

## An Interpenetrating Diamonoid Coordination Polymer of Ag(I) with Bis(3-pyridoxy)benzene in Aqueous Media

Moon Soon Cha, Shin A Kim, Kyung Ho Yoo,<sup>†</sup> Ki-Min Park,<sup>‡</sup> and Ok-Sang Jung<sup>\*</sup>

Department of Chemistry (BK21) and Center for Plastic Information System, Pusan National University, Pusan 609-735, Korea

<sup>\*</sup>E-mail: oksjung@pusan.ac.kr

<sup>†</sup>Korea Institute of Science and Technology, Seoul 136-791, Korea

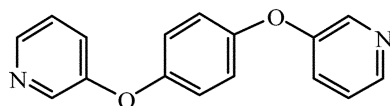
<sup>‡</sup>Research Institute of Natural Sciences, Gyeongsang National University, Jinju 660-701, Korea

Received September 30, 2005

**Key Words :** Aqueous media, Bis(3-pyridoxy)benzene,  $\beta$ -Cyclodextrin, Interpenetrated diamonoid structure, Silver(I) complex

The rational construction of functional coordination polymers with specific motifs in organic solvents is a fruitful field since the materials have various potential applications such as molecular separation, harmful materials adsorption, molecular containment, ion exchange, molecular recognition, and luminescent sensing.<sup>1-9</sup> Solubility of reactants is one of the most significant factors on the formation of such molecular materials.<sup>10-12</sup> We have demonstrated that various pyridyl ligands are useful spacer for desirable skeletons.<sup>13-17</sup> Among various skeletal structures, some diamonoid networks are of great interest in the field of supramolecular chemistry since they may have vacant spaces,<sup>18-20</sup> giving rise to interpenetration or guest inclusion. Such diamonoid networks may be obtained from the tetrahedral component through metal coordination, hydrogen bonding, donor-acceptor interactions, or van der Waals interactions.<sup>21-23</sup> Angles and lengths of potential bidentate spacers play key roles in the molecular construction of diamonoid materials.

In an effort to scrutinize the solubility effects on molecular constructions, the slow reaction of  $\text{AgCF}_3\text{SO}_3$  with a mixture of bis(3-pyridoxy)benzene (bpob) as a spacer and  $\beta$ -cyclodextrin as a water-solubilizing additive was carried out. The bpob is a potential linear N-donor bidentate spacer<sup>24,25</sup> and Ag(I) ion has been employed as the unit of a potential tetrahedral geometry.<sup>26</sup>



