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Synthesis and complexation properties of a synthetic receptor, *Z*-tetrabenzohexadehydro[16]annulene[†]

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Abstract—*Z*-Tetrabenzohexadehydro[16]annulene (**1**), a synthetic receptor, easily produces its silver(I) complexes both in solution and in the solid state. The X-ray analysis of the silver(I) complexes of **1** revealed unique structures of the dinuclear complexes.

Synthetic receptors have received considerable attention in recent years[1] because of their unique structures[2] and host/guest interactions,[3] and as a potential device for switches.[4] *Z*-Tetrabenzohexadehydro[16]annulene (**1**) possesses a concave π-system which could play a role in complexation for transition metal cations, as shown in Fig. 1. We now report the synthesis of **1** and its complex formation with a silver cation in solution and in the solid state.

Recently, we reported the synthesis of *all*-*Z*-tetrabenzo[16]annulene (**2**) and the X-ray structure of the silver(I) complexes.[5] Although **2** bears a stacked structure both in solution and in the solid state,[5a] the structures of its silver(I) complexes are flexible depending on the coordination conditions and crystal packing.[5b] The mobile structural change in **2** reflects the existence of four *Z*-double bonds. In contrast, *Z*-tetrabenzohexadehydro[16]annulene (**1**) exists as an equilibrium mixture of two conformers, and the spoon-like space in **2** can scoop up a metal cation effectively (Fig. 1).[6] The short radius of the elliptic inner space is ca. 5 Å, and hence the silver cation can be captured inside effectively like $\mathbf{1}\cdot M^+$, as shown in Fig. 1.

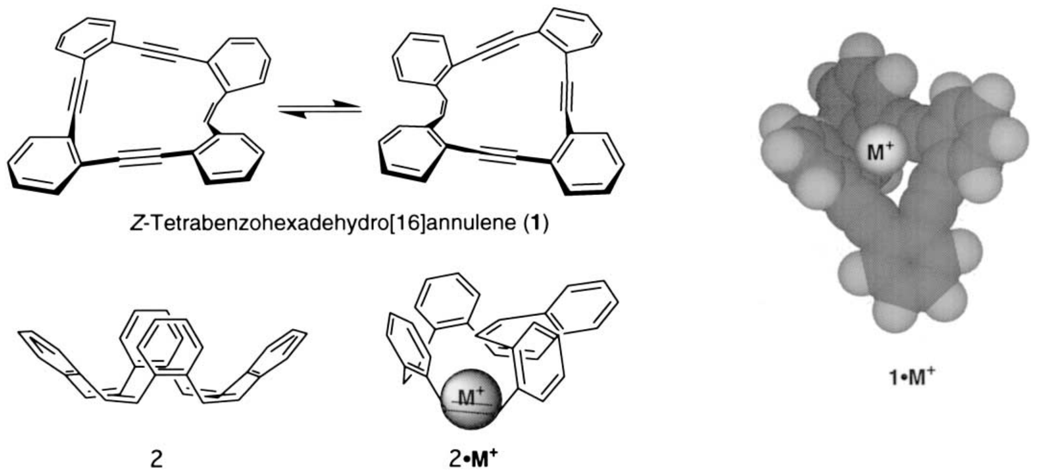

Figure 1. The conformations of **1**, **2**, and their complexes with M^+.

Keywords: annulenes; complexes; macrocycles; receptors; silver and compounds; X-ray crystal structures.

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[†] This paper is dedicated to Emeritus Professor Masazumi Nakagawa on the occasion of his 85th birthday.

