Alkylation of the S–C–S linkage. Towards lipophilic monoand ditopic heavy-metal receptors containing trithiane building blocks. Molecular structure of *cis*-2,4,6-tribenzyl-1,3,5-trithiane

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Abstract. Reaction of 1,3,5-trithiane with BuLi in THF at -50° C, followed by reaction with an equivalent amount of alkyl halide [*n*-hexyl (a), benzyl (b), *n*-dodecyl (c)] affords the corresponding lipophilic alkyl trithianes in moderate to good yields (25–75%). Reactions with xylylene dibromides (*ortho, meta, para*) proceeded analogously to afford potentially ditopic ligands in reasonable overall yields (30–50%). Alkylation of 1,3,5-trithiane with excess alkyl halide results in the stereoselective formation of all-*cis* di- or trisubstituted trithianes.

Investigation of the complexation behavior of these alkylated trithianes with Ag⁺ was done by means of conductometric titrations of AgO₃SCF₃ in MeCN and THF. The molecular structure of 2,4,6-tribenzyl-1,3,5-trithiane (**4b**) has been determined by X-ray crystallography. Crystal data for **4b**: trigonal, space group R-3 with a = b = 13.2287(7), c = 20.9177(2) Å, Z = 6, R = 0.030 ($R_w = 0.034$) for 1564 reflections.

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Introduction

Cyclic thioether ligands constitute a useful class of complexing agents for a variety of soft, heavy-metal ions^{1,2} and a few heavy-main-group elements. In this respect, these ligands may have important environmental and medicinal perspectives³. For instance extraction of harmful metal ions by means of complexation to thio-crown ethers may be used for the treatment of heavy-metal poisoning.

The complexation behavior of thiocrown ethers, however, strongly depends on ring size, flexibility, and most importantly, the conformational preorganization in solution⁴ (to a lesser extent the conformation in the solid state).

Thiocrown ethers are usually built up from S-C-C-S units (sometimes S-C-C-C-S) which gives rise, with few exceptions⁵, to the attainment of all-anti conformation for the sulfur atoms⁶. This all-anti arrangement causes the ligating sites to be directed exterior to the macrocyclic ring. As a result the effectiveness of the crown ether decreases because of the lack of preorganization.

In order to control the conformational preorganization of the thio-crown ethers, attempts have been undertaken to incorporate rigid building blocks in the molecular periphery of the *meso* (macro) cycle⁷. Important in this respect is the possibility to functionalize selectively the thio-crown ether and to control its solubility and complexation properties.

A prototype 'thio-crown ether' that can be selectively functionalized is 1,3,5-trithiane. In this case the three sulfur atoms are forced in an all-*cis* orientation imposed by rigid methylene units⁸, resulting in an overall chair

conformation of the trithiane ring. Furthermore, an advantage of this thioacetal is the fact that alkylation of the active methylene groups with a suitable electrophile⁹ (Eqn. 1) can be accomplished readily.

$$\begin{array}{c} \mathbf{R}_{1} & \mathbf{S} \\ \mathbf{R}_{2} & \mathbf{S} \end{array} \overset{H}{\xrightarrow{H}} \qquad \begin{array}{c} \mathbf{1} & \mathsf{Buli} \\ \mathbf{2} & \mathsf{RX} \end{array} \overset{R}{\xrightarrow{R_{1}}} \overset{R}{\xrightarrow{R_{1}}} \overset{R}{\xrightarrow{R_{2}}} \overset{R}{\xrightarrow{R_{1}}} \overset{R$$

In this paper, we describe the selective and stepwise alkylation of 1,3,5-trithiane with RX [R = n-hexyl (a), benzyl (b), *n*-dodecyl (c)] with an eye towards lipophilic and polyfunctionalized monotopic and ditopic heavy-metal receptors¹⁰.

Results and discussion

Parent 1,3,5-trithiane is poorly soluble in common organic solvents. However, via alkylation, its physical properties, *e.g.* solubility, can be progressively varied. In order to prepare derivatives that are better soluble we have alkylated⁹ 1,3,5-trithiane with RX [$\mathbf{R} = n$ -hexyl (**a**), benzyl (**b**) and *n*-dodecyl (**c**)]. 1,3,5-Trithiane is alkylated, as illustrated in Scheme 1, by quenching of the *in-situ* prepared 2-lithio derivative with a suitable alkyl halide. The best results have been obtained when the reaction was carried out in THF.

