Silver(I) Complex of a Crown Thioether Retaining the Transoid S−C−C−S Ligand Conformation☆

Rolf Gleiter*[a], Harald Röckel[a], and Bernhard Nuber[b]

Organisch[a]- und Anorganisch[b]-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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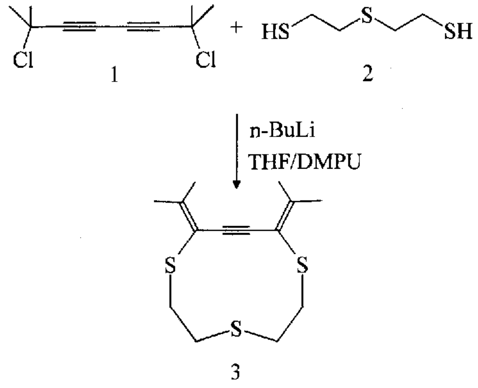
The crown thioether **3** with the novel diisopropylidene building block was synthesized by an S_N' cyclization reaction of 2,7-dichloro-2,7-dimethylocta-3,5-diyne (**1**) with 3-thiapentane-1,5-dithiol (**2**). Ligand **3** shows all the sulfur centers in exodentate positions. Reaction of **3** with Ag^I triflate and triphenylphosphane yielded the tetrahedral complex **4**, which shows unique spectroscopic data in solution. Crystallization furnished two different crystal forms (**4a** and **4b**). Both are different conformers which are stable in the solid state. **4a** exhibits a crown-like structure of the thioether ligand with cisoid S−C−C−S chains. To our knowledge **4b** is the first silver(I) complex with a crown thioether retaining the transoid S−C−C−S conformation in the metal complex.

Crown thioethers were investigated extensively because of their ability to complex and stabilize first-, second-, and third-row metals in low oxidation states. Important work on the complexation of copper ions for example was carried out by Rorabacher and Ochrymowycz[1]. The complexation properties of crown thioethers make them attractive as models for enzymes on the one hand and as candidates for ligands for industrial metal catalysts on the other. Recently, Cooper reviewed the conformation of cyclic thioethers as well as their coordination compounds with several metals[2].

One essential feature of the free ligands is the exodentate position of the sulfur donor atoms in most compounds. The important exception is 1,4,7-trithiacyclononane (9-S-3)[3] in which the sulfur atoms are preorganized in an endodentate fashion prone to metal complexation. This orientation is due to the sterical constraints in the 9-membered ring. Because of this preorganization 9-S-3 yields a number of stable complexes in contrast to other, more flexible crown thioethers[2]. Much efforts have been made to synthesize analogous compounds with preorganized endodentate sulfur atoms by introducing rigid units in the macrocyclic rings. However, most of these compounds prefer a conformation with exodentate sulfur units[4].

Recently, we synthesized crown thioethers with an unsaturated diisopropylidene-alkyne unit as building block[5]. One example of these novel compounds is **3** which was synthesized by a new S_N' cyclization reaction of the conjugated diyne **1** with the dithiol **2** (Scheme 1). In this tridentate compound there are two different types of sulfur atoms: two are adjacent to an organic π system, the third is flanked by saturated carbon atoms. These sulfur centers should exhibit different donor strengths because of the effect of p-π conjugation and therefore give rise to different complexation properties.

Scheme 1



In this paper we discuss the X-ray structure of the free ligand **3** which is ideal as capping ligand in complexes with tetrahedral geometry. For this purpose we carried out the synthesis and analyzed the structures of Ag^I triflate complexes with triphenylphosphane as coligand occupying the fourth coordination site. We were especially interested in the influence of the rigid building block, the diisopropylidene-alkyne π system, on the complexation properties of the new ligand.

Results and Discussion

The X-ray structure of **3** shows a conformation with a statistical disorder at C6, C7, S1, and S3. This yields two different positions for the chain between C3 and C8 giving rise to two conformers **3a** and **3b**; one of them, **3a**, is shown in Figure 1. (The sulfur atoms S1a, S1b and S3a, S3b could be anisotropically refined, whereas the thermal parameters of the carbon atoms could be refined only isotropically.) Both conformers have the anticipated shape: the diisopro-

