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The First Sandwich Complex with an Octa(thioether) Coordination Sphere: Bis(maleonitrile-tetrathia-12-crown-4)silver(I)

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Dedicated to Professor Eberhard Hoyer on the occasion of his 75th birthday

Keywords: Crown compounds / S ligands / Sandwich complexes / Silver

The new tetrathiacrown ethers maleonitrile-tetrathia-12-crown-4 (mn12S_4) and maleonitrile-tetrathia-13-crown-4 (mn13S_4) have been prepared and characterised by X-ray crystallographic analysis. These crown ethers form 2:1, 3:2 and 1:1 complexes with AgY (Y = BF_4, PF_6). The crystal structures of $[Ag(mn12S_4)_2]BF_4$ (**3a**), $[Ag(mn13S_4)_2]BF_4$ (**4a**) and $[Ag_2(mn13S_4)_3](PF_6)_2$ (**6b**) have been determined. Compound **3a** contains the centrosymmetric sandwich complex cation $[Ag(mn12S_4)_2]^+$ where each mn12S_4 ligand is coordinated to the Ag centre in an *endo* manner through all four S atoms. The 2:1 complex $[Ag(mn12S_4)_2]^+$ is the first sandwich complex with a tetrathiacrown ether and the first complex with an octa(thioether) coordination sphere. The crystal structure of compound **4a** also reveals a 2:1 complex. This complex, $[Ag(mn13S_4)_2]^+$, exhibits a half-sandwich structure. One mn13S_4 ligand coordinates to Ag^+ by all four S donor atoms and the other 13S_4 crown by only one S atom. Compound **6b** contains a dinuclear Ag complex. The Ag complexes **3a**,**b**–**8a**,**b** were also studied by electrospray ionisation mass spectrometry. Collision-induced dissociation (CID) was used to compare the relative stability of 2:1 complexes $[AgL_2]^+$ and 1:1 complexes $[AgL]^+$ (L = mn12S_4, mn13S_4). The ^{13}C NMR chemical shifts of 2:1 and 1:1 Ag complexes and their corresponding free ligands were also estimated and compared. The free energy of the barrier of ring inversion ($\Delta G^{\ddagger}$) for $[Ag(mn12S_4)_2]^+$ was determined to be 64 kJ mol^{-1}.

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Introduction

The classical crown ether, 12-crown-4 (12O_4), forms sandwich complexes with a number of metal ions.[1] In these complexes, for example $[Na(12O_4)_2]Cl\cdot 5H_2O$,[2] $[Mn(12O_4)_2][Br_3]_2$,[3] $[Li(12O_4)_2][PPh_2]$,[4] $[Ag(12O_4)_2][AsF_6]$,[5] $[Fe(12O_4)_2][PF_6]_2$,[6] $[In(12O_4)][SbCl_6]\cdot 3CH_3CN$,[7] and $[Zn(12O_4)_2][ZnCl_3H_2O]_2$,[8] the metal ion is coordinated to eight oxygen atoms to form an octa(oxygen) coordination sphere which is not accessible with acyclic ligands. In early studies of crown ether chemistry the structures of bis(12-crown-4)–metal ion sandwich complexes and the properties of the coordinated metal ions were of interest. Later, the ability of 12-crown-4 to coordinate metal ions in sandwich structures was used to separate cations from carbanions in an organometallic compound, such as in the substituted cyclopentadienide salt $[Li(12\text{-crown-}4)_2][1,2,4\text{-}(Me_3Si)_3\text{-}C_5H_2]$,[9] to stabilize salts, such as $[Na(12O_4)_2][\{(CO)_5Mo\}_2Sn(Cl)_2]$,[10] to synthesise new inorganic polymers, such as $[Cd(12O_4)_2][Cd_2(SCN)_6]$,[11] and to construct novel molecular conductors from supramolecular cations.[12] 12-Crown-4 generally forms sandwich complexes because its cavity (1.2–1.4 Å[13]) is too small to accommodate the metal ion. Moreover, free 12-crown-4 is already preorganized for the formation of sandwich complexes. The global minimum of 12-crown-4 has been shown to be the so-called "square" conformation, which has four identical *gauche*,*gauche*,*anti* conformations for the individual O–C–C–O groups. 12-Crown-4 also adopts a "square" conformation in the solid state.[14] In this conformation all four oxygen atoms are orientated in an endodentate fashion,[15] which is perfect for a sandwich structure.[16]

The cavities of the analogous tetrathia-12-crown-4[17] (12S_4) and tetraaza-12-crown-4[18] (12N_4H_4) are also too small to accommodate a metal ion, although so far there are no known sandwich complexes with these tetradentate macrocycles. In the case of tetrathia-12-crown-4, this is because of the exodentate orientation of all four sulfur atoms in the free ligand.[17]

For the synthesis of sandwich complexes with tetradentate S_4- or N_4-crown ether compounds, preorganized derivatives are necessary. With the help of 2,11-diaza[3.3](2,6)-

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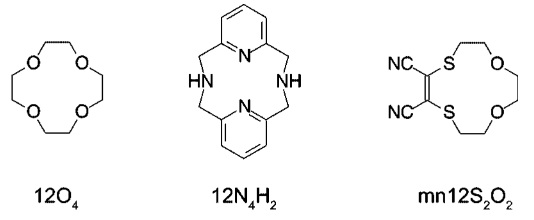
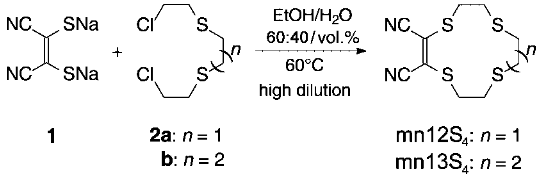
pyridinophane ($12N_4H_2$, Scheme 1), Krüger et al. have synthesised Fe^{II},[19a] Fe^{III}[19a] and Co^{II}[19b] sandwich-like complexes with N_8 coordination spheres. The rigid pyridinophane $12N_4H_2$ is a preorganized macrocyclic N_4 ligand that forces a metal ion in a sandwich complex to have a coordination number of eight.



Scheme 1. Tetradentate macrocycles for 2:1 complexes (macrocycle/metal ion) with coordination number eight: 12-crown-4 ($12O_4$), 2,11-diaza[3.3](2,6)pyridinophane ($12N_4H_2$), maleonitrile-dithia-12-crown-4 ($mn12S_2O_2$).

