A hamburger-shaped helical stacking of disk-shaped ligands mediated by silver(II) ions†

Ho Yong Lee,[a] Jaejoon Park,[b] Myoung Soo Lah[b] and Jong-In Hong*[a]

Received (in Cambridge, UK) 17th August 2007, Accepted 19th September 2007
First published as an Advance Article on the web 2nd October 2007
DOI: 10.1039/b712717k

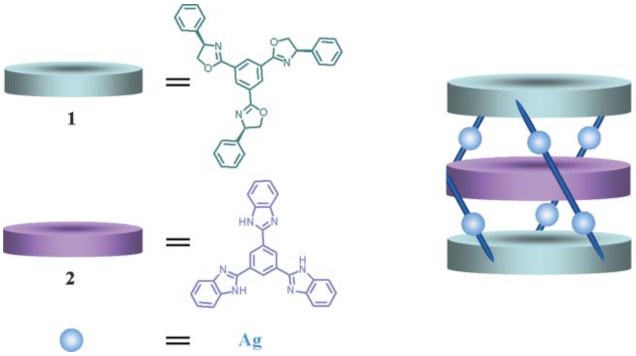
We describe a hamburger-shaped helical structure of chiral and achiral *C*$_3$-symmetric disk-shaped ligands mediated by silver ions.

There is a great deal of interest in the construction of helical supramolecular structures by synthetic oligomers,[1] metal–ligand complexes[2] and hydrogen-bonded assemblies.[3] Among these works, chiral amplification has been widely studied in the region of helical polymers[4] and hydrogen-bonded supramolecular structures.[5] However, the induction of helicity using metal–ligand interaction is still relatively rare. Recently, propeller-shaped supramolecular structures with helicity have been described by Shionoya *et al.*;[6] these include helical structures with *P* and *M* geometries, a heterotopic formation of a sandwich-shaped complex, and a molecular ball bearing. Those systems are based on *P* and *M* conversion of a racemic helical structure. However, the rationales for hetero-recognition and helicity control between disk-shaped ligands are still ambiguous, and there has been no report of a crystal structure for a heteromeric complex between disk-shaped ligands. Previously, we reported the completely stereospecific self-assembly of a propeller-shaped supramolecular capsule induced by a rigid chiral tris(oxazoline) unit acting as a trismonodentate ligand and Ag(I) metal ions having a tetrahedral coordination geometry.[7] Herein, we describe a simple method to prepare a heteromeric hamburger-shaped structure having unidirectional helicity from chiral and achiral *C*$_3$-symmetric disk-shaped ligands mediated by silver ions, and its crystal structure.

Our strategy is based on the chirality transfer from a chiral disk-shaped molecule to an achiral one. A chiral moiety (**1**) interacts with a benzimidazoline group (**2**) in one direction to generate a unidirectional helical complex in the process of crystallization.‡

Single crystals of $[Ag_6\mathbf{1}^{R}_2\cdot\mathbf{2}](OTf)_3\cdot 3MeOH$, suitable for X-ray analysis were obtained by slow evaporation of a MeOH solution containing $\mathbf{1}^{R}$, **2**, and Ag(OTf).§ We obtained the same crystal stucture of $[Ag_6\mathbf{1}^{R}_2\cdot\mathbf{2}](OTf)_3\cdot 3MeOH)$ with various ratios of $\mathbf{1}^{R}$, **2** and Ag(OTf) ($\mathbf{1}^{R}$:**2**:Ag(OTf) = 1 : 1 : 3, 2 : 1 : 6, and 1 : 2 : 9). The hamburger-shaped structure, in which the deprotonated form of **2** is sandwiched between two $\mathbf{1}^{R}$ molecules mediated by 6 silver ions, might be preferred in the process of crystalization.

