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all-Z-Tetrabenzo[16]- and Pentabenzo[20]annulenes, π-Cavitands Binding to Silver Cation

Yoshiyuki Kuwatani, Tadahiro Yoshida, Kenji Hara, Masato Yoshida, Haruo Matsuyama, and Masahiko Iyoda*

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

iyoda-masahiko@c.metro-u.ac.jp

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ABSTRACT

Crystal structures of the silver complexes derived from tetrabenzo[16]annulene with AgOTf and $AgClO_4$ are different, although these two complexes show similar ^1H NMR spectra reflecting a similar clathrate structure in solution. The silver complex of pentabenzo[20]annulene with $AgClO_4$ adopts a clathrate structure both in the solid state and in solution.

Cylindrical π-conjugated molecules[1] attract continuing attention because of the synthetic challenges,[2] unique structures,[3] host/guest interactions,[4] and organic materials with interesting electric properties.[5] Recently, we reported the synthesis of *all-Z*-[*n*]benzo[4*n*]annulenes **1**−**3**, bowl-shaped hydrocarbons with a medium-size concavity (Figure 1).[6]

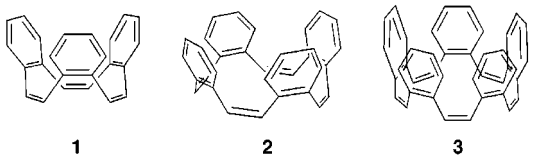

Figure 1.

Since tribenzo[12]annulene **1** formed a stable 1:1 complex with AgOTf,[6a] we investigated a host ability of larger

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tetrabenzo[16]- and pentabenzo[20]annulenes **2** and **3** to incorporate metal ions in their cavity.

Polymeric and self-organized metal complexes can be regarded as new solids with interesting physical and chemical properties based on crystal engineering.[7] In these new crystalline networks, silver(I) ions play an important part for the construction of multidimensional coordination compounds.[8] In addition, cyclophanes include a silver cation through cation−π interactions to produce "π-prismands".[9] In contrast to rigid frameworks of the known π-ligands such as cyclophanes[9] and [12]annulenes,[6a,10] we expected that flexible annulenes **2** and **3** can suit their shape to form metal complexes.

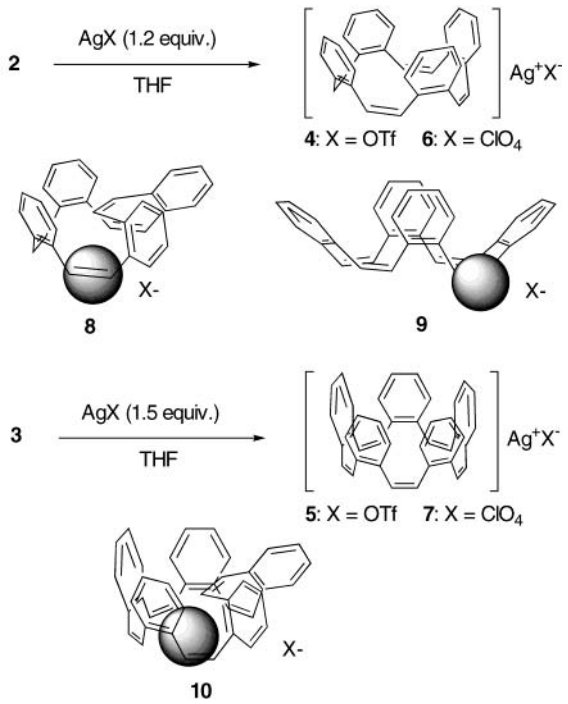
For the preparation of the silver complex of **2**, the reaction of **2** with AgOTf (1.2 equiv) in THF produced the corresponding 1:1 complex **4** in 73% yield. In a similar manner, the 1:1 complex **5** was obtained in 60% yield by the reaction of **3** with AgOTf (1.5 equiv) in THF. The 1:1 complexes (**6** and **7**) can be prepared similarly by mixing **2** and **3** with $AgClO_4$. The complexes **5**, **6**, **7**, and **8** are light- and air-sensitive like normal silver−alkene complexes.