Approaches to the preorganisation of twelve-membered S_4 macrocycles for sandwich complexation have, until now, not been carried out. However, tetrathiacrown ethers with larger cavities, for example with thirteen and fourteen members, have been modified at their periphery with different groups (cyclohexyl, phenyl, methyl, benzo, hydroxy) to preorganize the macrocyclic ligands for the "in-cavity" complexation.[20]

Previously, we have found that 1,4-dithiacrown ethers are stabilized in endodentate conformations by incorporating the rigid maleonitrile unit between the two sulfur atoms. The resulting maleonitrile-dithiacrown ethers[21] are preorganized S_2O_n coronands (n = 2–5) for the complexation of Ag^+,[22a,22b,23a] Tl^+,[22c] Cs^+,[21c] Na^+,[22d] $HgCl_2$,[22c,23b] and MCl_3 (M = Sb, Bi)[22d] in "in-cavity" sandwich or half-sandwich structures with mixed ether/thioether coordination spheres. The twelve-membered maleonitrile-dithia-12-crown-4 ($mn12S_2O_2$, Scheme 1) forms a sandwich complex $[Ag(mn12S_2O_2)_2]^+$ with Ag^+.[22a] The overall environment surrounding Ag^I in $[Ag(mn12S_2O_2)_2]^+$ is that of a distorted cubic S_4O_4 set of donors. In this paper we report on the synthesis of the maleonitrile-tetrathiacrown ethers $mn12S_4$ and $mn13S_4$ (Scheme 2). These new tetrathiacrown ethers are preorganized S_4 macrocycles for the preparation of sandwich and half-sandwich complexes. Maleonitrile-tetrathia-12-crown-4 ($mn12S_4$) forms the sandwich complex $[Ag(mn12S_4)_2]^+$ with Ag^I, which is the first complex with an octa(thioether) coordination sphere.



Scheme 2. Synthesis of the maleonitrile-tetrathiacrown ethers $mn12S_4$ and $mn13S_4$.

Results and Discussion

Using the high-dilution technique, the maleonitrile-tetrathiacrown ethers $mn12S_4$ and $mn13S_4$ were obtained by treating disodium 1,2-dicyanoethene-1,2-dithiolate[24] (**1**) with 1,8-dichloro-3,6-dithiaoctane[25] (**2a**) and 1,9-dichloro-3,7-dithianonane[25] (**2b**), respectively, in ethanol/water solution (Scheme 2). The dichlorides **2a** and **2b** were prepared by chlorination of the corresponding diols with $SOCl_2$ in $CHCl_3$ and were cyclized with the dithiolate **1** without isolation.

The crystal structures of the two new tetrathiacrown ethers were obtained by X-ray crystallographic analysis; details of data collection and refinement are given in the Experimental Section. The crystal structure of $mn12S_4$ is shown in Figure 1 from two different views. The rigid maleonitrile fragment forces the orientation of the sulfur atoms

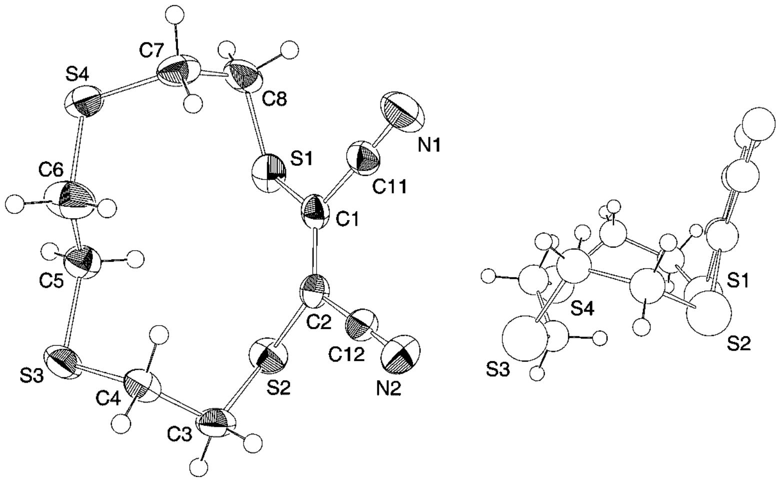


Figure 1. T7o different views of the molecular structure of maleonitrile-tetrathiacrown ether $mn12S_4$. Selected torsion angles [°] of free $mn12S_4$ and of coordinated $mn12S_4$ (in square brackets) in $[Ag(mn12S_4)_2]^+$ (Figure 3): S1–C1–C2–S2 1.68(18) [–0.7(3)], C1–C2–S2–C3 –135.65(12) [–137.37(19)], C2–S2–C3–C4 71.47(12) [65.8(19)], S2–C3–C4–S3 69.07(13) [69.2(2)], C3–C4–S3–C5 –92.51(12) [–162.59(17)], C4–S3–C5–C6 –67.56(15) [61.2(2)], S3–C5–C6–S4 –176.83(10) [64.8(2)], C5–C6–S4–C7 –106.43(10) [–151,46(19)], C6–S4–C7–C8 104.79(13) [148.49(19)], S4–C7–C8–S1 –68.65(14) [–66.4(2)], C7–C8–S1–C1 –68.38(13) [–57.7(2)], C8–S1–C1–C2 150.33(13) [139.36(19)].

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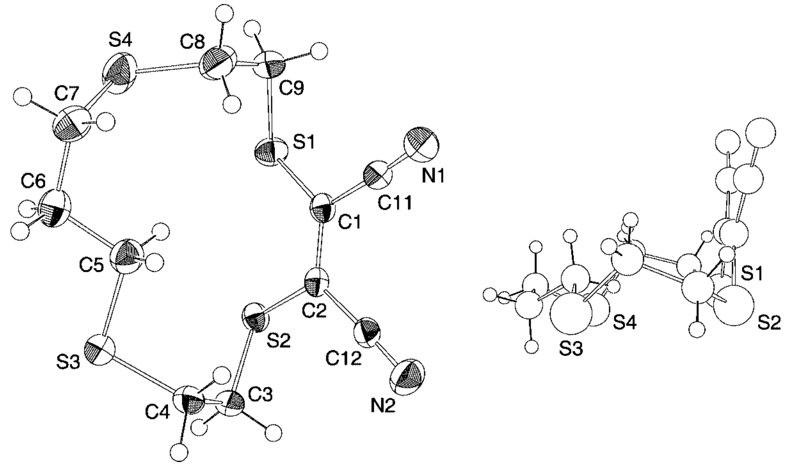


