Introduction

Antimony(III) and bismuth(III) halides behave like borderline Lewis acids. They provide not only complexes with crown ethers [1–4], but also with their thia analogues [2c, 5, 6]. Therefore complexes with mixed S/O coordination spheres should also be known, but to our knowledge no examples of this class have been published.

Recently, we synthesized the maleonitrile-dithia-crown ethers mn-12S$_2$O$_3$ – mn-21S$_2$O$_5$ (mn = maleonitrile) [7a-c] and showed that they are pre-organized S$_2$O$_{1+n}$-coronands (n = 1–4) which force B, AB and A class metal ions into novel mixed S/O coordination spheres. We reported on the Ag$^+$ sandwich complexes [Ag(mn-12S$_2$O$_2$)$_2$]Y (Y = PF$_6$, ClO$_4$) and [Ag(mn-15S$_2$O$_3$)$_2$]PF$_6$ [7d], and the „in cavity“ complexes [Ti(mn-18S$_2$O$_4$)]PF$_6$ [7e] and [CS(mn-21S$_2$O$_5$)]SbCl$_6$ [7c]. In addition to a S$_2$O$_{1+n}$ cavity (n = 1–4), maleonitrile-dithiacrown ethers provide the N atoms of both nitrile groups as exocyclic donors. In the polymeric disilver(I) complex [Ag$_2$(mn-15S$_2$O$_3$)]$_2$(ClO$_4$)$_2$ one silver centre is coordinated to the two sulphur and three oxygen atoms of mn-15S$_2$O$_3$ and the other one linearly to two nitrogen atoms of two mn-15S$_2$O$_3$ molecules [7f].

In this paper we wish to describe the synthesis and the crystal structures of the antimony and bismuth trichloride complexes of maleonitrile-dithia-15-crown-5 [MCl$_3$(mn-15S$_2$O$_3$)] [M = Sb(1), Bi(2)] and maleonitrile-dithia-18-crown-6 [MCl$_3$(mn-18S$_2$O$_4$)] [M = Sb(3), Bi(4)] which have half-sandwich arrangements, as well as the sand-
wich-like sodium complex of maleonitrile-dithia-18-crown-6 [Na(mn-18S2O4)2]SbCl6 [(5)SbCl6].

**Experimental Part**

All experiments were carried out under argon in dry solvents. Maleonitrile-dithia-15-crown-5 and maleonitrile-dithia-18-crown-6 were prepared by known procedures [7a]. Infrared spectra were obtained on a Nicolet 205 ET-IR. 1H and 13C NMR spectra were recorded at 250.13 and 75.48 MHz (Bruker ARX 300) in CD3NO2 using the solvent or TMS as internal standard. DEP (Direct Exposure Probe) -MS experiments were carried out on a Finnigan SSQ 710 operating with the relevant Finnigan-MAT software. The complexes 1 - 4 were introduced as acetonitrile solutions. A drop of an acetonitrile solution was placed on a rhenium-wire. After evaporation of the solvent the rhenium-wire was heated very quickly (heating rate 1600 °C/min) to 500 °C forcing the complexes into the gas phase. The conditions for electron impact (EI) ionization were electron energy 70 eV, trap current 200 μA and source temperature 150 °C.

**Synthesis of complexes**

[MCl3(L)]; M = Sb, Bi; L = mn-15S2O3, mn-18S2O4

To 0.3 mmol of the maleonitrile-dithiacrown ether (mn-15S2O3: 90 mg, mn-18S2O4: 103 mg) in 6 ml of MeCN, 0.3 mmol trichloride (SbCl3 = 69 mg, BiCl3 = 95 mg) in 6 ml of MeCN were added. The solution was heated to 60 °C for 1 h. After cooling of the solutions their volume was reduced in vacuo to 0.5 ml in order to crystallize the complex. The precipitate was filtered off, washed with diethyl ether (2x2 ml) and dried in vacuo for 2 h.