The second and third alkylations of 1,3,5-trithiane are accomplished easily by application of essentially the same method⁹ as was used for the preparation of **2a-c**. The



yields of the various substituted trithianes are compiled in Table I.

The alkylations proceed in high stereospecificity as is clear from the ¹H-NMR and ¹³C-NMR data. In all the cases, the cis isomers were obtained as the main product (>95%). Even for the trisubstituted compounds only traces of *trans* isomer were present in the final product. This phenomenon has been explained by a higher stability of the equatorial anion; for example H/D exchange occurs most readily at the equatorial position^{9d.e.}. In order to establish unambiguously the stereochemistry of the trisubstituted trithianes we determined the X-ray structure of 4b. The molecule is highly symmetry and possesses a threefold (C_3) axis (Figure 1). The three benzyl substituents are equatorially placed on the rigid trithiane skeleton and the S atoms are, due to the non-flexible methylene spacers, all-cis in the chair conformation of the six-membered ring $[C1b-S1-C1-S1b = -65.65(8)^\circ, S1 C1-S1b = 114.35(7)^{\circ}$]. The C-S bond distance [C1-S1 =1.8112(12) Å] is normal and compares well with the distances found in related trithianes⁸.

Trisubstituted trithianes have been prepared alternatively by a three-fold condensation¹⁴ of aldehydes with H_2S . However, in addition to lower yields, mixtures of the various isomers are formed (Eqn. 2) that are difficult to separate by crystallization or chromatography.



Conductometric titration¹¹ experiments with a MeCN solution of AgO₃SCF₃ and the various trithianes indicate similar coordination profiles with Ag⁺. In Figure 2, the molar conductivity (λ_m) is plotted against the molar ratio [L]/[Ag⁺] [L(igand) = **2b**, **3b**, **4b**]. In agreement with results obtained¹² for unsubstituted 1,3,5-trithiane, the effect of addition of ligand on the conductivity of the AgO₃SCF₃ solution is small. The diagram shows a series of rather shallow curved lines indicating a relatively weak coordination of the three benzyl derivatives in MeCN. This is reinforced by the fact that the relative drop of the molar conductivity is small, meaning that the mobility of

Table I Yields of alkyl-substituted trithianes (%).

R	2	3	4
n-hexyl (a)	82	36	76
benzyl (b)	86	59	54
n-dodecyl (c)	55	77	79



Figure 1. PLUTON plot of **4b** Selected bond distance (Å) and angles (°). C1-S1 = 1.8112(12), C1b-S1-C1-S1b = 65.65(8), S1-C1-S1b = 114.35(7). (b refers to atoms adjacent to the numbered segment S1, C2, etc. This unit is repeated three times in the trithiane ring).

the complexed Ag^+ ion is only slightly lowered relative to the free ion. **2b** appears to be less effective than the more bulky **3b** and **4b**. Although steric factors might control the effectiveness of the ligand, the metal coordination seems not to be affected dramatically by an increase of the bulkiness.

No clear breaks are present in the diagram that can suggest the formation of discrete $Ag^+(L)_n$ species. These ligands fail to compete effectively with MeCN¹³ for the Ag^+ ions.

Variation of the substituents on the trithiane ring only slightly affects the complexation properties of the ligands. Comparison of the titration curves of the **4a**, **4b** and *cis*-2,4,6-trimethyl-1,3,5-trithiane (**6a**) shows the trihexyl derivative **4a** to work most effectively (Figure 3). Most likely, the lowered mobility of the Ag^+ (**4a**) complex is reflected in the steeper drop of A_m .

A major disadvantage encountered thus far in the trithiane approach is the relatively weak complexation of this system to heavy metal ions. The extreme rigidity of the trithiane skeleton prevents efficient "wrapping around" the metal. Although S³-bonded trithianes are known¹⁵, trithiane usually works as an unidentate or bridging ligand. In order to prepare trithiane-based receptors that are able to encapsulate a metal ion, we employed xylylene dibromide as alkylating agent (Eqn. 3).



Figure 2. Plot of the molar conductivity (Λ_m) versus ratio $[L] / [AgCF_3SO_3]; L = 2b$ (°), 3b (\triangle), 4b (\Box).