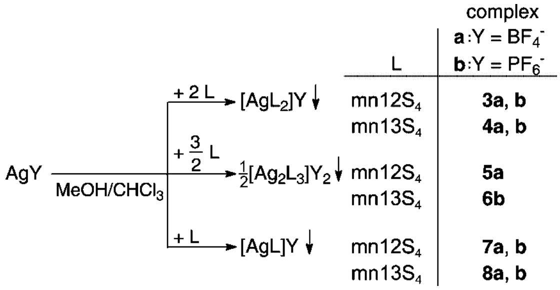
Figure 2. Two different views of the molecular structure of maleonitrile-tetrathiacrown ether mn13S$_4$. Selected torsion angles [°] of free mn13S$_4$ and of coordinated mn13S$_4$ (in square brackets) in the half-sandwich complex [Ag(mn13S$_4$){mn13S$_4$(A)-κ^1-S4A}]$^+$: S1–C1–C2–S2 –2.2(3) [–2.0(2)], C1–C2–S2–C3 –148.29(19) [–146.12(17)], C2–S2–C3–C4 61.8(2) [62.76(18)], S2–C3–C4–S3 61.8(2) [65.93(19)], C3–C4–S3–C5 –101.7(2) [–162.76(16)], C4–S3–C5–C6 –169.01(19) [76.69(19)], S3–C5–C6–C7 –174.14(19) [88.1(2)], C5–C6–C7–S4 67.9(3) [–92.8(2)], C6–C7–S4–C8 –107.1(2) [–73.67(19)], C7–S4–C8–C9 148.76(19) [163.15(16)], S4–C8–C9–S1 –67.5(2) [–62.9(2)], C8–C9–S1–C1 –71.8(2) [–62.67(19)], C9–S1–C1–C2 157.60(19) [145.28(17)].

S1 and S2 toward the macrocyclic ring centre (endodentate orientation). Sulfur atom S4 is in a half endo-/half exodentate position, while S3 is fully exodentate.

The preferred conformers of both mn12S$_4$ and mn13S$_4$ were also studied by molecular modelling in the gas state.[26] Two of the three most stable conformations of mn12S$_4$ show orientations for the S-donor atoms as observed in the crystal structure. In conclusion, both the results of the X-ray crystallographic analysis and of the molecular modelling reveal that free mn12S$_4$ adopts preferred conformations in which three of the four S donor atoms are already in an endodentate orientation. Similar positions for the sulfur atoms were also observed in free mn13S$_4$; in the corresponding crystal structure (see Figure 2), S1, S2 and S3 proved to be orientated in an endodentate fashion, and only S4 is exodentate.

Ag^I complexes of the studied tetrathiacrown ethers were obtained by mixing a solution of the crown ether in chloroform with a methanolic solution of AgBF$_4$ or AgPF$_6$. The macrocycles and silver salts were allowed to react in 2:1, 3:2 and 1:1 molar ratios, yielding the Ag^I complexes of corresponding compositions (**3a**,**b**–**8a**,**b**; Scheme 3). The IR spectra of these new Ag^I complexes show the typical ligand and anion bands (see Experimental Section); there is no hint of a coordination of the nitrile groups or anions to the silver cation. Therefore, the silver ions in compounds **3a**,**b**–**8a**,**b** should only be coordinated by the S atoms of the ligands. The crystal structures of the compounds [Ag(mn12S$_4$)$_2$]BF$_4$ (**3a**), [Ag(mn13S$_4$)$_2$]BF$_4$ (**4a**) and [Ag$_2$(mn13S$_4$)$_3$](PF$_6$)$_2$ (**6b**) were determined by X-ray crystallographic analysis; the corresponding data are summarised in the Experimental Section.

Compound **3a** contains the centrosymmetric complex cation [Ag(mn12S$_4$)$_2$]$^+$, with Ag^I sandwiched between the two mn12S$_4$ molecules. Each mn12S$_4$ ligand is coordinated to the Ag^I centre in an *endo* manner through all four S atoms. Two tetradentate mn12S$_4$ macrocycles force the Ag^I centre to have a closed octa(thioether) coordination sphere. The S$_8$ set of donors exhibits a distorted cubic geometry. The Ag–S bond lengths in the centrosymmetric cation [Ag(mn12S$_4$)$_2$]$^+$ are of different lengths, with four of them being shorter [2.5861(7), 2.7804(6) Å] than the other ones [3.2664(7), 3.2137(7) Å]. This kind of gradation is typical of Ag^I complexes with S$_8$ coordination spheres. For example, in the centrosymmetrical sandwich complex bis(tetraethylcyclotetraarsathiane)silver(I) [Ag{*cyclo*-(C$_2$H$_5$AsS)$_4$}$_2$]$^+$, four Ag–S distances are short [2.716(7), 2.767(5) Å] and four long [3.218(6), 3.328(9) Å].[27] Also, in the recently synthesised complex bis(η^4-cyclooctasulfur)silver(I) [Ag(η^4-S$_8$)$_2$]$^+$, four Ag–S distances are shorter (2.68–2.99 Å) than the other four (3.20–3.31 Å).[28] In the three complexes [Ag(mn12S$_4$)$_2$]$^+$, [Ag{*cyclo*-(C$_2$H$_5$AsS)$_4$}$_2$]$^+$ and [Ag(η^4-S$_8$)$_2$]$^+$ the four short Ag–S distances lie in a plane.



Scheme 3. Synthesis of the Ag^I complexes.

In the sandwich complex [Ag(mn12S$_4$)$_2$]$^+$, the Ag$^+$ ion is located 1.6543(4) Å above the best least-squares plane of the four mn12S$_4$ S atoms. The sandwich complexation of the Ag$^+$ ion by two mn12S$_4$ molecules is possible because the Ag$^+$ ion cannot be accommodated in the cavity of a single crown mn12S$_4$ (1.0–1.25 Å). Moreover, the free mn12S$_4$ S atoms already assume orientations which should be favourable for sandwich complexation. This expectation is confirmed by similar conformations of the free and coordinated mn12S_4 in the solid state. A comparative conformation analysis reveals only distinct differences for the $C(4)H_2$–S3–$C(5)H_2$–$C(6)H_2$ group, namely *a*, g^- and *a* in the free and g^-, g^- and g^- in the coordinated ligand (see caption of Figure 3). The bis(maleonitrile-tetrathia-12-crown-4)silver(I) complex is the first sandwich complex with a tetrathiacrown ether and the first complex with an octa(thioether) coordination sphere.

