Silver(I) Sandwich Complexes of Oxa-Crowned Derivatives of Dithiomaleonitrile

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The coordination chemistry of the four oxa-crowned derivatives of dithiomaleonitrile mn-$12S_2O_2$, mn-$15S_2O_3$, mn-$18S_2O_4$, and mn-$21S_2O_5$ as well as of the acyclic bis(methylthio)maleonitrile mn-S_2 with Ag^I was investigated by X-ray structural and spectroscopic methods. The 2:1 complexes (ligand/Ag^I) $[Ag(mn\text{-}12S_2O_2)_2]PF_6$, **[1]**$PF_6$, $[Ag(mn\text{-}15S_2O_3)_2]PF_6$, **[2]**$PF_6$, and $[Ag(mn\text{-}S_2)_2]PF_6$, **[6]**$PF_6$, and the 1:1 complexes $[Ag(mn\text{-}15S_2O_3)]ClO_4$, **[3]**$ClO_4$, $[Ag(mn\text{-}18S_2O_4)]PF_6$, **[4]**$PF_6$, and $[Ag(mn\text{-}21S_2O_5)]PF_6$ **[5]**PF_6, were obtained with $AgPF_6$ or $AgClO_4$ in MeOH. The stoichiometry of the macrocyclic Ag^I complexes and the coordination mode of mn-S_2O_{n+1} coronands ($n = 1-4$) is determined by the length of the macrocyclic oligoethylene chain. – The mn-crown dithioethers mn-$12S_2O_2$ and mn-$15S_2O_3$ form with $AgPF_6$ the new sandwich complexes $[Ag(mn\text{-}12S_2O_2)_2]PF_6$, **[1]**$PF_6$, and $[Ag(mn\text{-}15S_2O_3)_2]PF_6$, **[2]**$PF_6$. **[1]**$PF_6$ crystallises in the triclinic space group $P\bar{1}$. In the centrosymmetric cation $[\mathbf{1}]^+$ each mn-$12S_2O_2$ ligand is coordinated to the Ag^I centre in an *endo* manner via both S atoms and one O atom. The distance of the second O atom of mn-$12S_2O_2$ to Ag^I is somewhat longer than a normal $Ag-O_{ether}$ bond. The overall environment around Ag^I in $[\mathbf{1}]^+$ is that of a distorted cubic S_4O_4 set of donors. **[2]**PF_6 crystallises in the monoclinic space group *C2/c*. In the centrosymmetric cation $[\mathbf{2}]^+$ silver(I) is planar-coordinated by the four S atoms of both mn-$15S_2O_3$ molecules. The six O atoms of both mn-$15S_2O_3$ ligands show only long-range interactions to the Ag^I ion. They surround Ag^I almost vertically to the planar S_4 set of donors in a crown-like manner. – The crystal structures of the 1:1 complexes $[Ag(mn\text{-}18S_2O_4)]PF_6$, **[4]**$PF_6$, and $[Ag(mn\text{-}21S_2O_5)]PF_6$, **[5]**$PF_6$, consist of linear chain polymers. **[5]**PF_6 forms an N-bridged chain polymer of endocyclic $[Ag(mn\text{-}21S_2O_5)]^+$ units with $S_1O_4N_{Nitrile}$ coordination at the Ag^I centre. In the 2:1 complex $[Ag(mn\text{-}S_2)_2]PF_6$, **[6]**$PF_6$, each mn-$S_2$ acts as a monodentate $N_{Nitrile}$ donor. – ^{13}C-NMR studies in nitromethane solution confirm that the Ag^I ions in the complexes of the mn-crown dithioethers remain coordinated. However, the Ag^I ion in complex of mn-S_2 is decoordinated.

Crown thioether metal complexes can exhibit unusual coordination numbers, redox behavior, and spectroscopic properties[1]. In the 1:1 complexes of crown thioethers 18S6 (1,4,7,10,13,16-hexathiacyclooctadecane) or bzo$_2$-18S6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadecane) with $AgPF_6$[2,3] and in the 2:1 sandwich complex of 9S3 (1,4,7-trithiacyclononane) with $AgClO_4$[4] or $AgCF_3SO_3$[5] the ligands impose a hexakis(thioether) environment on Ag^I.

Ag^I has a relatively low affinity for oxygen donors although complexes containing crown ethers are known[6–8]. Reaction of $AgAsF_6$ with ethylene oxide in sulfur dioxide yields the sandwich complex of 12-crown-4 with silver(I) $[Ag(12\text{-crown-}4)_2](AsF_6)$[7]. Mixed thioether/ether coordination spheres on Ag^I were recently described by Blake et al. for 1:1 complexes with S/O crowns $15S_2O_3$ (1,4,7-trioxa-10,13-dithiacyclopentadecane)[9] and $18S_2O_4$ (1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane)[10]. The 1:1 complex with $15S_2O_3$ is a S-bridged linear chain polymer of $[Ag(15S_2O_3)]^+$ units with $S_2O_3S_{bridged}$ coordination at Ag^I, while $18S_2O_4$ forms a binuclear species $[Ag_2(18S_2O_4)]^{2+}$ in which each Ag^I is tetrahedrally coordinated by two S and two O atoms. Attempts to isolate a 2:1 complex of $15S_2O_3$ with Ag^I failed. Metal-free macrocycles $15S_2O_3$ and $18S_2O_4$ adopt conformations in which the S donors lie in *exo* positions[11]. On endocyclic complexation with Ag^I the conformation of the ligands must alter dramatically and this suggests that introduction of stereochemical constraints in the form of bulky or rigid groups might enhance the endocyclic coordination possibilities of mixed S/O crowns.

We synthesized the oxa-crowned derivatives of dithiomaleonitrile mn-$12S_2O_2$, mn-$15S_2O_3$, mn-$18S_2O_4$[12], and mn-$21S_2O_5$[13] (for ligand abbreviations see Figure 1). In contrast to those in the saturated analogues $12S_2O_2$, $15S_2O_3$, and $18S_2O_4$[11], the sulfur atoms in the uncomplexed unsaturated macrocycles mn-$12S_2O_2$, mn-$15S_2O_3$[14], and mn-$18S_2O_4$[13] have restricted exodentate conformations which should enhance the formation of endocyclic complexes. This should be useful for enforcing Ag^I and other metal centres into unknown thioether/ether coordination spheres. In order to clarify this assumption we prepared Ag^I complexes of mn-S_2O_{n+1} coronands (n: 1–4) and characterised their structures by X-ray analyses and spectroscoic methods. With $[Ag(mn\text{-}12S_2O_2)_2]PF_6$, **[1]**$PF_6$, we obtained the first sandwich complex with a mixed thioether/ether coordination sphere. $PdCl_2$[15–17], and $HgCl_2$ complexes[13,18] of mn-crown dithioethers were recently described by us and Sibert et al.

