2396 *Organometallics* **2008,** *27,* 2396–2398

Communications

Diverse Intermolecular Interactions in Metal−Organic Frameworks Constructed with the New Supramolecular Synthon Ag_n−L−Ag_n (n = 4, 5) (H_2L = 2,2′-Bis(prop-2-ynyloxy)biphenyl)

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Received February 21, 2008

Summary: The three silver(I) coordination polymers $[(Ag_2L)(AgNO_3)_6(H_2O)]$ (**1**), $[(Ag_2L)_{0.5}(AgCF_3CO_2)_4(H_2O)_2]$ (**2**), *and* $[(Ag_2L)(AgCF_3CO_2)_7(CH_3CN)_3(\mu_2\text{-}H_2O)]$ (**3**) *have been constructed from the flexible multifunctional dianionic ligand L* (H_2L = *2,2′-bis(prop-2-ynyloxy)biphenyl), providing experimental evidence of coexisting uncommon intermolecular interactions (cation−π and π−π in* **1**; *cation−π and anion−π in* **2**; *C≡N···π and C−H···π in* **3**) *that stabilize their framework structures.*

The metal−π interaction has been amply exploited in building novel molecular and framework architectures that may exhibit a variety of useful electrical and electrochemical properties.[1,2] Several other unconventional intermolecular interactions (H···H, anion−π, lp−π, and argentophilic) also have these traits.[3–7] Since the term "anion−π interaction" was used to describe the interaction between the permanent quadrupole of C_6F_6 and various anions in 2002,[4a] it has aroused considerable attention, owing to its relevance to anion recognition and transport with medicinal and environmental applications.[4,5] Meanwhile, the significance of attractive interactions between electron-rich neutral molecules and aromatic π systems have also been recognized.[6]

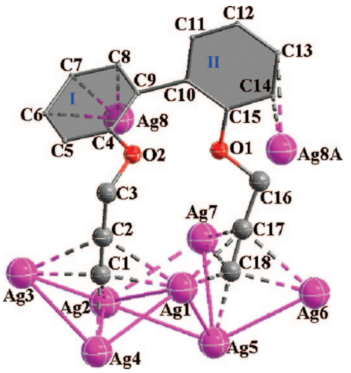

Figure 1. Coordination mode of L in **1**. Details are given in the Supporting Information. Symmetry code: (A) 1 + *x*, *y*, *z*.

Noting that experimental evidence of the coexistence of the aforementioned noncovalent supramolecular interactions is mostly lacking, we have designed the new dianionic ligand L (H_2L = 2,2′-bis(prop-2-ynyloxy)biphenyl), which has two pendant arms, each bearing a terminal ethynide moiety attached to the conformational flexible biphenyl skeleton. The reaction of H_2L with silver salts is expected to generate metal−organic frameworks (MOFs) consolidated by argentophilic,[7] silver(I)−ethynediyl,[8] and silver(I)−aromatic interactions,[2,9] and the aromatic rings of L are potentially capable of partaking in π-related interactions.

Herein we report the syntheses[10] and structural characterization[11] of three new silver(I) double salts derived from $[Ag_2L]_n$ as a starting material, namely $[(Ag_2L)(AgNO_3)_6(H_2O)]$ (**1**), $[(Ag_2L)_{0.5}(AgCF_3CO_2)_4(H_2O)_2]$ (**2**), and $[(Ag_2L)(AgCF_3CO_2)_7(CH_3CN)_3(\mu_2\text{-}H_2O)]$ (**3**), in which L adopts different coordination modes to silver(I) atoms.

In the crystal structure of **1**, the dianionic ligand L adopts a synclinal conformation, in which the torsion angle C4−C9−C10−C15 is 73.22° (Figure 1 and Figure S1 (Supporting Information)). The independent ethynide groups coordinate to a Ag_7 cluster with different μ_4-η^1:η^1:η^2:η^2 and μ_4-η^1:η^2:η^2:η^2 coordination modes. The edge-to-centroid distance between two proximal phenyl rings from two different L ligands is 3.711 Å, indicating the existence of a significant edge-to-face π−π

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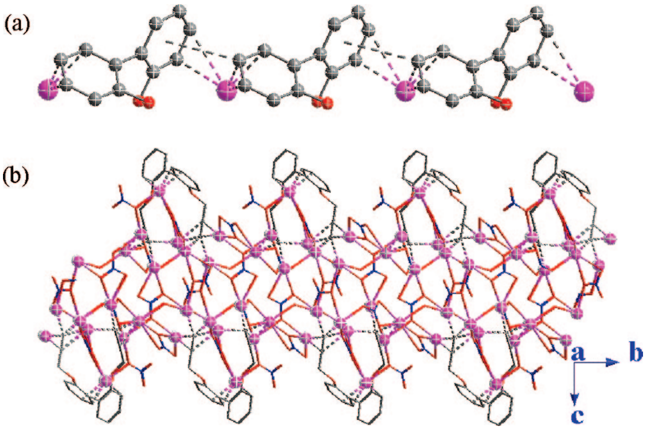

Figure 2. (a) Polymer chain in **1** showing both silver−aromatic and edge-to-face $\pi-\pi$ interactions along the *a* axis. (b) Double-layer structure of **1**. Color scheme for atoms: Ag, purple; C, black; O, red; N, blue.

