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Anion-Controlled Endo- and Exocyclic Disilver(I) Complexes of an S_2O_3 Macrocycle

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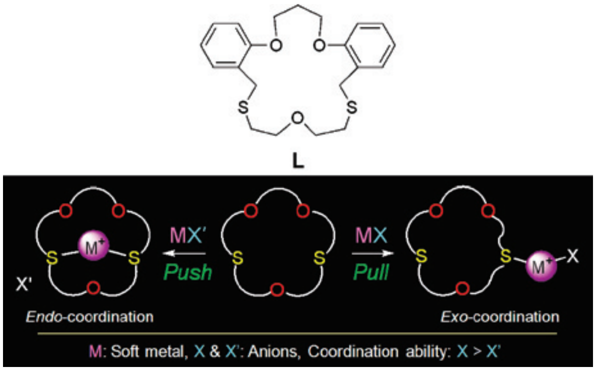
Anion-controlled endo- and exocyclic complexes were afforded in the reactions of an S_2O_3 macrocycle with $AgPF_6$ and $AgClO_4$, respectively. The two coordination modes that provide the Ag ion position inside (by PF_6^-) or outside (by ClO_4^-) the macrocyclic cavity are explained by the anion-coordination ability toward the metal cation. Furthermore, each Ag center bridges two ligands via a regular coordinative bond or by π coordination, forming a cyclic dimeric-type product. NMR titrations of the complex system in solution were also carried out.

Sulfur-containing macrocycles, called thiacrowns or thiamacrocycles, often form not only endocyclic complexes but also exocyclic ones in which the metal ions exist inside or outside the macrocyclic cavity, respectively.[1] In the thiacrowns, the S···S repulsion in the ring stabilizes the trans torsion about the S−C−C−S unit. Thus, the exoconformation tends to lead the product not toward the large distortion of the ring, which is energetically unfavorable, but rather toward the exocoordinated product with multiple M−S bonds.[2] Indeed, a range of mono- and multinuclear complexes of thiamacrocycles with exocoordination have been reported by us[3] and others.[4]

Chart 1. Diagrams of Anion-Controlled Endo- and Exocoordination Modes



We have suggested that such endo- and exocoordination could be controllable.[5] We recently proposed an *N*-azo-coupled NS_2O_2 macrocycle system, which illustrates how the coordinating ability of the anion controls a color change through the formation of endo- or exometal complexes.[5] Not only are we interested in investigating the factors that influence the self-assembly of metal complexes into distinct endo- or exocoordinated products, but also we want to advance our understanding of a methodology of emerging significance in macrocyclic chemistry that may serve as a potent controllable phenomenon.

As part of ongoing efforts, we have focused our attention on the anion species that would potentially influence the coordinated metal ion position.[6] This approach enabled us to prepare two distinct complexes of the S_2O_3 macrocycle **L**, with their coordination modes being anion-controllable as depicted in Chart 1. In an extension of the solid-state

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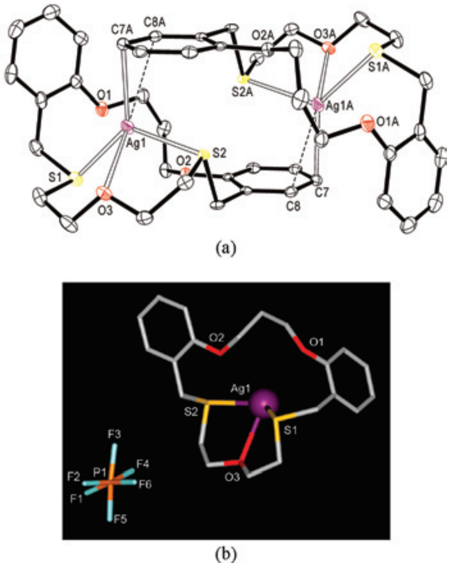

Figure 1. Endocyclic structure of (a) disilver(I) complex **1**, $[Ag_2\mathbf{L}_2](PF_6)_2$, and (b) its asymmetric unit.

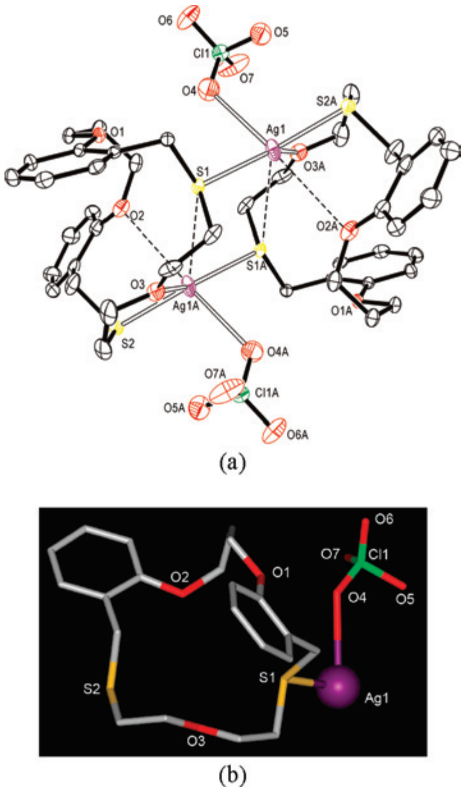

Figure 2. Exocyclic structure of (a) disilver(I) complex **2**, $[Ag_2\mathbf{L}_2(ClO_4)_2]\cdot0.5H_2O$, and (b) its asymmetric unit.

