Self-Assembly of a Chiral Three Dimensional Architecture Composed of Two Different Silver(I) Helical Chains Connected by Bitopic Tris(pyrazolyl)methane Ligands

Daniel L. Reger,*[a] Radu F. Semeniuc,[a] and Mark D. Smith[a]

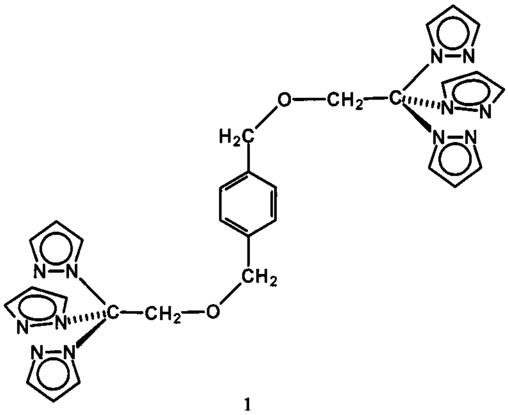
Keywords: Helical structures / Ligand design / Silver / Self-assembly

The coordination polymer $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2\text{-}Ag_2(BF_4)_2\}_n$ contains two opposite chirality metallohelicates, formed by a κ^2, κ^1 bonding arrangement of each tris(pyrazolyl)methane unit, that are linked with the bitopic ligand into 2D sheets. The 3D supramolecular structure is formed by C–H···F weak hydrogen bonds that also order the solvent molecules.

Helical structures have received increasing attention because of their structural similarities to nucleic acids and proteins. Potential applications, such as asymmetric catalysis and nonlinear optical materials,[1] have also increased the interest in the synthesis and characterization of these types of structures. Helical organization has been driven by the formation of covalent bonds in metal complexes[1a,2] and intermolecular forces, mainly hydrogen bonding.[3] Most known structures consist of discrete molecules or ions,[1a,1b,4] although examples of coordination polymers with helical structures are also known.[2,5] We report here a unique supramolecular architecture formed by using a new bitopic ligand to link two different metallohelicates having opposite chirality.

We are developing supramolecular chemistry using a new class of multitopic ligands, formed from linking two or more tris(pyrazolyl)methane units[6] in a single molecule, a study made possible by our recent progress on the preparation and reaction chemistry of tris(pyrazolyl)methane ligands.[7] Our first example is $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ (**1**, Scheme 1). This ligand was designed to have the unique capability of linking metals into chiral polymer chains with a κ^2, κ^1 bonding arrangement while also linking these chains with the flexible side arms of a 1,4-bis(ethoxymethyl)benzene bridge.

The reaction of $p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2$ with $AgBF_4$ in a 1:2 ratio in THF yields $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Ag_2(BF_4)_2\}_n$ (**2**), a coordination polymer that contains two types of bridged helical chains. Crystals of **2** suitable for X-ray diffraction[8] were grown by vapor-phase diffusion of Et_2O into an acetonitrile solution. The left side of Figure 1 shows a drawing of one of the two polymer chains. Each Ag(1) is three-coordinate, κ^2-bonded to a tris(pyrazolyl)methane unit in one ligand and κ^1-bonded to a second from a different ligand, forming polymer chain **1**. The polyhedron involving the Ag(1) atom is a flattened trigonal pyramid [sum of the N−Ag(1)−N bond angles = 347°], with a significant distortion caused by the restricted angle [83.43(11)°] of the κ^2-bonded ligand.



1

Scheme 1. 1,4-Bis[tris(pyrazolyl)ethoxymethyl]benzene

The right side of Figure 1 shows a drawing of the polymer chain formed by Ag(2). Each Ag(2) is four-coordinate. As with Ag(1), each silver(I) is κ^2-bonded to one tris(pyrazolyl)methane unit and κ^1-bonded to a second, forming polymer chain **2**. In addition, there is an acetonitrile molecule bonded to each Ag(2). The polyhedron involving the Ag(2) atom is a distorted tetrahedron with a large distortion caused by the restricted angle [77.40(11)°] of the κ^2-bonded ligand. The CH_3CN molecules bonded to the Ag(2) atoms are alternatively above and below the chain, as pictured (see also Figure 3b).

