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Exo-Coordination-Based Supramolecular Silver(I) Complexes of S_2O Macrocycles: Effect of Ligand Isomerism on the Structural Diversity

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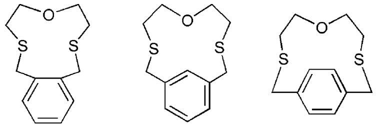
An isomeric series of S_2O macrocycles incorporating a xylyl group at the ortho (**L**^{1}), meta (**L**^{2}), and para (**L**^{3}) positions were employed to examine the influence of the ring rigidity on silver(I) coordination modes in resulting supramolecular complexes (**1**–**3**); **L**^{1} and **L**^{3} afforded sandwich (**1**; Ag:**L**^{1} = 1:2) and infinite 1-D (**3**) complexes, respectively; otherwise, **L**^{2} gave the 1-D polymer (**2a**), 2:3 club sandwich (**2b**), and unique 2:4 bridged dinuclear complex (**2c**) complexes, in which their topologies vary with the solvent used.

The structural modification of macrocycles and the careful selection of the metal salt system make it possible to produce a large number of coordination topologies.[1] In the course of our ongoing studies of the sulfur-containing mixed-donor macrocycles,[2] we explore the possibility of generating ligand rigidity-controlled coordination products through the modification of the macrocycles. Generally, thia and thiaoxa macrocycles show an *exodentate* arrangement of sulfur donors.[3] Thus, we are interested in the small macrocycles with sulfur donors and an aromatic subunit simultaneously. In connection with these reasons, the positional isomers **L**^{1}–**L**^{3} were chosen as model systems. Because the order of their conformational ring rigidity is known as **L**^{1} < **L**^{2} < **L**^{3}, due to the position of the xylyl substituent,[4] we reasoned that these may induce the rigidity-controlled products with soft metals such as silver(I).



L^1 **L**^{2} **L**^{3}

L^1 and **L**^{2} were prepared as previously reported.[5] **L**^{3} was prepared similarly (see the Supporting Information). In complexation, $AgPF_6$ (1 equiv) was used to exclude the anion coordination.[6] Using these reaction systems, we obtained a range of supramolecular complexes **1**–**3** with different topologies (Scheme 1), and their structures were characterized by X-ray analysis (Figures 1–3). In an extension of the solid-state study, NMR titrations were undertaken to explore the complexations in solution (Figure 4).

Reaction of **L**^{1} with $AgPF_6$ in methanol afforded the sandwich complex[7] of formula $[Ag(\mathbf{L}^1)_2](PF_6)$ (**1**; Figure 1). **1** is centrosymmetric, with the silver(I) at a crystallographic inversion center. The silver(I) center sits in a distorted tetrahedral coordination sphere, with each ligand coordinated in bidentate fashion via two exodentate sulfur donors. The S–Ag–S bite angles vary from 98.85(4) to 115.94(5)° partially because of the additional Ag···O [3.321(3) Å] interactions. The Ag–S distances (2.576–2.627 Å) are slightly shorter than those of other similar systems.[7] This particular sandwich complex seems to be obtained because of the less rigid conformation of **L**^{1} compared to **L**^{2} or **L**^{3}. Four of all torsion angles between donors with gauche conformations also could be evidence for the relatively larger flexibility.

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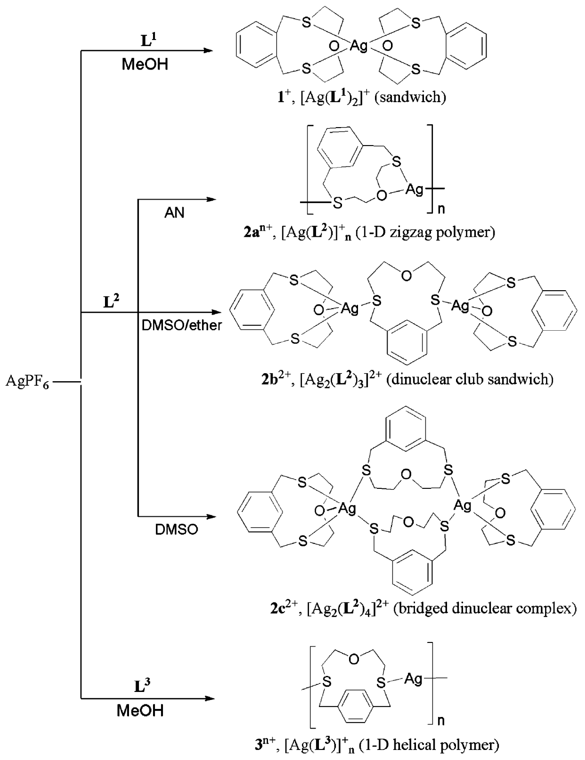
Scheme 1. Compounds Prepared