bpob

### Experimental Section

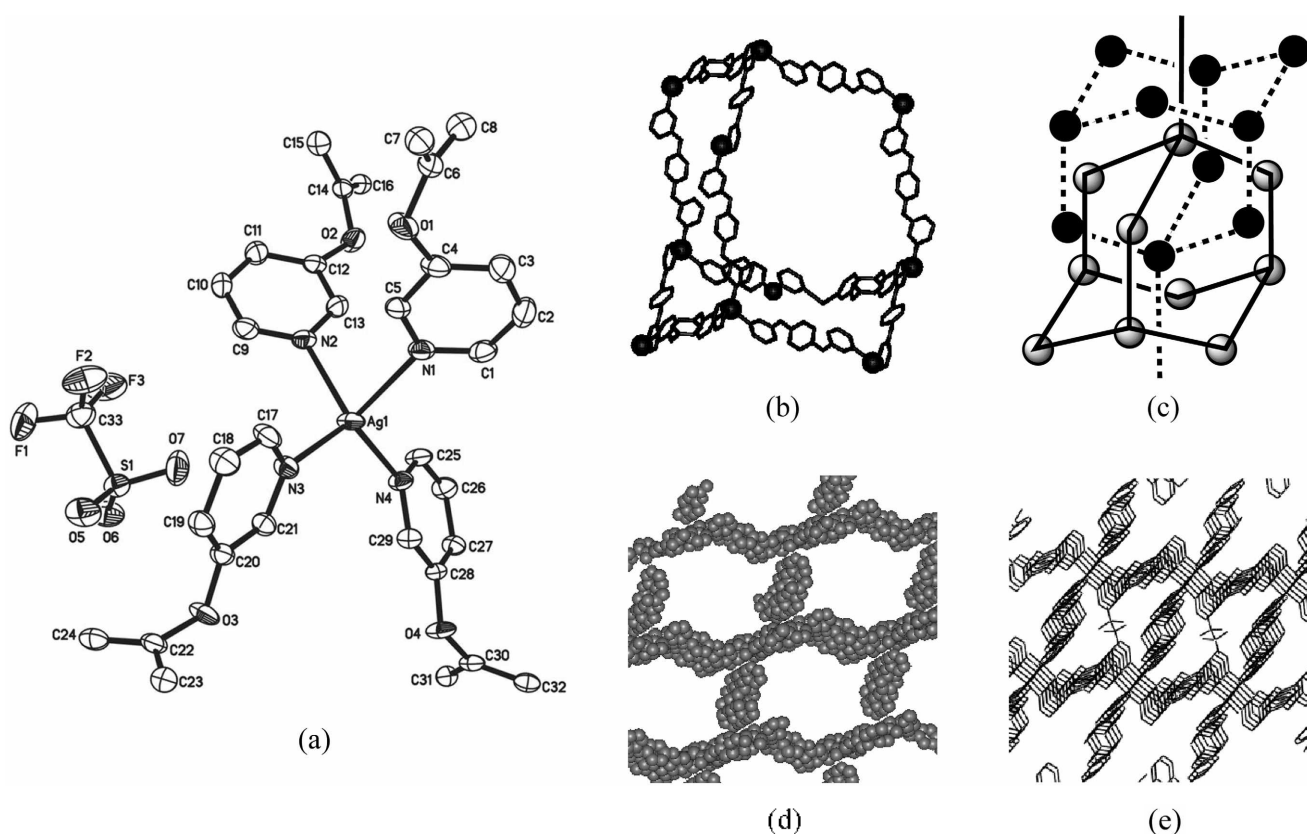
**Synthesis of  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$ .** A solid of bpob (53 mg, 0.20 mmol) was added into  $\beta$ -cyclodextrin (227 mg, 0.20 mmol) in 20 mL of water, and the suspension was stirred at 50 °C. After 2 h, the aqueous suspension was turned to aqueous solution. The aqueous solution was slowly diffused into a methanol solution (20 mL) of  $\text{AgCF}_3\text{SO}_3$  (26 mg, 0.10 mmol). Colorless crystals of  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$

formed at the interface, and were obtained in 6 days in 75% yield. mp > 250 °C (dec). Anal. Calcd for  $\text{C}_{33}\text{H}_{24}\text{N}_4\text{O}_7\text{SF}_3\text{Ag}$ : C, 50.46; H, 3.08; N, 7.13. Found: C, 50.10; H, 3.07; N, 7.16. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CF}_3\text{SO}_3)$ , 1252 (s); 864 (m).

**Crystal data for  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$ .** X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix.  $\text{C}_{33}\text{H}_{24}\text{N}_4\text{O}_7\text{F}_3\text{SAg}$ : triclinic,  $P1$  bar,  $a = 8.4183(4) \text{ \AA}$ ,  $b = 11.3125(5) \text{ \AA}$ ,  $c = 6.9550(8) \text{ \AA}$ ,  $\alpha = 78.265(1)^\circ$ ,  $\beta = 89.849(1)^\circ$ ,  $\gamma = 88.065(1)^\circ$ ,  $V = 1570.0(1) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.651 \text{ Mg m}^{-3}$ ,  $F(000) = 792$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu = 0.778 \text{ mm}^{-1}$ , crystal size  $0.30 \times 0.20 \times 0.10 \text{ mm}^3$ ,  $R$  ( $wR2$ ) = 0.0492 (0.1162) on 7096 unique reflections with  $I > 2\sigma(I)$ , GOF = 1.087, 442 parameters refined. Sheldrick, G. M. SHELXS-97 and SHELXL-97: Programs for Structure Determination and Refinement; University of Göttingen, Germany, 1997. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request by quoting the deposition number CCDC 268589.