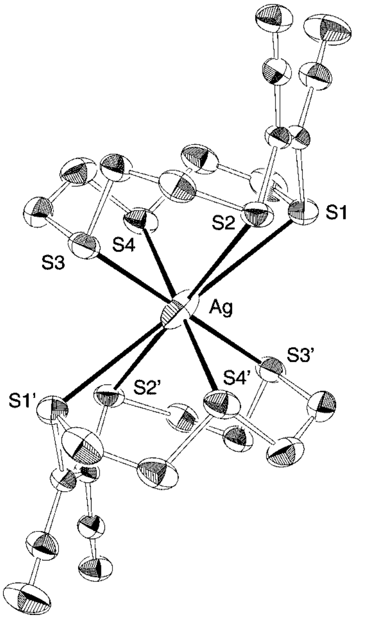


Figure 3. Molecular structure of the sandwich complex cation $[Ag(mn12S_4)_2]^+$ in compound **3a**. Selected bond lengths [Å]: Ag–S1 3.2664(7), Ag–S2 3.2137(7), Ag–S3 2.5861(7), Ag–S4 2.7804(6). For selected torsion angles see caption of Figure 1.

The crystal structure of $[Ag(mn13S_4)_2]BF_4$ (**4a**) reveals a 2:1 complex of the thirteen-membered maleontrile-tetrathia-13-crown-4 with silver(I) (Figure 4). As opposed to the sandwich complex $[Ag(mn12S_4)_2]^+$, the $[Ag(mn13S_4)_2]^+$ complex exhibits only a half-sandwich structure. One mn13S_4 ligand coordinates silver(I) by all four S-donor atoms and the other mn13S_4 molecule by only one S atom, resulting in an overall S_5 environment around Ag^I with a distorted square-pyramidal coordination geometry. The Ag–S bond lengths [2.5020(5)–2.9475(6) Å] are normal for penta(thioether)-coordinated Ag^+ ions (2.550–2.995 Å[29]). In the present complex the Ag^I is located only 0.9881(3) Å above the best least-squares plane of the fourfold-coordinated mn13S_4, which means that the Ag^+ ion dips markedly into the mn13S_4 cavity and more than half of its coordination sphere is already shielded. Thus, the second mn13S_4 ligand in this complex can only act as a monodentate ligand. The mn13S_4 cavity (1.3–1.45 Å) is too large to form a sandwich complex with silver(I), so the twelve-membered homolog mn12S_4 is the only one with the right cavity dimensions for preparing sandwich complexes.

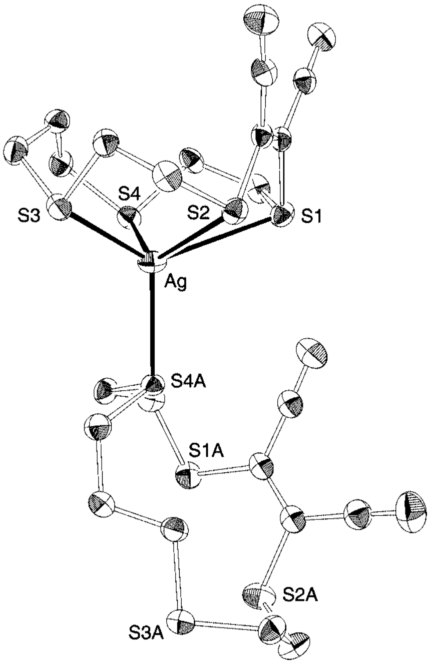


Figure 4. Molecular structure of the half-sandwich complex $[Ag(mn13S_4)\{mn13S_4(A)\text{-}\kappa^1\text{-}S4A\}]^+$ in compound **4a**. Selected bond lengths [Å]: Ag–S1 2.9475(6), Ag–S2 2.8100(6), Ag–S3 2.5508(6), Ag–S4 2.5647(6), Ag–S4A 2.5020(5). For selected torsion angles of the fourfold coordinated mn13S_4 molecule see the caption of Figure 2.

$[Ag_2(mn13S_4)_3](PF_6)_2$ (**6b**) contains the dinuclear Ag^I complex $[\{Ag1(mn13S_4)\}\{Ag2[mn13S_4(B)]\}\{\mu_2\text{-}mn13S_4\text{-}(A)\text{-}\kappa^1\text{-}S4A,\text{-}\kappa^1\text{-}S3A\}]$ (see Figure 5). The two half-sandwich moieties $[Ag1(mn13S_4)]^+$ and $[Ag2\{mn13S_4(B)\}]^+$ are connected by the third mn13S_4 molecule through the S atoms S4A and S3A. Both Ag^I centres therefore have a distorted square-pyramidal coordination geometry, as was already observed for the Ag^I centre in the complex $[Ag(mn13S_4)_2]^+$.

Electrospray ionisation was used to study the complexes **3a**,**b**, **4a**,**b**, **7a**,**b** and **8a**,**b**. Both $[AgL_2]^+$ and $[AgL]^+$ complexes are observed in the mass spectra with different intensities (see Table 1). The loss of the anions (PF_6^- and BF_4^-) seems to be the dominant ionisation process.[30] Additionally, the mn12S_4 and mn13S_4 ligands form 3:2 complexes **5a** and **6b** but with very low ion intensities (total ion current < 50 counts) in the mass spectra.

Collision-induced dissociation (CID) measurements were carried out to compare the relative stability of the $[AgL_2]Y$ and $[AgL]Y$ complexes. The $[AgL_2]Y$ complexes decompose easily by the elimination of one ligand ion. Increasing the collisional energy lowers the relative abundance of the peak of the $[AgL_2]^+$ complex ion, but raises the relative abundance of the peak of the $[AgL]^+$ complex ion. The collision voltage was gradually increased until the relative intensity of the 1:1 complex ion as well as that of the 2:1 complex ion was only 50%: the collision voltages thus obtained give an estimate of the dissociation energies of the corresponding complexes, which are generally higher for the $[AgL]^+$ complexes (22–25 eV) than for the corresponding $[AgL_2]^+$

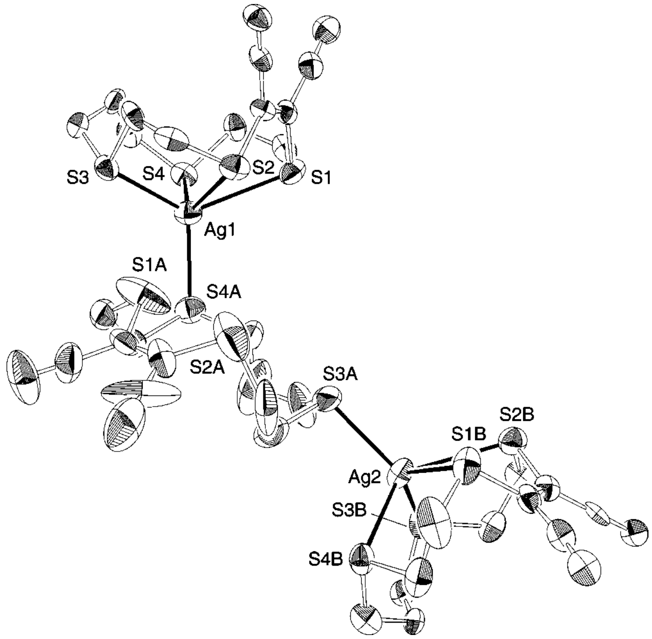


Figure 5. Molecular structure of the dinuclear complex [{Ag1(mn13S$_4$)}{Ag2(mn13S$_4$(B))}{μ$_2$-mn13S$_4$(A)-κ^1-S4A-κ^1-S3A}]$^{2+}$ in compound **6b**. Selected bond lengths [Å]: Ag1–S1 2.888(3), Ag1–S2 2.908(3), Ag1–S3 2.556(3), Ag1–S4 2.597(3), Ag1–S4A 2.484(3), Ag2–S1B 2.840(3), Ag2–S2B 2.904(3), Ag2–S3B 2.581(3), Ag2–S4B 2.613(3), Ag2–S3A 2.540(4).