We suppose that the increased acidity of the NH in benzimidazoline, upon the coordination of Ag(I) ions, and a compact structure of $Ag_6\mathbf{1}^{R}_2\cdot\mathbf{2}$ formed through additional CH–π interactions originating from between chiral oxazoline phenyl rings, compared to that of $Ag_3\mathbf{1}^{R}\cdot\mathbf{2}$, may cause **1** to crystallize in a deprotonated form. As a result, two cage-like structures are formed. The overall helicity and structure of the two cages between $\mathbf{1}^{R}$ and **2** are equal within error; however, the bond angles and bond lengths are slightly different. The N–Ag–N bonds are almost linear (Fig. 1). The three central phenyl rings of $\mathbf{1}^{R}$ and **2** are almost planar, with interplane distances of 4.61 Å and 4.81 Å, respectively, which results in an absence of aromatic stacking



Scheme 1

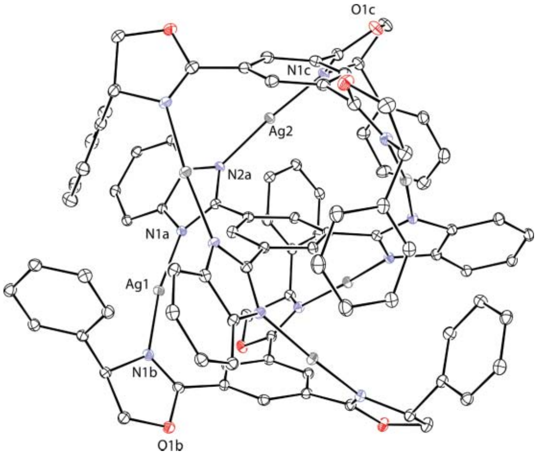


Fig. 1 Crystal structure of $Ag_6\mathbf{1}^{R}_2\cdot\mathbf{2}$; all the hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ag(1)–N(1A) 2.092(3), Ag(1)–N(1B) 2.114(3), Ag(2)–N(2A) 2.101(3), Ag(2)–N(1C) 2.118(3), N(1A)–Ag(1)–N(1B) 168.95(11), N(2A)–Ag(2)–N(1C) 171.30(11).

---

[a] *Department of Chemistry, Seoul National University, Seoul 151-747, Korea. E-mail: jihong@snu.ac.kr; Fax: (+82)-2-889-1568; Tel: (+82)-2-874-5902*
[b] *Department of Chemistry and Applied Chemistry, College of Science and Technology, Hanyang University, Ansan, Kyunggi-Do 426-791, Korea*

† Electronic supplementary information (ESI) available: crystallographic data in CIF. See DOI: 10.1039/b712717k

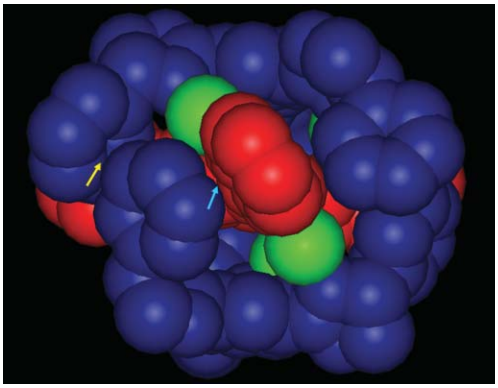


Fig. 2 CPK representation of the crystal structure of $M\text{-Ag}_6\mathbf{1}^{\boldsymbol{R}}{}_2\cdot\mathbf{2}$. **1**: blue, **2**: red, Ag: green. Yellow arrows: CH–π between chiral oxazoline phenyl rings; sky blue arrows: CH–π interactions between the phenyl rings of the benzimidazoline and CH of the chiral oxazoline phenyl ring. All the hydrogen atoms are omitted for clarity.

interaction. The central phenyl rings are twisted from the helix axis by approximately 60°. The overall crystal structure is stabilized by six CH–π interactions between the phenyl rings of the benzimidazoline and the CH of the chiral oxazoline phenyl ring, and three CH–π interactions between chiral oxazoline phenyl rings (Fig. 2). The crystal structure shows an enantiomerically pure $M\text{-Ag}_6\mathbf{1}^{\boldsymbol{R}}{}_2\cdot\mathbf{2}$ devoid of a diastereomer ($P\text{-Ag}_6\mathbf{1}^{\boldsymbol{R}}{}_2\cdot\mathbf{2}$) or homodimer ($\mathrm{Ag}_3\mathbf{1}^{\boldsymbol{R}}{}_2$ or $\mathrm{Ag}_3\mathbf{2}_2$).