To investigate the structures of the silver complexes **4**−**7** in solution, VT ^{1}H NMR spectra of **4** and **5** were measured in $CDCl_3$ or in CD_2Cl_2. Interestingly, the ^{1}H NMR spectra of **4** in $CDCl_3$ at 25 °C or higher temperatures show very broad signals, but they become sharp at −30 °C. On the basis of the ^{1}H NMR spectrum at −30 °C, the formation of **8** can be anticipated instead of **9** and other possible structures (Scheme 1) and the conformation of the tetrabenzo[16]-annulene moiety in **4** may be flexible. The silver complex **8** has a C_s symmetry, and the appearance of olefinic proton signals at a remarkably high field (δ 4.50) suggests that the olefinic hydrogens of **8** are located in the shielding region of the opposing benzene ring. It is noteworthy that two olefinic signals at δ 7.04 and 7.50 are doublets of doublets, in which smaller coupling (1.5 and 3 Hz) can be assigned to Ag−^{1}H coupling. Although no Ag−^{1}H coupling [^{107}Ag−^{1}H and ^{109}Ag−^{1}H couplings may be closely related value] is usually observable due to the fast exchange of silver atom in complexes, the olefinic protons of **4** show Ag−^{1}H coupling indicative of the presence of a fairly static, stable complex in solution.[11] The structural flexibility of **2** enables the silver complex to adopt a conformation like **8** in solution.

Although **3** shows a conformational change very rapidly in solution, the conformation of **3** is fixed significantly by a silver cation to form the complex **10**. Thus, the ^{1}H NMR spectra of **10** in $CDCl_3$ at 25 °C or higher temperatures show an extremely broad signal at δ 6.8−7.7, reflecting a slow conformational change. At −60 °C or lower temperatures, the spectra clearly indicate the formation of the silver complex **10** which has a C_s symmetry. In this conformation shown in Scheme 1, the two olefinic proton signals shift to upper field (δ 5.66 in $CDCl_3$ or 5.64 in CD_2Cl_2) due to the shielding effect of the neighboring benzene rings, whereas the two sets of AB-type quartet signals (δ 7.02 and 7.48 with J = 11.0 Hz and δ 7.44 and 7.55 with J = 12.0 Hz in CD_2Cl_2) are ascribed to the olefinic protons oriented in the same direction. The silver atom in **10** may be present in the center of the cavity formed by the five olefinic bonds.

The crystal structures of **4**, **6**, and **7** were determined by the X-ray diffraction method.[12] Single crystals of **4** containing

Scheme 1. Formation of Complexes **4**−**7**



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1 equiv of hexane were obtained and examined by X-ray crystallographic analysis (Figure 2). The complex **4** is a 1:1:1

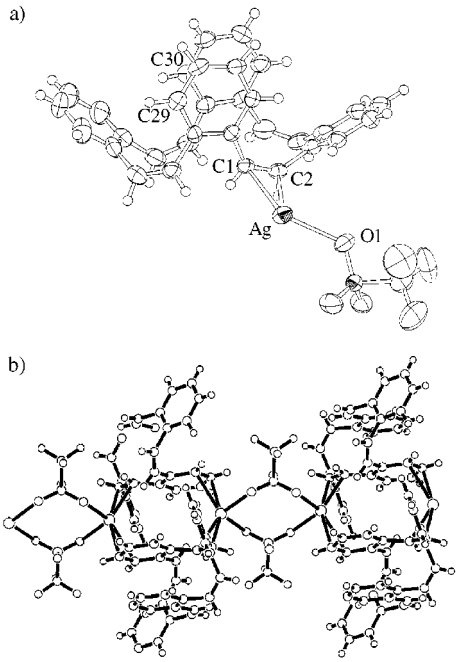

Figure 2. The molecular structure of **4**. (a) ORTEP drawing of **4** in 50% thermal ellipsoid, omitted solvent molecule for clarity. (b) Packing diagram. Selected bond lengths [Å]: Ag−O1, 2.411(4); Ag−O3, 2.467(4); Ag−C1, 2.445(6); Ag−C2, 2.447(6); Ag−C29, 2.684(6); Ag−C30, 2.432(6); C1−C2, 1.358(8); C29−C30, 1.398(9).