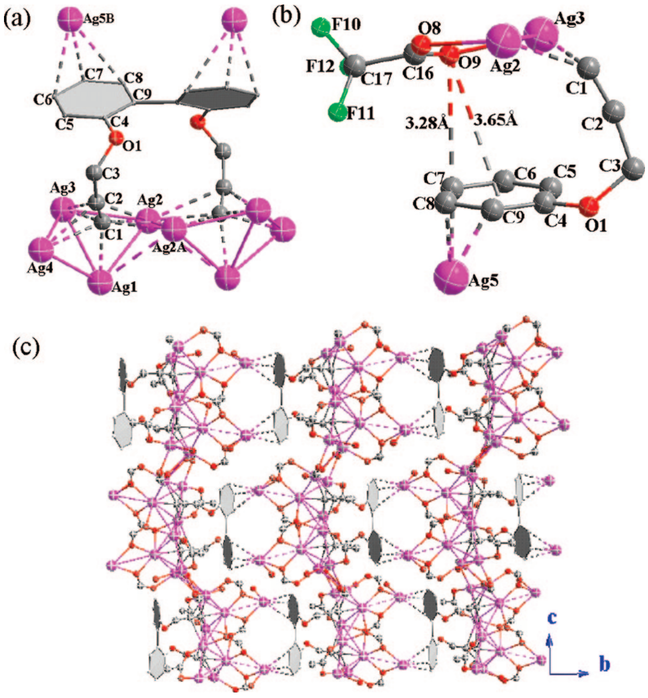

Figure 3. (a) Coordination mode of L in **2**. Details are given in the Supporting Information. Symmetry code: (A) *x*, *y*, $^1/_2 - z$; (B) *x*, 1 + *y*, *z*. (b) Silver−aromatic and anion−π interactions. (c) Layer structure of **2**. Color scheme for atoms: Ag, purple; C, black; O, red. Terminal CF_3 groups are omitted for clarity.

stacking interaction (Figure 2a).[12] Ligand L may be regarded to exhibit a less symmetrical μ_2-η^3:η^2 bonding mode composed of an η^3 silver−aromatic interaction with one ipso (C7) and two ortho carbon atoms (C6 and C8) of the phenyl ring I, together with an η^2 interaction with ipso and ortho carbon atoms (C13 and C14) of phenyl ring II. The respective Ag−C bond lengths of 2.393, 2.996, 2.570, 2.668, and 3.049 Å all fall within the range of silver−aromatic interactions.[13] The Ag_7 aggregates are additionally linked together through the bridging nitrate ions and edge-to-face $\pi-\pi$ stacking to give a double layer (Figure 2b). Such layers are associated together through offset face-to-face $\pi-\pi$ stacking (spacing 3.43 Å)[12] between two adjacent phenyl rings II and C−H···O hydrogen bonds between O20 of one nitrate and two carbon atoms (C12 and C13) of phenyl ring II in neighboring layers to give a 3D supramolecular structure (Figure S2 (Supporting Information)).

In contrast to complex **1**, L in **2** lies on a crystallographic 2-fold axis and takes a symmetric anticlinal conformation with a C4−C9−C9′−C4′ torsion angle of 142.44°. The ethynide group coordinates to a Ag_8 cluster of symmetry 2 with the μ_5-η^1:η^1:η^2:η^2:η^2 coordination mode (Figure 3a and Figure S3 (Supporting Information)). Three phenyl carbon atoms (C6, C7,

