

Triangular and Tetrahedral Array of Silver(I) Ions by a Novel Disk-Shaped Tridentate Ligand: Dynamic Control of Coordination Equilibrium of the Silver(I) Complexes

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The multimetal array, controlled by predesigned multidentate ligands, has received increasing attention with respect not only to supramolecular architecturing but also to equilibrium control of a prototypical dynamic library.^{1,2} This strategy has opened ways to create novel functions that have not previously been achieved by the ligands or the metal ions only. With an interest in finding new multidentate ligand frameworks, we set out to synthesize a novel disk-shaped tridentate ligand **1**,³ which is capable of arranging to metal centers in a variety of fashions (Figure 1). This ligand was designed so that three methyl groups could force the neighboring benzimidazolyl groups out of the plane of the central aromatic ring. As a consequence, metal ions should be arrayed on the disk plane with metal–metal distances of several angstroms. Herein we describe the potential ability of **1** to arrange Ag⁺ ions reversibly in a two-dimensional (2-D) triangular and a three-dimensional (3-D) tetrahedral fashion. The Ag⁺ complexes of **1** were proven to assume both sandwich-shaped Ag₃I₂ and tetrahedral Ag₄I₄ structures which are in a controllable dynamic equilibrium in solution, depending on the ratio of **1** to Ag⁺ ions. The structure of the latter tetrahedral complex was also confirmed by its single-crystal X-ray analysis.

The solution behavior of **1** with AgOTf was studied by the ¹H NMR titration experiment. Upon addition of equimolar AgOTf to **1** ([AgOTf]/[**1**] = 1.0) in a 1:1 CDCl₃–CD₃OD solution, the ¹H NMR spectrum of the mixture displayed only one set of new highly symmetrical signals (Figure 2b). When 0.5 equiv of AgOTf was further added to the mixture ([AgOTf]/[**1**] = 1.5), the other set of signals completely replaced those before addition with downfield shift (Figure 2d). Further addition of AgOTf (up to 2 equiv) did not change the spectrum at all. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra of these complexes showed the signals corresponding to Ag₄I₄ and Ag₃I₂ complexes when [AgOTf]:[**1**] = 1:1 and 3:2, respectively.⁴ The ESI mass spectrum of a mixture of [AgOTf]:[**1**] = 1:1 contains peaks for multiply charged cationic species missing two or three triflate counteranions. The two main peaks at *m/z* 1302.2 and 818.4 are assignable to the cationic species, [Ag₄I₄·(OTf)₂]²⁺ and [Ag₄I₄·(OTf)]³⁺, respectively, verifying the presence of Ag₄I₄ complex in solution. In contrast, the ESI mass spectrum of a mixture of [AgOTf]:[**1**] = 3:2 displayed only three main peaks at *m/z* 1559.0, 648.0, and 419.6, corresponding to the species [Ag₃I₂·(OTf)₂]⁺, [Ag₃I₂·(OTf)]²⁺, and [Ag₃I₂]³⁺, respectively. These results indicate the formation of both Ag₃I₂ and Ag₄I₄ complexes in solution depending on the ratio [AgOTf]/[**1**]. Plot of [Ag₄I₄]/([Ag₄I₄] + [Ag₃I₂]) and [Ag₃I₂]/([Ag₄I₄] + [Ag₃I₂]) as a function of [AgOTf]/[**1**] (Figure 3) based

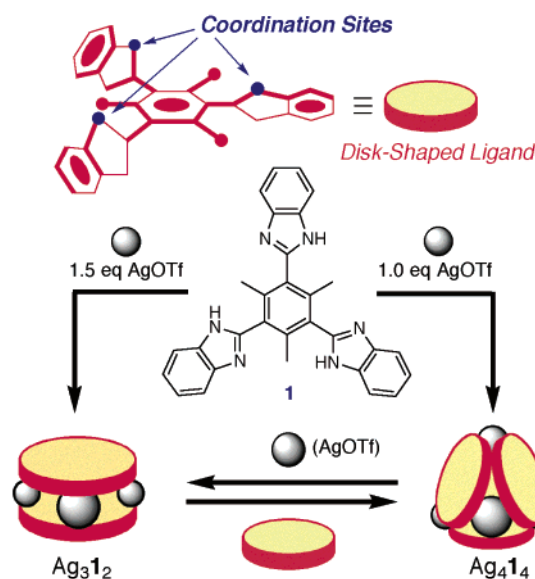


Figure 1. Schematic representation of the reversible conversion between tetrahedral Ag₄I₄ and sandwich-shaped Ag₃I₂ complexes.