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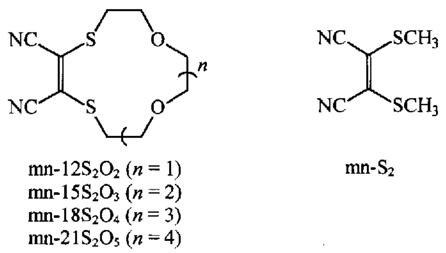
Figure 1. Used ligands and abbreviations (mn = maleonitrile)



Preparation of the Complexes

Ag^I complexes of mn-S_2O_{n+1} coronands (n = 1−4) were obtained with $AgPF_6$ or $AgClO_4$ in MeOH. At molar ratios of 1:1 and 2:1 macrocycles and silver salts were allowed to react. Reaction of mn-$12S_2O_2$ with $AgPF_6$ affords pale yellow crystals of the 2:1 complex [Ag(mn-$12S_2O_2$)$_2$]PF_6, **[1]**PF_6, in high yields irrespective of the molar ratio of the reactants. **[2]**ClO_4 is synthetically accessible by using $AgClO_4$. In contrast to macrocycle mn-$12S_2O_2$, mn-$15S_2O_3$ forms 1:1-complex [Ag(mn-$15S_2O_3$)]PF_6 with one equiv. of $AgPF_6$. [Ag(mn-$15S_2O_3$)]PF_6 could only be isolated as an oil. We therefore prepared the 1:1 complex of mn-$15S_2O_3$ with $AgClO_4$ [Ag(mn-$15S_2O_3$)]ClO_4, **[3]**ClO_4, which readily crystallises as colourless cubes. $AgPF_6$ and two equiv. of mn-$15S_2O_3$ form the 2:1 complex [Ag(mn-$15S_2O_3$)$_2$]PF_6, **[2]**PF_6. Reactions of the larger macrocycles mn-$18S_2O_4$ and mn-$21S_2O_5$ with $AgPF_6$ at molar ratios of 1:1 and 2:1 always yield the 1:1 complexes [Ag(mn-$18S_2O_4$)]PF_6, **[4]**PF_6, and [Ag(mn-$21S_2O_5$)]PF_6, **[5]**PF_6.

A crystalline 2:1 complex [Ag(mn-S_2)$_2$]PF_6 **[6]**PF_6, was accessible by treatment of 1 or 2 equiv. of mn-S_2 with $AgPF_6$ in CH_2Cl_2/MeOH.

The silver complexes obtained are stable in air and show no appreciable sensitivity to light in the solid state. The complexes are soluble in nitromethane and acetonitrile.

IR Spectra

IR spectra of the new Ag^I complexes in the range of 4000−400 cm^{-1} show the typical ligand and anion bands. Changes in the IR spectra of the free ligands are observed for the CN stretching frequencies. Upon coordination of mn-$15S_2O_3$, mn-$18S_2O_4$, and mn-$21S_2O_5$ with Ag^I in 1:1 complexes **[3]**ClO_4, **[4]**PF_6, and **[5]**PF_6 and of mn-S_2 to Ag^I in the 2:1 complex **[6]**PF_6, the CN stretching frequencies and their number increase (see Table 1). Thus, for **[5]**PF_6 three CN stretching bands are observed at 2247, 2232, and 2210 cm^{-1}, as compared to two at 2210 and 2200 cm^{-1} in the free macrocycle mn-$21S_2O_5$. However, there are only little changes in all CN stretching frequencies upon coordination of mn-$12S_2O_2$ and mn-$15S_2O_3$ to Ag^I in the 2:1 complexes **[1]**PF_6 and **[2]**PF_6.

Molecular and Crystal Structures

The crystallographic data of complexes [Ag(mn-$12S_2O_2$)$_2$]PF_6, **[1]**PF_6; [Ag(mn-$15S_2O_3$)$_2$]PF_6, **[2]**PF_6; [Ag(mn-$21S_2O_5$)]PF_6, **[5]**PF_6, and [Ag(mn-S_2)$_2$]PF_6, **[6]**PF_6, are summarised in Table 2.

Table 1. CN stretching frequencies in Ag^I complexes and free ligands [cm^{-1}]

Compound	ν(C≡N)[a]
[1]PF_6	2229 (w), 2216 (w)
mn-$12S_2O_2$	2222 (w), 2208 (m)
[2]PF_6	2229 (w), 2215 (m), 2202 (w)
[3]ClO_4	2241 (w), 2226(w), 2217 (w), 2201 (w)
mn-$15S_2O_3$	2225 (w), 2215 (m), 2204 (w)
[4]PF_6	2250 (w), 2230 (w), 2214 (w)
mn-$18S_2O_4$	2225 (w), 2210 (m)
[5]PF_6	2247 (w), 2232 (w), 2210 (w)
mn-$21S_2O_5$	2210 (m), 2200 (m)
[6]PF_6	2239 (w), 2224 (w), 2210 (m), 2205 (m), 2201 (m)
mn-S_2	2208 (m), 2200 (m)

[a] In KBr.

[Ag(mn-$12S_2O_2$)$_2$]PF_6, **[1]**PF_6

The asymmetric unit contains two half-cation molecules and one anion, thus forming a unit cell with two slightly different complex molecules A and B. The silver atoms are found in special positions. Both A and B are 2:1 ligands towards Ag^I species, in which Ag^I is sandwiched between two mn-$12S_2O_2$ molecules (Fig. 2: complex A). The corresponding dimensions of complex molecules A and B are very similar. In the centrosymmetric complex cation **[1]**$^+$ each mn-$12S_2O_2$ ligand is coordinated to the Ag^I centre in an *endo* manner via both S atoms [2.667(1)−2.821(1) Å] and one O atom [A: 2.591(3), B: 2.635(4) Å]. The bond lengths for Ag−S agree reasonably well with corresponding values of Ag^I complexes of crown thioethers[2,4,5,19−21] and S/O mixed-crowns[9,10] which lie usually in the range of 2.4−2.8 Å. The Ag−O distances fall in the range of Ag−O bond lengths, 2.4−2.65 Å, observed in macrocyclic Ag^I complexes of crown ethers[6−8] and S/O mixed crowns[9,10]. The distance of the second O atom of mn-$12S_2O_2$ to Ag^I [A: 2.811(3), B: 2.861(5) Å] is longer than a normal Ag−O$_{\text{ether}}$ bond[6−10]. Thus, the overall environment around Ag^I in **[1]**$^+$ is that of a distorted cubic S_4O_4 set of donors. The anion PF_6 has no contact with Ag^I.

[Ag(mn-$15S_2O_3$)$_2$]PF_6, **[2]**PF_6

Half a molecule of the complex cation and half of the anion molecule form the asymmetric unit of the crystal lattice. Both the Ag^I ion and the central P atom of the anion are in special positions. In the centrosymmetric cation **[2]**$^+$ silver(I) is complexed in a sandwich fashion by two mn-$15S_2O_3$ molecules (Fig. 3a). Each mn-$15S_2O_3$ ligand is coordinated to the Ag^I centre via both S atoms [2.654(2), 2.717(1)] giving a planar arrangement of four S donors at the metal ion.