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(10) *Caution!* Silver ethynide complexes are potentially explosive and should be handled in very small amounts with extreme care. Synthesis of $[Ag_2L]_n$: H_2L (0.6 g, 2.29 mmol) was dissolved in acetonitrile (50 mL). Then silver nitrate (0.778 g, 4.58 mmol) and triethylamine (0.634 mL, 4.58 mmol) were added with vigorous stirring and the mixture was stirred overnight under a nitrogen atmosphere in darkness. The pale yellow precipitate that formed was collected by filtration, washed thoroughly with acetonitrile (3 × 10 mL) and deionized water (2 × 10 mL), and then stored in wet form at−10 °C in a refrigerator. Yield: about 1.48 g (∼81%). IR: ν 2054 cm^{-1} (m, $\nu_{C\equiv C}$). Synthesis of $[(Ag_2L)(AgNO_3)_6(H_2O)]$ (**1**): $AgNO_3$ (0.34 g, 2 mmol) was dissolved in deionized water (1 mL). Then $[Ag_2L]_n$ (∼30 mg) solid was added to the solution. After it was stirred for about 2 h, the solution was filtered and the filtrate left to stand in the dark at room temperature for several days. During this time colorless blocklike crystals of **1** were deposited in about 75% yield. Anal. Calcd for $C_{18}H_{14}Ag_8N_6O_{21}$: C, 14.29; H, 0.93; N, 5.55. Found: C, 14.01; H, 0.97; N, 5.28. IR: ν 2063 cm^{-1} (w, $\nu_{C\equiv C}$). Upon heating, compound **1** melts from 135 to 136 °C and then turns black and explodes. Synthesis of $[(Ag_2L)_{0.5}(AgCF_3COO)_4(H_2O)_2]$ (**2**): $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in deionized water (1 mL). Then $[Ag_2L]_n$ (∼45 mg) solid was added to the solution. After it was stirred for about $^1/_2$ h, the solution was filtered and the filtrate stored at ∼10 °C in the refrigerator. One week later, colorless needlelike crystals of **2** were deposited in about 60% yield. Anal. Calcd for $C_{17}H_{10}Ag_5F_{12}O_{11}$: C, 17.64; H, 0.87. Found: C, 17.21; H, 0.92. IR: ν 2119 cm^{-1} (w, $\nu_{C\equiv C}$). Compound **2** transforms to a powder at 106 °C and decomposes above 260 °C. Synthesis of $[(Ag_2L)(AgCF_3COO)_7(CH_3CN)_3(\mu_2\text{-}H_2O)]$ (**3**): $AgCF_3CO_2$ (0.440 g, 2 mmol) and $AgBF_4$ (0.382 g, 2 mmol) were dissolved in a mixture of deionized water (1 mL) and acetonitrile (0.2 mL). Then $[Ag_2L]_n$ (∼50 mg) solid was added to the solution. After it was stirred for about $^1/_2$ h, the solution was filtered and left to stand in the dark at room temperature. After several days, colorless platelike crystals of **3** were deposited in about 45% yield. Anal. Calcd for $C_{38}H_{23}Ag_9F_{21}N_3O_{17}$: C, 21.10; H, 1.07; N, 1.94. Found: C, 20.85; H, 1.13; N, 1.57. IR: ν 2063 cm^{-1} (w, $\nu_{C\equiv C}$). Compound **3** melts from 68 to 70 °C.

(11) Crystal data for **1**: $C_{18}H_{14}Ag\ _8N_6O_{21}$, $M_r = 1513.31$, triclinic, space group $P\bar{1}$, $a = 7.627(1)$ Å, $b = 10.237(1)$ Å, $c = 20.343(2)$ Å, $\alpha = 89.231(3)°$, $\beta = 79.744(3)$ °, $\gamma = 88.209(2)°$, $V = 1562.2(3)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 3.217$ g cm^{-3}. The structure converged for 5451 unique reflections ($R_{int} = 0.0353$) and 3966 observed reflections with $I > 2\sigma(I)$ to give R1 = 0.0475, wR2 = 0.1097, and a goodness of fit value (*S*) of 1.032. Crystal data for **2**: $C_{17}H_{10}Ag_5F_{12}O_{11}$, $M_r = 1157.60$, monoclinic, space group $P2_1/c$, $a = 11.607(2)$ Å, $b = 12.299(2)$ Å, $c = 22.497(2)$ Å, $\beta = 120.287(2)°$, $V = 2773.2(6)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 2.773$ g cm^{-3}. The structure converged for 5155 unique reflections ($R_{int} = 0.0361$) and 4467 observed reflections with $I > 2\sigma(I)$ to give R1 = 0.0408, wR2 = 0.1032, and $S = 1.057$. Crystal data for $[Ag_2(L)(AgCF_3COO)_7(CH_3CN)_3(\mu_2\text{-}H_2O)]$ (**3**): $C_{38}H_{23}Ag_9F_{21}N_3O_{17}$, $M_r = 2163.43$, triclinic, space group $P\bar{1}$, $a = 11.789(3)$ Å, $b = 15.211(4)$ Å, $c = 18.017(5)$ Å, $\alpha = 70.960(5)°$, $\beta = 73.919(6)°$, $\gamma = 72.171(5)°$, $V = 2850.5(13)$ Å^3, $Z = 2$, $T = 293$ K, $D_c = 2.520$ g cm^{-3}. The structure converged for 9991 unique reflections ($R_{int} = 0.0314$) and 6723 observed reflections with $I > 2\sigma(I)$ to give R1 = 0.0538, wR2 = 0.1310, and $S = 1.033$. Silver atom Ag8 has two disordered positions with a site occupancy ratio of 0.9:0.1. Selected crystals were used for data collection at 293 K with Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $2° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package.