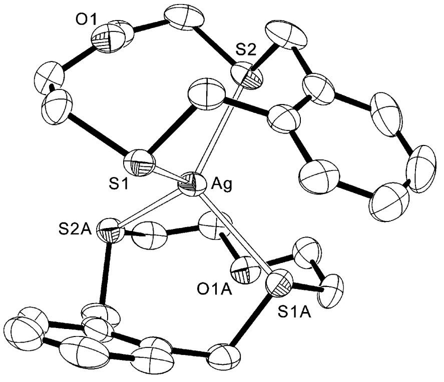


Figure 1. Sandwich (1:2) structure of **1**, [Ag(**L**^{1})$_2$](PF$_6$). Hydrogen atoms and noncoordinating anions are omitted.

Moreover, the NMR titration also confirms the formation of the corresponding species with 1:2 stoichiometry (Ag$^+$/**L**^{1}) in solution (Figure 4a,b).

Interestingly, reactions of **L**^{2} with AgPF$_6$ afforded the three types of solvent-free complexes (**2a**−**c**), in which their topologies and stoichiometries vary with the solvents used (Figure 2). First, **2a** crystallizes in a 1-D zigzag polymer consisting of [Ag(**L**^{2})](PF$_6$) units in acetonitrile (Figure 2a). Each silver(I) is in a distorted trigonal plane with coordination sites occupied by one S atom and one O atom from one **L**^{2} and by one S atom from an adjacent **L**^{2}, resulting in a Y-shaped geometry: the bond angles were from 77.33(6)° of S1−Ag1−O1 to 162.04(3)° of S2A−Ag1−S1.

On the other hand, by vapor diffusion of diethyl ether into the reaction mixture containing **L**^{2} and AgPF$_6$ in dimethyl sulfoxide (DMSO), **2b** crystallizes in a very rare dinuclear club sandwich complex[8] [Ag$_2$(**L**^{2})$_3$](PF$_6$)$_2$ with an **L**−M−**L**′−M−**L** (**L** = terminal ligand and **L**′ = connecting ligand)

