

Anion- π -Interaction-Directed Self-Assembly of Ag(I) Coordination Networks

Xiao-Ping Zhou, Xuanjun Zhang, Shi-Hong Lin, and Dan Li*

Department of Chemistry and Multidisciplinary Research Center, Shantou University,
Guangdong 515063, P. R. China

Received November 21, 2006; Revised Manuscript Received January 27, 2007

ABSTRACT: Reactions of AgX with 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tpt) yielded three 3D highly symmetric isostructural coordination polymers (X = ClO₄⁻, BF₄⁻, and PF₆⁻) and a dimer (X = CF₃COO⁻), respectively. In the coordination polymers, anion- π interactions are found between the multiatomic anions and tpt ligands. Systematic variation including synthetic methods, ratios of reactants, and solvents provides synthetic evidence proving that anion- π interactions play a decisive role in assembly of the coordination polymers.

Noncovalent supramolecular interaction such as π - π stacking and cation- π interaction, involving aromatic rings, is of critical importance for chemical and biological recognition.^{1,2} Recently, a new type of noncovalent interaction “anion- π interaction”, dealing with anions and electron-deficient aromatic rings (i.e., hexafluorobenzene, *s*-triazine, and *s*-tetrazine), has been found³ and is attracting increasing attention.⁴ Usually, it was regarded that the electron-donating character of anions and their expected repulsion with aromatic rings may block the interactions between anions and aromatic rings. However, theoretical studies revealed that noncovalent interactions between anions and electron-deficient π systems are energetically favorable.^{3,4a-d} Crystallographic and NMR data also provided evidence of their existence in the solid state and in solution, respectively.^{4d-j}

The roles of anions in self-assembly processes involve template effect (size, shape), coordination abilities, and hydrogen bonding interactions with receptors.⁵ Such character of anions is usually considered for designing the functional molecular receptors and coordination polymers. In contrast, relatively innocent anion- π interactions have been rarely used as a controlling factor to direct the assembly of metal complexes,^{4k} especially for highly dimensional coordination polymers. Previous literature reported that *s*-triazine rings in some metal complexes are good receptors for Cl⁻ anions.^{4g,4h} Few examples of multiatomic anions, such as ClO₄⁻, BF₄⁻, and PF₆⁻ were observed. In our continuing study of d¹⁰ metal complexes with 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tpt),⁶ we found that multiatomic anions (ClO₄⁻, BF₄⁻, and PF₆⁻) determine the self-assembly of Ag-tpt coordination polymers through anion- π interactions. Although it was proved that factors such as reaction temperature, ratio of reactants, counterions, and solvents influence the self-assembly of resulting supramolecular compounds, systematically synthetic evidence for the determination of anion- π interactions on directing the self-assembly of metal complexes is lack.

Reactions of AgX (X = ClO₄⁻, **1**; BF₄⁻, **2**; and PF₆⁻, **3**) with tpt gave the corresponding coordination polymers {[Ag(tpt)X]_n}. Systematic variation including synthetic methods, ratios of reactants, and solvents did not affect the result of the assembly reactions (see the Supporting Information for details). For example, first, with different synthetic methods, including conventional solution reactions at room temperature and in the atmosphere, critical solvothermal reactions at high temperature and in autogenous pressure, and layer diffusion method, the reactions of AgX with tpt all gave the corresponding compounds {[Ag(tpt)X]_n}. Furthermore, with different ratios of reactants (AgX:tpt, ranging from 4:1 to 1:1) under solvothermal conditions, only products of **1–3** (AgX:tpt = 1:1) were found. Finally, stirring the mixture of AgX and tpt in different solvents, acetonitrile, methanol, ethanol, and acetone, we also obtained {[Ag(tpt)X]_n} as a sole product. Interestingly, when the counteranion was changed to CF₃COO⁻, an oligomer {[Ag₂(tpt)(CF₃-

COO)₂(H₂O)[Ag₂(tpt)(CF₃COO)₂]}·0.5H₂O (**4**) was obtained (see the Supporting Information).

