

## Solid-State Stabilization of Discrete Triple-Stranded Silver (I) Helicates

Guo Dong, Pang Ke-Liang, Duan Chun-Ying,\* Zhao Yong-Gang, and Meng Qing-Jin\*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

(Received July 1, 2002; CL-020546)

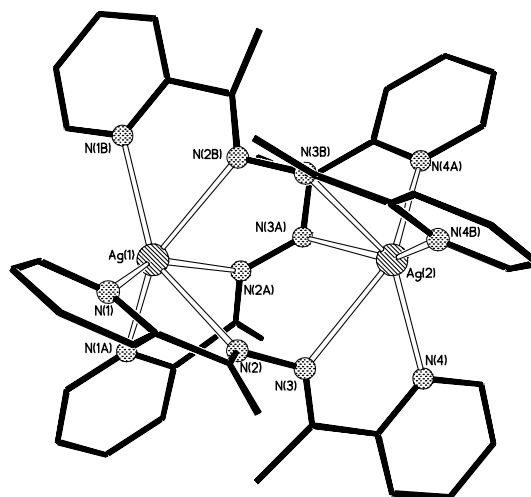
Novel triple-stranded binuclear helical complexes of silver(I) with various coordination modes are generated from the simple imine-based rigid ligand L (pyridylmethylketazine) via self-assembly in the presence of concentrate silver salts upon crystallization.

Over the past decade, the coordination motif has been established as a powerful tool in the design and self-assembly of a wide variety of supramolecular aggregates.<sup>1</sup> The application of metal-ligand interactions has proved particularly fruitful and complex molecular architectures<sup>2</sup> (such as helicates, knots, catenanes, and boxes) have well been assembled. Mixing ligands and metal ions may yield mixtures of complexes resulting from the reversible combination of the different constituents. For silver(I) ion, the stereochemistry of silver(I) complexes appears to be modulated by many factors such as the nature of the ligands, solvents, steric requirements of anions, etc.<sup>3–5</sup> More interestingly, a series of unprecedented aggregates of silver(I) have been prepared in silver-rich environments through thermodynamic assembly processes.<sup>6</sup>

In our previous studies, we prepared a discrete silver(I)-based double helicates<sup>7</sup> derived from L (pyridylmethylketazine) and  $\text{AgClO}_4$  in 1 : 1 molar ratio, in which each ligand binds two Ag atoms in bis-bidentate coordination modes. To test the effect of ion-rich environment on the assembly of complexes, we herein synthesized two discrete fantastic triple helical complexes of silver(I) via self-assembly in the presence of great excessive assistant ions.

When reaction ligand L with  $\text{AgClO}_4$  (molar ratio = 1 : 1) gives double-helicate  $[\text{Ag}_2\text{L}_2][\text{ClO}_4]_2$ ,<sup>7</sup> interaction ligand L with  $\text{AgClO}_4$  in same molar ratio, however, generates a triple-helical complex  $[\text{Ag}_2\text{L}_3][\text{ClO}_4]_2 \cdot (\text{H}_2\text{O})_3$  **1**<sup>8</sup> in the presence of excessive  $\text{NaClO}_4$ . The elemental analytical data is consistent with the formation of triple helice. The crystal structure of **1** reveals that it is a crystallographic  $C_3$  symmetric binuclear triple helicate (Fig. 1).<sup>9</sup>