**[SbCl3(mn-15S2O3)] (1)**

Yield 136 mg (86%), pale pink prisms, m.p. 145–150 °C. – IR (KBr): ν [cm-1] = 2226 (w), 2216 (w), 2199 (sh, vv) (CN); 1506 (m) (C=C); 1130 (s), 1105 (vs), 1083 (s), 1055 (m) (COC); 1000 (s); 914 (s). – DEP-MS (EI, 70 eV): m/z (%) = 300.2 (100) [mn-15S2O3]+; 491 (15) [SbCl3(mn-15S2O3)]+; 525.2 (3) [M]+.

C12H16Cl8N2O15Sb (528.49)
Calcd C 27.27 H 3.05 N 5.30%.
Found C 27.22 H 2.97 N 5.16%.

**[BiCl3(mn-15S2O3)] (2)**

Yield 162 mg (88%), pink prisms, m.p. 180–195 °C. – IR (KBr): ν [cm-1] = 2226 (w), 2216 (w), 2198 (sh, vv) (CN); 1509 (m) (C=C); 1098 (vs), 1076 (s), 1054 (m) (COC); 999 (s); 917 (s). – DEP-MS (EI, 70 eV): m/z (%) = 300.2 (100) [mn-15S2O3]+; 579.2 (0.2) [BiCl3(mn-15S2O3)]+.

C12H16BiCl8N2O15Sb (615.73)
Calcd C 23.41 H 2.62 N 4.55%.
Found C 23.47 H 2.56 N 4.45%.

**[SbCl3(mn-18S2O4)] (3)**

Yield 141 mg (82%), colourless prisms, m.p. 120–130 °C. – IR (KBr): ν [cm-1] = 2223 (w), 2213 (w), 2197 (w) (CN); 1510 (m) (C=C); 1121 (m), 1087 (vs), 1058 (m), (COC). – DEP-MS (EI, 70 eV): m/z (%) = 344.2 (100) [mn-18S2O4]+; 535 (13) [SbCl3(mn-18S2O4)]+.

C14H20Cl14N2O15Sb (572.55)
Calcd C 29.37 H 3.52 N 4.89%.
Found C 29.30 H 3.46 N 4.82%.

**[BiCl3(mn-18S2O4)] (4)**

Yield 146 mg (74%), pale yellow prisms, m.p. 155–160 °C. – IR (KBr): ν [cm-1] = 2224 (w), 2212 (w), 2199 (w) (CN); 1511 (m) (C=C); 1117 (m), 1079 (vs), 1068 (vs), 1050 (s), (COC). – DEP-MS (EI, 70 eV): m/z (%) = 344.2 (49) [mn-18S2O4]+; 623.15 (~ 0.6) [BiCl3(mn-18S2O4)]+.

C14H20BiCl14N2O15Sb (659.78)
Calcd C 25.49 H 3.06 N 4.25%.
Found C 25.10 H 3.01 N 4.13%.

**[Na(mn-18S2O4)2]SbCl6 (5) SbCl6**

NaCl (5.9 mg, 0.1 mmol) was dissolved with SbCl3 (0.026 ml, 0.2 mmol) in 2 ml of MeCN and a solution of mn-18S2O4 (69 mg, 0.2 mmol) in 2 ml of MeCN was added. The mixture was kept at r.t. for 24 h and possible products of SbCl3 hydrolysis were filtered off. The volume of the pale yellow filtrate was reduced in vacuo at 25 °C to 1 ml and layered with an equal volume of diethyl ether. At 6 °C yellow crystals precipitated which were separated, washed with 1 ml of cold MeCN and dried in vacuo.

Yield 96 mg (92%), yellow prisms, m.p. 112–116 °C (MeCN). – IR (KBr): ν [cm-1] = 2224 (w), 2212 (m), 2198 (w) (CN); 1505 (m) (C=C); 1167 (m), 1122 (vs), 1113 (s), 1059 (vs), 1038 (m) (COC).