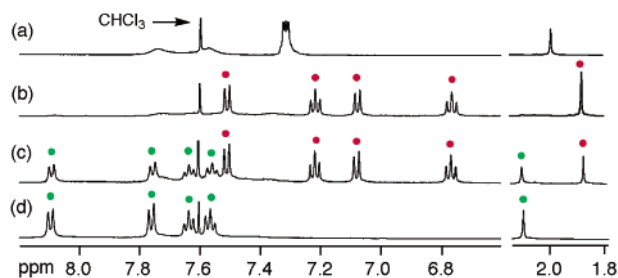


Figure 2. ¹H NMR spectra of the mixture of **1** and AgOTf (500 MHz, [**1**] = 21.3 mM, CDCl₃:CD₃OD = 1:1 (v/v)): (a) [AgOTf] = 0 mM, (b) [AgOTf] = 21.3 mM, (c) [AgOTf] = 24.0 mM, and (d) [AgOTf] = 32.0 mM.

on these ¹H NMR spectral changes shows that the sum of [Ag₄I₄] and [Ag₃I₂] is constant and that these two species are complementary to each other in the concentration. In addition, the conversion between the two products is quantitative and completed within a few minutes.

¹⁹F NMR study of **1** suggested the presence of an encapsulated triflate anion inside the Ag₄I₄ complex. ¹⁹F NMR spectrum of Ag₄I₄ (see Supporting Information) displayed two separate signals as two singlets, δ 92 ppm (3F) and 85 ppm (9F), whereas in the cases of Ag₃I₂ and AgOTf only one signal (δ 85 ppm) was observed for each.⁵ These results suggest that one triflate anion is encapsulated in the Ag₄I₄ complex and that the exchange of the triflate anions

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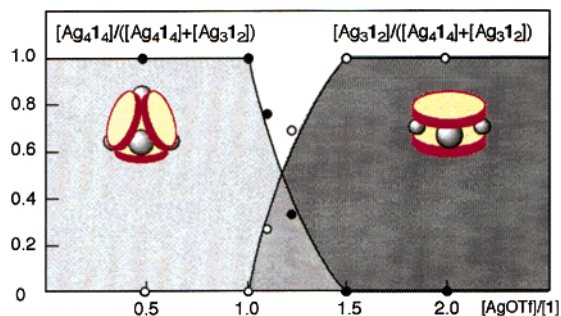


Figure 3. Plot of $[\text{Ag}_4\text{I}_4]/([\text{Ag}_4\text{I}_4]+[\text{Ag}_3\text{I}_2])$ (filled circles) and $[\text{Ag}_3\text{I}_2]/([\text{Ag}_4\text{I}_4]+[\text{Ag}_3\text{I}_2])$ (open circles) versus $[\text{AgOTf}]/[\mathbf{1}]$.

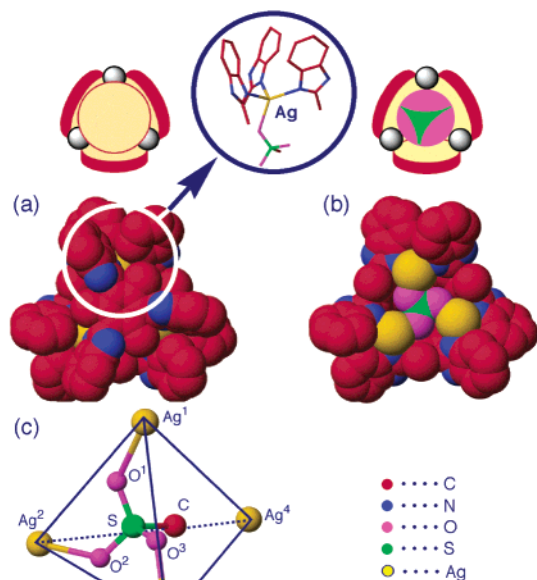


Figure 4. (a) Molecular structure of Ag_4I_4 complex, (b) a view of the cavity in which one ligand is omitted, and (c) Ag^+ ions arranged in a tetrahedral fashion and a CH_3SO_3^- anion coordinating to three of the four Ag^+ ions (Ag^1 , Ag^2 , and Ag^3) from the inside.

between the inner and outer cavity is rather slow compared with the NMR time scale. The significant downfield shift observed with the encapsulated triflate anion is probably due to desolvation effect or coordination effect of anion to Ag^+ ions.