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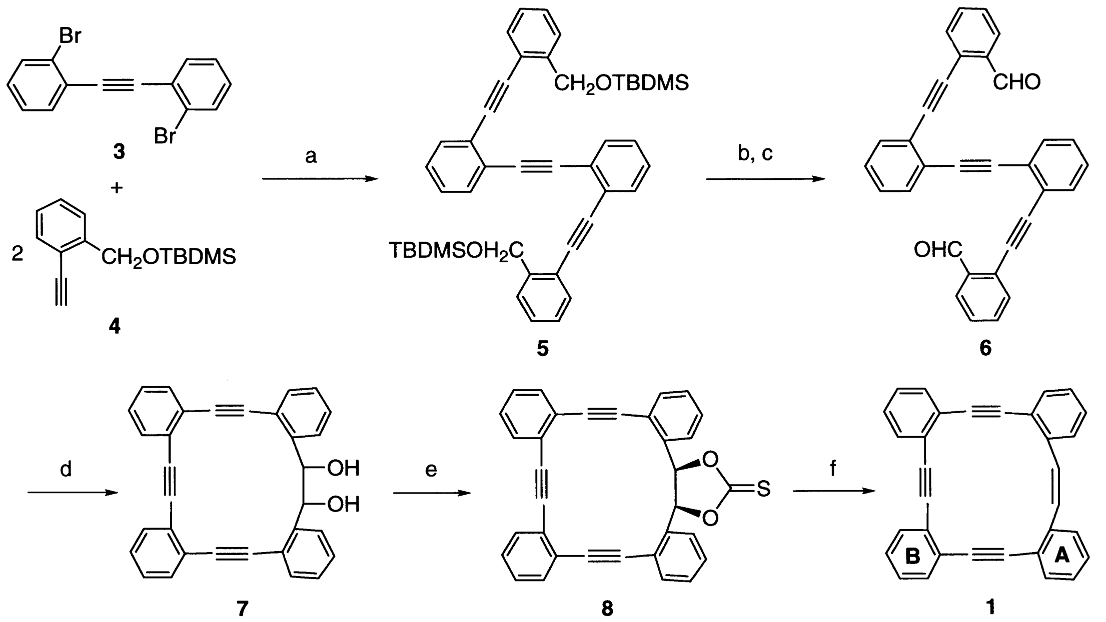
The synthesis of **1** was carried out according to the reaction sequence outlined in Scheme 1. The Sonogashira coupling of bis(2-bromophenyl)ethyne **3**[7] with **4** (2.52 equiv.) in refluxing Et_3N for 2 h afforded the triyne **5** (84%).[8] Removal of the *t*-butyldimethylsilyl (TBDMS) group in **5** (80%), followed by Dess–Martin oxidation (91%) yielded the dialdehyde **6**. The intramolecular pinacol coupling of **6** with a low-valent vanadium complex[9] generated from $VCl_3(THF)_3$ and Zn in CH_2Cl_2–DMF at room temperature produced selectively the *erythro*-**7** (84%) together with a small amount of the *threo*-isomer (5.5%). The reaction of *erythro*-**7** with 1,1′-thiocarbonyldiimidazole (TCDI) in refluxing toluene for 16 h afforded the thionocarbonate **8** (92%), which, on treatment with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DMPD)[10] in refluxing benzene for 14 h, produced the desired **1** in 68% yield.

The MOPAC PM3 calculations indicate that **1** has a twisted structure, as shown in Fig. 1. Since the ^1H and ^{13}C NMR spectral data of **1** at −90°C show a C_s structure, rapid interconversion takes place even at low temperatures. Although the ^1H NMR spectrum of **1** was unchanged by adding CuOTf, the addition of silver(I) salts (excess) caused a marked low-field shift of the olefinic and aromatic proton signals. These results indicate that **1** forms stable complexes with many silver(I) salts. Thus, a solution of **1** and a silver salt (1.4–2.0 eqiuv.) in THF was stirred for 30 min at room temperature, followed by removal of the solvent to afford a crude salt. A pure silver salt was obtained in moderate to good yields by recrystallization from hexane–CH_2Cl_2 or benzene–CH_2Cl_2, as shown in Table 1. In $CDCl_3$ solutions of the silver salts, signals of the olefinic and aromatic protons shift markedly to low-field as compared to those of **1** [**1**: δ 7.01 (s, olefinic), 7.12–7.61 (m, Ar A), and 7.12–7.31 (m, Ar B)]. On the basis of the Job plot's experiments, a 1:1 complex formed in solution when **1**·$(AgClO_4)_2$ and **1**·$(AgOCOCF_3)_2$ were dissolved in $CDCl_3$. The VT NMR experiments indicated that the ^1H NMR spectra of **1**·$(AgClO_4)_2$ and **1**·$(AgOCOCF_3)_2$ broadened at −60°C, and very broad spectra were observed at −90°C, due to the conformational change even at low tempera-



Scheme 1. Synthesis of **1**. (a) $Pd(PPh_3)_4$, CuI, Et_3N; (b) HF, CH_3CN, rt; (c) Dess–Martin reagent (2.25 equiv.), CH_2Cl_2, rt; (d) $VCl_3(thf)_3$, Zn, CH_2Cl_2, DMF, rt; (e) thiocarbonyldiimidazole (TCDI), toluene, reflux; (f) 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DMPD), benzene, reflux.