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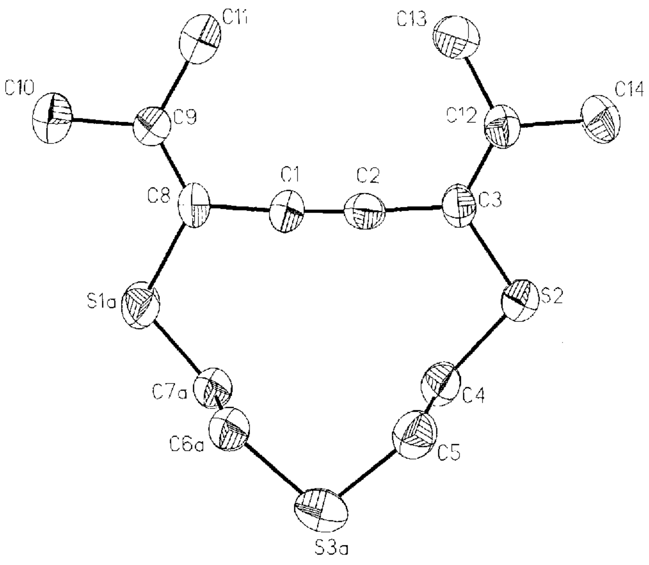
pylidene-alkyne unit is planar with a *cis* orientation of the two isopropylidene groups. The angles at the triple bonds are 176.2 and 176.7°, respectively. The sulfur atoms S1 and S2 next to the π bonds are in the plane of the isopropylidene-alkyne unit and adopt the favorable exodentate position. The third sulfur atom, S3, is *anti*-orientated to both S1 and S2. This is expressed e.g. by the two dihedral angles in **3a** which amount to 167.2° for S2−C4−C5−S3a and 172.0° for S1a−C7a−C6a−S3a.

Figure 1. Conformer **3a** in the crystal; selected bond lengths [Å] and bond angles [°]: S2−C3 1.744(10), S2−C4 1.787(8), C1−C2 1.888(11), C1−C8 1.417(11), C3−C12 1.340(12), C4−C5 1.470(13), C5−S3a 1.745(30); C2−C1−C8 176.2(10), C1−C2−C3 176.7(10), S2−C3−C2 120.5(6), S2−C3−C12 118.7(6), S2−C4−C5 113.2(7), C4−C5−S3a 124.7(16), C5−C3a−C6a 102.0(22)

3a



For complexation of a cation one would expect that the *anti* orientation of the sulfur atoms has to change to a more favorable cisoid, endodentate conformation. This conformational change was observed for all crown thioethers investigated to date[2].

Crystallization of the silver(I) complex from an acetonitrile/ether solution yielded colorless crystals in two macroscopic modifications. X-ray experiments with these crystals revealed that **4** crystallizes in two conformers, which are stable in the solid state (Figure 2). The first conformer (**4a**) was a typical silver crown thioether complex with a tridentate ligand and triphenylphosphane as coligand. Similar complexes were investigated by Loeb et al.[7]. The formerly exodentate sulfur atoms of the ligand **3** are now in an endodentate position, and the ligand is twisted along the carbon-carbon bond to adopt a crown-like *cis* conformation which is favorable for complexing the silver ion. The S1−C−C−S3 dihedral angle amounts to 70.4°. The bond lengths between silver(I) and the π-bonded sulfur atoms amount to 2.752(3) and 2.643(3) Å, respectively. The silver−S3 bond length amounts to 2.572(4) Å. This value is in the range of many observed bond lengths in silver complexes of crown thioethers[2,7]. The linear arrangement of the triple bonds is deformed by 7.9 and 11.4° due to the strain in the seven-membered chelate Ag−S1−C28−C27−C26−C25−S2. The fourth complexation site is occupied by the triphenylphosphane ligand which adopts normal bond lengths and bond angles. The phosphane ligand is in a staggered orientation with respect to the two isopropylidene groups.

In the second conformer (**4b**) the phosphane ligand is in an eclipsed orientation with respect to the isopropylidene groups of the crown thioether. Bond lengths and bond angles of this ligand again show no deviations from reported values[7]. The main difference in comparison with **4a** is found in the conformation of the macrocyclic thioether ligand. The ligand retains the transoid sulfur-sulfur conformation of the S1−C21−C22−S3 and S2−C24−C23−S3 chains, respectively, which is indicated by the S1−C−C−S3 dihedral angles amounting to 151.1°. This behavior is unusual for crown thioethers. The bond lengths between the silver(I) atom and the π-bonded sulfur atoms S1 and S2 are unexpectedly long. They are 2.750(2) and 2.971(2) Å, respectively, and therefore are in the range of the van der Waals radii of silver(I) and sulfur (2.98 Å). The distance between the silver atom and S3 is found to be 2.500(2) Å, a bond length similar to those found in **4a**. Once again the angle at the triple bond is deformed by 9.2 and 9.8°, respectively. In both silver complexes the bond lengths between silver and the sulfur atoms adjacent to the double bonds (average: 2.70 Å for **4a** and 2.86 Å for **4b**) are longer than those between silver and the sulfur atoms bound to two saturated aliphatic carbon atoms [2.572(4) Å for **4a** and 2.500(2) Å for **4b**]. This can be attributed to the result of π-p conjugation which diminishes the donor strength of the sulfur atoms. Similar results were found by Rorabacher and Ochrymowycz who investigated the complexation constants of phenyl-substituted crown thioethers[8].