Table 2. Summary of crystallographic details, data collection and refinement

Compound	**[1]**PF_6	**[2]**PF_6	**[5]**PF_6	**[6]**PF_6
Formula	$C_{20}H_{24}AgF_6N_4O_4PS_4$	$C_{24}H_{32}AgF_6N_4O_6PS_4$	$C_{16}H_{24}AgF_6N_2O_5PS_2$	$C_{12}H_{12}AgF_6N_4PS_4$
Form. wght.	765.51	853.61	641.33	593.33
Cryst. size [mm]	0.5 x 0.23 x 0.23	0.76 x 0.32 x 0.3	0.66 x 0.38 x 0.22	0.64 x 0.64 x 0.24
Cryst. system	triclinic	monoclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	C2/c	$P2_12_12_1$	$P\bar{1}$
a [Å]	9.299(1)	19.396(4)	11.661(2)	9.219(1)
b [Å]	11.211(1)	9.721(2)	12.924(2)	10.865(1)
c [Å]	16.237(1)	19.490(4)	16.003(1)	11.891(1)
α [°]	98.11	90	90	104.72
β [°]	102.59(1)	114.39(3)	90	101.52(1)
γ [°]	114.45(1)	90	90	109.69(1)
V [$Å^3$]	1452.0(3)	3346.9(2)	2411.8(6)	1030.0(2)
Z	2	4	4	2
d_c [Mg/m^3]	1.751	1.694	1.766	1.913
μ [mm^{-1}]	1.11	0.98	1.15	1.52
F(000)	768	1728	1288	584
T [°K]	298	298	213	298
Radiation	λ = 0.71073 Å (Mo-K_α), graphite monochromator			
Diffractometer	Siemens P4			
Data collecting mode	omega-scan			
Scan range (2Θ) [°]	4.14-45.00	4.58-45.00	4.06-45.00	3.72-45.00
hkl range	0/10, -11/10, -17/17	0/22, 0/11,-22/ 20	-13/13, 15/15, -19/19	0/10, -11/10, -13/13
Refl. collected	4026	2267	3628	2886
Refl. independent	3746	2191	3103	2685
Refl. observed	3277	1817	2939	2456
Observ. criterion	2σ (I)			
Refined param.	410	210	322	300
R1 (2σ (I))	0.0391	0.0471	0.0339	0.0374
R1 (all data)	0.0455	0.0580	0.0368	0.0407
wR2 (all data)	0.0983	0.1296	0.0824	0.0997
GooF	1.027	1.029	1.050	1.099

The overall coordination geometry at Ag^I cannot be described in simple terms because the three O atoms of mn-$15S_2O_3$ show long-range interactions [3.339(4), 3.336(4), 3.077(4) Å]. The Ag^I centre is surrounded by the six O atoms of both mn-$15S_2O_3$ ligands almost vertically to the planar S_4 set of donors in a crown-like manner (Fig. 3b). The least-square plane defined by the six macrocyclic O atoms and the planar AgS_4 moiety cut at an angle of 80.23°. As already observed for sandwich complex $[\mathbf{1}]^+$, the PF_6 anion has no contact with the Ag^I centre.

$[Ag_n(mn\text{-}21S_2O_5)_n](PF_6)_n$, **[5]**$PF_6$

The crystal structure of **[5]**PF_6 consists of a linear chain polymer of endocyclic 1:1 units $[Ag(mn\text{-}21S_2O_5)]^+$ with links between the units provided by a $Ag-N_{nitrile}$ bond (Fig. 4). The Ag^I ion in $[Ag_n(mn\text{-}21S_2O_5)_n]^{n+}$ is best described as being at the centre of a distorted pentagonal pyramidal array of one S, four O, and one N donor atoms. Four of the five macrocyclic O atoms are coordinated [2.451(4)−2.628(4) Å] along with only one of the two available S atoms [2.602(1) Å]. The sixth ligand is an N atom from the nitrile moiety of an adjacent $[Ag(mn\text{-}21S_2O_5)]^+$ unit [2.367(5) Å]. The uncoordinated atoms S2 and O5 are at distances of 4.687 and 5.088 Å from the Ag^I centre.

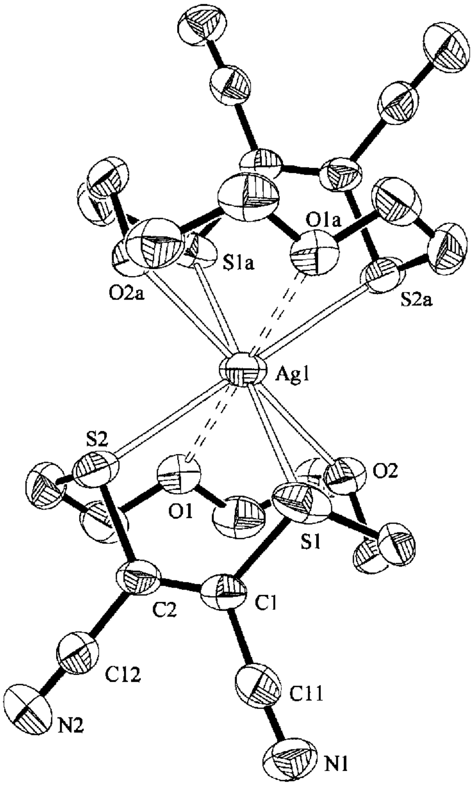
$[Ag(mn\text{-}S_2)_2]PF_6$, **[6]**$PF_6$

[6]PF_6 crystallises in the triclinic space group $P\bar{1}$ with two different ligand molecules per asymmetric unit. Each Ag^I ion is bound to two mn-S_2 ligands by two $Ag-N_{nitrile}$ bonds [2.242(4), 2.245(4) Å] (Fig. 5). The second nitrile functionality and one S atom of each ligand are close enough to display weak interaction with silver(I) [Ag1···N12″ 2.693(6) and Ag1···S11′ 2.872(3) Å] and to distort the N−Ag−N coordination from linear to a bent one [158.0(2)°]. Moreover, there are two Ag···F distances [3.04(2), 3.19(3) Å] indicating weak interactions of the anion PF_6 with the Ag^I centre (van der Walls distance Ag···F 3.86 Å). One S atom of each mn-S_2 remains uncoordinated [5.732(1) Å].

NMR-Spectroscopic Studies

^1H- and ^{13}C-NMR spectra of the Ag^I complexes and ligands were recorded in $MeNO_2$. In the ^{13}C-NMR spectra of the Ag^I mn-crown dithioether complexes all of the macrocyclic methylene carbon resonances are shifted relative to those in the spectra of the free macrocycles (see Table 3). The ^{13}C spectrum of **[6]**PF_6 shows only uncoordinated mn-S_2 indicating complete dissociation of this complex.