complexes (0–6 eV). Obviously, under electrospray conditions the tetrathiacrown ethers mn12S$_4$ and mn13S$_4$ form much more stable 1:1 complexes than 2:1 complexes.[31] Only minor differences in the CID measurements were observed in the fragmentation of the [AgL] complexes with mn12S$_4$ and mn13S$_4$. In the CID experiments of the [AgL]$^+$ ions, fragmentation occurred in the same way, mainly involving cleavage of the bond between the sulfur atoms and the carbon atom attached to the ethylene unit.

^{13}C NMR spectroscopic investigations of both the complexes **3a**, **4a**, **7a** and **8a** and the free ligands mn12S$_4$ and mn13S$_4$ in solution ([D$_3$]nitromethane) showed no evidence for any equilibrium formation in the case of the complexes or of conformational changes in the case of the free ligands; only one set of signals could be observed at room temperature. The complexation with silver ions changed the chemical shifts of all signals with respect to those of the free ligands. Except for the C atoms in the γ-position to the double bond, the 12-membered complexes **3a** and **7a** and the 13-membered complexes **4a** and **8a**, the difference of the chemical shifts is larger in the 1:1 complex than in the 1:2 complex. Also, the direction of the complex-induced difference of chemical shifts is always the same. However, the signals of the C atoms in the γ-position in the 1:2 complexes are always found downfield with regard to the 1:1 complexes (see Tables 2 and 3).

Table 2. ^{13}C NMR chemical shifts and shift differences [ppm] of the 12-membered tetrathiacrown ether mn12S$_4$.

	mn12S$_4$	**7a**	Δδ(**7a** – mn12S$_4$)	**3a**	Δδ(**3a** – mn12S$_4$)
C=C	125.2	125.7	+0.5	125.7	+0.5
C≡N	114.2	112.8	–1.4	113.3	–0.9
C-5	38.5	35.2	–3.3	36.5	–2.0
C-6	34.7	33.7[a]	–1.0	35.0	+0.3
C-7	35.9	34.0[a]	–1.9	35.3	–0.6

[a] Or reversed.

Table 3. ^{13}C NMR chemical shifts and shift differences [ppm] of the 13-membered tetrathiacrown ether mn13S$_4$.

	mn13S$_4$	**8a**	Δδ(**8a** – mn13S$_4$)	**4a**	Δδ(**4a** – mn13S$_4$)
C=C	124.1	124.2	+0.1	124.4	+0.3
C≡N	114.0	112.7	–1.3	113.3	–0.7
C-3	37.8	35.3[a,b]	–2.5	36.4	–1.4
C-2	33.5	34.3[a]	+0.8	34.7	+1.2
C-13	33.2	35.2[b]	+2.0	34.8	+1.6
C-12	30.3	26.5	–3.8	28.4	–1.9

[a] Or reversed. [b] Or reversed.

The ^{1}H NMR spectra of **7a** and **8a** show strongly broadened lines at room temperature. The low-temperature spectra of these compounds gave significant splitting of all groups of signals only in the case of **7a**, which permitted the determination of the free energy of the barrier of ring inversion ($\Delta G^{\ddagger}_{338}$ = 64 kJ mol^{-1}). The coalescence temperature of **8a** is very close to room temperature, and cooling to the melting point of the solution gave an insufficient splitting of the signals to estimate the difference of the chemical shifts. Thus, the barrier of ring inversion in **7a** is higher than in the 1:2 complex [Ag(mn12S$_2$O$_2$)$_2$]$^+$, which was determined previously to be 51 kJ mol^{-1}.[32] The presence of four S atoms, as well as a generally stronger bonding of the cation in the 1:1 complex **7a**, led us to expect such a behaviour. In general, the complexation in 12-membered ring systems leads to a strongly increased barrier of the ring inversion by fixing the donor atoms. As a comparison, the barriers for cyclododecane (ca. 29 kJ mol^{-1}),[33] substituted cyclododecanes (ca. 34–37 kJ mol^{-1})[34] and cyclododecene (ca. 29 and 40 kJ mol^{-1})[35] should be highlighted.

Table 1. Positive-ion ES-MS data for the 2:1 complexes recorded in MeCN solution. Cone voltage: 20 V; collision energy: 3 eV.

Complex	Ions (*m*/*z*, %)	
[Ag(mn12S$_4$)$_2$]BF$_4$ (**3a**)	[Ag(mn12S$_4$)$_2$]$^+$ (684, 100)	[Ag(mn12S$_4$)]$^+$ (395, 50)
[Ag(mn13S$_4$)$_2$]BF$_4$ (**4a**)	[Ag(mn13S$_4$)$_2$]$^+$ (711, 80)	[Ag(mn13S$_4$)]$^+$ (410, 100)
[Ag(mn12S$_4$)$_2$]PF$_6$ (**3b**)	[Ag(mn12S$_4$)$_2$]$^+$ (684, 20)	[Ag(mn12S$_4$)]$^+$ (395, 100)
[Ag(mn13S$_4$)$_2$]PF$_6$ (**4b**)	[Ag(mn13S$_4$)$_2$]$^+$ (711, 100)	[Ag(mn13S$_4$)]$^+$ (410, 95)

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Conclusion

The maleonitrile-tetrathia-12-crown-4 is the first preorganized tetradentate thiacrown ether that forms sandwich complexes with the coordination number eight. At present we are investigating the complexing properties of mn12S_4 and mn13S_4 for other metal ions.