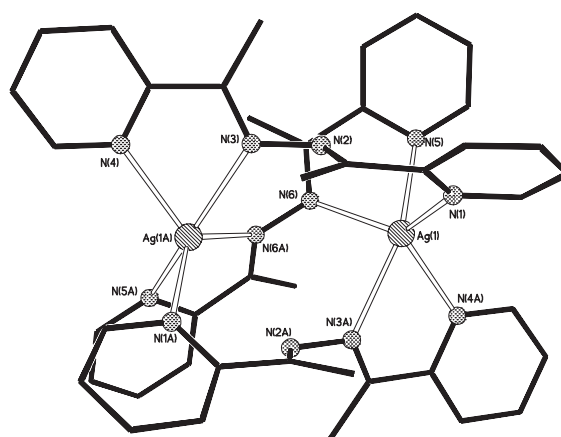
This complex crystallizes in the cubic crystal system with space group  $I_{23}$ , and only one third of the triple helicate is found in an asymmetry unit. The silver(I) atoms occupy at crystallographic 3-fold axis special positions with a metal...metal separation of ca. 4.54 Å, and the mean-square line passing through the metal ions of the helix shows a crystallographic 3-fold symmetry. The ligands of the helice are strongly disordered with each atoms of the ligand statistically occupied on two positions. Each ligand coordinates to Ag atoms by bis-dentate pyridylimine units. Each metal center is bound to three pyridylimine units in *fac* configuration to attain two different  $C_3$  pseudo-octahedral geometries with three equivalent Ag–N (pyridyl) and Ag–N (CH=N) bonds, respectively. The Ag–N bond lengths are in the range of 2.51–2.64 Å and the lengths to both imine and pyridine units are significantly different. The bis-didentate pyridylimine



**Figure 1.** Molecular structure of the triple helicate **1** with hydrogen atoms, solvents and anions omitted for clarity. Selected bond lengths (Å): Ag(1)–N(1) 2.532(7), Ag(1)–N(2) 2.618(8), Ag(2)–N(4) 2.521(9), Ag(2)–N(3) 2.681(10).

units are essentially planar. Helical twisting in the bis-didentate strand is dramatic about the central N–N bond ( $111.7^\circ$ ). Though numerous helical silver(I) complexes have been assembled,<sup>5c,5a,10</sup> discrete triple-stranded helical complexes of silver(I) were rarely documented up to the present.<sup>3</sup>

To provide other evidence supporting the above suggestion, we choose  $\text{AgPF}_6$  react with L (Ag(I) : L = 1 : 1) in ion-rich environment and obtain triple-stranded helicate  $[\text{Ag}_2\text{L}_3][\text{PF}_6]_2$  (Fig. 2) in a high yield.<sup>11</sup> The silver(I) centers are coordinated in



**Figure 2.** Molecular structure of the triple helicate **2** with hydrogen atoms and anions omitted for clarity. Selected bond lengths (Å): Ag(1)–N(1) 2.496(4), Ag(1)–N(6) 2.551(4), Ag(1)–N(5) 2.649(5), Ag(1)–N(4A) 2.537(4), Ag(1)–N(3A) 2.670(5), symmetry code A:  $1 - x, y, -0.5 - z$ .

an unusual five-coordinate distorted trigonal bipyramidal environment. One ligand uses all four donor atoms to coordinate as bis didentate ligand to the two metal centers, the other two ligands uses only three donors and coordinate as a didentate to one metal and monodentate to the other with a noncoordinated imine residue acting as a spacer unit between the binding sites. The structure is thus distinct from that observed in compound **1**. It is said that the difference in helical geometries on the two structures is based on the influence of the counter anion. In addition, although complex **2** and the related  $[\text{Ag}_2\text{L}_3][\text{PF}_6]_2$  complex reported by Honnon et al.<sup>3</sup> are almost same both in the molecular formation and molecular geometry, their crystals have different cell parameters. It seems that the difference in cell parameters is mainly controlled by difference in  $\pi$ - $\pi$  stacking interactions between pyridymethylketazine moieties. However, when the mixture of ligand L and silver(I) acetate (1 : 1) was treated with  $\text{NH}_4\text{PF}_6$ , two different complexes  $[\text{Ag}_n\text{L}_m][\text{PF}_6]_n$  and  $[\text{Ag}_2\text{L}_3][\text{PF}_6]_2$  appeared.<sup>3</sup> And only when the experiment was carried out with  $\text{Ag}(\text{I}) : \text{L} = 2 : 3$ , pure  $[\text{Ag}_2\text{L}_3][\text{PF}_6]_2$  was obtained. This result confirmed the power exerted by ion-rich environments on the crystallization of the products. A 1 : 1 combination of L with  $\text{Ag}(\text{I})$  generates in solution an equilibrating mixture of the self-assembled inorganic architectures, which converts into the single species  $[\text{Ag}_2\text{L}_3]$  in the solid state upon crystallization in high-dense salt solutions.

