Short Communication

Effect of conformation of cyclic sulfide ligands on the mode of complexation to silver salts

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Abstract

The cyclic trisulfide 1,3,5-trithiane has a flattened chair conformation. It forms with $AgSO_3CF_3$ a dimeric complex wherein each silver is tetracoordinated bearing three sulfides and one triflate ion as ligands. On the other hand 1,4-dithiane, which also has a chair conformation, forms an infinite polymer with AgO_2CCF_3 wherein each silver is coordinated to two different dithianes and two different CF_3CO_2 ligands.

The structures of metal complexes with ligands bearing multiple sulfide ligating sites have become of increasing interest now that synthetic access to many macrocyclic sulfides (thiocrown ethers) is possible [1]. In such systems the sulfides are usually separated by $(CH_2)_n$– chains where n is in most cases 2 or 3. In larger macrocycles (roughly 10- to 18-membered rings) this leads to 'inside–outside' conformations and coordination (often unidentate) exterior (exodentate) to the macrocyclic ring [2]. We have reported previously the structures of silver complexes of thiocrown ethers [3].

We are interested in the relation between conformation and the mode of complexation. The attempts at design of receptor ligands are dependent on this information.

The thioketal, 1,3,5-trithiane (**1**), is a prototype 'thiocrown ether'. In this case a single methylene group separates the sulfide sites in the six-membered (not macrocyclic) ring. The somewhat flattened chair-like conformation of **1** (Fig. 1)** is clearly one in which all three sulfides are positioned on the same side of the plane formed by the three carbon atoms [4]. An accurate redetermination of the structure of **1** is shown in Fig. 1 [4b].

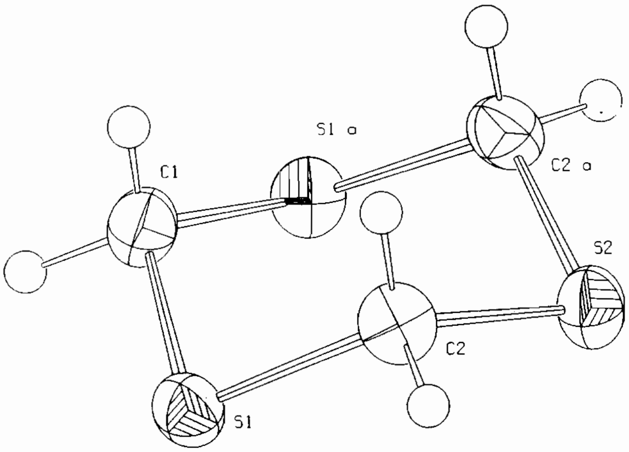
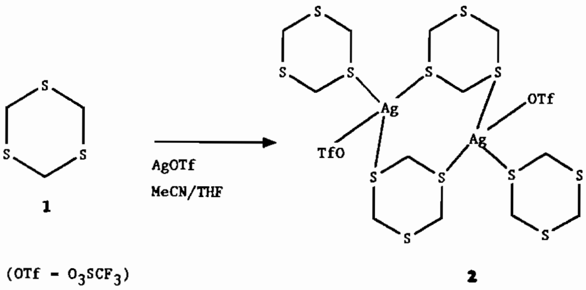


Fig. 1. ORTEP drawing (50% probability) of **1**. Selected bond distances (Å) and angles (°): S(1)–C(1) = 1.803(2); S(1)–C(2) = 1.801(2); S(2)–C(2) = 1.806(2); C(1)–S(1)–C(2) = 99.52(13); C(2)–S(2)–C(2a) = 98.91(10); S(1)–C(2)–S(2) = 115.50(12); S(1)–C(1)–S(1a) = 115.72(15).

Complexation of **1** with $AgCF_3SO_3$ in THF leads to precipitation of dimeric $[(CF_3SO_3)(C_3H_6S_3)_2Ag]_2$ (**2**) as shown in eqn. (1).