Experimental Section

General: All operations were performed under dry argon using standard equipment and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. 1,8-Dichloro-3,6-dithiaoctane,[25] 1,9-dichloro-3,7-dithianonane[25] and disodium (*Z*)-1,2-dicyanoethene-1,2-dithiolate[24] were prepared according to published procedures. Elemental analyses (C, H, N, S) were performed with an Elementar Vario EL elemental analyzer. NMR spectra were recorded with a Bruker Avance 500 or an Avance 300 spectrometer. For preparing the complex solutions, 15 mg was dissolved in 0.7 mL of deuterated chloroform or [D$_3$]nitromethane. Chemical shifts are referenced to TMS (for ^{1}H) or to the solvent (^{13}C). All 1D and 2D COSY and HMQC pulse sequences were taken from the standard Bruker software. IR spectra were recorded with a Thermo Nicolet NEXUS FTIR instrument. UV/Vis measurements were carried out with an Analytik Jena Specord S 100 spectrophotometer with sealed quartz cuvettes. The ESI and CID spectra were recorded with a Micromass Q-TOF$_{\text{micro}}$ mass spectrometer in positive electrospray mode.

Synthesis of Maleonitrile-tetrathiacrown Ethers mn12S_4 and mn13S_4: A solution of disodium (*Z*)-1,2-dicyanoethene-1,2-dithiolate (11.72 g, 63 mmol) in water (0.8 L) was added to a solution of 1,8-dichloro-3,6-dithiaoctane (13.14 g, 60 mmol; synthesis of mn12S_4) or 1,9-dichloro-3,7-dithianonane (13.98 g, 60 mmol; synthesis of mn13S_4) in ethanol (1.2 L). The solution was stirred at 60 °C for 60 h and the polymeric reaction products were filtered off. The filtrate was concentrated, the residue dissolved in chloroform, the solution washed twice with water and dried with magnesium sulfate. The drying agent was removed by filtration and the filtrate concentrated in vacuo. The residual brown oil was chromatographed on a silica gel 60 gravity column (3 cm diameter × 50 cm length), and was eluted with chloroform to give the maleonitrile-tetrathiacrown ether.

1,4,7,10-Tetrathiacyclododec-2-ene-2,3-dicarbonitrile (mn12S_4): Yield: 3.4 g (18.7%). R_f = 0.49 (chloroform). M.p. 182 °C (chloroform). IR (KBr): $\tilde{\nu}$ = 2222 m, 2208 m (C≡N); 1504 m (C=C) cm^{-1}. UV (chloroform): $\lambda_{\max}$ (logε) = 316 sh, 347 (3.97) nm. ^{1}H NMR (CDCl$_3$): δ = 2.88 [m, 4 H, C(6)H$_2$], 2.96 [s, 4 H, C(8)H$_2$], 3.37 [m, 4 H, C(5)H$_2$] ppm. ^{13}C NMR: See Table 2. ESI(HR)-MS: *m*/*z* calcd. for $C_{10}H_{12}N_2S_4$ [M]$^+$ 287.9883; found 287.9881. $C_{10}H_{12}N_2S_4$ (288.46): calcd. C 41.64, H 4.19, N 9.71, S 44.46; found C 42.38, H 4.24, N 9.62, S 44.47.

1,4,7,10-Tetrathiacyclotridec-5-ene-5,6-dicarbonitrile (mn13S_4): Yield: 3.05 g (16%). R_f = 0.33 (chloroform). M.p. 152–153 °C (chloroform). IR (KBr): $\tilde{\nu}$ = 2221 m, 2209 m (C≡N); 1507 m (C=C) cm^{-1}. UV (chloroform): $\lambda_{\max}$ (logε) = 297 sh, 347 (4.09) nm. ^{1}H NMR (CDCl$_3$): δ = 1.79 [m, 2 H, C(12)H$_2$], 2.73 [t, $^3J_{H,H}$ = 7.4 Hz, 4 H, C(13)H$_2$], 2.87 [m, 4 H, C(2)H$_2$], 3.35 [m, 4 H, C(3)H$_2$] ppm. ^{13}C NMR: See Table 3. ESI(HR)-MS: *m*/*z* calcd. for $C_{11}H_{15}N_2S_4$ [M + H]$^+$ 303.0118; found 303.0133. $C_{11}H_{14}N_2S_4$ (302.49): calcd. C 43.68, H 4.67, N 9.26, S 42.40; found C 44.04, H 4.54, N 9.14, S 41.92.

Synthesis of Ag^I Complexes 3a,b–8a,b: A methanolic solution of AgY (Y = BF$_4$, PF$_6$) was added to a stirred solution of the maleonitrile-tetrathiacrown ether in chloroform. After a few seconds, yellow crystals formed and were isolated by filtration.

[Ag(mn12S_4)$_2$]BF$_4$ (3a): Formed from mn12S_4 (28.8 mg, 0.1 mmol) in CHCl$_3$ (2 mL) and AgBF$_4$ (9.7 mg, 0.05 mmol) in MeOH (1 mL). Yield: 68 mg (88%). M.p. 194–196 °C. IR (KBr): $\tilde{\nu}$ = 2222 m, 2212 m (C≡N); 1510 m (C=C); 1083 s, 1061 s, 1052 s (B–F) cm^{-1}. ^{1}H NMR (CD$_3$NO$_2$): δ = 3.18 [s, 4 H, C(8)H$_2$], 3.21 [m, 4 H, C(6)H$_2$], 3.56 [m, 4 H, C(5)H$_2$] ppm. ^{13}C NMR: See Table 2. ESI(HR)-MS: *m*/*z* calcd. for $C_{20}H_{24}AgN_4S_8$ [M – BF$_4$]$^+$ 682.8818; found 682.8812. $C_{20}H_{24}AgBF_4N_4S_8$ (771.59): calcd. C 31.13, H 3.14, N 7.26, S 33.24; found C 30.51, H 3.00, N 6.92, S 32.35.

[Ag(mn12S_4)$_2$]PF$_6$ (3b): Formed from mn12S_4 (28.8 mg, 0.1 mmol) in CHCl$_3$ (2 mL) and AgPF$_6$ (12.6 mg, 0.05 mmol) in MeOH (2 mL). Yield: 52 mg (63%). M.p. 193 °C. IR (KBr): $\tilde{\nu}$ = 2222 m, 2213 m (C≡N); 1512 m (C=C); 835 s, 558 m (P–F) cm^{-1}. ESI(HR)-MS: *m*/*z* calcd. for $C_{20}H_{24}AgN_4S_8$ [M – PF$_6$]$^+$ 682.8818; found 682.8825. $C_{20}H_{24}AgF_6N_4PS_8$ (829.75): calcd. C 28.95, H 2.92, N 6.75, S 30.91; found C 28.63, H 2.78, N 6.48, S 31.30.