In summary, adding great excessive assistant salts to the solutions of corresponding  $\text{Ag}(\text{I})$  salts and ligand L may lead to the formation of unusual triple helical silver(I) complexes in the solid state. The self-assembly of such polynuclear species is a complex process of dynamic combinatorial chemistry (DCC), and triple helicates may be trapped by crystallization in the presence of suitable ancillary anions and neutral ligands. Such a strategy is in a way for extension of Lehn's virtual combinatorial library (VCL) concept.<sup>12</sup> We are currently extending our studies to apply this principle to more sophisticated supramolecular arrays.

This work was supported by the National Natural Science Foundation of China. We also thank Mr. Liu Yong-jiang for collecting the crystal data.

## References and Notes

- 1 a) J. M. Lehn, "Supramolecular Chemistry Concepts and Perspectives," VCH, Weinheim (1995), pp 139–160. b) G. F. Swiegers and T. J. Malefeste, *Chem. Rev.*, **100**, 3483 (2000). c) B. Hasenknopf, J. M. Lehn, B. O. Kneisel, G. Baum, and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, **35**, 1838 (1996).
- 2 a) C. Piguet, G. Bernardinelli, and G. Hopfgartner, *Chem. Rev.*, **97**, 2005 (1997). b) J. Xu, T. N. Parac, and K. N. Raymond, *Angew. Chem., Int. Ed.*, **38**, 2878 (1999). c) C. Dietrich-Buchecker, G. Rapenne, and J. P. Sauvage, *Coord. Chem. Rev.*, **186**, 167 (1999). d) M. Fujita, *Acc. Chem. Res.*, **32**, 53 (1999). e) E. C. Constable, *Prog. Inorg. Chem.*, **42**, 67 (1994).
- 3 J. Hamblin, A. Jackson, N. W. Alcock, and M. J. Hannon, *J. Chem. Soc., Dalton Trans.*, **2002**, 1635.
- 4 a) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Am. Chem. Soc.*, **117**, 4562 (1995). b) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, **34**, 1895 (1995). c) P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis, and S. B. Wild, *Chem. Commun.*, **1998**, 1153.
- 5 a) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, and T. Kulke, *Chem. Commun.*, **1998**, 2659. b) M. L. Tong, X. M. Chen, B. H. Ye, and L. N. Ji, *Angew. Chem., Int. Ed.*, **38**, 2237 (1999). c) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, and M. Schröder, *Coord. Chem. Rev.*, **183**, 117 (1999).
- 6 a) Q. M. Wang and T. C. W. Mak, *J. Am. Chem. Soc.*, **122**, 7608 (2000). b) Q. M. Wang and T. C. W. Mak, *J. Am. Chem. Soc.*, **123**, 1501 (2001). c) Q. M. Wang and T. C. W. Mak, *J. Am. Chem. Soc.*, **123**, 7594 (2001).
- 7 D. Guo, C. He, C. Y. Duan, C. Q. Qian, Q. J. Meng, Z. M. Wang, and C. H. Yan, *New J. Chem.*, **26**, 796 (2002).