Figure 2. Molecular structure of $[Ag(mn\text{-}12S_2O_2)_2]^+$-A in [**1**]$PF_6$ [H atoms omitted; ORTEP, 50% probability level][a]



[a] Selected bond lengths [Å] and angles [°]: [**1**]$^+$-A: Ag1−S1 2.789(1), Ag1−S2 2.779(1), Ag1−O2 2.591(3), Ag1···O1 2.811(3); S1−Ag1−S2 71.5(1), O2−Ag1−S1 69.1(1), O2−Ag1−O1 62.5(1), O1−Ag1−S2 66.5(1); the corresponding parameters of [**1**]$^+$-B: Ag2−S3 2.821(1), Ag2−S4 2.667(1), Ag2−O3 2.635(4), Ag2···O4 2.861(5); S3−Ag2−S4 74.6(1), O3−Ag2−S4 70.9(1), O3−Ag2−O4 60.1(2), O4−Ag2−S3 64.4(1).

In the ^{1}H-NMR spectra of macrocyclic Ag^I complexes all methylene proton resonances are shifted to lower frequencies upon complexation (CH_2S: $\delta = 0.17-0.32$, CH_2O: $\delta = 0.01-0.24$).

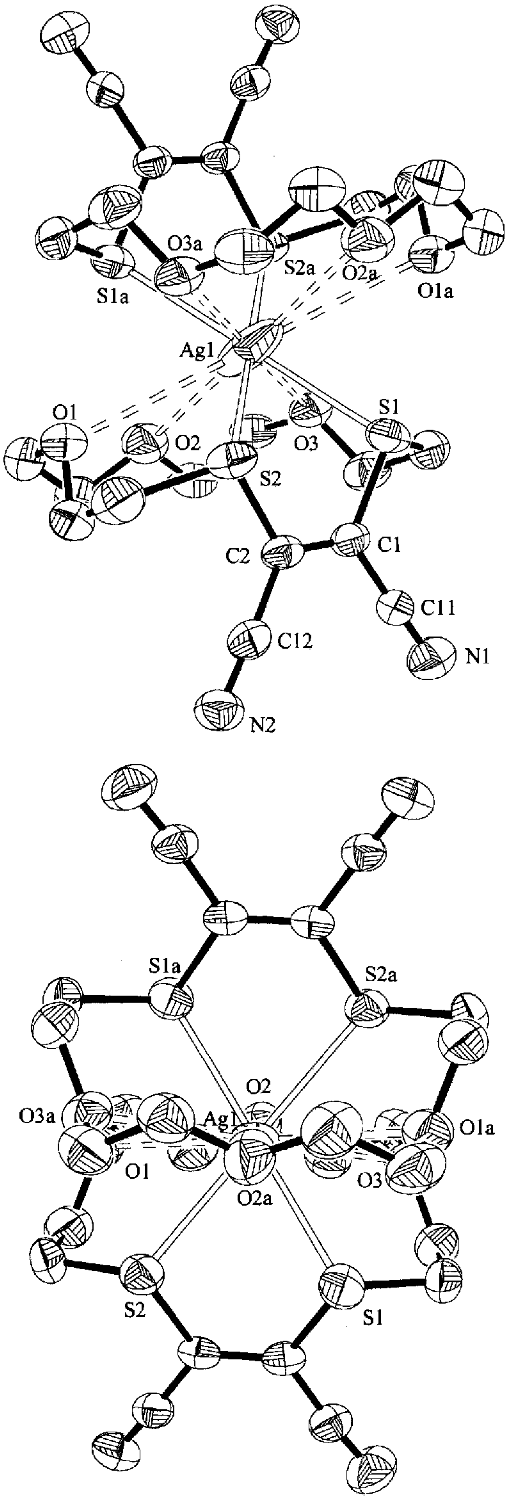
Discussion

The stoichiometry of the macrocyclic Ag^I complexes and the coordination mode of oxa-crowned derivatives of dithiomaleonitrile mn-$12S_2O_2$ to mn-$21S_2O_5$ are determined by the length of the macrocyclic oligooxyethylene chain.

Ag^I complexes of mn-crown dithioethers mn-$12S_2O_2$ − mn-$21S_2O_5$ were obtained by reaction of one or two equiv. of macrocycle with $AgPF_6$ or $AgClO_4$ in MeOH. Whilst the 12-membered mn-$12S_2O_2$ as the smallest macrocycle in this range forms the 2:1 complex [**1**]PF_6 only with the larger macrocycles mn-$18S_2O_4$ and mn-$21S_2O_5$ the 1:1 complexes [**4**]PF_6 and [**5**]PF_6 are obtained. The medium-size mn-crown dithioether mn-$15S_2O_3$ forms both a 2:1 complex [**2**]PF_6 and a 1:1 complex [**3**]ClO_4.

In the IR spectra of complexes [**3**]ClO_4−[**6**]PF_6 the highest ν(CN) frequencies are 16−37 cm^{-1} higher than those of the free ligands and indicate the coordination of nitrile to Ag^I. Kubota and Johnston found that the shift of the ν(CN) frequencies at 2249 cm^{-1} in pure glutaronitrile (gn) to 2274

Figure 3. Molecular structure of $[Ag(mn\text{-}15S_2O_3)_2]^+$ in [**2**]PF_6 [H atoms omitted; ORTEP, 50% probability level]; in two views a) parallel to the macrocyclic plane of mn-$15S_2O_3$ b) perpendicular to the AgS_4 unit[a]



[a] Selected bond lengths [Å] and angles [°]: Ag1−S1 2.654(2), Ag1−S2 2.717(1), Ag1···O1 3.339(4), Ag1···O2 3.336(4), Ag1···O3 3.077(4); S1−Ag1−S2 70.9(1).

