_1 = 0.0458$, $wR_2 = 0.1053$
T_{min}, T_{max}	0.847, −0.379	0.978, −0.423	0.784, −0.434

were corrected for Lorentz and polarization effects and absorption corrections were applied with the SADABS program.[5] Structures were solved by direct method and subsequent difference-Fourier syntheses using the program SHELXTL[6]. All non-hydrogen atoms were refined anisotropically and H atoms were placed at calculated positions and thereafter refined with $U_{iso}(H) = 1.2U_{eq}(C)$. Table 3 shows the crystal data and structural determination details.

CCDC reference numbers 284338–284340.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513293b

References

1 (*a*) H. O. Davies, J. R. Dilworth, D. V. Griffiths, J. R. Miller and Y. Zheng, *Polyhedron*, 1999, **18**, 459; (*b*) L. G. A. van de Water, Hoonte, W. L. F. Driessen, J. Reedijk and D. C. Sherrington, *Inorg. Chim. Acta*, 2000, **303**, 77; (*c*) M. Tanaka, M. Nakamura, T. Ikeda, K. Ikeda, H. Ando, Y. Shibutani, S. Yajima and K. Kimura, *J. Org. Chem.*, 2001, **66**, 7008; (*d*) L. G. A. van de Water, W. Buijs, W. L. Driessen and J. Reedijk, *New J. Chem.*, 2001, **25**, 243; (*e*) M. Tanaka, T. Ikeda, Q. Xu, H. Ando, Y. Shibutani, M. Nakamura, H. Sakamoto, S. Yajima and K. Kimura, *J. Org. Chem.*, 2002, **67**, 2223; (*f*) C. Caltagirone, A. Bencini, F. Demartin, A. Devillanova, A. Garau, F. Isaia, V. Lippolis, P. Mariani, U. Papke, L. Tei and G. Verani, *Dalton Trans.*, 2003, 901.
2 (*a*) Y. Habata and S. Akabori, *J. Chem. Soc., Dalton Trans.*, 1996, 3871; (*b*) Y. Habata, T. Saeki, A. Wanatabe and S. Akabori, *J. Heterocycl. Chem.*, 1999, **36**, 355; (*c*) Y. Habata, T. Saeki, S. Akabori, X. X. Zhang and J. S. Bradshaw, *Chem. Commun.*, 2000, 1469; (*d*) Y. Habata, T. Saeki, S. Akabori, X. X. Zhang and J. S. Bradshaw, *J. Heterocycl. Chem.*, 2001, **38**, 253; (*e*) Y. Habata and S. Akabori, *J. Heterocycl. Chem.*, 2001, **38**, 471; (*f*) Y. Habata, T. Saeki and S. Akabori, *J. Heterocycl. Chem.*, 2001, **38**, 585; (*g*) Y. Habata, Y. Yamashita and S. Akabori, *J. Chem. Soc., Dalton Trans.*, 2001, 966; (*h*) Y. Habata, S. Akabori, X. X. Zhang, R. M. Izatt and J. S. Bradshaw, *J. Heterocycl. Chem.*, 2001, **38**, 1329; (*i*) Y. Habata and S. Yamada, *J. Inclusion Phenom. Macrocyclic Chem.*, 2004, **49**, 17.
3 J. J. H. Edema, J. Buter and M. Kellogg, *Tetrahedron*, 1994, **50**, 2095.
4 A. J. Blake, W. Li, V. Loppolis, A. Taylor and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1998, 2931.
5 G. M. Sheldrick, *Program for adsorption correction of area detector frames*, Bruker AXS Inc, Madison, WI, USA, 1996.
6 *SHELXTL*™*, version 5.1*, Bruker AXS Inc., Madison, WI, USA, 1997.