Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 4765–4767 **4765**
DOI: 10.1021/ic100317p

Structure of Silver(I) Complex Prepared from Azobenzenonaphthalenophane, Photochemical Coordination Change of Silver(I) and Silver(I)-Induced Acceleration of *Z*−*E* Thermal Isomerization of Azobenzene Unit

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Received February 16, 2010

A Ag^I complex was prepared from azobenzenonaphthalenophane as a photoreactive multidentate ligand. The coordination of Ag^I was reversibly controlled by photoisomerization of the azobenzene unit, and at the same time, Ag^I accelerated the *Z*−*E* thermal isomerization of the azobenzene unit.

Supramolecular chemistry is of great current interest because of its intriguing structural diversity and its potential application.[1] In this regard, studying the variety of products from the self-assembly processes between labile metal ions and flexible multidentate ligands is a topic of interest.[2] Macrocyclic ligands, such as crown ethers,[3,4] calixarenes,[5] cyclophanes,[6] and naphthalene,[7] have been investigated as multidentate ligands for various metal complexes. As a candidate photoreactive unit, azobenzene has been widely employed by virtue of its superior characteristics when undergoing reversible *E*−*Z* photoisomerization upon UV and visible light illumination.[3,8−11] Ag^I is a documented versatile coordination sphere that can take coordination numbers from two to six, and it is marked by its ability to interact with both soft π-donor and hard donor (i.e., N, O, and S) cavities.[3−8,12] Ag^I perturbation of the *E*−*Z* photoisomerization of azobenzene has been reported, but Ag^I is a poor catalyst because of its small complexing constant $K \sim 6\ M^{-1}$.[11] Furthermore, only a single crystal structure of a Ag^I complex, $[Ag(\mu\text{-}trans\text{-azobenzene})[H_2O][BF_4]]_n$, in which the Ag^I ion is coordinated with the nitrogen atom of azobenzene, has been reported so far.[13] Other metal complexes with azobenzene ligands, in which the metal-coordinated N atom of azobenzene and/or the σ bond of an arene are present, have been reported.[14] To the best of our knowledge, metal−organic complexes based on cyclic azobenzene compounds that involve both direct coordination of the azobenzene nitrogen atom and cation−π interactions have not been reported so far. We focused on the

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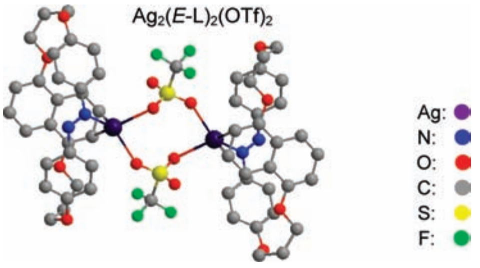
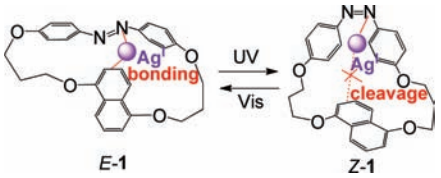


Figure 1. Crystal structure of dimeric Ag^I complex *E*-**1**.

Scheme 1. Schematic Illustration of Photoresponsive Cleavage/Binding of Cation−π Bond



characteristic cation−π interaction of Ag^I in terms of sensitivity to environmental change, as we expected it to provide new opportunities for photoresponsive materials. In this paper, we report on the synthesis, novel crystal structure, complexing ability, and thermal and photochemical behavior of the Ag^I complex prepared from [5.5](4,4′)azobenzeno(1,5)naphthalenophane (L). In this complex, the cleavage/binding of the cation−π bond was reversibly controlled by photoisomerization of an azobenzene unit with the metal-coordinated N atom of azobenzene (Scheme 1).

L was obtained by the reduction of the dinitro compound, 1,5-bis(2-(4-nitrophenoxy)propoxy)naphthalene.[15] *E*-L was isolated using silica gel column chromatography. *E*-L and $Ag(CF_3SO_3)$ (AgOTf) were dissolved in THF and stirred at room temperature for a period of 10 min. Then, the complex was crystallized overnight in THF and hexane. Orange crystals of **1** suitable for X-ray crystal structural analysis were obtained (see the Supporting Information).