Table 1. Preparation and ^1H NMR data of silver complexes derived from **1**[a]

Ag salt	Yield	Ratio[b]	^1H NMR (δ in $CDCl_3$)[c]
AgOTf	66	1:1	7.55 (s, olefin); 7.13–7.76 (m, Ar A); 7.28–7.46 (m, Ar B)
$AgClO_4$	81	1:2	7.77 (s, olefin); 7.22–7.81 (m, Ar A); 7.32–7.50 (m, Ar B)
$AgBF_4$	81	1:1	7.79 (s, olefin); 7.26–7.82 (m, Ar A); 7.31–7.52 (m, Ar B)
$AgSbF_6$	81	1:1	7.77 (s, olefin); 7.32–7.86 (m, Ar A); 7.37–7.55 (m, Ar B)
$AgOCOCF_3$	60	1:2	7.55 (s, olefin); 7.13–7.76 (m, Ar A); 7.28–7.46 (m, Ar B)
$AgNO_3$	42	1:1	7.40 (s, olefin); 7.13–7.63 (m, Ar A); 7.25–7.43 (m, Ar B)

[a] The complexes were prepared in THF, and recrystallized from n-C_6H_{14}–CH_2Cl_2 or C_6H_6–CH_2Cl_2.

[b] The ratio of **1** and Ag salt was determined by elemental analysis.

[c] The ^1H NMR spectra of crystalline silver salts were measured in $CDCl_3$ at room temperature.

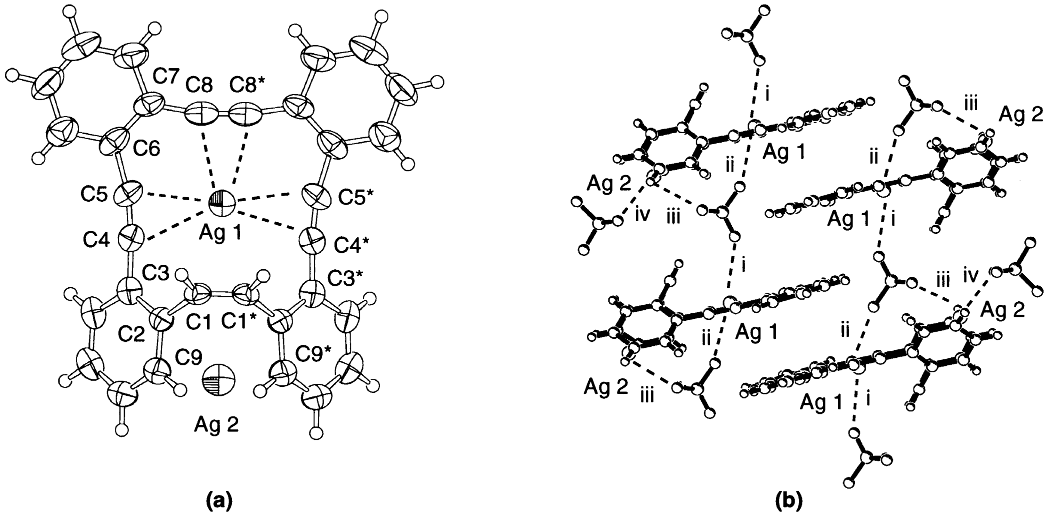


Figure 2. ORTEP diagram of $\mathbf{1}\cdot(AgClO_4)_2$. (a) Molecular structure of **1**. Perchlorate ions are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–C4 2.63(1), Ag1–C5 2.55(1), Ag1–C8 2.500(9), Ag2–C9 2.507(9), C1–C1* 1.29(2), C1–C2 1.51(1), C2–C3 1.38(1), C3–C4 1.43(1), C4–C5 1.21(1), C6–C7 1.39(2), C7–C8 1.43(2), C8–C8* 1.17(2), C3–C4–C5 174(1), C4–C5–C6 168(1), C7–C8–C8* 170.9(5). (b) Packing diagram. The dashed lines correspond to the Ag–O bonds: (i) Ag1–O4 2.94(1) Å; (ii) Ag1–O5 2.75(1); (iii) Ag2–O6 2.77(3); (iv) Ag2–O1 2.74(2).

tures. The chemical shifts of the olefinic and aromatic protons in the silver complexes reflect an effect of the silver cation, and the complexation of $AgClO_4$ and $AgBF_4$ with **1** is stronger than that of $AgNO_3$, AgOTf, and $AgOCOCF_3$.