Summary

The ligand **3** is the first example of a macrocyclic tridentate thioether which is able to form stable complexes with a cation retaining its inherent transoid S−C−C−S conformation. The X-ray structure of **4b** shows that it is not necessary for **3** to preorganize in a cisoid crown-like conformation to form a stable silver complex, as is mentioned for many other crown thioethers that act as a complexing ligand. We think that this result can be rationalized on the assumption that the two conformations exhibit an energy minimum even in solution. One reason is the weak sterical demand of the d^{10}-silver(I) metal ion at the ligand. The energy gain in **4a** by forming shorter silver-sulfur bonds is lost because of the unfavorable cisoid conformation for the ligand. On the other hand, the energy loss in **4b** due to the weak silver-sulfur bonds is compensated by an energy gain in the ligand, adopting the favorable transoid ligand conformation.

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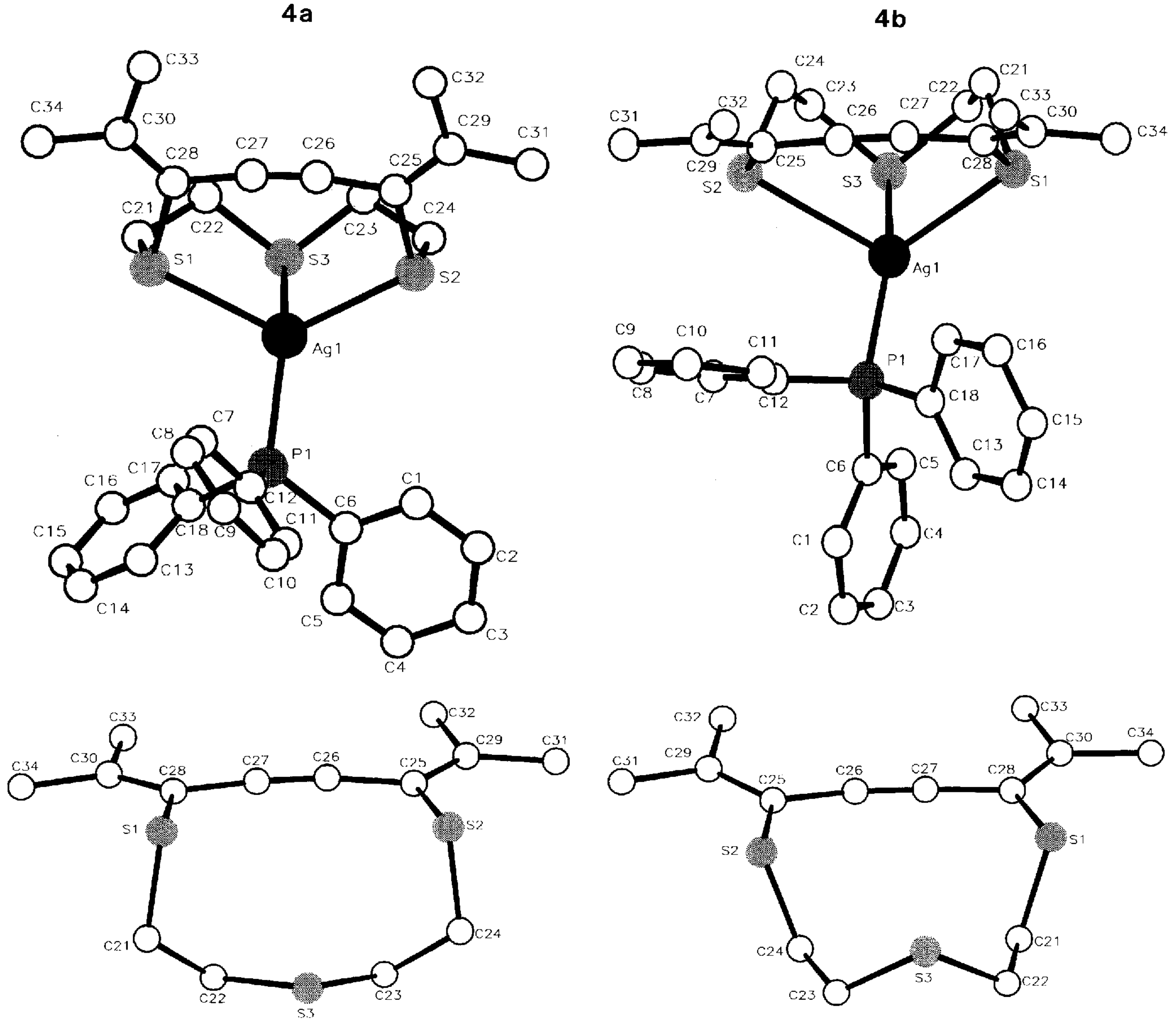
Figure 2. Molecular structures of **4a** and **4b** (top) and the respective macrocyclic ligand in **4a** or **4b** (bottom, Ag^+ and PPh_3 are omitted) in the crystal; selected bond lengths [Å] and bond angles [°] of **4a**: Ag1–S1 2.752(3), Ag1–S2 2.643(3), Ag1–S3 2.572(4), Ag1–P1 2.410(3); S1–Ag1–S2 123.3(1), S1–Ag1–S3 83.5(1), S1–Ag1–S3 85.2(1), S1–Ag1–P1 107.6(1), C26–C25–C29 125.5(8), C25–C26–C27 168.6(11), C24–S2–C25 102.2(5), C22–S3–C23 102.7(4), S2–C25–C26 112.5(7); **4b**: Ag1–S1 2.750(2), Ag1–S3 2.500(2), Ag1–P1 2.387(2); S1–Ag1–S3 83.7(1), S1–Ag1–P1 119.9(1), S3–Ag1–P1 151.0(1), C26–C25–C29 124.8(5), C25–C26–C27 170.8(6), C24–S2–C25 101.6(3), C22–S3–C23 103.9(4), S2–C25–C26 113.0(5)