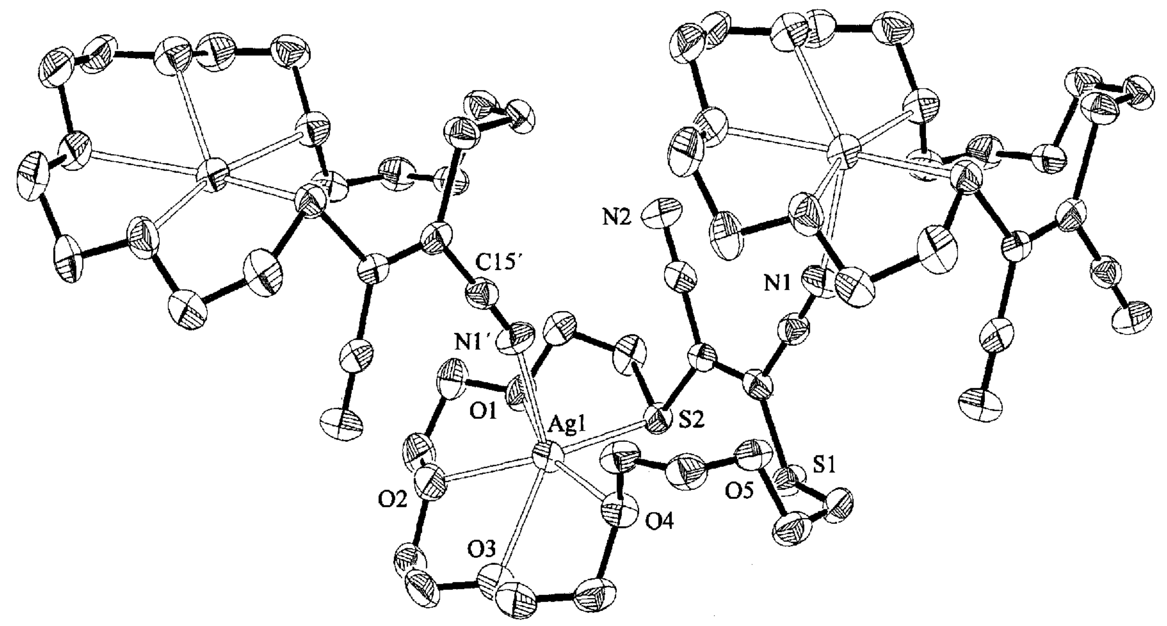


Figure 4. Part of crystal structure of $[Ag_n(mn\text{-}21S_2O_5)_n]^{n+}$ in [**5**]PF_6 [H atoms omitted; ORTEP, 50% probability level][a]

[a] Selected bond lengths [Å] and angles [°]: Ag1–N1' 2.367(5), Ag1–S2 2.602(1), Ag1–O1 2.628(4), Ag1–O2 2.539(4), Ag1–O3 2.451(4), Ag1–O4 2.611(4); Ag1–N1'–C15' 159.8(5), S2–Ag1–O1 69.9(1), O1–Ag1–O2 64.4(1), O2–Ag1–O3 66.9(1), O3–Ag1–O4 69.5(1), O4–Ag1–S2 91.3(1).

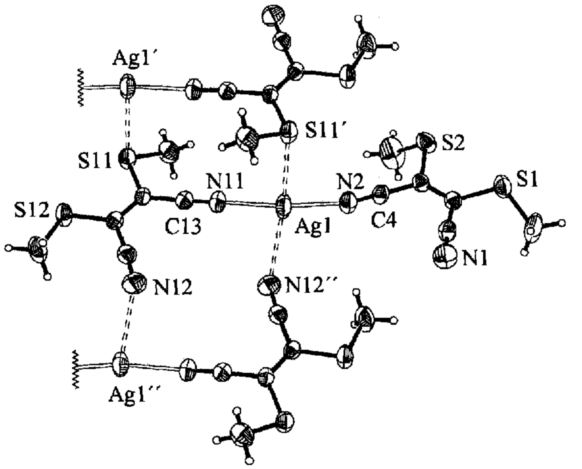


Figure 5. Part of crystal structure of $[Ag(mn\text{-}S_2)_2]^+$ in [**6**]PF_6 [without atom positions of lower s.o.f.; ORTEP, 50% probability level][a]

[a] Selected bond lengths [Å] and angles [°]: Ag1–N11 2.242(4), Ag1–N2 2.245(4), Ag1···S11' 2.872(3), Ag1···N12'' 2.693(6); N2–Ag1–N11 158.0(2), Ag1–N2–C4 166.9(4), Ag1–N11–C13 176.9(4).

Table 3. Selected ^{13}C-NMR data of Ag^I complexes and ligands in $MeNO_2$

Compound	SCH_2	SCH_2CH_2O	OCH_2CH_2O
[**1**]PF_6	37.5	66.3	68.9
mn-$12S_2O_2$	37.2	71.5	69.7
[**2**]PF_6	37.0	69.9	71.0, 71.4
[**3**]ClO_4	38.1	67.6	70.8, 71.0
mn-$15S_2O_3$	36.3	70.9	71.2, 71.7
[**4**]PF_6	37.0	68.6	70.6, 71.1, 71.5
mn-$18S_2O_4$	36.4	70.4	71.7, 71.8, 71.9
[**5**]PF_6	38.5	68.1	70.26, 70.33, 71.1, 71.4
mn-$21S_2O_5$	36.8	70.0	71.6, 71.9, 72.0, 72.1

cm^{-1} in the complex $[Ag(gn)_2]ClO_4$ is indicative of Ag–N bonds[22].

In order to clarify the whole coordination mode of mn-crown dithioethers and acyclic mn-S_2 in the synthesized Ag^I complexes, X-ray analyses were carried out. The crystal structure determination of [**1**]PF_6 and [**2**]PF_6 revealed that $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ are the centrosymmetric sandwich complex cations $[Ag(mn\text{-}12S_2O_2)_2]^+$ and $[Ag(mn\text{-}15S_2O_3)_2]^+$. In $[\mathbf{1}]^+$ each 12-membered mn-$12S_2O_2$ molecule acts as a tridentate ligand through two S and one O donor. The second O donor of mn-$12S_2O_2$ is near enough to Ag^I to display long-range interactions with the metal ion forming an overall coordination sphere of four thioether and four ether donors at the Ag^I centre (Fig. 2). A comparison of structural features of the free ligand mn-$12S_2O_2$[14] and the complexed ligand in $[\mathbf{1}]^+$ indicates that there is relatively little distortion of the ligand upon complexation. In free mn-$12S_2O_2$ the exodentate orientation of the sulfur atoms is restricted since the sulfur atoms are in an integral part of the rigid 1,2-dicyano-1,2-dithioethene unit. A measure of this intrinsic property is the angle between the middle plane of the atoms of the 1,2-dicyano-1,2-dithioethene moiety and the middle plane of the atoms of the ring fragment S1,C8···C3,S2. It amounts in free mn-$12S_2O_2$ to 70.2(1)° and in complexed mn-$12S_2O_2$ to 87.1(1) and 77.6(1)° for $[\mathbf{1}]^+$-A and [**1**]-B. This means that for free mn-$12S_2O_2$ the orientation of both S donors for coordinating Ag^I in [**1**]$^+$ is preorganised.

15-Membered mn-crown dithioether mn-15S_2O_3 also change its structural dimensions only slightly upon sandwich complexation with Ag^I. In marked contrast to [**1**]$^+$, the Ag^I in [**2**]$^+$ is only coordinated by the four S donors of both mn-15S_2O_3 molecules giving an unusual planar S_4 environment around d^{10} ion Ag^I (Fig. 3). Such a fragment is also formed in [**1**]$^+$, but moreover additional apical Ag–O bonds are observed. In [**2**]$^+$ all six O atoms of both mn-15S_2O_3 molecules which surround Ag^I in a crown-like manner are too far away from the Ag^I centre to form Ag–O bonds. But the Ag···O long-range interactions to the Ag^I centre should stabilise the sandwich structure [**2**]$^+$, too. The Ag^I ion is too small to form Ag–O bonds with the 15-membered mn-15S_2O_3 in [**2**]$^+$. Anisotropic displacement parameters of the Ag ion exceed those of all other atoms in the complex cation [**2**]$^+$ and yield a thermal ellipsoid elongated perpendicular to the AgS_4 plane (Fig. 3a). This elongation may reflect mobility of the silver out of the "uncomfortable" AgS_4 plane into the direction of the O donors. None of the other crystal structures show this effect.