C28H40Cl16NaO4Sb2 (1046.34)
Calcd C 32.14 H 3.85 N 5.35%.
Found C 32.11 H 3.78 N 5.23%.
Structure determinations

Crystals of 1 and 2 were obtained by keeping the acetonitrile solutions of mn-15S2O3 with SbCl3 and BiCl3 (compare synthesis of complexes) at 6 °C. After 3 d 1 crystallized in pale pink blocks, and within a day 2 began to deposit in pink blocks. The volume of the acetonitrile solutions of mn-18S3O4 with SbCl3 and BiCl3 (see synthesis of complexes) was reduced to 0.5 ml and 1 ml, respectively, and layered with an equal volume of diethylether to provide slow deposition of the products at 6 °C. After 7 d prismatic crystals of 3 and after 3 d pale yellow prisms of 4 were isolated. A suitable single crystal of (5)SbCl6 was obtained from a preparation very similar to that described above.

The crystals were sealed onto a glass fibre and mounted on a Siemens P4 automated four circle diffractometer (MoKα radiation; λ = 0.71073 Å, T = 298 K). Table I provides a summary of the crystal data, data collection, and refinement parameters for complexes 1–4 and (5)SbCl6. The structures were solved by direct methods (XS program for crystal structure solution, version 4.2 für MS-DOS, Copyright Siemens Analytical X-ray Inst. Inc.) and refined by full-matrix least-squares methods (SHELXL-93). Non-H atoms were refined with anisotropic displacement parameters. All H atoms were placed into theoretical positions and were refined by using the riding model.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103067 [SbCl3(mn-15S2O3)] (1), CCDC-103087 [BiCl3(mn-15S2O3)] (2), CCDC-103089 [SbCl3(mn-18S3O4)] (3), CCDC-103088 [BiCl3(mn-18S3O4)] (4) and CCDC-100914 [Na(mn-18S3O4)2]SbCl6 (5)SbCl6. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336–333; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and infrared spectra

The complexes [MCl3(mn-15S2O3)] {M = Sb(1), Bi(2)} and [MCl3(mn-18S3O4)] {M = Sb(3), Bi(4)} were obtained from the reaction of antimony and

Table I. Summary of the crystal data, data collection, and refinement parameters for complexes 1 - 4 and (5)SbCl6.

<table>
<thead>
<tr>
<th></th>
<th>SbCl3(mn-15S2O3)</th>
<th>BiCl3(mn-15S2O3)</th>
<th>SbCl3(mn-18S3O4)</th>
<th>BiCl3(mn-18S3O4)</th>
<th>Na(mn-18S3O4)2]SbCl6</th>
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<td>formula</td>
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<td>C12H10BiCl2N2Sb</td>
<td>C14H10Cl2N2Sb</td>
<td>C14H10BiCl2N2Sb</td>
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<td>1.14/1.13</td>
<td>0.28/0.38</td>
<td>0.65/0.75</td>
<td>0.78/0.61</td>
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</table>
bismuth trichloride with maleonitrile-dithia-15-crown-5 and maleonitrile-dithia-18-crown-6:

\[
\text{MCl}_3 + L \rightarrow [\text{MCl}_3(L)] \quad (M = \text{Sb, Bi}; \quad L = \text{mn-15S}_2\text{O}_3, \text{mn-18S}_2\text{O}_4).
\]

The compound \([\text{Na(mn-18S}_2\text{O}_4)_2]\text{SbCl}_6\) (5) was formed in the reaction of maleonitrile-dithia-18-crown-6 with sodium-hexachloroantimonate irrespective of the molar ratio of the reactants (2:1, 1:1 or 1:2). Sodium-hexachloroantimonate was prepared in situ from sodium chloride and antimony pentachloride:

\[
\text{NaCl} + \text{SbCl}_5 + 2 \text{mn-18S}_2\text{O}_4 \rightarrow [\text{Na(mn-18S}_2\text{O}_4)_2]\text{SbCl}_6.
\]

The use of acetonitrile as reaction medium proved to be favorable. 1–4 and (5)SbCl₆ were obtained in good yields (74–92%). The compounds are soluble in acetonitrile and nitromethane.