The crystal structure of **1** revealed the formation of a dimer structure, which involves Ag^I and *E*-L in a 1:1 molar ratio (*E*-**1**, Figure 1). Crystallographic inversion center sites occur in the middle of Ag(1)$\cdots$Ag(1′), and the intermetallic separation distance is 5.78 Å. The Ag(1) site exhibits a distorted tetrahedral geometry comprising a nitrogen atom of an azobenzene unit, an η^2-naphthalene in L, and two bidentate triflate moieties. The observed Ag−C(naphthalene) bond distances are 2.631(2) and 2.570(2) Å. These values are close to those found in Ag^I complexes constructed from [2.2.2]paracyclophane (2.5−2.7 Å),[6] and from calix[4]- and calix[6]-arene (2.399(4)−2.542(8) Å),[5] which result from cation−π interactions. For L, the slight increase in the C=C (η^2) bond distance during complexing with Ag^I (from 1.404(3) to 1.423(3) Å) is indicative of a decrease in double bond character and an increase in electron donating character of the naphthalene ring. The Ag−N bond distance is 2.339(2) Å, whose value is similar to those found in $[Ag(\mu\text{-}trans\text{-azobenzene})[H_2O][BF_4]]_n$ (2.36(2) and 2.37(2) Å).[13] The bond angles at the $\{AgN(C{=}C)O_2\}$ tetrahedral site range from 86.85(6)° to 139.15(7)°. With respect to the naphthalene rings, the N=N vectors of the azobenzene units are tilted by 6° in *E*-**1**, and by 30° and 33° in *E*-L. The configuration between the azobenzene and naphthalene units may be optimized to form a more stable Ag^I dinuclear complex. The structural features of the azobenzene unit (see the Supporting Information) show that the cyclic azobenzene, which is bidentate to a Ag center, is affected significantly by a partial distortion in *E*-**1**. No intermolecular interactions were observed, such as a [$\pi\cdots\pi$] interaction or hydrogen bonding in either *E*-**1** or *E*-L. Unfortunately, a suitable crystal of *Z*-**1** was not obtained in our experiments.

The absorption maxima of *E*-L in a THF solution at 298 K occurred at 359 nm (π−π*, ε = 19 400 M^{-1} cm^{-1}) and 455 nm (n−π*, ε = 2500 M^{-1} cm^{-1}). Titration of 40 μM *E*-L with AgOTf in a THF solution resulted in spectral changes consisting of two parts (Figure S2, Supporting Information). The first part was the addition of a solution with a concentration of less than 20 mol equiv of AgOTf ([AgOTf] ≤ 800 μM), which showed a decrease in absorbance without any shifts in peak maxima. The second part was the addition of a solution with a concentration of over 20 mol equiv of AgOTf ([AgOTf] ≥ 800 μM), which showed a red shift in the π−π* transition band and an overlap with the *n*−π* transition band that had almost the same absorption intensity at the peak maxima. According to the absorption spectra of *E*-**1** using KBr pellets and CH_2Cl_2 solution, the absorption spectrum of *E*-**1** in THF is the limiting spectrum of the second reaction ([AgOTf] = 40 mM). In THF, another silver complex with a different composition may be produced in the first stage. The absorption maximum and the molar extinction of *E*-**1** in THF were 385 nm and ε = 14 000 M^{-1} cm^{-1} per azobenzene unit, respectively. This value of ε is less than that of *E*-L. With 500 mol equiv of AgOTf, 92% of *E*-L exists as *E*-**1** in a THF solution ([L] = 40 μM) at 298 K. In this case, the stability constant, *K*, of *E*-**1** was estimated to be *K* = 580 M^{-1} (see the Supporting Information).