4a

4b

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Experimental

Synthesis of **3**: To a solution of the dithiol **2** (1.69 g, 11 mmol) dissolved in THF/DMPU (10:1), which was cooled to −70 °C, a solution of 13.8 ml (22 mmol) of *n*BuLi (1.6 mol in hexane) was added dropwise. After completion of the addition the suspension of the dilithium salt was heated to reflux. To the deprotonated dithiol, a solution of 2,7-dichloro-2,7-dimethylocta-3,5-diyne (**1**) (2.22 g, 10 mmol) in 50 ml of the solvent mixture was added over a period of 5 h. The reaction mixture was heated for further 12 h, cooled and treated with 50 ml of water. After the addition of diethyl ether, DMPU was extracted with ten portions of 30 ml of water each. The combined extracts were dried with Na_2SO_4, the solvent was evaporated, and the residue was chromatographed (silica gel/CCl_4) to yield **3** as a colorless solid. Further purification could be achieved by crystallization of **3** from CH_2Cl_2/ethanol (1:2). Yield: 42%. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.89 (s, 6H), 2.04 (s, 6H), 2.70–2.76 (m, 4H), 2.99–3.05 (m, 4H). – ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.38, 24.57, 89.29, 110.74, 142.90. – EI-MS, *m/z* (%): 284 [M^+] (100). – $C_{14}H_{20}S_3$ (284.4): calcd. C 59.10, H 7.09; found C 58.94, H 7.11.

Synthesis of the Silver(I) Complex: To a solution of **3** (426 mg, 2.5 mmol) and triphenylphosphane (393 mg, 2.5 mmol) in 40 ml of acetonitrile, a solution of Ag^I triflate (385.5 mg, 2.5 mmol) in 20 ml of acetonitrile was added dropwise over a period of 20 min at room temp. The mixture was stirred for 2 h, and most of the acetonitrile was removed in vacuo. Addition of diethyl ether and cooling to −30 °C yielded the tetrahedral silver complex **4** (1.8 g, 89%). – ^1H NMR (300 MHz, CD_3CN): δ = 1.97 (s, 6H), 2.00 (s, 6H), 3.09 (m, 8H), 7.42–7.53 (m, 15H). – ^{13}C NMR (75.46 MHz,

CD_3CN): δ = 22.10, 24.96, 32.39, 34.35, 93.24, 108.70, 129.92 ($J_{C,P}$ = 10.2 Hz), 131.62 ($J_{C,P}$ = 33.3 Hz), 134.27 ($J_{C,P}$ = 2.8 Hz), 134.27 ($J_{C,P}$ = 16.4 Hz), 153.62. – FD-MS, *m/z*: 653 [M^+ of the cation]. – $C_{33}H_{35}AgF_3O_3PS_4$ (803.7): calcd. C 49.32, H 4.39, S 15.96; found C 49.41, H 4.83, S 15.61.