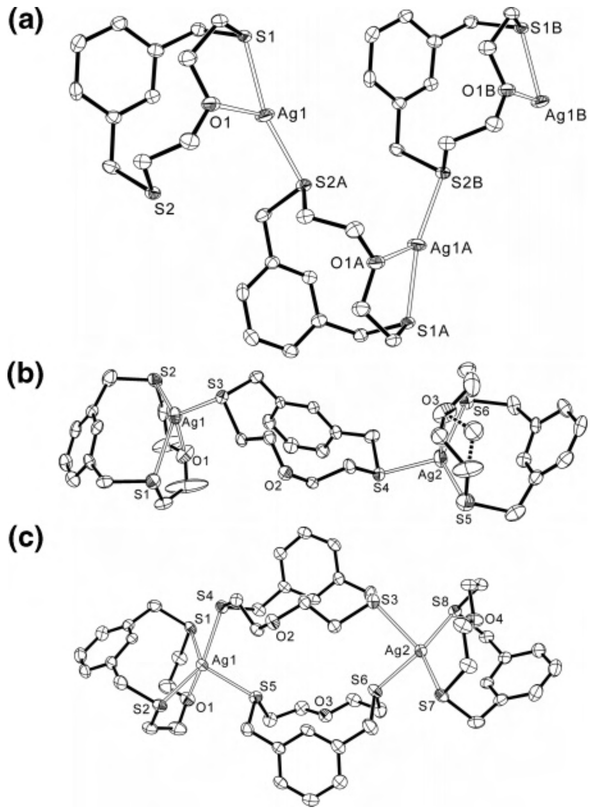


Figure 2. (a) Zigzag structure of **2a**, {[Ag(**L**^{2})](PF$_6$)}$_n$, (b) club sandwich (2:3) structure of **2b**, [Ag$_2$(**L**^{2})$_3$](PF$_6$)$_2$, and (c) bridged dinuclear complex (2:4) structure of **2c**, [Ag$_2$(**L**^{2})$_4$](PF$_6$)$_2$. Hydrogen atoms and noncoordinating anions are omitted.

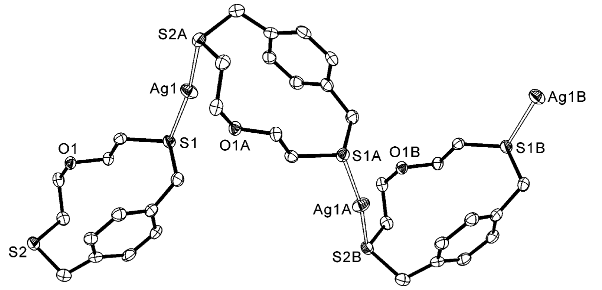


Figure 3. Zigzag structure of **3**, {[Ag**L**^{3}](PF$_6$)}$_n$. Hydrogen atoms and noncoordinating anions are omitted.

array (Figure 2b). As we understand, only one example of the club sandwich complex (M$_2$**L**$_3$) between soft metal ions and macrocycles has been reported until now.[8d] Each silver(I) is in a distorted tetrahedral environment with coordination sites occupied by the facial mode of two S atoms and one O atom from one terminal ligand in bent arrangement adopting an endodentate conformation and by one exodentate S atom from the connecting ligand. The Ag−S distances in the terminal ligands [2.584(2)−2.723(3) Å] are longer than those in the connecting ligand [2.486(3) and 2.501(3) Å]. Two terminal ligands show a similar bent arrangement adopting an endo coordination. However, all of donors in the connecting

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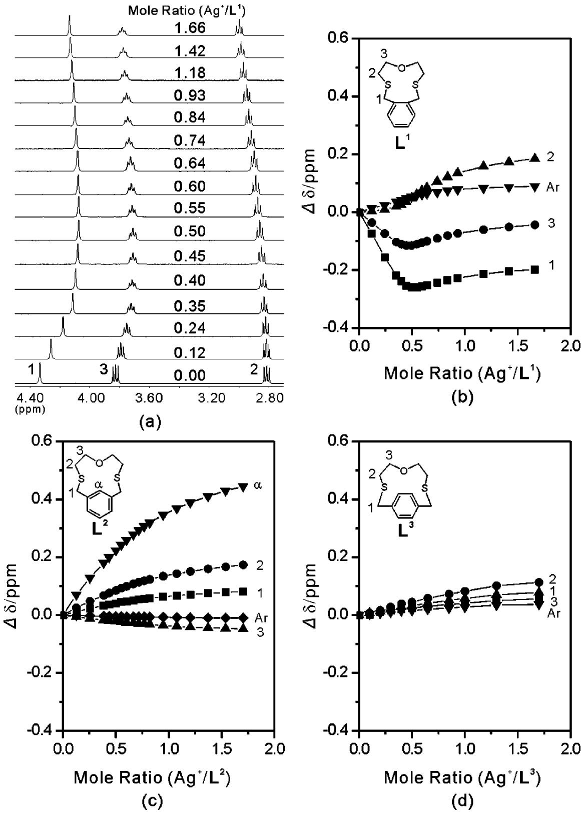

Figure 4. (a) Aliphatic region of ^1H NMR spectra of L^1 by stepwise addition of $AgPF_6$ in CD_3CN and the ^1H NMR titration curves for (b) L^1, (c) L^2, and (d) L^3 with $AgPF_6$. For labeling of protons, see each formula in this figure.

ligand have an exodentate conformation because of the fully stretched arrangement and are quite similar to the free form.[4b]

