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FULL PAPER

Reactions and complexation properties of 1,6-diaminohex-3-yne and 1,4-bis(2-aminoethyl)benzene

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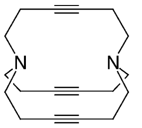
1,6-Diaminohex-3-yne (**3**) reacts with silver triflate to yield a complex consisting of two silver ions and two molecules of 2-(2′-aminoethyl)-1-pyrroline (**6**). The silver ions form bridges between the primary amino group of one ligand and the imino group of the 1-pyrroline heterocycle of the other ligand. X-Ray investigations confirm this structure and show that the triflate anions are placed above and below the center of the plane spanned by the organic ligands and the silver ions. The reaction of 1,4-bis(2-aminoethyl)benzene (**4**) with silver triflate yields in the solid state an infinite chain composed of **4** and Ag^+. X-Ray investigations reveal a loop-like arrangement of the chain in the solid state.

1 Introduction

Many ditopic organodiamino and diimino compounds form intermolecular coordination polymers with silver ions providing a wide variety of fascinating one-, two- and three-dimensional structures.[1] As building blocks in these structures one recognizes linear N ··· Ag ··· N bridges. This behavior is contrasted by 1,(*k*+2)-diazabicyclo[*k.l.m*]alkanes with rigid elements such as alkyne or benzene units in the chains. These cage molecules form stable intramolecular complexes with Ag(I) and Cu(I) ions.[2,3] Examples for such cavities are 1,8-bicyclo[6.6.6]eicosa-4,11,17-triyne (**1**)[4] and the π-prismand **2**[3] and their silver complexes.[2,3] To find out how the building blocks of **1** and **2**, 1,6-diaminohex-3-yne (**3**)[3] and 1,4-bis(2-aminoethyl)benzene (**4**)[3] behave towards silver ions we reacted them with silver triflate. Since the resulting species were not anticipated we report their structures.



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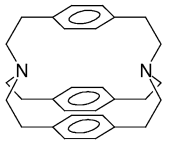

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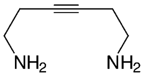

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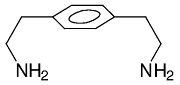

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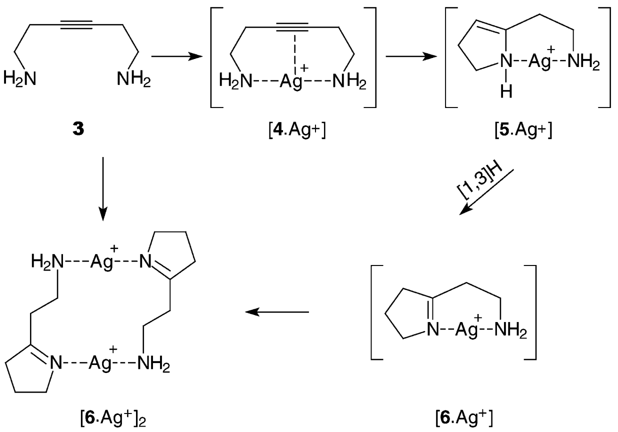
2 Results

The reaction of **3** with silver triflate at room temperature in methylene chloride yielded 2-(2′-aminoethyl)-1-pyrroline (**6**), complexed with Ag^+ in quantitative yield as colorless, light-sensitive crystals. The assignment of the structure of **6** is based on its NMR spectra. High resolution mass spectrometric (FAB^+) investigations reveal that two molecules of **6** are complexed with two molecules of silver triflate. The structure given in Scheme 1 for the product $[\mathbf{6}\cdot Ag^+]_2$ is based on X-ray investigations (see below). The formation of the aminoethylpyrroline derivative from **3** can be rationalized by a silver supported intramolecular hydroamination reaction to yield in a first step to $[\mathbf{5}\cdot Ag^+]$ (Scheme 1). This intermediate might rearrange to $[\mathbf{6}\cdot Ag^+]$ *via* an intramolecular hydrogen shift, which subsequently forms the more stable dimeric complex $[\mathbf{6}\cdot Ag^+]_2$.