General X-ray Diffraction Data Collection and Solution: Data were collected with a Syntex R3 diffractometer at room temperature. The structures were solved by using direct methods (**3**) and Patterson Fourier analysis (**4a, b**). The calculations were performed with the SHELXTL PLUS[6] program.

Table 1. Crystal data and data collection parameters

	3	**4a**	**4b**
mol formula	$C_{14}H_{20}S_3$	$[C_{32}H_{35}AgS_3P]SO_3CF_3$	$[C_{32}H_{35}AgS_3P]SO_3CF_3$
fw	284	804	804
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
cell dimensions			
a, Å	16.30(1)	11.562(7)	11.813(3)
b, Å	4.959(3)	11.534(6)	12.006(4)
c, Å	19.33(1)	15.74(1)	13.925(5)
α, °		96.99(6)	108.25(2)
β, °	108.26	104.34(6)	96.44(3)
γ, °		115.87(4)	106.98(2)
V, $Å^3$	1483.8	1765.1	1748.2
Z	4	2	2
T, K	296	296	296
d_{calc}, g·cm^3	1.27	1.51	1.53
linear abs, μ, mm^{-1}	0.46	0.88	0.89
F(000)	608.00	820.00	820.00
radiation, Å	λ(Mo Kα), = 0.71073	λ(Mo Kα), = 0.71073	λ(Mo Kα), = 0.71073
scan type	ω	ω	ω
reflections measured	h, 0 - 18; k, 0 - 6; l, -22 - 22	h, 0 - 16; k, -15 - 15; l, -21 - 21	h, 0 - 14; k, -14 - 14; l, -16 - 16
2θ range, deg	3.0 < 2θ < 46.0	3.0 < 2θ < 55.0	3.0 < 2θ < 48.0
no of rflns measd	2360	8131	5523
abs cor	empirical, 4 rflns	empirical, 7 rflns	empirical, 6 rflns
range of transmission	0.87 - 1.00	0.93 - 1.00	0.91 - 1.00
no of unique obsd data	1236, I > 2.5σ(I)	4787, I > 2.5σ(I)	3885, I > 2.5σ(I)
no of parameters	172	366	407
R(F)	0.075	0.090	0.051
R_W(F)	0.069	0.076	0.044
GOOF	3.22	2.77	1.79
ρ, residual, e·Å(max/min)	0.51	1.95	0.58

X-ray Structure of $C_{14}H_{20}S_3$ (**3**): The colorless needles suitable for X-ray analysis were obtained by crystallization from an ethanolic solution of **3** at −30 °C. The dimensions of the crystal were 0.25 × 0.30 × 0.95 mm^3. The unit cell was determined and refined from 25 reflections (5.6 < 2Θ < 23°). The structure was solved by assuming a statistical distortion at C6 and C7. Relevant crystal and data collection parameters are given in Table 1[9]. Selected bond lengths and bond angles are summarized in Figure 1[9].

X-ray Structure of **4a** *and* **4b**: Crystallization of **4** from diethyl ether yielded two macroscopically different crystals. They were separated mechanically and used for X-ray analysis. **4a**: The dimensions of the colorless crystals were 0.16 × 0.25 × 0.95 mm^3. The unit cell was determined and refined from 20 reflections (4.0 < 2Θ < 21.0°). Relevant crystal and data collection parameters are given in Table 1[9]. Selected bond lengths and bond angles are summarized in Figure 2. **4b**: The crystal dimensions were 0.25 × 0.35 × 0.40 mm^3. The unit cell was determined and refined from 22 reflections (3.7 < 2Θ < 21.0°). Relevant crystal and data collection parameters are given in Table 1. Selected bond lengths and bond angles are summarized in Table 1[9].

☆ Dedicated to Prof. *Marianne Baudler* on the occasion of her 75th birthday.

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[9] Further details of the structure determination are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CDD 404565 for **3**, CSD 404566 for **4a**, and CSD 404567 for **4b**, the names of the authors, and the journal citation.

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