A Well Characterized Example of Conversion of Molecular Configuration Depending on the Existence of Intermolecular Interactions

Qin-Yu Zhu,[†] Yong Zhang,[†] Jie Dai,*[†,††] Guo-Qing Bian,[†] Ding-Xian Jia,[†]
Jia-Sheng Zhang,[†] and Lin Guo[†]
[†]*Department of Chemistry & Chemical Engineering, Suzhou University, SuZhou 215006, P. R. China*
[††]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*

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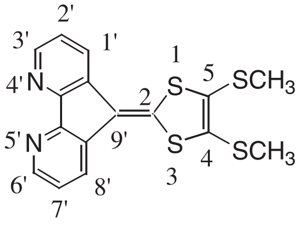
A new complex $[Ag(L)_2]ClO_4{\cdot}2CH_2Cl_2$ (**1**) (L = 4′, 5′-diaza-9′-(4,5-dimethylthio-1,3-dithiole-2-ylidene)fluorene) was synthesized. It was confirmed by ^1H NMR and X-ray structure determination that when the molecules crystallize out from solution, a conversion of molecular configuration occurs because of the strong intermolecular interactions.

In inorganic or orgnometalic chemistry, great efforts have been reported to design and prepare supramolecules or complexes having $\pi\cdots\pi$ stacking,[1] S···S contact[4] and hydrogen bonding.[3] Most of these studies are concentrated on the solid-state chemistry (crystal structures). Few of them are concerned with the role of the intermolecular forces in the processes of crystallization.

We are interested in the crystal engineering with weak intermolecular forces.[4] Recently, 4′,5′-diaza-9′-(4,5-dimethylthio-1,3-dithiole-2-ylidene)fluorene (L, Scheme 1) was selected as one of this kind ligand, which is basically a planar molecule and includes two pyridine rings.[5] Its coordination chemistry is similar to 1,10-phnanthroline and 2,2-bipyridine.[4d] Besides, this ligand also includes a conjugated sulfur-rich moiety that is expected to change the relative donor/acceptor properties of the ligand and the intermolecular interaction in its solid state.

Lately, an interesting experimental result was found in studying Ag(I) complexes of this ligand. The complex $[Ag(L)_2]ClO_4{\cdot}2CH_2Cl_2$ (**1**) was simply synthesized by reaction of ligand L with $AgClO_4{\cdot}H_2O$ in a mixed solution of acetonitrile and dichloromethane.[7]



Scheme 1.

The complex **1** consists of $[Ag(L)_2]^+$ cation and perchlorate anion.[8] The crystal structure of the cation is illustrated in Figure 1. The silver atom is coordinated by two nitrogen atoms from two ligands in a linear geometry, in which the N(1)–Ag–N(1) angle is just 180.00°. Although the linear coordination compounds are very common for Ag(I) complex, there is a lack of this kind crystal data for this type ligands, such as 2,2′-bipyridine and phenathroline complexes. In contrast, a number of four coordinated Ag(I) complexes are reported.[6] The crystal structure of $[Ag(bipy)_2(NO_3)]{\cdot}H_2O$ consists of chains with the coordinated nitrate group acting as a bridging ion and the Ag atom is strongly coordinated to all four pyridyl N atoms.[9] On the other hand, Burke indicates that complexes of the type $[M(bpy)_2]^{n+}$ and $[M(phen)_2]^{n+}$ are unable to adopt a square-planar configuration because of steric interaction between α–H and the N atoms.[10] Thus the planar structure of the linear coordinated $[Ag(L)_2]^+$ is very unique and reasonable in structure chemistry of Ag(I). The two Ag–N(1) distances in **1** are equivalent (2.203(4) Å) and two other nitrogen atoms of diaza in fluorene are not coordinated and the distance from Ag to N(2) is 2.738 Å.

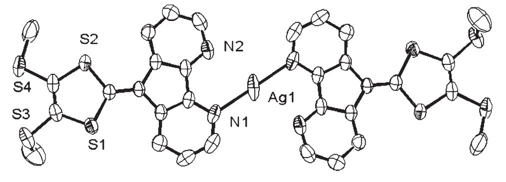
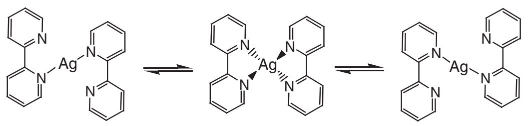


Figure 1. ORTEP view of the cation structure of **1**. Ag(1)–N(1), 2.023(4) Å; N(1)–Ag–N(1), 180.00(2)°.

^1H NMR spectrum of the complex $[Ag(L)_2]ClO_4$ in $CDCl_3$ revealed clearly three set of aromatic hydrogen signals. The two doublets signals at 8.78 and 8.24 ppm are assigned to the ^1H at 3′, 6′ and 1′, 8′ ring sites of the fluorene, respectively (Scheme 1). The signal at 7.55 with quarto-split is assigned to the ^1H at 2′ and 7′ ring sites. A single signal at 2.63 ppm is due to the methyl group (^1H NMR spectrum of free L: 8.68d, 8.06d, 7.39q, 2.58s ppm in $CDCl_3$).