(1)

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Crystal data for the free ligand **1, $C_3H_6S_3$: (T = 302 K; Enraf-Nonius CAD4T rotating anode; transparent, colorless crystal, M = 138.26) $C_3H_6S_3$, orthorhombic $Pcmn$, a = 5.261(3), b = 7.6680(3), c = 14.0347(7) Å, V = 566.18(5) Å^3, Z = 4, D_c = 1.622 g cm^{-3}, μ(Mo Kα) = 11.1 cm^{-1}, λ(Mo Kα) = 0.71073 Å, $1 < \theta < 27.5°$, R_F = 0.025, R_w = 0.034 for 620 reflections with $I > 2.5\sigma(I)$; $w = \sigma^2(F)$, GOF = 0.48. The data were corrected for absorption (DIFABS). The structure was solved by direct methods (SHELXS86) and refined by full matrix least-squares (SHELX76) whereby all positional parameters were refined.

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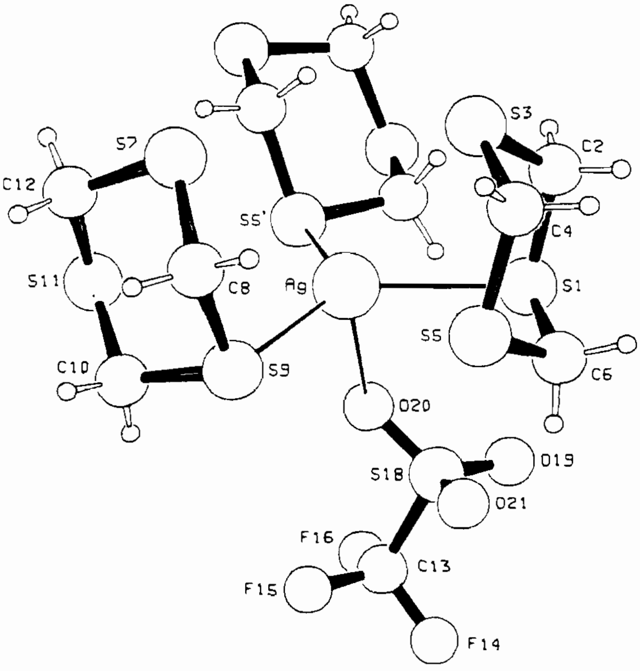

Fig. 2. Perspective drawing of complex **2**. Selected bond distances (Å) and angles (°): Ag–S(1) = 2.584(1); Ag–S(5) = 2.511(1); Ag–S(9) = 2.491(1); Ag–O(20) = 2.960(3); S(1)–Ag–S(5) = 103.71(4); S(1)–Ag–S(9) = 131.09(4); S(1)–Ag–O(20) = 81.42(7); S(5)–Ag–S(9) = 123.47(3).

A solution of $AgCF_3SO_3$ (1.07 mmol in 150 ml THF) was gently added to a solution of **1** (2.48 mmol in 75 ml of THF) at room temperature. The resulting mixture was allowed to stand for two days after which time off-white crystals of **2** were obtained in 63% yield. Complex **4** was prepared similarly. Complex **2** was also obtained when a large excess of ligand (>3 equiv.) was used or when MeCN or MeOH was used as solvent.

The structure of **2*** is shown in Fig. 2. For clarity only half of the molecule is illustrated.

The bond distances between Ag and S are quite similar in **2**: Ag–S(1) = 2.584(1), Ag–S(5) = 2.511(1), Ag′–S(1) = 2.584(1), Ag′–S(5) = 2.511(1) Å.