The synthesis of the ditopic trithianes **5a-c** (Figure 4) is straightforward; essentially the same methodology was employed as for the synthesis of **2a-c**. In these systems various orientations of the trithiane rings are possible. The presence of the two basket-like coordination sites might be, in principle, suitable for a twofold complexation of metal ion.

In contrast to the monoalkylated trithianes, bistrithianes **5a-c** are poorly soluble in MeCN. The conductometric titrations have been carried out in THF to circumvent this problem. A schematic diagram of $\Lambda_m vs$. the molar ratio $[L]/[Ag^+(X)^-]$ (X = CF₃SO₃, L = **5a**, c) produces curved lines with shallow minima at ratio $[L]/[Ag^+(X)^-]$ that may be attributed to formation of Ag(L)⁺ species, probably with an $\{Ag_2(L)\}^{2+}$ core. The bistrithianes **5a**, c do not differ strongly in their coordination properties as is indicated by the diagram.

The smooth increase of Λ_m observed for AgCF₃SO₃ within the range [L]/[Ag⁺] = 0.5-2.0 (Figure 5) indicates, furthermore, a weak complexation of **5a** and **5c** with AgCF₃SO₃ in THF is most likely due to the orientation of the two trithiane moieties within the molecule. The two pendant trithiane moieties do not act as chelating ligands probably due to the fact that an energetically unfavorable conformational rearrangement is necessary to attain a chelate structure. Therefore, **5a** and **5c** resemble simple monoalkylated trithianes in their coordination properties. The shallow lines may be furthermore indicative of a less efficient competition with solvent molecules¹³ relative to more flexible thiocrown ethers^{2,7d}.

However, the *meta* derivative **5b** behaves as desired as is clear from the conductometry diagram. Initially, no significant effect is monitored. At ratio $[L]/[AgCF_3SO_3] = 0.5$ a sudden increase of Λ_m is seen which stops roughly at a ratio $[L]/[AgCF_3SO_3] = 1$. The sigmoid behavior strongly suggests an equilibrium between an $\{Ag_2(CF_3SO_3)_2(L)\}^{2+}$ and an $\{Ag(L)\}^+$ species (Eqn. 4). This furthermore sug-



Figure 3. Plot of the molar conductivity versus ratio $[L]/[AgCF_3SO_3]$; $L = 4a (\Box), 4b (\Delta), 6a (\circ).$

gests that the orientation of the trithiane moieties in **5b** is suitable for the encapsulation of an Ag^+ ion.



Further work on the chemistry of trithiane-based heavy metal receptors is in progress and will be the subject of forthcoming articles.

Experimental

1,3,5-Trithiane and organic halides were purchased from Aldrich and used as received. Solvents were dried and distilled according to standard procedures prior to use. All reactions were carried out under inert atmosphere (N₂). The alkylations of 1,3,5-trithiane were carried out following a slightly adapted literature procedure⁸. ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian 200-MHz spectrometer. Infrared data were obtained from a Perkin-Elmer 781 spectrometer at 70 eV. Conductometric experiments were performed in HPLC-UV-grade MeCN or THF (Janssen Chimica) according to literature methods¹¹ with a Philips platinum electrode PW 9512/01 and a Wayne Kerr Autobalance Universal Bridge B642.

Preparation of 2-hexyl-1,3,5-trithiane (2a) (typical example)

A suspension of 1,3,5-trithiane (2.60 g, 18.7 mmol) in 100 ml of THF was cooled to -40° C. Subsequently, 11.8 ml BuLi (1.6 M) was added dropwise to the solution. The temperature was kept between -40 and -25° C. The solution was allowed to reach room temperature and stirring was continued for 45 min. The solution was cooled again to -20° C and 1-bromohexane (3.2 g, 19 mmol) was added during 45





Figure 5. Plot of λ_m versus ratio $[L] / [AgCF_3SO_3]$; $L = 5\mathbf{a} (\Box)$, $5\mathbf{b} (\Delta)$, $5\mathbf{c} (\diamond)$, $2\mathbf{b} (\circ)$.