Scheme 2. Interconversion of molecular configurations of **1** in $CDCl_3$.

Based on the ^1H NMR results, the reasonable structure of the complex in chloroform must be a tetrahedral coordination sphere, in contrast to the structure in solid state discussed above. That is to say both of the aza nitrogen atoms in a fluorene are coordinated to the Ag(I) in solution of **1**, that insures the symmetrical distribution of the electron density on carbon atoms of the C_{2v} fluorene moiety. The tetrahedral geometry has been also found in the solid state of some silver(I)-bipyridyl compounds.[6b] However, the NMR results of **1** could also be explained as a quick interconversion of the molecular configuration (Scheme 2), even in this case, the tetrahedral coordination intermediate should still be dominant species. Thus both of the cases explained above are supported the existence of tetrahedral cations. Unfortunately, low temperature ^{1}H NMR measurement was not succeeded for the low solubility of **1**.

Now the problem we want to know is why the planer structure of **1** is more stable in crystal than the tetrahedral structure. Figure 2a shows the interplanar interactions; by those strong interactions the molecules are stacked in 1-D column structure. The Ag(1)···S(1) distance (3.414 Å) is shorter than the sum of van der Waals radii of Ag and S atoms. The $\pi\cdots\pi$ stacking between the fluorene planes is about 3.37 Å. These strong intermolecular forces play an important role in determination of the molecular configuration and molecular packing. It is noteworthy that to ensure both the $\pi\cdots\pi$ stacking and the Ag(1)···S(1) interaction operating efficiently, two of the fluorene planes in pairs are almost completely overlapped, whereas the Ag(1)···S(1) interactions bevel to the plane. Figure 2b displays the inter-planar interactions looking along the long axis of the molecules. The C(9)···C(15) stacks (3.37 Å) are ac. perpendicular to the molecular plane.

In the crystal, every two of the neighbored 1-D structures are paralleled to each other and the molecules are arranged in Λ pattern with dihedral angle 47.95° (See ESI), forming layered structure. The ClO_4^- and CH_2Cl_2 are located between the layers, at 1, 0, 0 and 2, 0, 0 planes. Weak O···H–C hydrogen bond is found between the fluorene moieties and the perchlorate ions, which connects and further stabilizes the close packed layer-structure. No significant interaction is found for the solvated CH_2Cl_2.

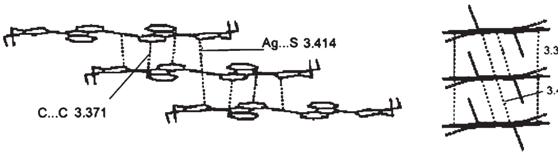


Figure 2. Inter-planar $\pi\cdots\pi$ stacking and Ag(1)···S(1) interaction in complex **1**.

Fluorescence spectra show that the ligand emits strong fluorescence at 365 nm (λ_{ex} 300 nm, $CHCl_3$). This fluorescence band is still observed and dose not be changed when the complex formed, but its intensity decreases owing to the fluorescence quenching of Ag(I). The result that the fluorescence emission at 365 nm does not be changed before and after the coordination is basically consistent with the conclusion of the tetrahedral configuration of the complex in solution. Since the energy levels of the ligand will be significantly affected by the extended conjugating structure, if the molecular configuration is taken a plane.

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7 $[Ag(L)_2]ClO_4{\cdot}2CH_2Cl_2$ (**1**). To an acetonitrile solution of $AgClO_4{\cdot}H_2O$ (0.1 mmol, 20.76 mg) was slowly dropped CH_2Cl_2 solution of the ligand L (0.1 mmol, 36 mg). An orange precipitate formed was filtrated, washed and finally dried in vacuo (Yield 61%). Anal. Calcd for $C_{34}H_{28}N_4AgCl_5O_4S_8$: C, 37.30; H, 2.58; N, 5.12% Found: C, 37.12; H, 2.38; N, 5.49%.

8 X-ray Crystallography. Unique reflections (4739) were collected by ω scan mode and 3392 reflections with $I > 3\sigma(I)$ were used in the succeeding refinement. The structure was solved by DIRDIF99. The final cycle of refinement converged at $R = 0.050$, $wR = 0.124$. monoclinic system, $C2/c$, $a = 25.589(4)$, $b = 8.2764(8)$, $c = 22.363(4)$ Å, $\beta = 117.876(6)$, $C_{34}H_{28}AgCl_5N_4O_4S_8$, $M_r = 1098.20$, $V = 4186.6(11)$ Å^3, $Z = 4$, $D_{calcd} = 1.736$ mg/m^3, $\mu = 12.42$ cm^{-1}, $F(000) = 2192.00$, $S = 1.00$.

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