metal-to-ligand-to-anion tertiary system (Figure 2a), but 1 equiv of hexane also exists independently in the lattice interstice. Each silver ion is coordinated to the C1−C2 double bond of one molecule and to the C30 aromatic carbon of another at Ag−C distances ranging from 2.432(6) to 2.447(6) Å (average 2.44 Å). The average Ag−C distance (2.44 Å) is similar to those of the reported silver complexes with alkenes and arenes,[13−16] whereas the C1−C2 double bond [1.358(8) Å] and the C29−C30 bond [1.398(9) Å] are elongated by 0.03 and 0.02 Å, respectively, reflecting the coordination of the silver ion to the sp^2 carbons. As shown in Figure 2b, the two silver ions are sandwiched between two tetrabenzo[16]annulene moieties to form a head-to-tail dimer. In addition, the structure contains a dinuclear core, $Ag_2(O_3SCF_3)_2$, in which each silver(I) ion is tetrahedrally coordinated to two oxygen atoms of the two different triflate anions and two distinct annulene ligands to form a coordination polymer. The distorted rhombic ring formed by bridging of the two O−S−O linkages between pairs of silver atoms leads to Ag···Ag and S···S distances of 5.49 and 4.02 Å, respectively.

In contrast to the infinite coordination polymer of the triflate **4**, the perchlorate **6** formed a discrete complex in the crystal. As shown in Figure 3, the crystal structure of **6**

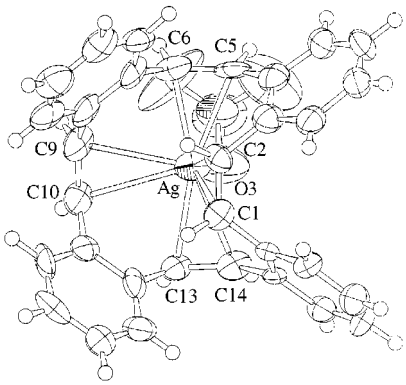

Figure 3. The molecular structure of **6**. Selected bond lengths [Å]: Ag−O3, 2.53(1); Ag−C1, 3.09(1); Ag−C2, 3.08(1); Ag−C5, 2.54(1); Ag−C6, 2.43(1); Ag−C9, 2.76(1); Ag−C10, 2.78(1); Ag−C13, 2.41(1); Ag−C14, 2.52(1); C1−C2, 1.34(2); C5−C6, 1.39(2); C9−C10, 1.31(2); C13−C14, 1.36(2).

is consistent with the ^{1}H NMR spectrum which suggests C_s-symmetric structure in solution. The Ag(I) ion in the complex is located "inside" the annulene cage, the conformation of which is different from the ground-state structure of annulene **2**, probably due to the effective coordination. The coordination geometry of the complex is a distorted square-pyramid with an apical olefin ligand C9−C10 in a distance of 2.69 Å (between Ag and the midpoint of the two carbons). The percholorate ion occupies one of the basal position with a distance of 2.53(1) Å. The olefin ligand C1−C2 opposite to perchlorate is coordinated to Ag ion in a relatively long distance of 3.01 Å which suggests weak coordination due to the trans effect. The other two basal olefin ligands, C5−C6 and C13−C14, have normal coordination distances of 2.38 and 2.37 Å, respectively. The elongation of olefinic bond is mainly observed in the basal ligands (C1−C2,