The residual two trithiane molecules are connected to the silver atom through only one sulfur atom with the fairly normal bond distance of Ag–S(9) = 2.491(3) Å, comparable with those found in $[Ag(CF_3SO_3)$12-thiocrown-3] (2.463(2) and 2.477(2) Å) [5] $[Ag_3$(9-thiocrown-3]$^{3+}$ (2.696(3) Å) [6] and $[Ag(CF_3CO_2)(\mu$-1,3-dithiane)$]_n$ (2.509(1) and 2.5785(7) Å) [7]. The Ag–O distance is quite long (O(20)–Ag = 2.960(3) Å) compared to the related complex $[Ag(CF_3SO_3)$12-thiocrown-3] (2.482(6) Å) [5b]. This may be a consequence of the steric repulsion by the trithiane ligands surrounding the central metal ion.

The geometry of ligand **1** in complex **2**, despite the different types of bonding, is quite similar and illustrates that virtually no conformational reorganization relative to the free ligand has occurred. The 1,3,5-trithiane molecule (**1**) acts as a unidentate ligand in spite of the seemingly suitable arrangement of the three sulfur atoms in the non-complexed form [4b].

The characteristic cyclohexane chair conformation [8] is found in 1,4-dithiane (**3**) where the S atoms are separated by two ethylene units allowing some degree of fluxionality. This compound forms with AgO_3CCF_3 a crystalline complex **4****, the sheet-like polymeric structure of which is illustrated in Fig. 3(a).

Owing to the rather strong coordinating properties of $CF_3CO_2^-$ ligand the structure is built up of Ag_2L_2 units interlinked by the sulfide ligand. In each individual dimer one oxygen atom of the carboxylate moiety bridges between two silver ions. Bond lengths and angles are in line with the representative data given for **2**. In **4** the energetically favorable chair form of the ligand appears to drive the complex formation to an infinite two-dimensional polymeric 1:1 network.

These relatively simple systems provide remarkable insight into how the conformation (preorganization) of an individual ligand is translated into a macroscopic crystal arrangement of their metal complexes.

Supplementary material

Atomic coordinates, bond lengths and bond angles including lists of F_o/F_c are available on request from the authors for all compounds listed.

Acknowledgement

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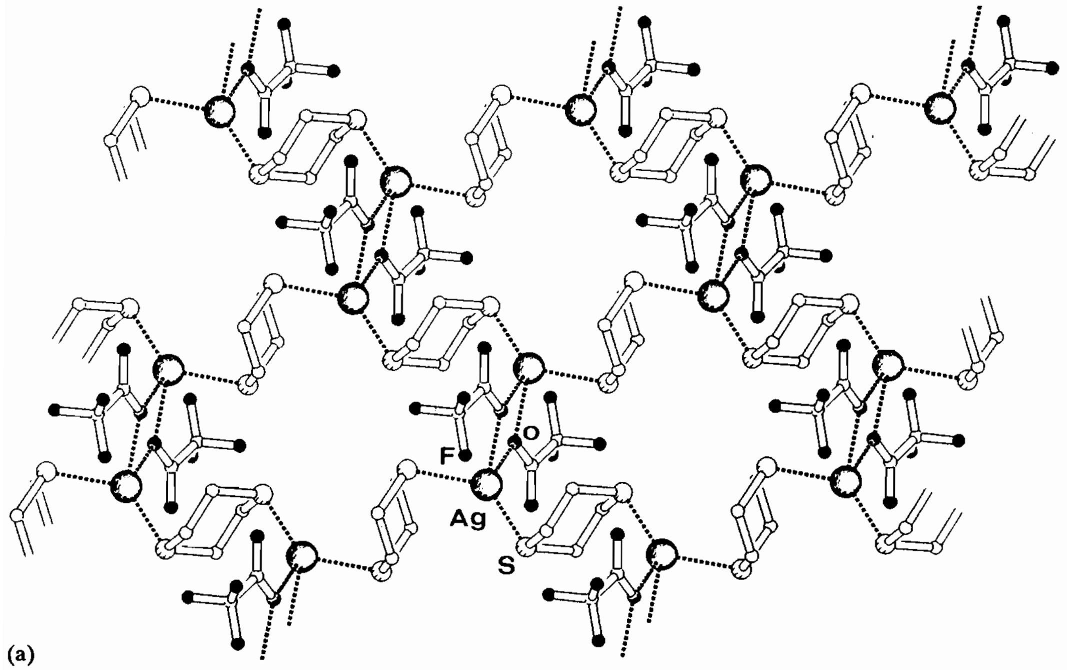
*Crystal data for **2**, $C_7H_{12}S_7F_3O_3Ag$: monoclinic, space group $P2_1/a$, $a = 11.445(d)$, $b = 12.121(1)$, $c = 12.966(1)$ Å, $\beta = 107.83(1)°$, $V = 1712.3(3)$ Å^3, $Z = 4$, $D_c = 2.069$ g cm^{-3}, μ(Mo Kα) = 20.17 cm^{-1}, $\lambda = 0.71073$ Å, $1 < \theta < 27.5°$, $R_F = 0.028$, $R_w = 0.035$ for 2982 ($I > 3\sigma(I)$) reflections collected on an Enraf-Nonius CAD 4 diffractometer at 138 K, $GOF = 1.68$.