### Results and Discussion

The treatment of an aqueous solution of  $\text{AgCF}_3\text{SO}_3$  with an aqueous solution of a mixture of bpob ligand and  $\beta$ -cyclodextrin (1 : 1) afforded the composition of  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$ . The bpob ligand is insoluble in water, but a mixture of bpob and  $\beta$ -cyclodextrin (1 : 1) is soluble in water, presumably owing to the presence of hydrogen bonds between bpob and  $\beta$ -cyclodextrin. Thus, the reaction was smoothly conducted in an aqueous solution. The reaction was originally accomplished in the 1 : 1 mole ratio of Ag(I) and bpob, but  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$  of 1 : 2 mole ratio was obtained as a product. That is, the product is not significantly affected by the mole ratios, indicating that  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$  formation is very favorable. In particular, the direct reaction of  $\text{AgCF}_3\text{SO}_3$  with a mixture of bpob and  $\beta$ -



**Figure 1.** Asymmetric unit showing a tetrahedral geometry (a), an adamantanoid cage unit (b), interlocked adamantanoid units of two independent diamondoid networks (c), skeletal structure (d), and interlocked (100) plane packing diagram (e) of  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$ .  $\text{Ag}(1)-\text{N}(3) = 2.264(3)$  Å,  $\text{Ag}(1)-\text{N}(4) = 2.272(3)$  Å,  $\text{Ag}(1)-\text{N}(2) = 2.356(3)$  Å,  $\text{Ag}(1)-\text{N}(1) = 2.397(3)$  Å,  $\text{N}(3)-\text{Ag}(1)-\text{N}(4) = 116.9(1)^\circ$ ,  $\text{N}(3)-\text{Ag}(1)-\text{N}(2) = 110.1(1)^\circ$ ,  $\text{N}(4)-\text{Ag}(1)-\text{N}(2) = 116.3(1)^\circ$ ,  $\text{N}(3)-\text{Ag}(1)-\text{N}(1) = 113.4(1)^\circ$ ,  $\text{N}(4)-\text{Ag}(1)-\text{N}(1) = 109.5(1)^\circ$ ,  $\text{N}(2)-\text{Ag}(1)-\text{N}(1) = 87.0(1)^\circ$ .

cyclodextrin did not give precipitation promptly, owing to good water-solubility of the reaction mixture. That is, the crystalline product forms slowly in aqueous solution. The crystalline product is insoluble in water and common organic solvents, and is stable for several weeks even in aqueous suspension.

The crystal structure of  $[\text{Ag}(\text{bpob})_2](\text{CF}_3\text{SO}_3)$  is shown in Figure 1. Each bpob spacer connects two silver(I) ions ( $\text{Ag}-\text{N} = 2.264(3)-2.397(3)$  Å) in a tetrahedral geometry around the  $\text{Ag}(\text{I})$  ion to form a diamondoid network. The adamantanoid motif exhibits a  $\text{Ag}\cdots\text{Ag}$  edge separation of 16 Å. Such a nano-cage motif causes the interpenetration of the networks. The triflate anion is nestled in a cavity ( $11.31 \times 16.96$  Å<sup>2</sup>). The triflate is a simple counteranion rather than an anionic ligand (the shortest  $\text{Ag}\cdots\text{O} = 4.10$  Å). The angles around  $\text{Ag}(\text{I})$  ion are slightly distorted from an ideal tetrahedral arrangement ( $\text{N}-\text{Ag}-\text{N} = 87.0(1)-116.9(1)^\circ$ ), probably owing to the presence of one counteranion per one  $\text{Ag}(\text{I})$  ion.

The formation of a 3D diamondoid network may be attributed to a suitable combination of the linear N-donor bidentate of bpob spacer and the capacity for the  $\text{Ag}(\text{I})$  ion to adopt a tetrahedral geometry. This is, the nano-sized adamantanoid cage of the diamondoid network induces the interpenetration instead of inclusion of solvent molecules.