min. The solution was warmed gradually to room temperature and the stirring was continued for 16 h. The mixture was treated with 50 ml of water and extracted with CHCl₃ (3×75 ml). The organic layer was separated and dried with MgSO₄. The solid residue obtained after evaporation of the organic solvent was recrystallized from CHCl₃/pentane (250 ml) yielding needle-shaped colorless crystals (m.p. 60-62°C); yield 2.9 mmol, 15.5%. IR (KBr, cm⁻¹): 2954 m, 1732 w, 1699 m, 1674 m, 1390 w, 1374 m, 1099 s, 905 m. Mass spectrum, m/e^+ (rel.int.%): 223.91(8.5), 222.88(7.6), 221.81(57.0), 139.90(13.5), 138.90(6.5), 137.89(100), 136.91(10.6), 91.98(37.7), 90.93(13.1), 87.04(27.1). Exact mass (m/e⁺) calcd. for C₉H₁₈S₃: 222.057; found: 222.057.

2b: M.p. 99–100.5°C. ¹H NMR (CDCl₃): 3.12 (d, 2H), 4.11 (AB system, 4H), 4.43 (t, 1H), 7.30 (m, 5H). ¹³C NMR (CDCl₃): 35.46 (t), 36.34 (t), 42.12 (t), 52.27 (d), 127.27 (d), 128.46 (d), 129.37 (d), 136.11 (q). IR (KBr, cm⁻¹): 3465, 2964 1451, 1384, 1220, 730, 695. Mass spectrum, m/e^+ (rel.int.%): 229.87(3.1), 228.86(2.9), 227.82(20.5), 137.91(30.3), 136.91(100), 90.93(34.9). Exact Mass (m/e^+) calcd. for C₁₀H₁₂S₃: 228.010; found 228.011.

2c. M.². 68–68.5°C. ¹H NMR (CDCl₃): 0.88 (t, 3H), 1.26 (s, 18H), 1.52 (m, 2H), 1.79 (m, 2H), 4.14 (s) + 4.18 (dd, AB system, total 4H), 4.22 (t, 1H). ¹³C NMR (CDCl₃): 14.09 (q), 22.65 (t), 29.13 (t), 29.47 (t), 31.88 (t), 35.42 (t), 35.69 (t), 35.89 (t), 36.27 (t), 51.43 (d), 53.20 (d). IR (KBr, cm⁻¹) 2918 s, 2851 m, 1466 m, 1376 w, 1179 m, 904 m, 721 w. Mass spectrum, m/e^+ (rel.int.%): 307.90(1.27), 306.90(1.45), 305.85(6.87), 258.90(2.26), 229.01(1.99), 227.02(1.63), 214.04(1.18), 213.03(2.26), 139.74(13.74), 137.93(100). Exact mass (m/e) calcd. for C₁₅H₃₀S₃: 306.151 found: 306.151.

Preparation of 2,4-dihexyl-1,3,5-trithiane (3a) (typical example)

A suspension of 1,3,5-trithiane (2.60 g, 18.7 mmol) in 100 ml of THF was cooled to -40° C. Subsequently, 11.8 ml BuLi (1.6 M) was added dropwise to the solution. The temperature was kept between -40 and -25° C. The solution was allowed to reach room temperature and stirring was continued for 45 min. The solution was cooled again to -20° C and 1-bromohexane (3.2 g, 19 mmol) was added during 30 min. The solution was warmed gradually to room temperature and the stirring was continued for 1 h. The mixture was again cooled to -50° C and 11.8 ml BuLi (1.6 M) was added dropwise to the solution. The temperature was kept at -40° C. The solution was allowed to reach room temperature and stirring was continued for 60 min. The solution was cooled again to -10° C and the second portion of 1-bromohexane (3.2 g, 19 mmol) was added during 30 min. The mixture was treated with 50 ml of water and extracted with CHCl₃

Table III Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of **4b**.

Atom	x	у	Z	$U(eq)(\mathring{A}^2)$
S (1)	0.35801(2)	0.54780(2)	0.02574(1)	0.0238(1)
C(1)	0.46412(10)	0.68905(10)	0.05751(6)	0.0212(3)
C(2)	0.58777(10)	0.71168(11)	0.04359(6)	0.0245(3)
<i>C</i> (3)	0.67578(10)	0.80380(11)	0.08801(6)	0.0227(3)
<i>C</i> (4)	0.75431(11)	0.91602(11)	0.06737(6)	0.0279(3)
C(5)	0.83107(11)	0.99958(12)	0.11030(7)	0.0333(4)
C(6)	0.82957(12)	0.97155(12)	0.17406(7)	0.0326(4)
C(7)	0.75233(11)	0.85958(12)	0.19480(6)	0.0296(4)
C(8)	0.67608(11)	0.77612(11)	0.15233(6)	0.0261(3)