Crystal data for **4 ($T = 302$ K; Enraf-Nonius CAD4T rotating anode) $C_4H_8S_2 \cdot Ag \cdot C_2F_3O_2$: needle shaped colorless crystal. Monoclinic space group $P2_1/n$, $a = 9.1343(3)$, $b = 7.7603(4)$, $c = 14.0965(4)$ Å, $\beta = 42.867(3)$, $V = 997.98(7)$ Å^3, $Z = 4$, $D_c = 2.270$ g cm^{-3}, μ(Mo Kα) = 24.2 cm^{-1}, λ(Mo Kα) = 0.71073 Å, $1.4 < \theta < 27.5°$. Data were corrected for absorption. The structure was solved by Patterson methods (SHELX86) and refined by full matrix least squares (SHELX76). H atoms were included at calculated positions. The structure converged at $R_F = 0.0226$, $R_w = 0.0281$, $w = \sigma^2(F)$ for 2046 reflections with $I > 2.5\sigma(I)$ and 128 parameters.



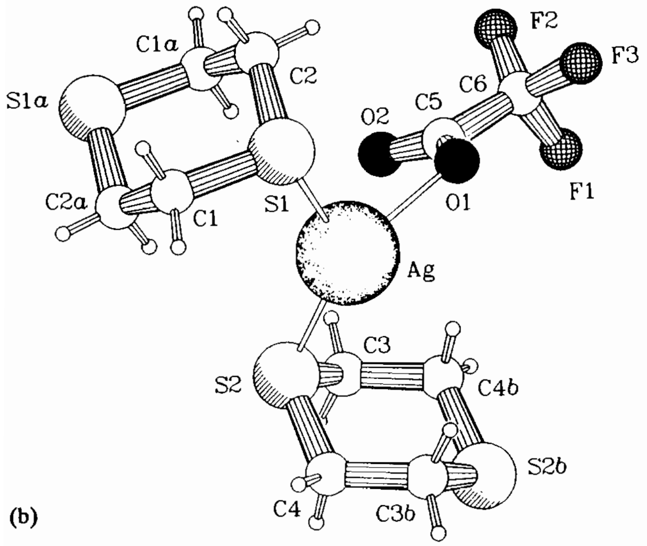


Fig. 3. (a) Drawing illustrating the two-dimensional network structure of **4**. (b) Coordination sphere around Ag(I) in **4**. Selected bond distances (Å) and angles (°): Ag–S(1) = 2.5110(7); Ag–S(2) = 2.4648(7); Ag–O(1) = 2.3496(19); Ag–O(1) = 2.5555(19); S(1)–Ag–S(2) = 132.43(2); S(1)–Ag–O = 99.28(6); S(1)–Ag–O(1) = 93.32(5); S(2)–Ag–O(1) = 122.47(6); S(2)–Ag–O(1) = 115.94(5).

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