The crystal structures of 1:1 complexes [**3**]ClO_4 and [**4**]PF_6 are very similar to those of [Ag(mn-15S_2O_3)]BF_4 and [Ag(mn-18S_2O_4)$_2$]BF_4, recently described by Sibert et al.[23]. Complex [**3**]ClO_4 crystallises as [Ag(mn-15S_2O_3)]BF_4 with two molecules per asymmetric unit. Both molecules are endocyclic 1:1 species with one as the monomeric form [Ag(Y)(mn-15S_2O_3)] (Y = ClO_4, BF_4, resp.) and the other as part of a polymer chain [Ag$_n$(mn-15S_2O_3)$_n$]$^{n+}$ in which adjacent units are connected by a Ag–$N_{nitrile}$ bond. The crystal structures of complex [**4**]PF_6 and [Ag(mn-18S_2O_4)$_2$]BF_4 consist of a linear chain polymers. As in the polymeric form of [**3**]ClO_4, endocyclic 1:1 units are bridged by a Ag–$N_{nitrile}$ bond. Selected bond lengths and distances of [**3**]ClO_4 and [**4**]PF_6 are compared with the corresponding data of the complexes of Sibert in Table 4[24].

The crystal structure of 1:1 complex [**5**]PF_6 consists of a linear chain polymer, too (Fig. 4). As mn-18S_2O_4 in [**4**]PF_6 and mn-15S_2O_3 in the polymeric form of [**3**]ClO_4, the mn-crown dithioether mn-21S_2O_5 acts in [**5**]PF_6 as bridging ligand forming an N-bridged polymer chain [Ag$_n$(mn-21S_2O_5)$_n$]$^{n+}$ consisting of endocyclic 1:1 units.

In the chain polymers of [**3**]ClO_4, [**4**]PF_6, and [**5**]PF_6 only one nitrile moiety of the mn-crown dithioether is coordinated to the Ag^I centre, the other remaining free. This is in accordance with the observation in the IR spectra that on coordination of mn-15S_2O_3, mn-18S_2O_4, and mn-21S_2O_5 with Ag^I in 1:1 complexes, the CN stretching modes are shifted towards higher wave number and increase in number.

Comparison of the coordination mode of mn-crown dithioether mn-12S_2O_2 – mn-21S_2O_5 in the complexes [**1**]PF_6 – [**5**]PF_6 revealed that with longer oligooxyethylene chain the affinity of Ag^I for sulfur atoms of the dithiomaleonitrile unit decreases. Whereas in sandwich complexes [**1**]$^+$ and [**2**]$^+$ and in 1:1 complex [**3**]ClO_4 both S donors are coordinated to Ag^I, there is only one S donor coordinated to Ag^I in [**4**]PF_6 and [**5**]PF_6. This should be a result of the larger number of macrocyclic O donors in mn-18S_2O_4 and mn-21S_2O_5 which can successfully compete with one S donor at the Ag^I centre. If only the dithiomaleonitrile moiety interacts with Ag^I as it was approached by treatment of one or two equiv. of mn-S_2 with $AgPF_6$, the 2:1 complex [**6**]PF_6 is always formed in which each mn-S_2 acts as a monodentate $N_{nitrile}$ donor (Fig. 5). Both S atom of mn-S_2 are not bound to the Ag^I centre as it was assumed for [Ag(mn-S_2)$_2$]ClO_4[25]; only one S atoms shows a longe-range interaction with the Ag^I ion. These results are in accordance with the earlier observations that the 1,2-dithioethene moiety of dithiomaleonitrile derivatives is a relatively weak chelate unit due to the strong electron-withdrawing effect of the cyano groups[25]. Nevertheless, as ^{13}C-NMR studies confirmed, the mn-crown dithioethers remain coordinated to the Ag^I centres in nitromethane solutions. The number of ^{13}C signals is indicative of C_{2h} symmetry of average structures of 2:1 complexes [**1**]$^+$ and [**2**]$^+$ and of C_s symmetry of those of 1:1 complexes [**3**]$^+$, [**4**]$^+$, and [**5**]$^+$. The carbon methylene resonances next to the S atoms are shifted downfield by only 0.3–1.8 ppm, indicating a very small polarisation of the C–S bond by means of Ag^I.

Table 4. Selected interatomic distances [Å] for [Ag(mn-15S_2O_3)]Y and [Ag(mn-18S_2O_4)]Y (Y = ClO_4, BF_4)

Complex	[Ag(mn-15S_2O_3)]Y		[Ag(mn-18S_2O_4)]Y	
	ClO_4	BF_4[23]	PF_6	BF_4[23]
	Monomeric Form			
Ag-S1	2.727(4)	2.732(2)		
Ag-S2	2.745(4)	2.718(2)		
Ag-O1	2.60(1)	2.750(6)		
Ag-O2	2.44(1)	2.399(5)		
Ag-O3	2.73(1)	2.579(6)		
Ag-$OClO_3$	2.43(2)			
Ag-FBF_3		2.46(1)		
		Polymeric Form		
Ag-S1	2.682(4)	2.711(2)	3.411(3)	3.315(3)
Ag-S2	2.727(3)	2.683(2)	2.560(2)	2.533(3)
Ag-O1	2.72(2)	2.802(6)	2.865(6)	2.859(1)
Ag-O2	2.56(1)	2.516(7)	2.654(5)	2.714(11)
Ag-O3	2.85(2)	2.682(7)	2.540(5)	2.533(3)
Ag-O4			2.594(5)	2.593(11)
Ag-N1′	2.29(1)	2.276(6)	2.345(5)	2.310(10)

The synthesis of Ag^I sandwich complexes [**1**]PF_6 and [**2**]PF_6 and our earlier results[15–17] show that the incorporation of the dithiomaleonitrile fragment into smaller crown-like macrocycles can profit from the unique coordination potential of this 1,2-dithioethene unit. It can be assumed that the mn-crown dithioethers mn-12S_2O_2 and mn-15S_2O_3 should be useful ligands for the synthesis of other metal complexes with sandwich or half-sandwich arrangement with novel thioether/ether mixed coordination spheres. The larger homologues in this range, e.g. mn-18S_2O_4 and mn-21S_2O_5, can probably be useful for the synthesis of heterobimetallic complexes.

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Experimental

All operations were carried out under argon by using Schlenk techniques. Solvents were dried by conventional methods. – NMR: Bruker AC 250 or Bruker ARX 300. – IR: Nicolet 205 FT-IR. – MS: Intectra AMD 402, FAB positiv with NBA as matrix substance.