 $(3 \times 75 \text{ m})$. The organic layer was separated and dried with MgSO₄. The solid residue obtained after evaporation of the solvent was recrystallized from CHCl₃/pentane yielding needle-shaped crystals; m.p. 78–79.5°C; yield 2.9 mmol, 36%. Mass spectrum, m/e^+ (rel.int.%): 308.92(2.2), 307.90(11.3), 306.89(14.5), 305.86(72.5), 258.85(28.1), 240.90(39.5), 212.95(36.0), 137.89(33.7), 136.86(37), 100.94(35.4), 87.00(64.5). Exact mass (m/e^+) calcd. for C₂₇H₅₄S₄: 306.151; found: 306.151.

3b: M.p. 92–92.5°C. ¹H NMR (CDCl₃): 3.12 (m, 4H), 4.04 (AB system, 2H), 4.39 (t, 2H), 7.30 (m, 5H). ¹³C NMR (CDCl₃): 37.31 (t), 41.86 (t), 54.00 (d), 127.25 (d), 128.43 (d), 129.39 (d), 136.26 (q). IR (KBr, cm⁻¹): 3028 m, 2918 m, 2864 m, 1600 w, 1585 m, 1492 s, 1446 s, 1435 s, 1187 m, 1029 m, 944 m, 766 m, 763 s, 741 s, 696 s. Mass spectrum (m/e⁺ (rel.int. %): 317.91(7.64), 316.88(5.3), 226.88(86.9), 149.01(51.5), 136.06(56.3), 134.80(57.0), 122.93(23.5), 104.06(27.8), 90.99(100), 90.86(15.7). Exact mass (m/e⁺) calcd. for $C_{17}H_{18}S_3$: 318.057 found: 318.057.

3c. M.p. 78–79.5°C. ¹H NMR (CDCl₃): 0.86 (t, 6H), 1.27 (m, 36H), 1.53 (m, 4H), 1.81 (t, 4H), 3.9–4.4 (m, 2H). ¹³C NMR (CDCl₃): 14.10 (q), 22.68 (t), 29.33 (t), 29.50 (t), 29.62 (t), 31.91 (t), 35.45 (t), 35.71 (t), 53.24 (d). IR (KBr, cm⁻¹): 2916 s, 2850 m, 1461 m, 1373 w, 1175 m, 908 m, 720 w. Mass spectrum, m/e^+ (rel. int. %): 467.85(2.0), 475.91(7.0), 474.88(12.5), 473.84(36.3), 408.93(77.3), 212.92(48.83), 86.99(49.2), 68.98(45.6). Exact mass (m/e^+) calcd. for $C_{27}H_{54}S_3$: 474.399; found: 474.339.

4a: $46-47^{\circ}$ C, ¹H NMR (CDCl₃): 0.89 (t, 9H) 1.29 (m, 18H) 1.57(m, 6H) 1.87 (m, 3H) 4.13 (t, 3H). ¹³C NMR (CDCl₃): 14.05 (q) 22.57 (t) 26.26 (t) 29.08 (t) 31.46 (t) 35.60 (t) 53.98 (d). IR (KBr, cm⁻¹): 2928 s, 2852 m, 1465 m, 1377 w, 1191 m, 904 m, 772 w, 723 m. Mass spectrum m/e^+ (rel.int. %): 391.92(4.7), 390.89(7.5), 389.84(28.9), 325.03(52.4), 129.93(57.8), 128.96(87.8), 97.07(30.3), 87.02(57.0). Exact mass (m/e^+) calcd. for $C_{21}H_{42}S_3$: 390.245; found: 390.245.

act mass (m/e^+) calcd. for $C_{21}H_{42}S_3$: 390.245; found: 390.245. **4b.** M.p. 164–165°C. ¹H NMR (CDCl₃): 3.12 (d, 6H), 4.25 (t, 3H), 7.28 (m, 15H). ¹³C NMR (CDCl₃) 41.51 (t), 54.56 (d), 127.13 (d), 128.37 (d), 129.45 (d), 136.40 (d). IR (KBr, cm⁻¹): 3026 m, 2914 m, 2867 m, 1601 w, 1585 m, 1493 s, 1449 s, 1436 s, 1189 m, 1028 m, 943 m, 765 s, 740 s, 699 s, 658 m. Mass spectrum, m/e^+ (rel.int. %): 408.80 (0.8), 407.80 (3.0), 316.81 (42.9), 135.98 (100), 143.92(91.3), 90.95(89.5). Exact Mass (m/e^+) calcd. for $C_{23}H_{18}S_3$: 408.104; found: 408.104.