The formation of Ag_4I_4 complex highly depends on the size and shape of counteranions employed. Upon addition of equimolar AgPF_6 to a solution of $\mathbf{1}$ in a 1:1 CDCl_3 – CD_3OD , Ag_3I_2 complex and free ligand $\mathbf{1}$ mainly formed, whereas Ag_4I_4 complex was generated only slightly as was observed in their ^1H NMR spectra. Further addition of AgPF_6 completed the formation of Ag_3I_2 complex. These results indicate that the stability of the Ag_4I_4 complex is gained by a template triflate anion in the core, leading to the exclusive formation of the Ag_3I_2 complex even when the ratio of Ag^+ to $\mathbf{1}$ is 1:1.

We first tried the X-ray analysis of crystals obtained from a mixture of $\mathbf{1}$ and AgOTf , but due to the disorder of solvent and anion molecules no sufficient data were obtained.⁶ The structure of Ag_4I_4 complex was finally determined when AgCH_3SO_3 was used in place of AgOTf as the Ag^+ source (Figure 4).^{7,8} The crystal structure revealed that four Ag^+ ions are tetrahedrally arranged by

four tridentate ligands $\mathbf{1}$ resulting in a tetrahedral Ag_4I_4 structure including a methanesulfonate anion in the cavity. Each Ag^+ ion binds to three imidazole nitrogen atoms of different ligands, and three of the four Ag^+ ions, Ag^1 to Ag^3 , display a distorted tetrahedral geometry having a $\text{Ag}-\text{O}$ (methanesulfonate) bond, whereas Ag^4 assumes a distorted trigonal planar coordination without a $\text{Ag}-\text{O}$ bond (Figure 4c). Thus, four Ag^+ ions are not equivalent; the $\text{Ag}-\text{Ag}$ distances between Ag^1 , Ag^2 , and Ag^3 are shorter (5.86 Å in average) than those of Ag^4-Ag^n ($n = 1-3$) distances (6.53 Å in average).⁹

In summary, a disk-shaped tridentate ligand $\mathbf{1}$ allows 2-D triangular and 3-D tetrahedral arrays of Ag^+ ions, highly dependent on the metal–ligand ratio. In addition, the dynamic equilibrium is accompanied by the encapsulation and the release of a triflate anion: in other words, the tetrahedral Ag_4I_4 complex encapsulates one triflate or one methanesulfonate anion in the cavity, whereas the sandwich-type Ag_3I_2 complex has no space for guest molecules. Such a controllable dynamic system will be potentially applicable to specific anion recognition and transport based on predesigned molecular motion.

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Supporting Information Available: Synthetic procedures for $\mathbf{1}$, ESI-TOF mass data for Ag_4I_4 and Ag_3I_2 , ^{19}F NMR spectra of $\text{Ag}_4\text{I}_4\cdot(\text{OTf})_4$ and $\text{Ag}_3\text{I}_2\cdot(\text{OTf})_3$ (PDF), and an X-ray crystallographic file for $\text{Ag}_4\text{I}_4\cdot(\text{OTf})_4$ (in CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (3) For preparation of $\mathbf{1}$, see Supporting Information.
- (4) ESI-TOF mass spectra of Ag_4I_4 and Ag_3I_2 are reported in the Supporting Information.
- (5) The chemical shifts were determined using C_6F_6 as the internal standard.
- (6) The tetrahedral structure was preliminarily obtained for the core Ag_4I_4 portion.
- (7) Crystal data for $\text{Ag}_4\text{I}_4\cdot(\text{CH}_3\text{SO}_3)_4$: $\text{C}_{124}\text{H}_{120}\text{Ag}_4\text{N}_{24}\text{O}_{18}\text{S}_4$, $M = 2794.17$. Trigonal, space group $R\bar{3}$, $a = b = 40.805(3)$ Å, $c = 60.529(0)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 87282.4$ Å³, $Z = 24$. Final R indicates ($I > 2\sigma(I)$): $R_1 = 0.0887$, $wR_2 = 0.1280$. GOF on $F^2 = 1.118$.
- (8) The crystal of $\text{Ag}_4\text{I}_4\cdot\text{CH}_3\text{SO}_3$ was obtained from a mixture of AgCH_3SO_3 and $\mathbf{1}$ in the ratio of 3:2 where Ag_3I_2 complex is predominantly formed in the solution. This is due to the equilibrium shift from Ag_3I_2 to of $\text{Ag}_4\text{I}_4\cdot\text{CH}_3\text{SO}_3$ through the crystallization process.
- (9) ^1H NMR spectrum of $\text{Ag}_4\text{I}_4\cdot\text{CH}_3\text{SO}_3^-$ was highly symmetrical at room temperature, and these signals did not show any changes even at low temperature (193 K). These results indicate that the encapsulated CH_3SO_3^- is rotating in the Ag_4I_4 capsule above 193 K.

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