IR spectra of 1–4 and (5)SbCl₆ in the range of 4000–400 cm⁻¹ show the typical ligand bands.

Upon coordination of mn-15S₂O₃ and mn-18S₂O₄ to MCl₃ and of mn-18S₂O₄ to Na⁺ most bands of the ligands are somewhat shifted to lower frequencies. This was clearly ascertained for the C-O stretching frequencies. The strongest band with asymmetric COC-stretching frequency character [3c] is shifted from 1143 (both mn-15S₂O₃ and mn-18S₂O₄) to 1105 (1), 1098 (2), 1087 (3), 1079 (4) and 1113 ((5)SbCl₆) cm⁻¹, suggesting that the oxygen atoms are involved in the coordination. Because only little changes were observed for all CN stretching frequencies and for the intensities of these bands for mn-15S₂O₃ and mn-18S₂O₄ nitrile coordination can be excluded. The similarity of the IR spectra of the two mn-15S₂O₃ complexes, 1 and 2, and again for the two mn-18S₂O₄ complexes, 3 and 4, lead us to expect analogous molecular structures.

**Crystal structures**

The single-crystal X-ray structures of compounds 1–4 show half-sandwich arrangements in which the maleonitrile dithiacrown ether is an endocyclic ligand for the antimony or bismuth atom of the pyramidal MCl₃ (M = Sb, Bi) units. The two mn-15S₂O₃ complexes as well as the two mn-18S₂O₄ complexes are isostructural. For illustration the molecular structures of 1 and 4 are depicted in Fig. 1 and 2.

In complexes 1 and 2 mn-15S₂O₃ is coordinated to the M centre through its three oxygen and two sulfur atoms. The oxygen and sulphur donor atoms are essentially coplanar, with maximum deviations of 0.14 Å from an idealized plane through the

Fig. 1. Two views of [SbCl₃(mn-15S₂O₃)] (1). ORTEP illustrations with the atoms represented by their 30% probability thermal ellipsoids.
S₂O₃ fragment both in 1 and 2. The structures of 1 and 2 show approximate C₅ symmetry (see 1 in Fig. 1). The M-O and especially the M-S interactions are weaker than those found in the complexes of SbCl₃ [1a] and BiCl₃ with 15-crown-5 [2c] and of BiCl₃ with pentathia-15-crown-5 (abbreviation 15S₅) [2c]. Table II lists the M-O and M-S contact distances of 1 - 4 and their mean values. For example, in [BiCl₃(mn-15S₂O₃)] (2) the mean Bi-O and Bi-S distances are 2.88(1) and 3.391(4) Å, the corresponding mean distances in [BiCl₃(15-crown-5)] and [BiCl₃(15S₅)] are 2.83(1) [2d] and 3.182(7) Å [2c], respectively. The comparatively long M-S contact distances in 1 and 2 point to weak interactions between M and the thioether S atoms S(1) and S(2).

The M-O interactions appear to be the main factor for the stabilization of complexes 1 and 2. Coordination of mn-15S₂O₃ to MCl₃ is possibly, because already in the free mn-15S₂O₃ the orientation of both the nonbonded electron pairs of the sulphur atoms and probably also of the oxygen atoms favours an endocyclic coordination. This presumption is supported by comparable conformations of both the free and the coordinated mn-15S₂O₃ in the crystal. A comparative conformational analysis of free and coordinated mn-15S₂O₃ reveals merely alterations for the subunits –S(1)–CH₂–CH₂–O(I)–CH₂– and –S(2)–CH₂–CH₂–O(3)–CH₂–, from sc, ap, ap and -sc, ap, ap [8] to -sc, ap, -sc and sc, ap, sc sequences (see Fig. 1).