4c. M.p. 53–53.5°C. ¹H NMR (CDCl₃): 0.89 (t, 9H), 1.24 (s, 54H), 1.55 (m, 6H), 1.86 (m, 6H), 4.12 (t, 3H). ¹³C NMR (CDCl₃): 14.09 (q), 22.66 (t), 26.30 9t), 26.05 (t), 29.32 (t), 29.49 (t), 29.61 (t), 31.89 (t), 35.43 (t), 35.70 (t), 53.92 9d). IR (KBr, cm⁻¹): 2917 s, 2825 s, 1464 m, 1376 m, 1195 s, 774 w, 721 m. Mass spectrum, m/e^+ (rel.int. %): 743.94 (5.0), 742.95 (8.4), 641.95(16.9), 579.04(10.3), 578.05(33.2), 577.06(71.6), 397.02(31.7), 395.02(24.0), 215.00(41.5), 213.99(38.9), 212.987(90.1), 100.94(32.3), 87.00(50.7). Exact mass (m/e^+) calcd. for $C_{39}H_{78}S_3$: 642.527; found: 642.527.

Table IV [Selected] bond distances (\mathring{A}) and bond angles (°) for 4b.

S(1)-C(1)	1.8112(12)	C(3)-C(8)	1.3949(18)
S(1)-C(1)b	1.8133(19)	C(4)–C(5)	1.392(2)
C(1) - C(2)	1.536(2)	C(5)-C(6)	1.382(2)
C(2) - C(3)	1.5117(18)	C(6)–C(7)	1.383(2)
C(3)-C(4)	1.3882(18)	C(7)–C(8)	1.3827(19)
C(1)-S(1)-C(1)b	99.97(6)	C(4)C(3)-C(8)	118.81(12)
S(1)-C(1)-C(2)	109.39(9)	C(3)-C(4)-C(5)	120.49(12)
S(1)-C(1)-S(1)a	114.35(7)	C(4)-C(5)-C(6)	120.18(13)
S(1)a-C(1)-C(2)	108.24(8)	C(5)-C(6)-C(7)	119.60(13)
C(1)-C(2)-C(3)	110.88(11)	C(6)-C(7)-C(8)	120.46(12)
C(2)-C(3)-C(4)	122.26(11)	C(3)-C(8)-C(7)	120.45(12)
C(2)-C(3)-C(8)	118.91(11)		

5a. M.p. 144–145.5°C. ¹H NMR (CDCl₃): 3.12 (d, 4H), 4.13 (AB system, 8H), 4.45 (t, 2H), 7.26 (s, 4H). ¹³C NMR (CDCl₃): 36.53 (t), 38.78 (t), 52.06 (d), 127.38 (d), 130.66 (d), 134.84 (q). IR (KBr, cm⁻¹): 2969 m, 2913 w, 2886 w, 1694 m, 1490 m, 1448 w, 1428 m, 1383 m, 1216 m, 766 m, 730 s. Exact mass (m/e^+) calcd. for $C_{14}H_{18}S_6$ 377.973: found: 377.972.

5b. M.p. 146.5–147.5°C. ¹H NMR (CDCl₃): 3.05 (d, 4H), 4.12 (AB system, 8H), 4.42 (t, 2H), 7.14 (m, 3H), 7.27 (s, 1H). ¹³C NMR (CDCl₃): 36.31 (t), 42.01 (t), 52.17 (d), 128.24 (d), 128.44 (d), 128.52 (d), 130.45 (d), 136.30 (q). IR (KBr, cm⁻¹): 2908 m, 2882 w, 1634 m, 1383 m, 1221 m, 1192 m, 733 s, 721 s, 699 s. Mass spectrum m/e^+ (rel. int. %): 379.68(1.9), 378.68(1.5), 377.69(6.5), 160.98(4.7), 138.89(13.5), 137.89(5.6), 136.91(100), 90.88(8.2). Exact mass (m/e^+) calcd. for C₁₄H₁₈S₆: 377.973 found: 377.973.