The crystal structures of the dinuclear complexes $\mathbf{1}\cdot(AgClO_4)_2$ and $\mathbf{1}\cdot(AgOCOCF_3)_2$ were determined by X-ray analysis (Figs. 2 and 3).[11] As shown in Fig. 2(a), the molecular structure of $\mathbf{1}\cdot(AgClO_4)_2$ has a crystallographic C_s symmetry with a mirror plane passing through the mid-point of the C(1)–C(1*) and C(8)–C(8*) bonds. The [16]annulene ring has a dipper-like structure, and the Ag(1) atom is located in the center of the annulene ring and is connected to three acetylenic bonds, whereas the Ag(2) atom binds to the C9 and C9* carbons. The C(3)–C(8) and C(3*)–C(8*) carbons are located on the plane, and the maximum atomic deviation from the least-squares plane is 0.04 Å. In contrast, the length of the olefinic bond C(1)–C(1*) is 1.34(2) Å, reflecting a coordination-free double bond character. The crystal packing contains a stacked diphenylacetylene unit, and the face-to-face distance is 3.9 Å (Fig. 2(b)). The annulene–$AgClO_4$ and the styrene–$AgClO_4$ moieties also stack together with the Ag–O bonds (the dotted lines i–iv in Fig. 2(b)) along with the diphenylacetylene column, and the distance of Ag(1)–Ag(1) and Ag(2)–Ag(2) is 7.90 Å.

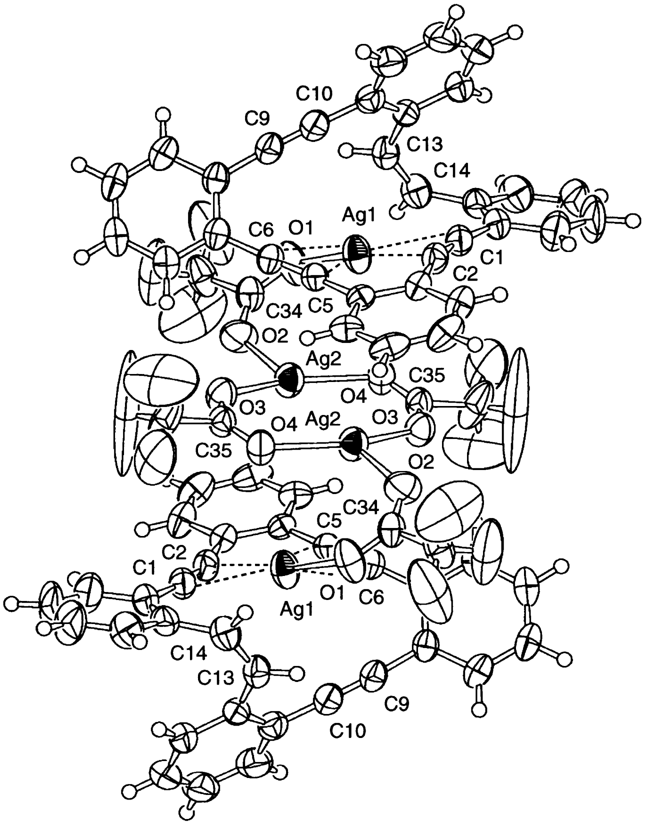


Figure 3. Packing diagram of $\mathbf{1}\cdot(AgOCOCF_3)_2$. Selected bond lengths [Å] and angles [°]: Ag1–C1 2.500(6), Ag1–C2 2.443(5), Ag1–C5 2.555(5), Ag1–C6 2.742(5), Ag1–C13 2.827(6), Ag1–C14 2.801(6), Ag1–O1 2.222(4), Ag2–O2 2.376(4), Ag2–O3 2.256(4), Ag2–O4 2.242(4), C1–C2 1.202(8), C2–C3 1.424(8), C3–C4 1.415(7), C4–C5 1.429(7), C5–C6 1.209(7), C9–C10 1.193(8), C13–C14 1.326(9), C1–C2–C3 167.6(6), C2–C1–C16 170.0(6), C4–C5–C6 166.8(6), C5–C6–C7 172.6(6), C8–C9–C10 175.7(6), C9–C10–C11 178.0(7).

As shown in Fig. 3, $\mathbf{1}\cdot(AgOCOCF_3)_2$ has an interesting packing structure. The [16]annulene ring has a twisted structure like $\mathbf{1}\cdot M^+$ in Fig. 1, and the Ag(1) atom binds to the two acetylenic bonds, presumably due to the weak cationic character of the Ag ion in $AgOCOCF_3$.[12] The distances (2.44–2.74 Å) of the Ag(1)–acetylene bonds in $\mathbf{1}\cdot(AgOCOCF_3)_2$ are similar to those (2.50–2.63 Å) of the Ag(1)–acetylene bonds in $\mathbf{1}\cdot(AgClO_4)_2$. The distances of Ag(1)–C(13) and Ag(1)–C(14) are

2.80–2.83 Å, reflecting a weak interaction between the Ag(1) ion and the olefinic bond. Interestingly, a planar eight-membered ring containing the two Ag(2) atoms is formed between the annulene–Ag(1) complexes, the maximum atomic deviation from the least-squares plane being 0.04 Å. All silver atoms in **1**·$(AgOCOCF_3)_2$ are connected with the acetate (O–C–O) bridges to form a triple-decker structure.