X-ray single-crystal measurements revealed that complexes **1–3** are isostructural and crystallize in cubic space groups *I43d*, *I43d*, and *Ia3d*, respectively.⁷ The difference in the space group between **1–3** may be mainly due to the different symmetric properties of the multiatomic anions (ClO₄⁻ and BF₄⁻ of *T_d*, and PF₆⁻ of *O_h*). In each of **1–3**, all the tpt ligands and silver cations are disordered for satisfying their highly symmetric properties (see Figure S2 in the Supporting Information). The occupancy of each silver atom, locating in two positions, is about 0.66. All the silver atoms adopt a tetrahedral coordination geometry (Ag–N 2.143(5)–2.406(5) Å), and each tpt ligand chelates three silver atoms. The tpt ligands link the silver atoms forming a 2-fold interpenetrating 3D coordination network (Figure 1). The two adjacent triazines of tpt ligands from the two corresponding interpenetrating coordination networks are parallel, separated by multiatomic anions ClO₄⁻, BF₄⁻, and PF₆⁻, with the distances of 8.62, 8.20, and 8.84 Å for **1–3**, respectively. Obviously, the distances between the adjacent tpt ligands depend on the size of the anions; however, the whole coordination network is not changed with different sizes or shapes of the anions. The 3D coordination network of **1–3** can be rationalized to be a SrSi₂ topologic (10, 3)-*a* net, when the tpt ligands are treated as 3-connect nodes and Ag⁺ cations as linkers (see Figure S3 in the Supporting Information). The (10, 3)-*a* net has also been presented in a Zn complex of 2,4,6-tri(4-pyridyl)-1,3,5-triazine reported by Robson and co-workers, in which the SiF₆²⁻ anions coordinate to Zn²⁺ cations.⁸

Notably, all the multiatomic anions in **1–3** reside above the central triazine rings of the tpt ligands are perfectly located on the C₃-axis above the rings (Figure 2). The distances between the O atoms of ClO₄⁻ and the centroids of the triazine rings are 3.157 and 3.821 Å, respectively, for O1 (O1A–1C) and O2, indicating the presence of anion- π interactions. The distances between F atoms of BF₄⁻ and the centroids of the triazine rings in **2** are 3.289 Å (F1A–1C···centroid) and 3.731 Å (F2–centroid), respectively. All the F atoms of PF₆⁻ are symmetrically identical, and the distances between the F atoms and the centroids of the adjacent triazine rings are all the same (3.732 Å). The distances of the anion- π interactions in **1–3** are slightly longer than the bonds of tetrazine with the multiatomic anions (2.840–3.265 Å)^{4j} but shorter than the shortest distances between the anions and the silver cations (Ag···O1 = 3.389 Å, Ag···O2 = 5.696 Å for **1**; Ag···F1 = 3.400 Å, Ag···F2 = 4.759 Å for **2**; Ag···F = 3.838 Å for **3**). However, they compare well with the π - π stacking distances of aromatic rings (3.3–3.7 Å). Interestingly, the multiatomic anions link the tpt receptors through anion- π interactions to form a 1D supramolecular array along varied directions, as shown in Figure 2. To the best of our knowledge, such a 1D supramolecular array of anion- π interaction is first observed.

Complex **4** crystallized in triclinic space group *P1*.⁹ In **4**, each tpt chelates two Ag⁺ ions (Ag–N = 2.216(7)–2.636(7) Å), and

* To whom correspondence should be addressed. E-mail: dli@stu.edu.cn.

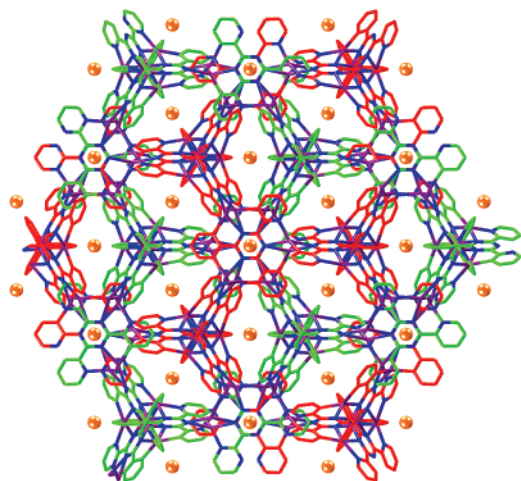


Figure 1. Three-dimensional 2-fold interpenetrating Ag-tpt coordination network of **1–3**. The golden spheres represent the anion ClO_4^- , BF_4^- , or PF_6^- . Hydrogen atoms are omitted for clarity.

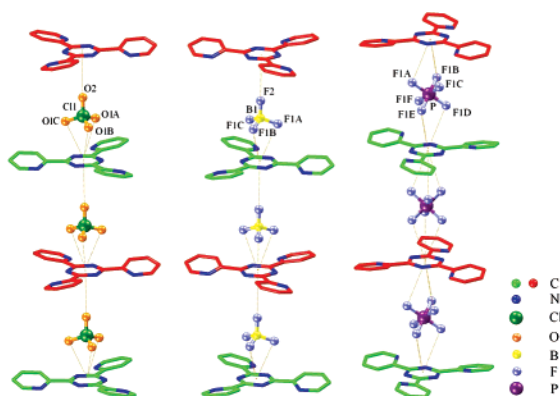


Figure 2. One-dimensional tpt supramolecular arrays constructed by the anion- π interactions in **1–3**. Silver and hydrogen atoms are omitted for clarity.