The shortest  $\text{Ag}\cdots\text{Ag}$  distance in the interpenetrated structure is 8.418 Å, which is a half distance of the  $\text{Ag}\cdots\text{Ag}$  separation through a bpob spacer (16 Å). The interpenetration of the title compound shows a simple interlocked adamantane units of two independent diamond-like nets as shown in Figure 1(c) in contrast to the structure of  $[\text{Ni}(\text{cyclan})_2][\text{TCM}]\cdot 2\text{DMF}\cdot 10\text{H}_2\text{O}$ ,<sup>19</sup> presumably owing to the short spacer and the presence of a bulky triflate counteranion. In particular, the  $\beta$ -cyclodextrin in the reaction solution is not an obstacle to form the interpenetrated 3D channel structure. The  $\beta$ -cyclodextrin in this reaction acts as a simple water-solubilizing additive rather than a reactant. Such a synthetic procedure is relevant in the synthesis of solid-state materials since the rational design and synthesis of solid materials has important ramifications for the development of new materials. The presence of hydrogen-bonds between bpob spacer and  $\beta$ -cyclodextrin may be attributed to the water-solubility. The product was not affected by changing the mole ratio of the reactants and prolonging the reaction time. Furthermore, raising the reaction temperature to 70 °C gave the same results.

In conclusion, the present interpenetrated diamondoid structure is robust and insoluble in common organic solvents and water. Our works have shown that  $\beta$ -cyclodextrin can be useful to a water-solubilizing additive instead of rotaxane

element in the coordination polymerization. This constitutes a green method the coordination polymerization without any organic solvent. Further procedures using  $\beta$ -cyclodextrin as a water-solubilizing agent are now in progress.

**Acknowledgments.** Support for this research was provided by KOSEF (R01-2004-000-10321-0) in Korea.

### References

1. Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.
2. Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289.
3. Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11813.
4. Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79.
5. Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417.
6. Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243.
7. Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313.
8. Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem. Eur. J.* **2005**, *11*, 3521.
9. Uemura, K.; Matsuda, R.; Kitagawa, S. *J. Solid State Chem.* **2005**, *178*, 2420.
10. Oh, M. H.; Carpenter, G. B.; Schweigart, D. A. *Organometallics* **2003**, *22*, 2364.
11. Li, C. J.; Zeng, Q.-D.; Wang, C.; Wan, L.-J.; Su, S. L.; Wang, C.-R.; Bai, C.-L. *J. Phys. Chem. B* **2003**, *107*, 747.
12. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3<sup>rd</sup> ed; Wiley-VCH: 2003.
13. Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, J. K.; Chae, H. K. *J. Am. Chem. Soc.* **2000**, *122*, 9921.
14. Jung, O.-S.; Kim, Y. J.; Kim, K. M.; Lee, Y.-A. *J. Am. Chem. Soc.* **2002**, *124*, 7906.
15. Jung, O.-S.; Lee, Y.-A.; Kim, Y. J.; Hong, J. *Cryst. Growth Des.* **2002**, *2*, 497.
16. Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Kang, S. W.; Choi, S. N. *Cryst. Growth Des.* **2004**, *4*, 23.
17. Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, K.-M.; Lee, S. S. *Inorg. Chem.* **2003**, *42*, 844.
18. Ma, B.-Q.; Sun, H.-L. *Inorg. Chem.* **2005**, *44*, 837.
19. Kim, H.; Suh, M. P. *Inorg. Chem.* **2005**, *44*, 810.
20. Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.
21. Thaimattam, R.; Shirma, C. V. K.; Clearfield, A.; Desiraju, G. R. *Cryst. Growth Des.* **2001**, *1*, 103.
22. Reddy, D. S.; Dewa, T.; Endo, K.; Aoyama, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 4266.
23. Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem. Eur. J.* **2002**, *8*, 1520.
24. McMorrin, D. A.; Steel, P. J. *Acta Crystallogr., Sec. C* **1998**, *54*, 1132.
25. Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Lee, J.-K.; Yoo, K. H. *Bull. Korean Chem. Soc.* **2000**, *21*, 39.
26. Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173.