For complex **1**, as well as for L, the *E* isomer only exists as an isomer in solution at room temperature when kept in the dark. However, upon light excitation, noticeable spectral changes were observed. Using light with a wavelength of 365 nm, the isomerization process takes place, converting the *E* to the *Z* isomer. According to ^1H NMR data using an *E*-**1** crystal dissolved in THF-d_8 ([*E*-L] = [Ag^+] = [OTf^-] = 2.1 mM), at least 77% of *E*-**1** is converted into *Z*-**1** using prolonged irradiation with light having a wavelength of 365 nm (see the Supporting Information). The ratio of *Z*-**1**/*E*-**1** = 77:23 is smaller than that of the L compound (*Z*-L/*E*-L = 95:5 in THF in the photostationary state monitored using the absorbance at 359 nm (Figure S3, Supporting Information)). When irradiated with light at a wavelength of 488 nm, *Z*-**1** is converted into *E*-**1**. The results of alternating irradiation of a THF solution of *E*-L (40 μM) with 500 mol equiv of AgOTf using light with wavelengths of 365 and 488 nm are shown in Figure 2, which shows that photochemical isomerization occurred reversibly over a period of 20 cycles.

Data from ^1H NMR studies on the complexation process of *E*-L and *Z*-L with AgOTf in a THF-d_8 solution are shown in the Supporting Information. A downfield shift of the aliphatic and aromatic protons was observed in both isomers. The chemical shift values (δ) of *E*-L and *Z*-L added from 0 to 10 mol equiv of AgOTf were obtained, and the values of $\Delta\delta$ in the aromatic region are shown in Figure 3. When the

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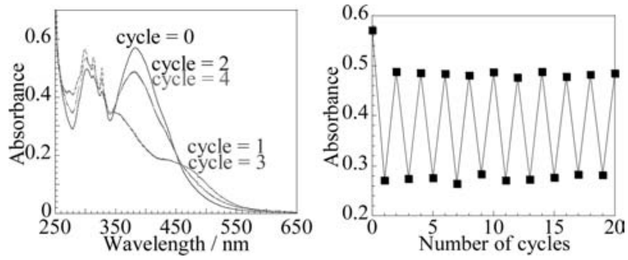

Figure 2. Absorption changes observed at 383 nm of *E*-L (40 μM) with 500 mol equiv of AgOTf (20 mM) in THF after alternating the irradiations at 365 nm (3 min) and 488 nm (3 min) over 20 cycles.

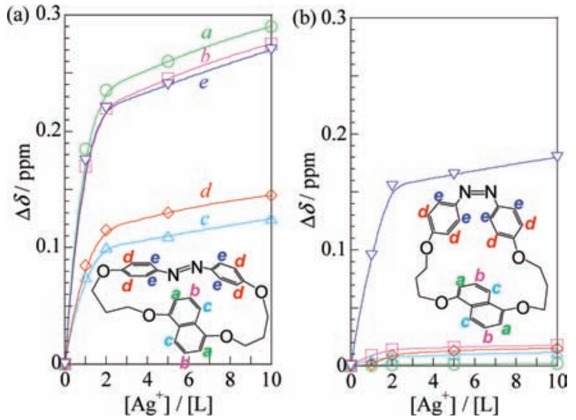

Figure 3. ^{1}H NMR titration curves for (a) *E*-L and (b) *Z*-L with AgOTf.

complexation-induced shifts in the same *E*-**1** compound are compared, the values of the protons on one side of the azobenzene unit (*e* in Figure 3a) and the two kinds of protons in the naphthalene unit (*a* and *b* in Figure 3a) are larger than the values of the other protons (*c* and *d* in Figure 3a). These results support *E*-L recognizing one Ag$^{\mathrm{I}}$ through one N atom of azobenzene and one C=C bond of the naphthalene unit, in both a THF solution and in a crystal. The *Z*-L coordinates to Ag$^{\mathrm{I}}$ by a single N atom, as evidenced by the large chemical shift of the values of the protons on one side of the azobenzene unit (*e* in Figure 3b). The photochemical isomerization of the azobenzene unit, *E*-**1** ↔ *Z*-**1** mentioned above, induces a change in coordination around the Ag$^{\mathrm{I}}$ ion, namely, L changes the conformation of Ag$^{\mathrm{I}}$ reversibly through the cleavage (*E*-**1** → *Z*-**1**) or binding (*E*-**1** ← *Z*-**1**) of the π−cation interaction. The stability constants of the *E*-**1** and *Z*-**1** complexes in THF-d$_8$ were estimated from the ^{1}H NMR data using the Benesi−Hildebrand equation (described in the Supporting Information). The equilibrium constant of *E*-**1**, $K = 630\ (\pm 60)\ \mathrm{M}^{-1}$ at 296 K, was obtained. This value is consistent with the value obtained from the absorbance data. The complexing ability of *E*-L with Ag$^{\mathrm{I}}$ is larger than that of [2.2.2]cyclophane (K(arom) $= 189\ \mathrm{M}^{-1}$ in CD$_3$OD).[6] For *Z*-**1**, the stability constant was estimated to be 1000 ($\pm$50) M^{-1} at 296 K. On comparing the value of $K \sim 6\ \mathrm{M}^{-1}$ of *trans*-azobenzene,[11] the strong complexing ability of azobenzenonaphthalenophanes *E*-L and *Z*-L can be clearly seen.