Acknowledgements

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8. All compounds gave satisfactory analytical and spectral data. For example, **6**: colorless needles, mp 158.2–159.6°C, MS m/z 434 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.33–7.36 (m, 2H, Ar) 7.38–7.44 (m, 10H, Ar), 7.60–7.66 (m, 4H, Ar), 7.80–7.82 (m, 2H, Ar), 10.60 (s, 2H, CHO); ^{13}C NMR ($CDCl_3$) δ 89.1, 92.3, 95.1, 124.9, 125.5, 126.67, 126.72, 128.56, 128.61, 128.9, 132.2, 132.3, 133.28, 133.33, 135.8, 191.5; IR (KBr) 2214, 1691 cm^{-1}. *Erythro*-**7**: colorless leaflets, mp 239°C (decomp), MS m/z 436 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.71 (br. s, 2H, OH), 5.76 (d, $J=1.8$ Hz, 2H, CH), 7.17 (m, 2H, Ar), 7.22 (m, 2H, Ar), 7.31 (m, 2H, Ar), 7.33 (m, 2H, Ar), 7.35 (m, 2H, Ar), 7.37 (dd, $J=7.8$, 1.1, 2H, Ar), 7.50–7.52 (m, 2H, Ar), 7.59–7.61 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 74.0, 91.4, 92.1, 92.6, 122.0, 125.1, 125.4, 127.3, 127.4, 128.0, 128.1, 128.2, 132.47, 132.50, 132.54, 140.4; IR (KBr) 3422, 2213 cm^{-1}. **8**: colorless leaflets, mp 215°C (decomp), FAB-MS m/z 479 (M^++1); ^{1}H NMR ($CDCl_3$) δ 5.30 (s, 2H, CH), 7.15–7.26 (m, 6H, Ar), 7.33–7.42 (m, 6H, Ar), 7.55 (dd, $J=7.7$, 1.3, 2H, Ar), 7.65 (dd, $J=7.6$, 1.2, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 84.2, 89.9, 92.3, 93.6, 122.3, 124.2, 124.7, 126.9, 128.2, 128.4, 128.7, 129.2, 132.4, 133.09, 133.11, 133.4, 192.0. **1**: colorless plates, mp 202°C (decomp), MS m/z 402 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 2H, CH=), 7.12–7.18 (m, 6H, Ar), 7.27–7.31 (m, 4H, Ar), 7.46–7.49 (m, 2H, Ar), 7.50–7.54 (m, 2H, Ar), 7.58–7.61 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ 92.56, 92.63, 93.3, 122.5, 125.1, 125.2, 126.8, 127.8, 127.9, 128.0, 128.8, 130.2, 132.8, 132.9, 133.4, 139.3; UV (solv.) λ_{max} (ε) 284 (127,000), 324 (36,400) nm.
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11. Crystal data for **1**·$(AgClO_4)_2$ and **1**·$(AgOCOCF_3)_2$. **1**·$(AgClO_4)_2$: $C_{32}H_{18}O_8Cl_2Ag_2$, $Mw=817.13$, monoclinic, space group $C2/m$ (No. 12), $a=25.133(3)$, $b=14.724(3)$, $c=7.902(2)$ Å, $\beta=98.65(2)°$, $V=2891(1)$ Å^3, $Z=4$, $D_c=1.877$ g cm^{-3}, $R_1=0.070$, $R_w=0.208$, GOF = 1.09 for 1858 reflections with $I>3.00\sigma(I)$. **1**·$(AgOCOCF_3)_2$: $C_{36}H_{18}O_4F_6Ag_2$, $Mw=844.26$, monoclinic, space group $P2_1/n$ (No. 14), $a=16.564(3)$, $b=8.924(3)$, $c=22.813(3)$ Å, $\beta=107.67(1)°$, $V=3213(1)$ Å^3, $Z=4$, $D_c=1.745$ g cm^{-3}, $R_1=0.042$, $R_w=0.068$, GOF = 1.35 for 4431 reflections with $I>3.00\sigma(I)$.
12. Attempts to determine the X-ray structures of **1**·AgOTf and **1**·$AgBF_4$ were unsuccessful until now.