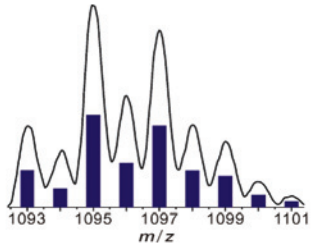

Figure 3. Observed isotope distribution for $[Ag_2\mathbf{L}_2(ClO_4)]^+$ in the FAB mass spectrum of **2**. The bars represent the predicted mass spectral distribution for this ion.

study, NMR titrations were undertaken to explore complexation in solution.

L was prepared according to our previously published method.[7] In complexation, $AgPF_6$ and $AgClO_4$ were used to examine the anion effect on the coordination modes. First, **L** dissolved in dichloromethane was treated with 1 equiv of each silver(I) salt in methanol. Slow evaporation of the solutions afforded the crystalline products suitable for X-ray analysis. Using these reaction systems, two complexes (**1**, PF_6^-, and **2**, ClO_4^-) were prepared and structurally characterized (Figures 1 and 2).

The X-ray analysis revealed that **1** is a disilver(I) complex of formula $[Ag_2\mathbf{L}_2](PF_6)_2$ in which each metal ion is accommodated inside the macrocyclic cavity (Figure 1). Because the structure in Figure 1a is generated through an inversion symmetry, the asymmetric unit of **1** contains one **L**, one Ag atom, and one PF_6^- (Figure 1b). The uncoordinated PF_6^- ion acts only as the counterion to balance the charge, with the closest distance between the Ag and F atoms being 6.098 Å. The Ag center is four-coordinate, being bound to two S and one O donors from one **L** at Ag−S distances ranging from 2.497(1) and 2.539(1) Å, with the macrocycle adopting an endoconformation. Notably, the coordination polyhedron is completed by one aromatic C atom (C7A) from an adjacent **L**, allowing the formation of a cyclic dimer. The Ag1−C7A distance, 2.619(5) Å, is well within the reported limits (2.47−2.77 Å) for Ag−π coordination.[3d,8] The next-closest contact between Ag and C is 2.807(5) Å for C8A (dashed line). Thus, the Ag atom coordination can be described as a distorted tetrahedral structure. Accordingly, **L** acts as a ditopic ligand coordinating to one Ag atom via two Ag−S bonds and another Ag atom via Ag−π coordination. The bond angles around the Ag atom vary from 72.3(1)° (O3−Ag1−S1) to 136.7(1)° (S1−Ag1−C7A) because of the formation of a five-membered ring and the additional Ag···C8A π interaction, respectively. The Ag1···O1 and Ag1···O2 distances are 3.470(4) and 3.402(3) Å, respectively, which are too long to be considered as a regular bond. With respect to the anion-coordination ability, the preferred endocoordination mode of **1** is due to the weak affinity of the PF_6^- ion toward the Ag^I center, allowing the approach of the benzo group to form a unique cyclic dimer. To our best understanding, this is the first characterized example of a macrocyclic complex with a cyclic dimer arrangement through π coordination.

In marked contrast to the metal ion position in **1**, the perchlorate complex **2** shows an exocoordinated dinuclear species of formula $[Ag_2\mathbf{L}_2(ClO_4)_2]\cdot0.5H_2O$ (Figure 2). The asymmetric unit contains one **L**, one Ag atom, and one ClO_4^-. In this case, the Ag atom that lies outside the cavity