Concerning the thermal isomerization of the *Z* to *E* isomer in THF, the first-order rate constant (k) of the reaction at 298 K was found to be $k = 6.0 \times 10^{-4}\ \mathrm{s}^{-1}$ for **1** (92%) and $k = 2.1 \times 10^{-5}\ \mathrm{s}^{-1}$ for L. Thus, Ag$^{\mathrm{I}}$ accelerates the *Z*−*E* thermal isomerization of the azobenzene unit. Using the values of k obtained at different temperatures, the thermodynamic parameters of the isomerization process of *Z*-L to *E*-L were obtained: $\Delta H^{\ddagger} = 19.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -12.8$ cal K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 23.3$ kcal mol^{-1}. For the isomerization of 92% *Z*-**1** into *E*-**1**, values of $\Delta H^{\ddagger} = 31.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = 34.4$ cal K^{-1} mol^{-1}, and $\Delta G^{\ddagger} = 21.3$ kcal mol^{-1} were obtained. This result shows that the large activation entropy made the conversion from *Z*-**1** to *E*-**1** easier despite the larger activation barrier for the process than that for the corresponding ligand L. A large activation enthalpy has been reported for the thermal isomerization from *Z* to *E* of an azobenzene dendrimer.[16] The large activation enthalpy and entropy for the process may suggest the possibility of a highly networked structure for *Z*-**1** such as a polymeric chain containing silver(I) centers bridged by the N atom of *Z*-L.[13] Otherwise, the possibility of the coordination of a THF molecule in *Z*-**1** cannot be denied. The newly observed accelation of *Z*−*E* thermal isomerization of the azobenzene unit by Ag$^{\mathrm{I}}$ must be related to the strong perturbations of the electronic state and structure for the azobenzene unit in both *E*-**1** and *Z*-**1** due to the direct coordination.

In conclusion, a Ag$^{\mathrm{I}}$ complex was prepared from [5.5](4,4′)azobenzeno(1,5)naphthalenophane (L) and was characterized. In *E*-**1**, Ag$_2$(E-L)$_2$(OTf)$_2$, the Ag$^{\mathrm{I}}$ ions have a rare coordination environment, which contains a nitrogen atom of an azobenzene and an η^2-naphthalene in L. From ^{1}H NMR data, photoisomerization of *E*-**1** into *Z*-**1** leads to the cleavage of the π−cation interaction, and vice versa. Namely, complex **1** enables Ag$^{\mathrm{I}}$ to change its coordination environment reversibly from photoisomerization of the multidentate azobenzene ligand. In addition, the thermal isomerization of the azobenzene unit is accelerated by Ag$^{\mathrm{I}}$ ions, which must be related to the strong perturbations of the electronic state and structure for the azobenzene unit in both *E*-**1** and *Z*-**1** due to direct coordination.

Acknowledgment. We would like to thank M. Gotoh for her help in crystal analysis. This work was supported by a Grant-in-Aid for Scientific Research in Priority Areas “New Frontiers in Photochromism (No. 471)” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Supporting Information Available: Crystallographic data in CIF format, synthesis details, absorption spectra, ^{1}H NMR spectra, determination of stability constants, and *Z*−*E* thermal isomerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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