[Ag(mn13S_4)$_2$]BF$_4$ (4a): Formed from mn13S_4 (30.2 mg, 0.1 mmol) in CHCl$_3$ (2 mL) and AgBF$_4$ (9.7 mg, 0.05 mmol) in MeOH (1 mL). Yield: 71 mg (88%). M.p. 190–191 °C. IR (KBr): $\tilde{\nu}$ = 2217 m, 2209 m (C≡N); 1512 m, 1504 m (C=C); 1069 s, 1052 s, 1035 s (B–F) cm^{-1}. ^{1}H NMR (CD$_3$NO$_2$): δ = 2.06 [m, 2 H, C(12)H$_2$], 3.02 [t, $^3J_{H,H}$ = 6.1 Hz, 4 H, C(13)H$_2$], 3.24 [m, 4 H, C(2)H$_2$], 3.59 [m, 4 H, C(3)H$_2$]. ^{13}C NMR: See Table 3. ESI(HR)-MS: *m*/*z* calcd. for $C_{22}H_{28}AgN_4S_8$ [M – BF$_4$]$^+$ 710.9131; found 710.9136. $C_{22}H_{28}AgBF_4N_4S_8$ (799.64): calcd. C 33.04, H 3.53, N 7.01, S 32.07; found C 32.90, H 3.42, N 6.63, S 32.59.

[Ag(mn13S_4)$_2$]PF$_6$ (4b): Formed from mn13S_4 (30.2 mg, 0.1 mmol) in CHCl$_3$ (2 mL) and AgPF$_6$ (12.6 mg, 0.05 mmol) in MeOH (2 mL). Yield: 57 mg (66%). M.p. 193–195 °C. IR (KBr): $\tilde{\nu}$ = 2225 m, 2216 m, 2210 m (C≡N); 1514 m, 1505 m (C=C); 840 s, 558 m (P–F) cm^{-1}. ESI(HR)-MS: *m*/*z* calcd. for $C_{22}H_{28}AgN_4S_8$ [M – PF$_6$]$^+$ 710.9131; found 710.9140. $C_{22}H_{28}AgF_6N_4PS_8$ (857.80): calcd. C 30.80, H 3.29, N 6.53, S 29.90; found C 30.77, H 3.20, N 6.44, S 30.34.

[Ag$_2$(mn12S_4)$_3$](BF$_4$)$_2$ (5a): Formed from mn12S_4 (21.6 mg, 0.075 mmol) in CHCl$_3$ (2 mL) and AgBF$_4$ (9.7 mg, 0.05 mmol) in MeOH (1 mL). Yield: 31 mg (33%). M.p. 172–185 °C. IR (KBr): $\tilde{\nu}$ = 2223 m, 2213 m (C≡N); 1511 m, 1502 m (C=C); 1053 s, 1037 s (B–F) cm^{-1}. ESI(HR)-MS: *m*/*z* calcd. for $C_{30}H_{36}Ag_2BF_4N_6S_{12}$ (< 1) [M – BF$_4$]$^+$ 1164.7781; found 1164.7758. $C_{30}H_{36}Ag_2B_2F_8N_6S_{12}$ (1254.7): calcd. C 28.72, H 2.89, N 6.70, S 30.66; found C 28.12, H 2.55, N 6.35, S 31.40.

[Ag$_2$(mn13S_4)$_3$](PF$_6$)$_2$ (6b): Formed from mn13S_4 (22.65 mg, 0.075 mmol) in CHCl$_3$ (2 mL) and AgPF$_6$ (12.6 mg, 0.05 mmol) in MeOH (2 mL). Yield: 42 mg (40%). M.p. 194.5–195.5 °C. IR (KBr): $\tilde{\nu}$ = 2223 m, 2211 m (C≡N); 1510 m, 1503 m (C=C); 845 s, 558 m (P–F) cm^{-1}. ESI(HR)-MS: *m*/*z* calcd. for $C_{33}H_{44}Ag_2F_6N_6PS_{12}$ (< 1) [M – PF$_6$ + 2 H]$^+$ 1266.8020; found 1266.8044. $C_{33}H_{42}Ag_2F_{12}N_6P_2S_{12}$ (1413.12): calcd. C 28.05, H 3.00, N 5.95, S 27.22; found C 27.81, H 2.92, N 5.83, S 28.40.

[Ag(mn12S_4)]BF$_4$ (7a): Formed from mn12S_4 (14.4 mg, 0.05 mmol) in CHCl$_3$ (1 mL) and AgBF$_4$ (9.7 mg, 0.05 mmol) in MeOH (1 mL). Yield: 18 mg (75%). M.p. 169–172 °C. IR (KBr): $\tilde{\nu}$ = 2227 m, 2215 m (C≡N); 1511 m, 1504 m (C=C); 1056 s (B–F) cm^{-1}. ^{1}H NMR: See text. ^{13}C NMR: See Table 2. ESI(HR)-MS: *m*/*z* calcd. for $C_{10}H_{12}AgN_2S_4$ [M – BF$_4$]$^+$ 394.8934; found 394.8959.

$C_{10}H_{12}AgBF_4N_2S_4$ (483.13): calcd. C 24.86, H 2.50, N 5.80, S 26.54; found C 24.62, H 2.34, N 5.63, S 27.20.

[Ag(mn12S$_4$)]PF$_6$ (7b): Formed from mn12S$_4$ (14.4 mg, 0.05 mmol) in $CHCl_3$ (1 mL) and $AgPF_6$ (12.6 mg, 0.05 mmol) in MeOH (2 mL). Yield: 18 mg (67%). M.p. 169.5–172 °C. IR (KBr): $\tilde{\nu}$ = 2226 m, 2216 m (C≡N); 1512 m, 1504 m (C=C); 839 s, 558 m (P–F) cm^{-1}. ESI(HR)-MS: *m/z* calcd. for $C_{10}H_{12}AgN_2S_4$ $[M - PF_6]^+$ 394.8934; found 394.8928. $C_{10}H_{12}AgF_6N_2PS_4$ (541.29): calcd. C 22.19, H 2.23, N 5.18, S 23.69; found C 22.25, H 2.13, N 5.13, S 24.48.

[Ag(mn13S$_4$)]BF$_4$ (8a): Formed from mn13S$_4$ (15.1 mg, 0.05 mmol) in $CHCl_3$ (1 mL) and $AgBF_4$ (9.7 mg, 0.05 mmol) in MeOH (1 mL). Yield: 21 mg (85%). M.p. 158–161 °C. IR (KBr): $\tilde{\nu}$ = 2224 m, 2214 m (C≡N); 1510 m, 1503 m (C=C); 1054 s (B–F) cm^{-1}. ^{1}H NMR: See text. ^{13}C NMR: See Table 3. ESI(HR)-MS: *m/z* calcd. for $C_{11}H_{14}AgN_2S_4$ $[M - BF_4]^+$ 408.9091; found 408.9115. $C_{11}H_{14}AgBF_4N_2S_4$ (497.16): calcd. C 26.58, H 2.84, N 5.63, S 25.79; found C 26.32, H 2.73, N 5.48, S 26.38.