The chirality of **1** should play a major role in the helicity determination. In the process of crystallization, the left-handed structure might be energetically favored by avoiding steric repulsion and maximizing favored interactions. Among favored interactions, CH–π interaction may be one of the important components because there are 9 CH–π interactions in the individual hamburger-shaped assembly.[8]

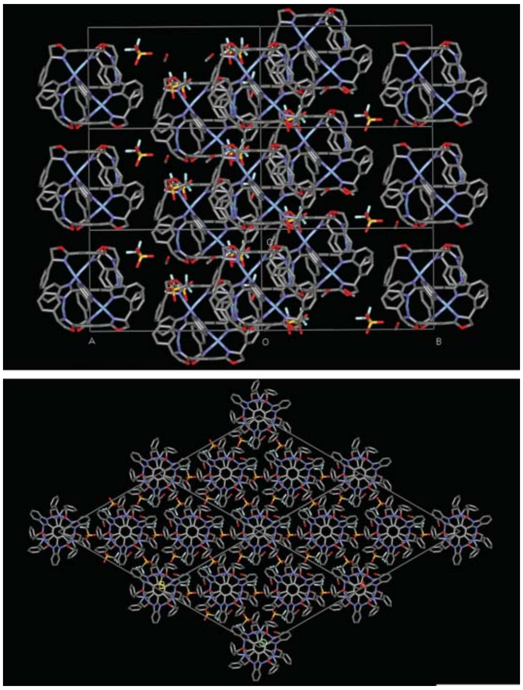


Fig. 3 Crystal packing pattern of $[\mathrm{Ag}_6\mathbf{1}^{R}{}_2\cdot\mathbf{2}](\mathrm{OTf})_3\cdot 3\mathrm{MeOH}$. C: gray, N: blue, O: red, F: light blue, S: orange, Ag: sky blue. All the hydrogen atoms are omitted for clarity.

The overall packing patterns are illustrated in Fig. 3. Helical assemblies are stacked along the crystallographic *c*-direction forming one-dimensional columnar structures. Adjacent assemblies are slightly distorted and separated by about 3.60 Å, which results in π–π interactions between discrete assemblies. MeOH and OTf anions interlinked *via* hydrogen bonds are located between one-dimensional columnar structures.

In conclusion, a hamburger-shaped helical complex can be prepared stereospecifically by the self-assembly of achiral tris(benzimidazoline) and chiral tris(oxazoline) ligands with coordinating silver ions. The overall helicity of the complex is determined by the chirality of the tris(oxazoline) ligand and crystal packing. The helicity induction ability of the chiral tris(oxazoline) ligand could be applied to construct more stacked helical structures and coordination polymers by combination with extended π-conjugated C_3-symmetric ligands.

Financial support from the MOCIE (Grant No. 10024945) is gratefully acknowledged. H.-Y.L. thanks the Ministry of Education for the award of the BK 21 fellowship.