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and C8) coordinate to the silver atom Ag5 by an unusual μ-η^3 mode[9,14] with bond lengths of 2.661, 2.345, and 2.874 Å, respectively. These moieties are further connected together through coordination interactions between silver atoms and trifluoroacetate ligands to produce a two-dimensional coordination/organometallic polymer (Figure 3c). Notably, the short distances (O9···C8 = 3.28 Å; O9···center = 3.65 Å) between one oxygen atom (O9) of the coordinated trifluoroacetate group and the phenyl ring indicate the existence of a weak anion–π stacking interaction[4,5,15,16] (Figure 3b). This may be rationalized by the fact that the π-electron density of the ring is polarized upon bonding to a positively charged silver(I) center. Recent calculation has made it clear that very favorable interaction energies, short equilibrium distances, and strong synergic effects can be achieved when different noncovalent interactions (cation–π, anion–π, and/or π–π) coexist in the same system.[17] Though the coexistence of cation–π and anion–π interactions has been found in organometallic cavitands,[18] to our knowledge complex **2** is the first structure that has both cation (Ag^I)–π and anion–π interactions in a metal–organic coordination polymer.

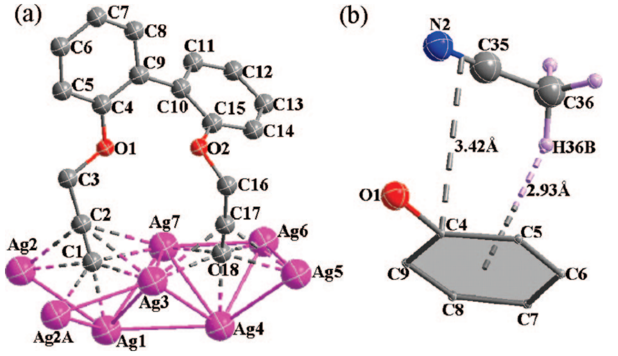

Figure 4. (a) Coordination mode of L in **3**. Symmetry code: (A) $2 - x$, $1 - y$, $1 - z$. (b) CH···π and CN···π interactions in **3**.

In complex **3**, L takes the synclinal conformation with a C4–C9–C10–C15 torsion angle of 69.11°. Two centrosymmetry-related L ligands are bound to a Ag$_{16}$ aggregate, in which the independent ethynide groups display different μ_5-η^1:η^1:η^2:η^2:η^2 and μ_5-η^1:η^1:η^1:η^2:η^2 coordination modes (Figure 4a and Figure S4 (Supporting Information)). Short distances between the nearly parallel acetonitrile ligand and phenyl ring indicate C–H···π and C≡N···π interactions, which are comparable with results in the literature[19,20] (Figure 4b). Though the first experimental proof for significant interactions between neutral electron-rich acetonitrile and electron-deficient aromatic rings has been reported recently,[6c] the concurrence of C–H···π and C≡N···π interactions for one acetonitrile molecule is a new mode that is crucial in the context of its host–guest supramolecular chemistry.[21] The formation of these noncovalent interactions may be related to the coordination of acetonitrile to the silver(I) ion (Ag9). The Ag$_{16}$ aggregates are further interconnected through bridging trifluoroacetate ligands and argentophilicity between symmetry-related Ag5 ions to give an infinite chain (Figure S5 (Supporting Information)).

The present study has established that L is an flexible multifunctional dianionic ligand with its biphenyl skeleton exhibiting synclinal and anticlinal conformations, and its tethered ethynide moieties can adopt μ_4- and μ_5-ligation modes upon bonding to silver(I) centers. The resulting Ag$_n$–L–Ag$_n$ (n = 4, 5) aggregate may be regarded as a new metallo-ligand supramolecular synthon for coordination/organometallic network assembly, which gains stability through manifestation of the less common intermolecular silver–ethynide, argentophilicity, cation (Ag^I)–aromatic, and anion–π interactions.

Acknowledgment. This work was supported by the Hong Kong Research Grants Council (Ref. No. CUHK 402405), the Wei Lun Foundation, and a Postdoctoral Research Fellowship (to S.-Q.Z.) from The Chinese University of Hong Kong.

Supporting Information Available: Figures and CIF files giving additional crystallographic data and detailed structural descriptions for **1**–**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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