Scheme 1

In Fig. 1a the molecular structure of $[\mathbf{6}\cdot Ag^+]_2$ is shown as derived from an X-ray investigation on a single crystal of the product. In the solid state two molecules of **6** are joined together *via* two silver ions. The distances between the organic moieties stay within the expected values. The average distances between the nitrogen and silver atoms (2.12 Å) are very similar to those values reported for unstrained silver amine complexes.[5] It is noteworthy that both N ··· Ag ··· N axes deviate from linearity by 9° (N ··· Ag ··· N = 171.1°, Fig. 1). This inward bending leads to a Ag ··· Ag distance of 3.23 Å in $[\mathbf{6}\cdot Ag^+]_2$ indicating an attractive interaction between the metals. In the case of lighter coinage metals copper and silver this phenomenon has been discussed on several occasions.[6,7] In Fig. 1b we show a side view of $[\mathbf{6}\cdot Ag^+]_2$ which reveals relatively short Ag ··· O distances (minimum distance 3.08 Å) and hydrogen bridges between the triflate oxygen atoms and the NH bonds (2.15 and 2.27 Å). Close Ag ··· O distances (3.00 Å) have been found in the one-dimensional coordination polymer between 5,5′dicyano-2,2′bipyridine with silver triflate.[8]

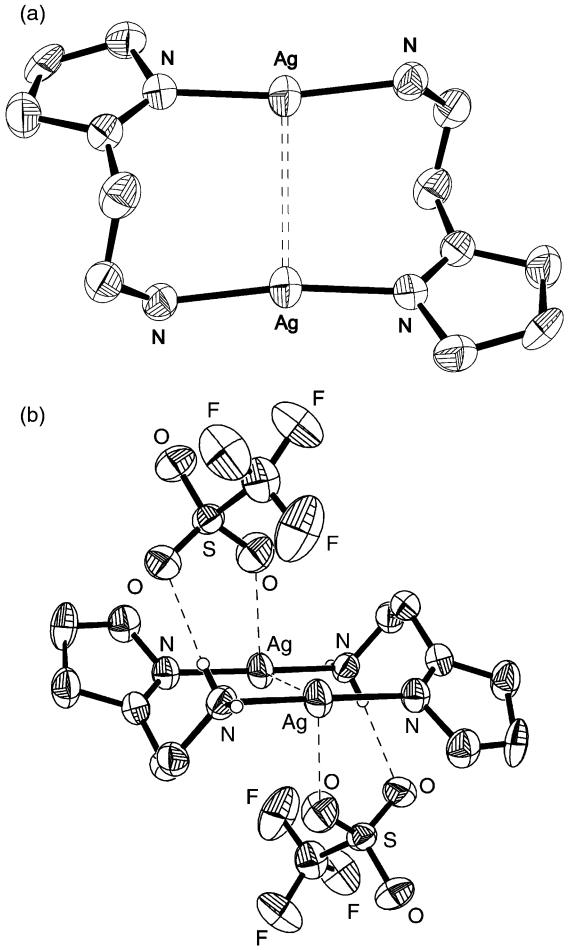


Fig. 1 (a) Molecular structure of $[\mathbf{6}{\cdot}AgCF_3SO_3]_2$ viewed from above. The hydrogen atoms and the anions were omitted for the sake of clarity. The plot is presented at 50% probability level; (b) side view of $[\mathbf{6}{\cdot}AgCF_3SO_3]_2$. Short distances between silver and oxygen as well hydrogen and oxygen are indicated.

The reaction of silver(I) triflate with **4** does not yield an intramolecular complex. We isolated a light-sensitive colorless compound which showed relatively broad lines in the ^1H NMR spectrum in methanol. This effect points towards oligomeric species. This assumption was supported by a mass spectrometric investigation. In the (FAB^+) mass spectrum multiple mass signals of the expected monomer could be detected. The resonance of the aromatic protons in the ^1H NMR spectrum of $[\mathbf{4}{\cdot}Ag^+]_n$ (δ = 7.21) in solution is shifted towards lower field as compared to the free ligand by 0.11 ppm. This suggests some proximity in solution between Ag^+ and the aromatic ring.