Notes and references

‡ *Synthesis and characterization data*: $\mathbf{1}^{\boldsymbol{R}}$: see reference 7, **2**: 1,3,5-benzenetricarboxylic acid (2 g, 9.5 mmol) and 1,2-phenylenediamine(3.4 g, 3.3 eq., 31.4 mmol) was added to polyphosphoric acid. The mixture was stirred at 180 °C for 8 h. After the mixture had cooled down to 100 °C, the resulting blue solution was poured into ice water with vigorous stirring, and filtered. After stirring the filtered solid in a saturated sodium bicarbonate solution for 24 h, the raw solid was washed with water, acetone and chloroform. The resulting solid was poured into deionized water and stirred for an additional 12 h. The precipitate was filtered and recrystallized in methanol to give rise to a grey solid (2.3 g, 56% yield). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): 13.35 (s, 3H), 9.11 (s, 3H), 7.77 (d, $J = 8.7$, 3H), 7.62 (d, $J = 8.7$, 3H), 7.32 (m, 3H), 7.28 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): 150.7, 144.2, 135.7, 132.2, 125.9, 123.4, 122.4, 119.4, 112.2. HRMS (FAB): calculated ($\mathrm{C}_{27}\mathrm{H}_{19}\mathrm{N}_6$) = 427.4881, found = 427.4899, $\mathrm{Ag}_6\mathbf{1}^{\boldsymbol{R}}{}_2\cdot\mathbf{2}$: Single crystals suitable for X-ray analysis were obtained by the slow evaporation of a MeOH solution containing various ratios of $\mathbf{1}^{\boldsymbol{R}}$, **2** and Ag(OTf) ($\mathbf{1}^{\boldsymbol{R}}$:**2**:Ag(OTf) = 1 : 1 : 3, 2 : 1 : 6, and 1 : 2 : 9, [Ag(OTf)] = 5.0 mM). The yields of the crystal formation are 28, 41, and 23%, respectively. Anal. calc. for $\mathrm{Ag}_6\mathrm{C}_{99}\mathrm{H}_{81}\mathrm{N}_{12}\mathrm{O}_{18}\mathrm{F}_9\mathrm{S}_3$: C, 45.02; H, 3.09; N, 6.36. Found: C, 45.17; H, 2.98; N, 6.31%.

§ *Crystal data*: $\mathrm{Ag}_6\mathrm{C}_{99}\mathrm{H}_{81}\mathrm{N}_{12}\mathrm{O}_{18}\mathrm{F}_9\mathrm{S}_3$ ($[\mathrm{Ag}_6\mathbf{1}^{\boldsymbol{R}}{}_2\cdot\mathbf{2}](\mathrm{OTf})_3\cdot 3(\mathrm{MeOH})$), M = 2641.16, colorless crystal 0.15 × 0.10 × 0.10 mm^3, trigonal, $R3$, $a = b = 25.470(4)$, $c = 13.028(3)$ Å; $V = 7319(2)$ Å^3, $Z = 3$, $\rho_{\mathrm{calcd}} = 1.798$ Mg m^{-3}, μ(synchrotron, $\lambda = 0.70000$ Å) = 1.337 mm^{-1}, $2\theta_{\max} = 60.59°$; 26304 measured 10160 unique reflections, of which 9868 observables [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares calculations with SHELXTL. The final $R1 = 0.0421$, w$R2 = 0.1099$ for reflections of $I > 2\sigma(I)$, $R1 = 0.0432$, w$R2 = 0.1112$ for all observed reflections. Crystallographic details for CCDC-610197 are in the supporting information†.

1 (*a*) J. C. Nelson, J. G. Saven, J. S. Moore and P. G. Wolynes, *Science*, 1997, **277**, 1793–1796; (*b*) D. J. Hill and J. S. Moore, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5053–5057; (*c*) K. Matsuda, M. T. Stone and J. S. Moore, *J. Am. Chem. Soc.*, 2002, **124**, 11836–11837; (*d*) L. Brunsveld, E. W. Meijer, R. B. Prince and J. S. Moore, *J. Am. Chem. Soc.*, 2001, **123**, 7978–7984; (*e*) H. Sigiura, Y. Nigorikawa, Y. Saiki, K. Nakamura and M. Yamaguchi, *J. Am. Chem. Soc.*, 2004, **126**, 14858–14864.

2 (*a*) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457–3497; (*b*) U. Knof and A. von Zelewsky, *Angew. Chem.*, 1999, **111**, 312–333, (*Angew. Chem., Int. Ed.*, 1999, **38**, 302–322); (*c*) E. V. Anokhina and A. Jacobson, *J. Am. Chem. Soc.*, 2004, **126**, 3044–3055; (*d*) M. Seitz, A. Kaiser, S. Stempfhuber, M. Zabel and O. Reiser, *J. Am. Chem. Soc.*, 2004,

126, 11426–11427; (*e*) X. Shi, G. Zhu, S. Qiu, K. Huang, J. Yu and R. Xu, *Angew. Chem.*, 2004, **116**, 6644–6647, (*Angew. Chem., Int. Ed.*, 2004, **43**, 6482–6485).