In a DMSO solution containing L^2 and $AgPF_6$, **2c** crystallizes very slowly (for 2 months) in an unprecedented bridged dinuclear complex of formula $[Ag_2(L^2)_4](PF_6)_2$ consisting of two silver(I) and four L^2 units (Figure 2c) in the category of the macrocyclic ligands. Only one Ag_2L_4-type metallacyclic complex with the acyclic ligand [$L = (CH_3)_4(CN)_2S_3$] was known.[10]

This is the first characterized bridged dinuclear complex between macrocycles and soft metal ions. Each silver(I) is surrounded by three macrocycles: two connecting ligands and one terminal ligand. Hence, it is noteworthy that the two silver(I) units in **2c** are doubly bridged by the two connecting ligands. Ag1 is in a five-coordinated environment with three coordination sites occupied by the facial mode of two S atoms and one O atom from one terminal ligand in bent arrangement adopting an endodentate conformation and by two exodentate S atoms from two connecting ligands. However, Ag2 is in a distorted tetrahedral geometry with two sites occupied by two S atoms in one terminal ligand in bent arrangement adopting an endodentate conformation and by two exodentate S atoms from the two connecting ligands. Interestingly, two connecting ligands show different conformations: e.g., the S···S distances are 5.043(2) and 6.596(1) Å, respectively. The Ag···Ag distance is 9.261(1) Å. The fast atom bombardment mass spectrum for **2c** showed a peak at *m*/*z* 587.06 (calculated value: 587.03) corresponding to $[Ag_2(L^2)_4]^{2+}$. The relative abundance of its isotope pattern is in good agreement with that of the simulated one (see the Supporting Information). The coordination polymer, $[Ag(L^2)(NO_3)]_n$, with chain structure has been reported by Casabó et al.[11]

Reaction of L^3 with $AgPF_6$ in methanol afforded the infinite 1-D complex of formula $\{[Ag(L^3)](PF_6)\}_n$ (**3**; Figure 3). Like **2a**, each exodentate macrocycle is bridging the silver(I). However, **3** is a helical chain,[12] which is distinct from the zigzag morphology of **2a**. The deviation of the S−Ag−S angle [168.29(3)°] from linear arrangement is due to the additional Ag···O interaction [2.925(2) Å], which also stabilizes the helical structure. Again, comparing the 1-D structures of **2a** and **3** afforded a good case for illuminating the effect of ring rigidity in the small macrocycles on the conformations of the exo-coordination products.

For comparison with those in solution, NMR titrations were carried out for the parallel system (Figure 4). Commonly, the peaks for H_1 and H_2 show relatively larger shift than those of H_3 and H_{ar}, indicating that silver(I) is strongly coordinated by S donors, similar to the case in the solid state. As mentioned, the results for L^1 (Figure 4a,b) clearly indicate the formation of the complex with a 1:2 (Ag^+/L^1) ratio, which is also similar to the case in the solid state. The other titration curves, however, show no clear break point in the range investigated, suggesting the coexistence of several species with different ratios.[9] Thus, the bridging potential of the macrocycles including L^2 is perhaps less surprising when one considers that diverse types of species can exist, at least depending on the mole ratio, in the solution state.

In conclusion, assembly of silver(I) with the S_2O macrocyclic isomers (L^1−L^3) provides a facile means of generating a new category of unique exo-coordination complexes (**1**−**3**) with diverse arrays, such as $(L-M)_n$ (**2a** and **3**), **L**−**M**−**L** (**1**), **L**−**M**−**L**−**M**−**L** (**2b**), and $L-M-L_2-M-L$ (**2c**). From these results, it is concluded that the influence of the ring rigidity of the macrocycles in complexation alters the ligand behavior and has important consequences for ligand binding. It may thus be used as a tool in ligand design. Further study on the serendipitous results for L^2 complexes derived from the different solvents is in progress.

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Supporting Information Available: Synthetic procedures, NMR titrations, and analytical data and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structures reported in this paper are also available at the Cambridge Crystallographic Data Centre, with the CCDC reference number 152821 (for **3**).

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