Table II. M-O and M-S contact distances (M = Sb, Bi) of complexes 1 - 4 and the corresponding mean values.

<table>
<thead>
<tr>
<th>M = Sb, Bi</th>
<th>[SbCl₃(mn-15S₂O₃)] (1)</th>
<th>[BiCl₃(mn-15S₂O₃)] (2)</th>
<th>[SbCl₃(mn-18S₂O₄)] (3)</th>
<th>[BiCl₃(mn-18S₂O₄)] (4)</th>
</tr>
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<tbody>
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<td>2.500(4)</td>
<td>2.389(2)</td>
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<tr>
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<td>2.88(1)</td>
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<td>2.81(1)</td>
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<td>2.95(1)</td>
<td>3.071(3)</td>
<td>2.68(1)</td>
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<tr>
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</table>

Fig. 2. [BiCl₃(mn-18S₂O₄)] (4).
While the maleonitrile-dithia-15-crown-5 forces half of the M centre of MCl₃ into a novel mixed O₃/S₂-coordination sphere, the larger maleonitrile-dithia-18-crown-6 only uses its four oxygen atoms for coordination to MCl₃. The resulting coordination spheres at M in 3 and 4 are comparable to those found in the 12-crown-4 complexes of MCl₃. In 4 the four oxygen donor atoms of mn-18S₂O₄ are precisely coplanar. In 3 the deviation from the idealized plane through the O₄ fragment of mn-18S₂O₄ amounts to 0.2 Å. The mean M-O distances in 3 and 4 are longer than those in their 12-crown-4 counterparts. The mean Sb-O distance in 3 is 3.013(3) (12-crown-4 2.83(4) [2d]), and the mean Bi-O distance in 4 is 2.86(1) Å (12-crown-4 2.70(1) [2c]). The oxygen atoms of maleonitrile-dithia-18-crown-6 interact with a metal centre not as strong as those of 12-crown-4 since they are donor atoms of a larger macrocyclic framework. On the one hand the rigid and sterically demanding dithiamaleonitrile unit of mn-18S₂O₄ prevents the oxygen atoms O(1) and O(4) from a shorter contact to a metal centre, while on the other hand it represents a preorganization for endocylic coordination.

The A class metal ion Na⁺ is not bound in the cavity of mn-18S₂O₄. Instead it is sandwich-like coordinated by two molecules of mn-18S₂O₄. Fig. 3 shows the centrosymmetrical sandwich complex cation [Na(mn-18S₂O₄)₂]⁺ (5). In this complex, mn-18S₂O₄ also acts as a macrocyclic tetradeutate O-donor ligand. The sodium atom is surrounded by the eight oxygen atoms of two mn-18S₂O₄ molecules occupying the corners of a distorted square antiprism. This coordination sphere is comparable to that found in the classical bis(12-crown-4)sodium complex [9]. In 5 the Na-O contact distances range from 2.80(1) to 3.11(1) Å (mean = 2.94(1) Å); they are approximately 0.45 Å longer than those in [Na(12-crown-4)]⁺ [9].

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**Fig. 3.** [Na(mn-18S₂O₄)₂]⁺ (5) in (5)SbCl₆. Selected distances [Å]: Na(1)-O(1) 2.98(1), Na(1)-O(2) 2.86(1), Na(1)-O(3) 2.82(1), Na(1)-O(4) 3.11(1).
macrocycles mn-18S₂O₄ adopt similar conformations in the Na⁺ sandwich complex 5 and in the MCl₃ half sandwich complexes 3 and 4. A comparison of the torsion angles of coordinated mn-18S₂O₄ in 3, 4, and 5 reveals the same conformational sequences: for the subunits -S(1)-CH₂-CH₂-O(1)- and -S(2)-CH₂-CH₂-O(4)-, sc, sc and sc, -sc, -sc, -sc, for -O(1)-CH₂-CH₂-O(2)- and -O(4)-CH₂-CH₂-O(3)-, ap, sc, ap and sc, ap, sc, and for -O(2)-CH₂-CH₂-O(3)-, -sc, -sc, ap.