The investigation of single crystals reveals that in the solid state the diamine **4** is connected *via* silver ions to a polymer with a loop-like arrangement of the chains (Fig. 2). The distance between silver ion and nitrogen atom (2.14 Å) is close to that found for other silver amine complexes.[5] The distance between silver atom and benzene center amounts to 3.30 Å. This distance is rather large compared to the values recorded for complexes between various cyclophanes with silver salts[9] and $C_6H_6{\cdot}AgAlCl_4$.[10] In these cases the distance between the metal and the center of the nearest C–C bond varies between 2.6 Å and 2.8 Å.[9,10] Nevertheless the folding of the polymer chain yields alternation of benzene rings and silver ions suggesting a weak interaction between both (see Fig. 2). Furthermore, the triflate anions are situated in channels between two chains of the coordination polymers, parallel to the *b*-axis. Hydrogen bonds between the NH protons and the oxygen atoms of the triflate anion result. There is no interaction between Ag^+ and the oxygen centers. The shortest distance between silver and oxygen amounts to 4.50 Å.

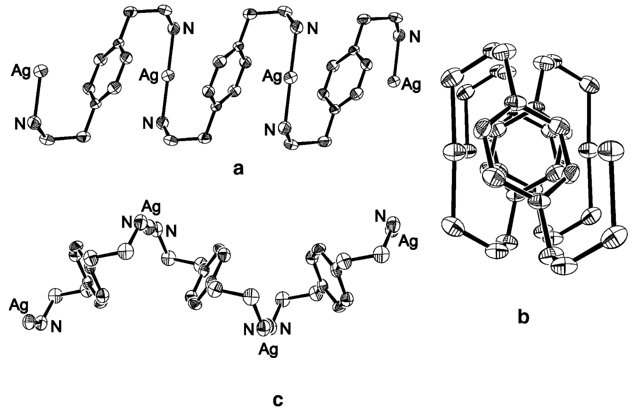


Fig. 2 Molecular structure of $[\mathbf{4}{\cdot}AgCF_3SO_3]_\infty$. For the sake of clarity the anions (CF_3SO_3) and the hydrogens were omitted. The plots are presented at 50% probability level. (a) view along the *a*-axis, (b) view along the *b*-axis, (c) view along the *c*-axis.

3 Conclusion

Our investigations reveal that the reaction between silver triflate and the building units of **3** and **4**, respectively, does not yield intramolecular complexes. The primary amine **3** reacts in an intramolecular hydroamination of the triple bond. The intramolecular complexation of **4** fails, probably due to the relative long distance between the nitrogen centers. Already in $[\mathbf{2}{\cdot}Ag^+]$ the silver ion is not situated in the center of the cavity, whereas in the silver complex of **1** this is the case.

4 Experimental

4.1 General methods

All reactions were carried out under an argon atmosphere with magnetic stirring in dry degassed methylene chloride. The ^1H and ^{13}C NMR spectra were recorded in CD_3OD with Bruker WH 300 and Avance 500 instruments, respectively. Mass spectra were obtained with a JEOL JMS 700 spectrometer.

4.2 General procedure for the complexation

One equivalent of the diamine (**3**,[3] **4**[11]) was added to one equivalent of silver(I) triflate in dry degassed methylene chloride under argon and stirred for one hour at room temperature with the exclusion of light. The solvent was removed *in vacuo* and the remaining white solid recrystallized from methanol yielding colorless light-sensitive crystals in both cases.

$[[\mathbf{6}{\cdot}Ag]_2{\cdot}2CF_3SO_3]$: mp 132 °C. decomp., yield: 100%. HRMS (FAB^+) *m*/*z* 590.9688, 586.9675, calc. for $C_{13}H_{24}{}^{109}Ag_2F_3N_4O_3S$ (M^+): 590.9616, calc. for $C_{13}H_{24}{}^{107}Ag_2F_3N_4O_3S$ (M^+): 586.9623; ^1H NMR (300 MHz) δ 2.09 (pseudo quint., 4H, ^3J = 7.5 Hz, 8.0 Hz), 2.74 (t, 4H, ^3J = 8.0 Hz), 2.90 (t, 4H, ^3J = 6.0 Hz), 3.12 (t, 4H, ^3J = 6.0 Hz), 3.97 (t, 4H, ^3J = 7.5 Hz); ^{13}C NMR (75 MHz) δ 23.1, 36.4, 40.5, 41.7, 63.6, 186.6. IR (KBr) $\tilde{\nu}_{max}$/cm^{-1} 2954 (m), 1641 (s), 1429 (w), 1260 (vs), 1172 (s), 1039 (s). Elem. Anal.: Found: C, 23.34; H, 3.59; N, 7.47. $C_{14}H_{24}Ag_2F_6N_4O_6S_2$ requires C, 23.78; H, 3.28; N, 7.59.