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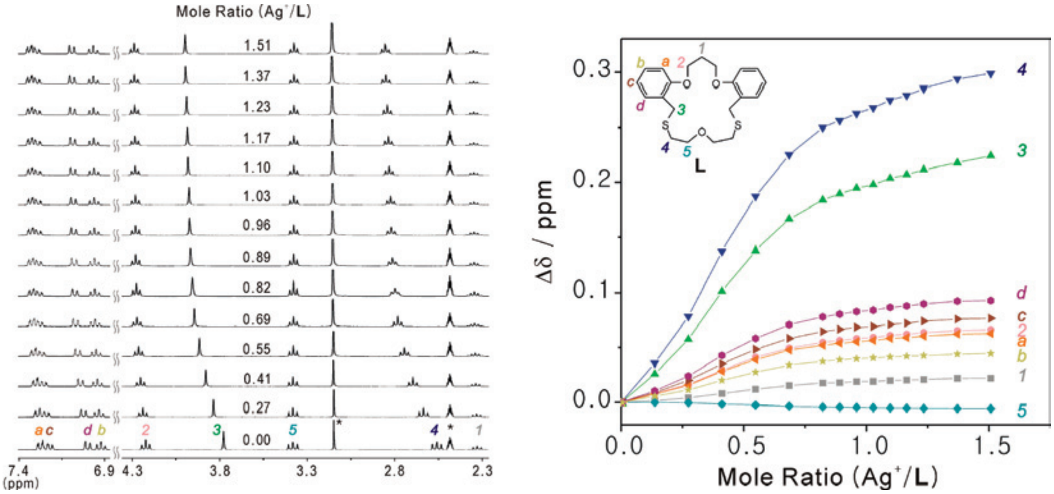

Figure 4. (a) ^{1}H NMR spectra of **L** by the stepwise addition of $AgPF_6$ and (b) titration curves for **L** with $AgPF_6$ in CD_3CN/DMSO-d_6 (1:1).

bridges two facing macrocycles, forming a cyclic dimer again. Accordingly, the Ag center is four-coordinated by two S atoms from one **L** and one S atom from another **L**. The fourth site is occupied by an O atom of ClO_4^- in a monodentate manner with a bond length [Ag1−O4 2.779(8) Å] that falls within the range observed for other monodentate perchlorate complexes of silver.[7,9] Surprisingly, the Ag atom is not in the center of the tetrahedral environment but is defected out of the S_2O trigonal plane by 0.012 Å opposite the perchlorate. This exceptionally large dislocation of the Ag atom may be due to the long-range Ag1···S1A and Ag1···O2A interactions [dashed lines, 3.474(2) and 3.289(5) Å]. The two O donors between aromatic units (O1 and O2) remain uncoordinated [Ag1···O1 4.952(4) Å; Ag1···O2 5.406(6) Å].

The fast atom bombardment (FAB) mass spectrum of **2** contains a peak at *m*/*z* 1093.05, which corresponds to $[Ag_2\mathbf{L}_2(ClO_4)]^+$. The relative abundance of its isotope pattern is in good agreement with that of the simulated one (Figure 3). Unlike the FAB mass data for complex **1** (Figure S1 in the Supporting Information), this result is also evidence for the formation of the monovalent dimer complex due to the anion coordination.

Consequently, a comparison of the coordination modes between the anion-free endo form in **1** and the anion-coordinated exo form in **2** supported the idea that the anion-coordination effect is a controlling factor. Undoubtedly, coordination of ClO_4^- toward the Ag atom inhibits the formation of the endo-type structure and induces or triggers the formation of the S−Ag−S linkage between the two ligand molecules by occupying the fourth coordinating site. Furthermore, the discriminated anion-coordination ability induces the dimerization of the complex in different modes, giving rise to the cyclic form.

For comparison of the behavior of these structures in solution, ^{1}H NMR titrations were performed for the parallel system in CD_3CN/DMSO-d_6 (1:1) (Figure 4a). Unlike in the solid state, the results for the NMR titration experiments with the two anions show no significant differences because the solvation in the dipolar aprotic solvent minimizes or removes the anion effect observed in the solid state. Thus, we present only the result of $AgPF_6$ as a representative example. The signals of the five methylene (H_{1-5}) and the aromatic (H_{a-d}) protons in **L** were well resolved and identified (Figure 4a). Upon stepwise additions of Ag^I, every proton of **L** except H_5 shifted downfield, suggesting stable complexation for the fast exchange system. The order of the magnitude of the chemical shift variation is $H_4 > H_3 > H_2 > H_1$, indicating that Ag^I is more strongly coordinated by S than O donors, which is similar to the case in the solid state. In addition, the chemical shifts for the aromatic protons H_{a-d} change from their uncomplexed ones. These changes are caused by both Ag−donor and Ag−π interactions.[3d,8] The titration curves show no clear break point over the range investigated, suggesting the coexistence of several species with different ratios including 1:1 or 2:2 (Ag^+/**L**).

In summary, the assembly of thiaoxamacrocycle with silver salts with different anions provides a facile means of generating discriminated macrocyclic disilver complexes with different coordination modes. From these results, it is concluded that the influence of the anion-coordination ability, at least in thiamacrocyclic complexation, alters ligand behavior and has important consequences for the topology of the complexes.

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Supporting Information Available: Synthetic procedures, analytical data, and X-ray crystallographic files (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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