[Ag(mn-12S$_2$O$_2$)$_2$]PF$_6$ ([**1**]PF$_6$): To a solution of 76.8 mg (0.3 mmol) of mn-12S$_2$O$_2$ in 12 ml of MeOH a solution of 37.8 mg (0.15 mmol) of AgPF$_6$ in 3 ml of MeOH is added. The yellow solution is kept at 0 °C for 12 h. The pale yellow both rhombic and rod-like crystals are filtered off and washed with 2 ml of MeOH. A rod-like crystal was used for single-crystal X-ray structural analysis. The rhombic species were either intergrown or twinned. – Yield 92 mg (83%), m.p. 218–225 °C (dec.) (MeOH). – IR (KBr): $\tilde{\nu}$ = 2229 (w) and 2216 (w) (CN), 1517 (w), (C=C), 1166 (w), 1140 (s), 1135 (s) and 1103 (m) (COC), 897 (w), 868 (m), 840 (s) and 559 (m) cm^{-1} (PF). – ^{1}H NMR (CD$_3$NO$_2$): δ = 3.56 (m, SCH$_2$, 4 H), 3.77 (m, SCH$_2$C*H*$_2$O, 4 H), 3.84 (s, OCH$_2$CH$_2$O, 4 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 37.5 (SCH$_2$), 66.3 (SCH$_2$CH$_2$O), 68.9 (OCH$_2$-CH$_2$O), 113.7 (CN), 126.4 (C=C). – MS; *m/z* (%): 621 (28) [[**1**]$^+$], 365 (100) [[**1**]$^+$ – mn-12S$_2$O$_2$]. – $C_{20}H_{24}AgF_6N_4O_4PS_4$ (765.5): calcd. C 31.38, H 3.16, N 7.32; found C 31.27, H 3.12, N 7.11.

[Ag(mn-12S$_2$O$_2$)$_2$]ClO$_4$ ([**1**]ClO$_4$): To a solution of 76.8 mg (0.3 mmol) of mn-12S$_2$O$_2$ in 12 ml of MeOH a solution of 31.2 mg (0.15 mmol) of AgPF$_6$ in 3 ml of MeOH is added. The yellow solution is kept at 0 °C for 12 h. The pale yellow rod-like crystals are filtered off and washed with 2 ml of MeOH, yield 87 mg (80%), m.p. 236–238 °C (dec.) (MeOH). – IR (KBr): $\tilde{\nu}$ = 2226 (w) and 2218 (w) (CN), 1512 (w) (C=C), 1138 (s), 1122 (s), 1104 (s), 1096 (s), 1087 (s) and 1056 (w) (COC) (ClO), 625 (m) (ClO). – ^{1}H NMR (CD$_3$NO$_2$): δ = 3.54 (m, SCH$_2$, 4 H), 3.76 (m, SCH$_2$C*H*$_2$O, 4 H), 3.82 (s, OCH$_2$CH$_2$O, 4 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 37.4 (SCH$_2$), 66.6 (SCH$_2$CH$_2$O), 68.9 (OCH$_2$CH$_2$O), 113.8 (CN), 126.4 (C=C). – MS; *m/z* (%): 621 (16) [[**1**]$^+$], 367 (100) [[**1**]$^+$ – mn-12S$_2$O$_2$]. – $C_{20}H_{24}AgClN_4O_8S_4$ (720.0): calcd. C 33.36, H 3.36, N 7.78; found C 33.51, H 3.22, N 7.53.

[Ag(mn-15S$_2$O$_3$)$_2$]PF$_6$ ([**2**]PF$_6$): To a solution of 90 mg (0.3 mmol) of mn-15S$_2$O$_3$ in 24 ml of MeOH a solution of 38 mg (0.15 mmol) of AgPF$_6$ in 3 ml of MeOH is added. The solution is kept in the dark at room temp. By slow concentration of the methanol solution to 10% of its original volume during a period of 4 weeks crystals suitable for X-ray analysis grow. The crystals are filtered off and washed with 1 ml of MeOH, yield 95 mg (74%), m.p. 120–152 °C (dec.) (MeOH). – IR (KBr): $\tilde{\nu}$ = 2229 (w), 2215 (m) and 2202 (w) (CN), 1508 (m) (C=C), 1170 (m), 1143 (s), 1129 (s), 1119 (s) and 1098 (m) (COC), 869 (m), 844 (s) and 559 (m) cm^{-1} (PF). – ^{1}H NMR (CD$_3$NO$_2$): δ = 3.49 (t, SCH$_2$, 4 H), 3.67 (m, OCH$_2$CH$_2$O, 8 H), 3.76 (t, SCH$_2$C*H*$_2$O, 4 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 37.0 (SCH$_2$), 69.9 (SCH$_2$CH$_2$O), 71.0 and 71.4 (OCH$_2$CH$_2$O), 114.0 (CN), 123.6 (C=C). – MS; *m/z* (%): 709 (7) [[**2**]$^+$], 409 (100) [[**2**]$^+$ – mn-15S$_2$O$_3$]. – $C_{24}H_{32}AgF_6N_4O_6PS_4$ (853.6): calcd. C 33.77, H 3.78, N 6.56; found C 33.65, H 3.75, N 6.37.

[Ag(mn-15S$_2$O$_3$)]ClO$_4$ ([**3**]ClO$_4$): To a solution of 75 mg (0.25 mmol) of mn-15S$_2$O$_3$ in 10 ml of MeOH a solution of 52 mg (0.25 mmol) of AgClO$_4$ in 5 ml of MeOH is added. The reaction mixture is kept in the dark at room temp. After 3 d pale yellow crystals suitable for X-ray analysis are filtered off and washed with 2 ml of MeOH, yield 89 mg (70%), m.p. 136–142 °C (dec.) (MeOH). – IR (KBr): $\tilde{\nu}$ = 2241 (w), 2226 (w), 2217 (w) and 2201 (w) (CN), 1524 (m) and 1504 (w) (C=C), 1169 (w), 1108 (s), 1099 (s), 1083 (s) and 1042 (m) cm^{-1} (COC) (ClO) 622 (m) (ClO). – ^{1}H NMR (CD$_3$NO$_2$): δ = 3.63 (t, SCH$_2$, 4 H), 3.82 (s, OCH$_2$CH$_2$O, 8 H), 3.83 (t, SCH$_2$C*H*$_2$O, 4 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 38.1 (SCH$_2$), 67.6 (SCH$_2$CH$_2$O), 70.8 and 71.0 (OCH$_2$CH$_2$O), 112.9 (CN), 123.7 (C=C). – MS; *m/z* (%): 409 (100) [[**3**]$^+$]. – $C_{12}H_{16}AgClN_2O_7S_2$ (507.7): calcd. C 28.39, H 3.18, N 5.52; found C 28.44, H 3.05, N 5.43.