$[\mathbf{4}{\cdot}AgCF_3SO_3]$: mp 139 °C, decomp. yield: 100%. HRMS (FAB^+) *m*/*z* 273.0376, 271.0360, calc. for $C_{10}H_{16}{}^{109}AgN_2$ (M^+): 273.0361, calc. for $C_{10}H_{16}{}^{107}AgN_2$ (M^+): 271.0365; ^1H NMR (500 MHz) δ 2.62 (t, 4H, ^3J = 6.7 Hz), 2.89 (t, 4H, ^3J = 6.7 Hz), 7.21 (s, 4H); ^{13}C NMR (125 MHz) δ 38.5, 45.2, 130.4, 138.1. IR (KBr) $\tilde{\nu}_{max}$/cm^{-1} 3262 (m), 2944 (w), 2861 (w), 1584 (m), 1452 (w), 1260 (vs), 1176 (s), 1035 (vs).

4.3 X-Ray crystallography and structure solution

Data were collected on a Bruker SMART CCD diffractometer at 200 K for $[\mathbf{4}{\cdot}AgCF_3SO_3]_n$ and a Nonius CAD4 diffractometer

Table 1 Crystal data for $[\mathbf{4}\cdot Ag^+]_n$ and $[\mathbf{6}\cdot Ag^+]_2$

	$[\mathbf{4}\cdot AgCF_3SO_3]_\infty$	$[\mathbf{6}\cdot Ag]_2\cdot 2CF_3SO_3$
Empirical formula	$C_{11}H_{16}AgF_3N_2O_3S$	$C_{14}H_{24}Ag_2F_6N_4O_6S_2$
M	421.9	738.24
Cryst. size/mm^3	0.28 × 0.06 × 0.02	0.35 × 0.25 × 0.15
Cryst. system	Orthorhombic	Monoclinic
Z	8	2
T/K	200	293
Space group	*Cmca*	$P2_1/n$
a/Å	16.2075(8)	9.901(3)
b/Å	10.3223(4)	11.362(3)
c/Å	18.2280(8)	10.975(3)
β/deg	90.0	100.98(3)
V/Å^3	3049.5(2)	1212.0(6)
D_{calc}/g cm^{-3}	1.84	2.02
Θ range/°	2.2 to 27.5	2.5 to 28.0
hkl values	$-20 \le h \le 21$ $-13 \le k \le 13$ $-23 \le l \le 23$	$0 \le h \le 13$ $0 \le k \le 14$ $-14 \le l \le 14$
μ/mm^{-1}	1.50	1.87
Reflns. collected	15125	3067
Unique reflns.	1816	2906
Reflns. obs., $I > 2\sigma(I)$	1035	2285
Max and min transmission	0.98/0.79	0.72/0.64
Variables	102	230
R (F)	0.036	0.031
R_w (F^2)	0.056	0.069
GOF (F^2)	1.00	1.04
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e A^{-3}	0.57, −0.47	0.39, −0.56

for $[\mathbf{6}\cdot AgCF_3SO_3]_2$, at 293 K. The structures were solved by direct methods ($[\mathbf{6}\cdot AgCF_3SO_3]_2$: SHELXS-97,[12] $[\mathbf{4}\cdot AgCF_3SO_3]_n$: SHELXTL[13]). The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full matrix least squares method.[12] The hydrogen atoms of $[\mathbf{4}\cdot AgCF_3SO_3]_n$ were considered at calculated positions. The hydrogen atoms of $[\mathbf{6}\cdot AgCF_3SO_3]_2$ were refined isotropically with the exception of the H atoms at C4 which were calculated. C4 as well as all F atoms were disordered at two positions (50 :50%). Empirical absorption corrections were applied in both data sets. The crystallographic data are listed in Table 1.

CCDC reference numbers 169018 and 169019.

See http://www.rsc.org/suppdata/dt/b1/b107450b/ for crystallographic data in CIF or other electronic format.

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