3 (*a*) M. L. Bushey, T. Nguyen, W. Zhang, D. Horoszewski and C. Nuckolls, *Angew. Chem.*, 2004, **116**, 5562–5570, (*Angew. Chem., Int. Ed.*, 2004, **43**, 5446–5453); (*b*) J. H. K. Ky Hirschberg, L. Brunsveld, A. Ramzi, J. A. M. Vekemans, R. P. Sijbesma and E. W. Meijer, *Nature*, 2000, **407**, 167–170; (*c*) L. Brunsveld, J. A. J. M. Vekemans, J. H. K. K. Hirschberg, R. P. Sijbesma and E. W. Meijer, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4977–4982.

4 (*a*) T. Nakano and Y. Okamoto, *Chem. Rev.*, 2001, **101**, 4013–4038; (*b*) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039–4070; (*c*) M. Ishikawa, K. Maeda, Y. Mitsutsuji and E. Yashima, *J. Am. Chem. Soc.*, 2004, **126**, 732–733.

5 (*a*) L. J. Prins, P. Timmerman and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 2001, **123**, 10153–10163; (*b*) L. Brunsceld, B. J. Folmer, E. W. Mijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4098.

6 (*a*) S. Hiraoka, T. Yi, M. Shiro and M. Shionoya, *J. Am. Chem. Soc.*, 2002, **124**, 14510–14511; (*b*) S. Hiraoka, M. Shiro and M. Shionoya, *J. Am. Chem. Soc.*, 2004, **126**, 1214–1218; (*c*) S. Hiraoka, K. Hirata and M. Shionoya, *Angew. Chem.*, 2004, **116**, 3902–3906, (*Angew. Chem., Int. Ed.*, 2004, **43**, 3814–3818); (*d*) S. Hiraoka, K. Harano, T. Tanaka, M. Shiro and M. Shionoya, *Angew. Chem.*, 2003, **115**, 5340–5344, (*Angew. Chem., Int. Ed.*, 2003, **42**, 5182–5185); (*e*) S. Hiraoka, M. Shiro and M. Shionoya, *J. Am. Chem. Soc.*, 2004, **126**, 1214–1218; (*f*) S. Hiraoka, T. Tanaka and M. Shionoya, *J. Am. Chem. Soc.*, 2006, **128**, 13038–13039.

7 H.-J. Kim, D. Moon, M. S. Lah and J.-I. Hong, *Angew. Chem.*, 2002, **114**, 3306–3309, (*Angew. Chem., Int. Ed.*, 2002, **41**, 3174–3177).

8 We compared the partial structure (M-Ag$_3\mathbf{1}^{R}\cdot\mathbf{2}$), obtained by removing one $\mathbf{1}^{R}$ ligand and three silver ions from the crystal structure, with the modeling structure of P-Ag$_3\mathbf{1}^{R}\cdot\mathbf{2}$, which has identical ligands but opposite helicity. Molecular modeling was carried out using Spartan '02 program (Wavefunction Inc.) to understand the reason for stereospecific helicity control. Bond lengths and angles are based on ref. 7 and crystal structure of M-Ag$_6\mathbf{1}^{R}_{2}\cdot\mathbf{2}$. The three CH–π interactions between the phenyl rings of benzimidazoline and the CHs of the phenyl rings of the chiral oxazoline seem to play an important role in the helicity determination. In the case of Ag$_3\mathbf{1}^{R}\cdot\mathbf{2}$ with M-helicity, a phenyl ring of the chiral oxazoline is oriented toward the electron-rich benzimidazoline ring to generate CH–π interactions. However, if the Ag$_3\mathbf{1}^{R}\cdot\mathbf{2}$ complex has P-helicity, the phenyl ring of the chiral oxazoline should be facing away from the coordinating silver ions between the aromatic planes. Therefore, no CH–π interactions are possible between the side phenyl rings. Instead, the modeling structure of Ag$_3\mathbf{1}^{R}\cdot\mathbf{2}$ with P-helicity shows only one π–π stacking between the central benzene rings (interplanar distance around 3.5 Å).