(12) X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with Mo Kα radiations. The structures were solved by Patterson method for **4** and by direct methods for **6** and **7** and refined using full-matrix least-squares analyses. Anisotropic thermal parameters were used for non-hydrogen atoms. **4**: $C_{39}H_{38}O_3F_3SAg$, $M_w = 751.65$, triclinic, space group *P*-1 (No. 2), $a = 11.591(5)$ Å, $b = 13.850(3)$ Å, $c = 10.408(2)$ Å, $\alpha = 99.59(2)°$, $\beta = 107.02(2)°$, $\gamma = 87.51(3)°$, $V = 1575.2(9)$ Å^3, $Z = 2$, $D_c = 1.585$ g cm^{-3}, $R = 0.049$, $R_w = 0.049$, GOF = 1.56 for 3595 reflections with $I > 3.0\sigma(I)$. **6**: $C_{32}H_{24}AgClO_4$, $M_w = 615.86$, monoclinic, space group *C*2/*c* (No. 15), $a = 31.49(2)$ Å, $b = 10.018(8)$ Å, $c = 20.92(1)$ Å, $\beta = 127.46(2)°$, $V = 5238(5)$ Å^3, $Z = 8$, $D_c = 1.562$ g cm^{-3}, $R = 0.065$, $R_w = 0.092$, GOF = 1.32 for 1441 reflections with $I > 2.0\sigma(I)$. **7**: $C_{40}H_{30}AgClO_4$, $M_w = 718.00$, monoclinic, space group $P2_1/a$ (No. 14), $a = 16.537(4)$ Å, $b = 12.306(4)$ Å, $c = 16.633(5)$ Å, $\beta = 105.73(2)°$, $V = 3258(1)$ Å^3, $Z = 4$, $D_c = 1.464$ g cm^{-3}, $R = 0.053$, $R_w = 0.057$, GOF = 1.95 for 3464 reflections with $I > 3.0\sigma(I)$.

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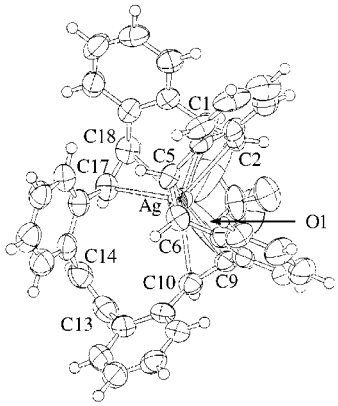

Figure 4. The molecular structure of **7**. Selected bond lengths [Å]: Ag−O1, 2.94(1); Ag−C1, 2.481(7); Ag−C2, 2.698(7); Ag−C5, 2.833(7); Ag−C6, 2.630(6); Ag−C9, 2.433(7); Ag−C10, 2.643(7); Ag−C17, 2.543(7); Ag−C18, 2.568(7); C1−C2, 1.346(9); C5−C6, 1.334(6); C9−C10, 1.366(9); C13−C14, 1.34(1); C17−C18, 1.348(10).

1.34(2) Å; C5−C6, 1.39(2) Å; C13−C14, 1.36(2) Å), whereas that of the apical ligand is not so remarkable (C9−C10, 1.31(2) Å). The formation of two different silver complexes of the annulene **2** can be attributed to the conformational instability of the annulene cage in complex **8**.

As shown in Figure 4, the crystal structure of **7** was also found to form a discrete complex similar to that of **6**. The Ag(I) ion is located inside the annulene cage, the conformation of which is similar to that of the free annulene in the crystal. Four double bonds were used for coordination to Ag, *i.e.*, the double bond C13−C14 is 4.09 Å apart from Ag(I). The coordination geometry of the complex is a distorted trigonal-bipyramid with an axial perchlorate ligand at a distance of 2.94(1) Å. Another axial ligand is the olefinic double bond C5−C6, the coordination distance of which is relatively longer (2.65 Å) than that of the equatrial ligands. Three equatorial ligands have similar coordination distances (2.45−2.50 Å) and elonged double bonds (1.346(9)−1.366(9) Å) which are longer than the axial ligand (1.334(9) Å). This pentacoordinate structure is not consistent with that in solution as descrived above. It can be explained by the rapid exchange of the two olefins (C13−C14 and C17−C18) at the equatorial position.

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Supporting Information Available: Experimental procedures and characterization data for the complexes **4** and **5**. X-ray crystallographic data for **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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