The M-Cl bonds and Cl-M-Cl angles in 1-4 are comparable to those found in the structurally analogous crown and thiacrown ether complexes [1a, 2a, 2c, 2d]. The Cl-M-Cl angles are reduced to those in the free chlorides, and the M-Cl bonds are slightly lengthened.

It is surprising that in the isostructural complexes 1 and 2 as well as 3 and 4 the mean Sb-O/S contacts in the SbCl₃ complexes 1 and 3 are longer than the Bi-O/S contacts in the BiCl₃ counterparts 2 and 4. The mean Sb-O and Sb-S distances in 1 are 0.075 and 0.068 Å longer than the corresponding distances in 2, and the mean Sb-O distance in 3 is 0.153 Å longer than the mean Bi-O distance in 4 (see Table II). Interestingly, these differences are close to those which were observed between the isostructural SbCl₃ and BiCl₃ complexes of 15-crown-5 and of 12-crown-4, 0.07 (1a, 2d) and 0.13 Å [2a, 2d], respectively. We assume that the characteristic lengthening of the mean M-O distances of isostructural crown and maleonitrile-dithiacrown ether complexes of MCl₃ from Bi to Sb may reflect a stereochemical activity of the Sb lone pair.

\[^{1}H\] and \[^{13}C\] NMR spectra

\[^{1}H\] and \[^{13}C\] NMR spectra of complexes 1-4 and (5)SbCl₆ in CD₃NO₂ confirm that mn-15S₂O₃ and mn-18S₂O₄ remain coordinated in nitromethane solutions. The shifts of the methylene proton and methylene carbon resonances of mn-15S₂O₃ and mn-18S₂O₄ upon complexation to both SbCl₃ and BiCl₃, and of mn-18S₂O₄ to Na⁺ are small (Δδ [ppm]: \[^{1}H\] NMR = 0.02 – 0.30, \[^{13}C\] NMR = -1.8 – 0.1). The number of \[^{13}C\] signals is indicative of C₃ symmetry for the average structures of complexes 1-4 and of C₁ symmetry for that of 5.

DEP-MS experiments

Under the conditions of the DEP-MS experiments a molecular ion was detected only for the complex [SbCl₃(mn-15S₂O₃)] (1). The EI spectrum of 1 shows the parent ion in low relative intensity (3%). The most striking features in the EI spectra of both SbCl₃ complexes 1 and 3 are [M-Cl]+ peaks of medium relative intensity (15 and 13%) for the monocationic complexes [SbCl₂(L)]+ (L = mn-15S₂O₃, mn-18S₂O₄). In the EI spectra of the BiCl₃ complexes 2 and 4, [M-Cl]+ peaks for monocationic complexes [BiCl₂(L)]+ (L = mn-15S₂O₃, mn-18S₂O₄) are also observed, but only with even lower relative intensities (~0.2 and 0.6%), suggesting that the SbCl₂⁺ complexes are more stable than their BiCl₂⁺ counterparts. This ranking indicates a stronger affinity of the cation SbCl₂⁺ for the oxygen atoms of mn-15S₂O₃ and mn-18S₂O₄.

Attempts to synthesize the monocationic complexes, following a method employed for [BiCl₂(15-crown-5)(CH₃CN)]SbCl₆ [10] and [SbCl₂(18-crown-6)]SbCl₆ [3c], from the trichlorides MCl₃ (M = Sb; Bi) with SbCl₃ in acetonitrile in the presence of mn-15S₂O₃ and mn-18S₂O₄ were unsuccessful.

Acknowledgement

Support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.
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