[Ag(mn13S$_4$)]PF$_6$ (8b): Formed from mn13S$_4$ (15.1 mg, 0.05 mmol) in $CHCl_3$ (1 mL) and $AgPF_6$ (12.6 mg, 0.05 mmol) in MeOH (2 mL). Yield: 19 mg (68%). M.p. 167–168 °C. IR (KBr): $\tilde{\nu}$ = 2225 m, 2214 m (C≡N); 1510 m, 1502 m (C=C); 840 s, 558 m (P–F) cm^{-1}. ESI(HR)-MS: *m/z* calcd. for $C_{11}H_{14}AgN_2S_4$ $[M - PF_6]^+$ 408.9091; found 408.9109. $C_{11}H_{14}AgF_6N_2PS_4$ (555.32): calcd. C 23.79, H 2.54, N 5.04, S 23.09; found C 24.08, H 2.48, N 5.01, S 23.7.

Electrospray Ionisation: The ligand and complex solutions (10^{-5} M) for the ESI investigations were prepared with CH_3CN or CH_3NO_2. All samples were injected (5–25 µL min^{-1}) with a Harvard syringe pump. The capillary voltage was set to 2.5 kV, with a cone voltage of between 15 and 35 V. The source temperature was 80 °C and the desolvation temperature 150 °C. The cone and desolvation gases (nitrogen) were delivered at 50 and 360 µL h^{-1}, respectively (Table 2). For MS/MS, after selection of the appropriate precursor ion, argon was used as the collision gas (approx. 5×10^{-5} mbar) and the gas cell was maintained between 3 and 40 eV. Elemental compositions were determined by accurate mass measurement with a standard deviation of less than 5 ppm.

X-ray Structure Determinations for mn12S$_4$, mn13S$_4$, 3a, 4a and 6b: Crystals of mn12S$_4$ and mn13S$_4$ suitable for the X-ray structure determination were obtained by slow crystallisation from a chloroform solution in a refrigerator at 6 °C. Single crystals of **3a** were selected from a nitromethane solution after standing at 6 °C for 4 d. A solution of **4a** was placed in the narrow region of a crystallisation tube and carefully covered with a heptane layer. After 5 d, yellow crystals, which were suitable for X-ray analysis, were obtained. Crystals of **6b** were grown at 6 °C from a methanol/nitromethane solution during a six-week period. The crystals were mounted on a glass fibre. Diffraction data for mn12S$_4$, mn13S$_4$, **3a** and **6b** were collected with a STOE IPDS-2 diffractometer (Table 4). Data for **4a** were collected with a STOE four-circle instrument. All measurements were performed at 210(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Spherical absorption corrections were applied for mn12S$_4$ and mn13S$_4$. For **4a**, an empirical absorption correction was performed. The structures were solved by direct methods (SHELXS-97)[36] and refined by full-matrix least-squares on F^2 using all reflections (SHELXL-97).[37] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in their expected positions and refined using a riding model. The packing of **3a** contains disordered tetrafluoroborate anions and two solvate molecules (nitromethane) with small occupancy factors, from which only one solvate molecule could be satisfactorily refined. Therefore only one was involved in the refinement; the other ones were disregarded with the SQUEEZE instruction of the PLATON[38] program. CCDC-266947 to -266951 (for mn12S$_4$, mn13S$_4$, **3a**, **4a** and **6b**,

Table 4. Crystallographic data for the structural analyses of compounds mn12S$_4$, mn13S$_4$, **3a**, **4a**, and **6b**.

	mn12S$_4$	mn13S$_4$	**3a**·2CH$_3$NO$_2$	**4a**	**6b**·2CH$_3$NO$_2$
Empirical formula	$C_{10}H_{12}N_2S_4$	$C_{11}H_{14}N_2S_4$	$C_{22}H_{30}AgBF_4N_6O_4S_8$	$C_{22}H_{28}AgBF_4N_4S_8$	$C_{35}H_{48}Ag_2F_{12}N_8O_4P_2S_{12}$
Formula mass	288.46	302.48	893.67	799.64	1535.21
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a [Å]	7.9925(5)	9.1375(8)	8.4720(8)	9.0222(6)	9.2270(3)
b [Å]	17.7229(9)	9.3531(5)	10.8770(10)	9.4131(8)	32.9208(17)
c [Å]	9.5906(6)	16.6903(15)	12.7790(11)	18.4532(14)	9.3795(3)
α [°]	90	90	66.830(6)	83.591(7)	90
β [°]	105.572(5)	95.761(7)	73.070(6)	89.939(6)	96.779(3)
γ [°]	90	90	73.370(6)	81.332(6)	90
V [Å^3]	1308.65(13)	1419.21(19)	1015.78(16)	1539.4(2)	2829.20(19)
Z	4	4	1	2	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.464	1.416	1.461	1.725	1.802
$F(000)$	600	632	413	808	1540
Θ range [°]	2.30–24.99	2.24–24.99	1.77–25.00	2.20–27.49	1.24–22.50
Index range	$-9 \le h \le 9$	$-10 \le h \le 10$	$-10 \le h \le 10$	$0 \le h \le 11$	$-9 \le h \le 9$
	$-20 \le k \le 20$	$-11 \le k \le 11$	$-12 \le k \le 12$	$-12 \le k \le 12$	$-35 \le k \le 35$
	$-11 \le l \le 11$	$-19 \le l \le 19$	$-15 \le l \le 15$	$-20 \le l \le 23$	$-10 \le l \le 10$
Reflections collected	19147	8242	10580	7391	26971
Independent reflections	2300	2489	3573	6969	7373
Data/restraints/parameters	2300/0/146	2489/0/155	3573/0/226	6969/0/362	7373/3/688
R_1, wR_2 $[I > 2\sigma(I)]$	0.0234, 0.0601	0.0343, 0.0816	0.0305, 0.0878	0.0277, 0.0766	0.0517, 0.1059
R_1, wR_2 (all data)	0.0285, 0.0618	0.0442, 0.0847	0.0358, 0.0895	0.0377, 0.0807	0.0771, 0.1144
S	1.039	1.042	1.060	1.027	0.953
$\Delta\rho_{\text{min.}}$, $\Delta\rho_{\text{max.}}$ [e Å^{-3}]	–0.203, 0.039	–0.522, 1.070	–0.488, 0.371	–0.771, 1.246	–0.632, 1.092

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respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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