5c. Mass spectrum; m/e^+ (rel.int. %): 379.94(0.53), 377.94(1.95), 239.97(1.06), 239.00(2.22), 194.05(1.42), 193.04(1.42), 181.97(1.77), 179.01(0.44), 159.96(2.13), 147.05(7.09), 136.97(32.36). Exact mass (m/e^+) calcd. for C₁₄H₁₈S₆: 377.973; found: 377.973.

X-ray data collection and refinement

X-ray data for 4b. A colorless, block-shaped crystal (0.3 \times 0.8×0.9 mm), was glued to the tip of a glass fiber and transferred to an ENRAF-NONIUS CAD4 Turbo diffractometer on rotating anode. Accurate cell parameters and an orientation matrix were determined by least-squares refinement of 25 well centered reflections (SET4) in the range $11.5^{\circ} < \Theta < 13.8^{\circ}$ C. The unit-cell parameters were checked for the presence of higher lattice symmetry¹⁶. Crystal data and details on data collection and refinement are given in Table III. Data were collected at 150K in $\omega/2\Theta$ mode with scan angle w = 0.89 + 0.35. tan(Θ°). Intensity data of 3549 reflections were collected in the range $2.0^{\circ} < \Theta < 27.5^{\circ}$, of which 1631 are independent. Data were corrected for $L_{\rm p}$ effects. Three periodically measured reference reflections (7 5 3, 2 -1 -7, 4 -5 -2) showed no significant linear decay (<1%) during 8 h of X-ray exposure time. Standard deviations of the intensities, as obtained by counting statistics, were increased according to an analysis of the excess variance of the reference reflections¹⁷: $\sigma^2(I) = [\sigma_{cs}^2(I) + 0.01, I]^2$. An empirical absorption/extinction correction was applied (DIFABS¹⁸, correction range 0.853–1.167). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92¹⁹). Refinement on F was carried out by full-matrix least-squares techniques (SHELX76²⁰). Hydrogen atoms were included in the refinement at calculated positions $(C-H = 0.98 \text{ \AA})$ riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; H atoms were refinement with one overall isotropic thermal parameter of 0.00333(14) Å². Weights were introduced in the final refinement cycles. Convergence was reached at R = 0.030, $R_w = 0.034$, $w = 1/\sigma^2(F)$, S = 1.46, for 83 parameters and 1564 reflections with $I > 2.5.\sigma(I)$. A final difference Fourier map showed no residual electron density: -0.24 and 0.29 e. Å⁻³. Neutral-atom scattering factors were taken from Cromer and Mann²¹, anomalous-dispersion corrections from Cromer and Liberman²². Geometrical calculations and illustrations were performed with PLATON²³. All calculations were performed on a DEC station 5000/125. Positional parameters are listed in Table IV.

Supplementary material available. Tables listing crystal structure data, structure factors, atomic positional parameters, anisotropic parameters, and complete bond distances for 4b (8 pages). Ordering information is given on any current masterhead page.

Conductometric measurements

In order to obtain information about the stoichiometry of the complexes in solution, the following procedures were used: The conductometry cell was charged with approximately 5.0-5.2 g of a solution of AgCF₃SO₃ in MeCN or THF (taken from a well-defined stock solution (1.018 mM)). This solution was titrated with a solution of the ligand in the same solvent. Care was taken to add maximally 0.5 ml ligand solution during the titration. The maximum dilution was calculated to be 7.8%.

Conductivities were measured at fixed temperature [25.0(1)°C] and the corresponding molar conductivities were computed. If complexation were restricted to certain discrete stoichiometries, an abrupt change of slope in the conductivity plot is to be expected. In MeCN, Onsager plots could be obtained for AgCF₃SO₃. According to Onsagers equation a limiting molar conductivity (Λ_{lim}) of 202.0(1) S. cm⁻¹ was measured for AgCF₃SO₃ in MeCN. For evaluation on the Onsager plots the values of *a* and *b* were taken from Ref. 11b. The molar conductivity of MeCN was determined to be sufficiently low (4.7. w⁻⁷ S. cm⁻¹).

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