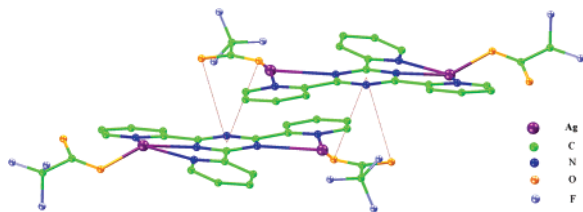


Figure 3. π -Supramolecular dimer in **4**.

the CF_3COO^- anions also coordinate to Ag^+ ions ($\text{Ag}-\text{O} = 2.210(6)-2.274(10) \text{ \AA}$). Compared with those in **1–3**, only limited O atoms of CF_3COO^- in **4** are involved in the anion- π interactions ($\text{O}\cdots\text{centroid} = 3.474-3.482 \text{ \AA}$), forming supramolecular dimers (Figure 3).

Referring to the synthetic reactions mentioned above, the effect of anion- π interactions on the preferred coordination frameworks is significant. In **1–3**, anion- π interactions involving all O or F atoms in ClO_4^- , BF_4^- , and PF_6^- , respectively, result in the same structural motifs regardless of the variation in synthetic methods and the anions (with different sizes and shapes). When the anion- π interaction is limited, i.e., in **4**, the influence is reduced.

TGA measurements of heated samples of **1–4** show that **1–3** are more thermally stable than **4** (Figure 4). The thermal behaviors of **1–3** are similar. **1–2** retain their structures to ca. 380°C , and **3** is stable until around 360°C . In contrast, **4** began to lose weight at a lower temperature of $\sim 240^\circ\text{C}$. The highly stable properties of **1–3** can be ascribed to the structural character of the 3D

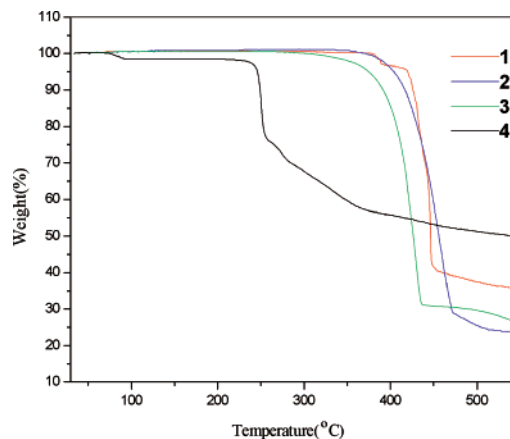


Figure 4. Thermogravimetry curves of complexes **1–4**.

interpenetrated coordination polymer, which is expected to be more stable than that of the oligomer **4**. For the isostructural **1–3**, the decomposing temperature of **3** is about 20°C lower than those of **1–2**. The main reason is possibly that the anion- π interactions of PF_6^- and triazine rings in **3** are weaker than those of ClO_4^- and BF_4^- and the rings in **1** and **2**.

In summary, systematic reactions provide synthetic evidence proving that anion- π interactions play a decisive role in the assembly of the 3D highly symmetric coordination networks of tpt and Ag(I) with varied anions. In each polymeric complex, an anion- π 1D supramolecular array is first observed.

Acknowledgment. This study was financially supported by the National Natural Science Foundation of China (Grants 20571050 and 20271031) and the Natural Science Foundation of Guangdong Province (Grant 021240).