- 8 Complex **1** (0.061 g, 0.06 mmol, yield 85%) was prepared by mixing the ethanol-acetonitrile ligand L (0.048 g, 0.2 mmol) and  $\text{AgClO}_4$  (0.041 g, 0.2 mmol) in the presence of  $\text{NaClO}_4$  (0.245 g, 2 mmol). Found: C, 42.3; H, 4.0; N, 14.0. Calcd for  $\text{C}_{42}\text{H}_{42}\text{Ag}_2\text{O}_8\text{N}_{12}\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ : C, 42.6; H, 4.1; N, 14.2%.  $^1\text{H}$  NMR[500 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  2.36(s, 6H,  $\text{CH}_3$ ), 7.58(t, 2H, py), 8.00(t, 2H, py), 8.24(d, 2H, py), 8.74(d, 2H, py). **CAUTION** : Although no problems were encountered in the present study, perchlorate salts of  $\text{Ag}(\text{I})$  complex with organic ligands are potentially explosive and should be handled with care!
- 9 Crystal data for **1**:  $\text{C}_{42}\text{H}_{48}\text{Ag}_2\text{O}_{11}\text{N}_{12}\text{Cl}_2$ ,  $M_r = 1183.56$ , Cubic,  $I_{23}$ ,  $a = 22.528(5)$ ,  $V = 11433(4) \text{ \AA}^3$ ,  $T = 193(2) \text{ K}$ ,  $Z = 8$ ,  $D_{\text{calcd}} = 1.375 \text{ Mg/m}^3$ ,  $F(000) = 4800$ ,  $\mu(\text{Mo K}\alpha) = 0.838 \text{ mm}^{-1}$ , 27290 reflections measured, 3363 independent reflections ( $R_{\text{int}} = 0.070$ ),  $R1 = 0.0731$ ,  $wR2 = 0.2167$  for 3059 observed reflections [ $I > 2\sigma(I)$ ]. Intensities of complex was collected on collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and reduced using SMART and SAINT program. A SADABS program was applied for absorption correction. The structure was solved by direct methods and refined on  $F^2$  using full-matrix least-squares methods using SHELXTL version 5.1.
- 10 a) M. J. Hannon, S. Bunce, A. J. Clarke, and N. W. Alcock, *Angew. Chem., Int. Ed.*, **38**, 1277 (1999). b) A. Erxleben, *Inorg. Chem.*, **40**, 2928 (2001). c) K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama, and M. Oda, *Inorg. Chem.*, **39**, 3301 (2000).
- 11 Synthesis of complex **2**: Ligand L (0.048 g, 0.2 mmol) reacted with  $\text{AgPF}_6$  (0.051 g, 0.2 mmol) by adding excessive  $\text{NH}_4\text{PF}_6$  (0.326 g, 2 mmol) in 25 mL ethanol-acetonitrile (2 : 1) to give a yellow solution. The filtrate was stood for several days and crystals (0.073 g, 0.06 mmol, yield 90%) suitable of **2** for X-ray diffraction determination were obtained. Found: C, 41.3; H, 3.4; N, 13.7. Calcd for  $\text{C}_{42}\text{H}_{42}\text{Ag}_2\text{F}_{12}\text{N}_{12}\text{P}_2$ : C, 41.3; H, 3.5; N, 13.8%.  $^1\text{H}$  NMR[500 MHz,  $(\text{CD}_3)_2\text{SO}$ ]:  $\delta$  2.36 (s, 6H,  $\text{CH}_3$ ), 7.59 (t, 2H, py), 8.01 (t, 2H, py), 8.24 (d, 2H, py), 8.75 (d, 2H, py). **Crystal data** for **2**:  $\text{C}_{42}\text{H}_{42}\text{Ag}_2\text{F}_{12}\text{N}_{12}\text{P}_2$ ,  $M_r = 1220.54$ , Monoclinic,  $C2/c$ ,  $a = 13.792(7)$ ,  $b = 25.295(12)$ ,  $c = 17.389(8) \text{ \AA}$ ,  $\beta = 92.84(7)^\circ$ ,  $V = 6059(5) \text{ \AA}^3$ ,  $T = 193(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.338 \text{ Mg/m}^3$ ,  $F(000) = 2440$ ,  $\mu(\text{Mo K}\alpha) = 0.773 \text{ mm}^{-1}$ , 13535 reflections measured, 5271 independent reflections ( $R_{\text{int}} = 0.126$ ),  $R1 = 0.069$ ,  $wR2 = 0.195$  for 4241 observed reflections [ $I > 2\sigma(I)$ ].
- 12 P. N. W. Baxter, J. M. Lehn, and K. Rissanen, *Chem. Commun.*, **1997**, 1323.