[Ag(mn-18S$_2$O$_4$)]PF$_6$ ([**4**]PF$_6$): To a solution of 86 mg (0.25 mmol) of mn-18S$_2$O$_4$ in 10 ml of MeOH a solution of 63 mg (0.25 mmol) of AgPF$_6$ in 5 ml of MeOH is added. The solution is kept in the dark at room temp. By slow concentration of the methanol solution to 5% of its original volume during a period of 4 weeks orange crystals suitable for X-ray analysis grow. The crystals are filtered off and washed with 1 ml of MeOH, yield 91 mg (61%), m.p. 180–190 °C (dec.) (MeOH). – IR (KBr): $\tilde{\nu}$ = 2250 (w), 2230 (w) and 2214 (w) (CN), 1510 (w) (C=C), 1175 (w), 1108 (s), 1095 (s) and 1085 (m) (COC), 878 (m), 839 (s), 799 (w) and 558 (m) cm^{-1} (PF). – ^{1}H NMR (CD$_3$NO$_2$): δ = 3.57 (m, SCH$_2$, 4 H), 3.73 (m, OCH$_2$CH$_2$O, 8 H), 3.76 (s, OCH$_2$CH$_2$O, 4 H), 3.82 (m, SCH$_2$C*H*$_2$O, 4 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 37.0 (SCH$_2$) 68.6 (SCH$_2$CH$_2$O), 70.6, 71.1 and 71.5 (OCH$_2$CH$_2$O), 113.5 (CN), 123.6 (C=C). – MS; *m/z* (%): 453 (100) [[**4**]$^+$]. – $C_{14}H_{20}AgF_6N_2O_4PS_2$ (597.3): calcd. C 28.15, H 3.38, N 4.69; found C 27.99, H 3.40, N 4.70.

[Ag(mn-21S$_2$O$_5$)]PF$_6$ ([**5**]PF$_6$): To a solution of 78 mg (0.2 mmol) of mn-21S$_2$O$_5$ in 8 ml of MeOH a solution of 51 mg (0.2 mmol) of AgPF$_6$ in 4 ml of MeOH is added. The solution is kept in the dark while it is stirred at 50 °C for 1 h. The reaction mixture is then kept in the dark at room temp. After 2 d pale pink crystals suitable for X-ray analysis are filtered off and washed with 1 ml of MeOH, yield 118 mg (91%), m.p. 184–186 °C (dec.) (MeOH). – IR (KBr): $\tilde{\nu}$ = 2247 (w), 2232 (w) and 2210 (w) (CN), 1510 (w) (C=C), 1175 (m), 1141 (s), 1122 (s), 1114 (s), 1093 (s) and 1064 (m) cm^{-1} (COC), 881 (m), 838 (s) and 558 (m) cm^{-1} (PF). – ^{1}H NMR (CD$_3$NO$_2$): δ = 3.63 (m, SCH$_2$, 4 H), 3.78 (s, OCH$_2$CH$_2$O, 4 H), 3.88 (m, OCH$_2$CH$_2$O, 12 H), 3.88 (t, SCH$_2$C*H*$_2$O, 4 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 38.5 (SCH$_2$), 68.1 (SCH$_2$CH$_2$O), 70.26, 70.33, 71.1 and 71.4 (OCH$_2$CH$_2$O), 113.7 (CN), 125.7 (C=C). – MS; *m/z* (%): 497 (100) [[**5**]$^+$]. – $C_{16}H_{24}AgF_6N_2O_5PS_2$ (641.3): calcd. C 29.97, H 3.77, N 4.37; found C 29.76, H 4.16, N 4.12.

[Ag(mn-S$_2$)$_2$]PF$_6$ ([**6**]PF$_6$): A solution of 63 mg (0.25 mmol) of AgPF$_6$ in 5 ml of MeOH is added to a solution of 85 mg (0.5 mmol) of mn-S$_2$ in 5 ml of CH$_2$Cl$_2$. The solution is kept in the dark while being stirred at room temp. for 1 h. Then the solution is reduced to a volume of 5 ml at 10 Torr and kept at 0 °C. After 5 d yellow rhombic crystals are filtered off and washed with 2 ml of MeOH, yield 96 mg (65%), m.p. 195–205 °C (dec.) (CH$_2$Cl$_2$/MeOH). – IR (KBr): $\tilde{\nu}$ = 2239 (w), 2224 (w), 2210 (m), 2205 (m) and 2201 (m) (CN), 1506 (w) and 1496 (m) (C=C), 869 (s), 839 (s) and 560 (m) cm^{-1} (PF). – ^{1}H NMR (CD$_3$NO$_2$): δ = 2.77 (s, SCH$_3$, 6 H). – ^{13}C NMR (CD$_3$NO$_2$): δ = 18.5 (SCH$_3$), 113.5 (CN), 123.2 (C=C). – MS; *m/z* (%): 449 (16) [[**6**]$^+$]. – $C_{12}H_{12}AgF_6N_4PS_4$ (593.3): calcd. C 24.29, H 2.04, N 9.44; found C 24.54, H 2.01, N 5.19.

Crystal Structure Determinations: Crystals of the complexes [**1**]PF$_6$, [**2**]PF$_6$, [**5**]PF$_6$, and [**6**]PF$_6$ were investigated with a Siemens P4 diffractometer after taking a rotational photo and performing a photo search to find a suitable reduced cell. The structures were solved by direct methods (XS programme for crystal structure solution, version 4.2 for MSDOS, Copyright 1990 Siemens Analytical X-ray Inst. Inc.) and refined by the full-matrix least-squares method of SHELXL-93[27]. For $[Ag(mn\text{-}21S_2O_5)]PF_6$ the temperature was set to 213 K at the controller unit; however, for refinement calculations a temperature of 223 K was assumed, thus taking into consideration the usual temperature gradient between nozzle and crystal. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions and were refined by using the riding model. The weighting scheme was calculated according to $\omega = 1/[\sigma^2(F_o^2) + (0.0334\ P)^2 + 1.8592\ P]$ for $[Ag(mn\text{-}12S_2O_2)_2]PF_6$, $\omega = 1/[\sigma^2(F_o^2) + (0.0424\ P)^2 + 12.1701\ P]$ for $[Ag(mn\text{-}15S_2O_3)_2]PF_6$, $\omega = 1/[\sigma^2(F_o^2) + (0.0293\ P)^2 + 0.00\ P]$ for $[Ag(mn\text{-}21S_2O_5)]^+$ and $\omega = 1/[\sigma^2(F_o^2) + (0.0451\ P)^2 + 1.6641\ P]$ for $[Ag(mn\text{-}S_2)_2]PF_6$, where $P = (Fo^2 + 2Fc^2)/3$ in all cases.

To be on the safe side absorption correction calculations were performed, although we did not expect much influence, since the absorption coefficient is fairly low in all cases. Indeed, the calculations did not yield a better quality of the findings.

The most important details are compiled in Table 2.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404454 [(**1**)PF_6], -404455 [(**2**)PF_6], -405099 [(**5**)PF_6] or -404458 [(**6**)PF_6], the names of the authors, and the journal citation.

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[24] Other details of the crystal structure of compounds $[Ag(mn\text{-}15S_2O_3)]ClO_4$, [**3**]$ClO_4$, and $[Ag(mn\text{-}18S_2O_4)_2]PF_6$, [**4**]$PF_6$, can be ordered from the authors or at Karlsruhe (CSD-404456 and CSD-404457).

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