Supporting Information Available: Synthetic procedure and XRD patterns for **1–4** in PDF format, and X-ray crystallographic files for **1–4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210.
- (2) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.
- (3) (a) Schneider, H.-J. *Angew. Chem., Int. Ed.* **1991**, *30*, 1417. (b) Schneider, H.-J.; Blatter, T.; Palm, B.; Pflingst, U.; Rüdiger, V.; Theis, I. *J. Am. Chem. Soc.* **1992**, *114*, 7704. (c) Schneider, H.-J.; Werner, F.; Blatter, T. *J. Phys. Org. Chem.* **1993**, *6*, 590. (d) Quiñero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3389.
- (4) (a) Mascal, M.; Armstrong, A.; Bartberger, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 6274. (b) Yaroslav, R. S.; Lindeman, S. V.; Rosokha, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 4650. (c) Frontera, A.; Saczewski, F.; Gdaniec, M.; Dziemidowicz-Borys, E.; Kurland, A.; Deyà, P. M.; Quiñero, D.; Garau, C. *Chem.-Eur. J.* **2005**, *11*, 6560. (d) Maheswari, P. U.; Modec, B.; Pevec, A.; Kozlevcar, B.; Massera, C.; Gamez, P.; Reedijk, J. *Inorg. Chem.* **2006**, *45*, 6637. (e) Casellas, H.; Massera, C.; Buda, F.; Gamez, P.; Reedijk, J. *New J. Chem.* **2006**, *30*, 1561. (f) Mooibroek, T. J.; Teat, S. J.; Massera, C.; Gamez, P.; Reedijk, J. *Cryst. Growth Des.* **2006**, *6*, 1569. (g) Demeshko, S.; Dechert, S.; Meyer, F. *J. Am. Chem. Soc.* **2004**, *126*, 4508. (h) Hoog, P. de; Gamez, P.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5815. (i) Berryman, O. B.; Hof, F.; Hynes, M. J.; Johnson, D. W. *Chem. Commun.* **2006**, 506. (j) Schottel, B. L.; Bacsá, J.; Dunbar, K. R. *Chem. Commun.* **2005**, 46. (k) Schottel, B. L.; Chifotides, H. T.; Shatruck, M.; Chouai, A.; Pérez, L. M.; Bacsá, J.; Dunbar, K. R. *J. Am. Chem. Soc.* **2006**, *128*, 5895.
- (5) (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (b) Vilar, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1460. (c) Hannon, M. J.; Painting, C. L.; Plummer, E. A.; Childs, L. J.; Alcock, N. W. *Chem.-Eur. J.* **2002**, *8*, 2225. (d) Campos-Fernández, C. S.; Schottel, B. L.; Chifotides, H. T.; Bera, J. K.; Bacsá, J.; Koomen, J. M.;

- Russell, D. H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2005**, *127*, 12909.
(e) Shatruk, M.; Chouai, A.; Dunbar, K. R. *Dalton Trans.* **2006**, 2184.
- (6) (a) Zhou, X.-P.; Li, D.; Wu, T.; Zhang, X. *Dalton Trans.* **2006**, 2435.
(b) Zhou, X.-P.; Li, D.; Zheng, S.-L.; Wu, T.; Zhang, X. *Inorg. Chem.* **2006**, *45*, 7119.
- (7) Crystal data for **1**: $C_{18}H_{12}AgClN_6O_4$, cubic, space group $\bar{I}43d$, $M_r = 519.66$, $a = b = c = 19.9271(7) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 7912.8(3) \text{ \AA}^3$, $Z = 16$, $\rho_{\text{calcd}} = 1.745 \text{ g cm}^{-3}$, $\mu = 1.193 \text{ mm}^{-1}$, $T = 123(2) \text{ K}$; $R_1 = 0.0483$, $wR_2 = 0.1292$ for all data. **2**: $C_{18}H_{12}AgBF_4N_6$, cubic, space group $\bar{I}43d$, $M_r = 507.02$, $a = b = c = 19.8773(4) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 7853.7(3) \text{ \AA}^3$, $Z = 16$, $\rho_{\text{calcd}} = 1.715 \text{ g cm}^{-3}$, $\mu = 1.081 \text{ mm}^{-1}$, $T = 173(2) \text{ K}$; $R_1 = 0.0622$, $wR_2 = 0.1499$ for all data. **3**: $C_{18}H_{12}AgBF_6N_6P$, cubic, space group $Ia\bar{3}d$, $M_r = 507.02$, $a = b = c = 20.4250(7) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 8520.9(5) \text{ \AA}^3$, $Z = 16$, $\rho_{\text{calcd}} = 1.762 \text{ g cm}^{-3}$, $\mu = 1.091 \text{ mm}^{-1}$, $T = 293(2) \text{ K}$; $R_1 = 0.1109$, $wR_2 = 0.2148$ for all data.
- (8) Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1996**, 1313.
- (9) Crystal data for **4**: $C_{44}H_{27}Ag_4F_{12}N_{12}O_{9.5}$, triclinic, space group $p\bar{1}$, $M_r = 1535.26$, $a = 10.7077(15) \text{ \AA}$, $b = 15.062(2) \text{ \AA}$, $c = 16.372(2) \text{ \AA}$, $\alpha = 80.844(2)^\circ$, $\beta = 72.760(2)^\circ$, $\gamma = 89.823(2)^\circ$, $V = 2487.1(6) \text{ \AA}^3$, $Z = 16$, $\rho_{\text{calcd}} = 2.050 \text{ g cm}^{-3}$, $\mu = 1.667 \text{ mm}^{-1}$, $T = 293(2) \text{ K}$; $R_1 = 0.1035$, $wR_2 = 0.2609$ for all data.

CG0608256