---

[a] Department of Chemistry and Biochemistry, University of South Carolina
Columbia, South Carolina 29208, USA
Fax: (internat.) +1-803/777-9521
E-mail: Reger@psc.sc.edu

1434−1948/02/0303−0543 $ 17.50+.50/0

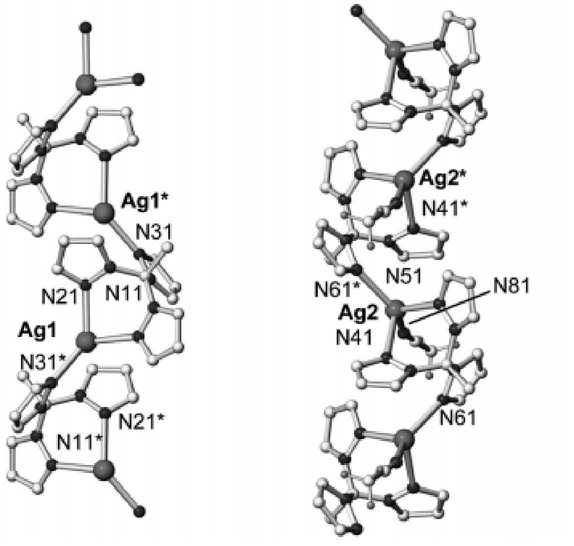


Figure 1. (a) Partial structure of **2** showing the polymeric chain formed by Ag(1); selected bonds (Å) and angles (deg.) are as follows: Ag(1)−N(11) 2.269(3), Ag(1)−N(21) 2.283(3), Ag(1)−N(31*) 2.196(4), N(11)−Ag(1)−N(21) 83.43(11), N(11)−Ag(1)−N(31*) 127.50(13), N(21)−Ag(1)−N(31*) 136.16(12); (b) the polymeric chain formed by Ag(2); selected bonds (Å) and angles (deg.) are as follows: Ag(2)−N(41) 2.405(3), Ag(2)−N(51) 2.380(3), Ag(2)−N(61*) 2.292(3), Ag(2)−N(81) 2.206(4), N(41)−Ag(2)−N(51) 77.40(11), N(41)−Ag(2)−N(61*) 107.07(11), N(41)−Ag(2)−N(81) 103.48(12), N(51)−Ag(2)−N(61*) 102.77(11), N(51)−Ag(2)−N(81) 124.19(13), N(61*)−Ag(2)−N(81) 128.28(12)

Figure 2 shows a space filling model of the backbone of both silver chains. In both cases the arrangement of the backbone is helical, but the chirality of each is opposite. Both helices are generated around crystallographic 2_1 screw axes along the *a* axis of the unit cell. For both, the distance between every other silver atom is equal and identical to the length of the *a* axis of the unit cell, 10.282 Å, making the pitches of both helicates identical.

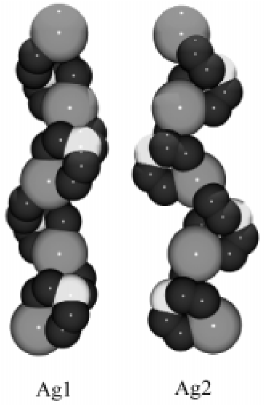


Figure 2. Space filling representation of the backbone of both silver chains, showing the helical arrangement; for the sake of clarity all atoms not directly related to the backbone chains have been omitted; the acetonitrile molecule is also excluded in the Ag(2) case

Figure 3a is a view perpendicular to the network formed by the alternating helical chains. The helical chains are connected by the 1,4-bis(ethoxymethyl)benzene bridging units with the ether groups in each ligand oriented on opposite sides of the aromatic ring. Although this part of the network is two dimensional, the structure has thickness. Figure 3b is the view in the same alignment of chains as in Figure 3a, viewed parallel to the network, showing two U-shape channels formed between the silver strands by the 1,4-bis(ethoxymethyl)benzene bridge. The dimensions of the channels are 5.8 × 3.6 Å, measured between the two methylene groups directly bonded to the phenyl ring and between these methylene groups and the central methine carbon atoms from the tris(pyrazolyl)methane units. There is also a cavity formed along the strand formed by the three-coordinate Ag(1) because of the parallel orientation of the flattened trigonal pyramids.

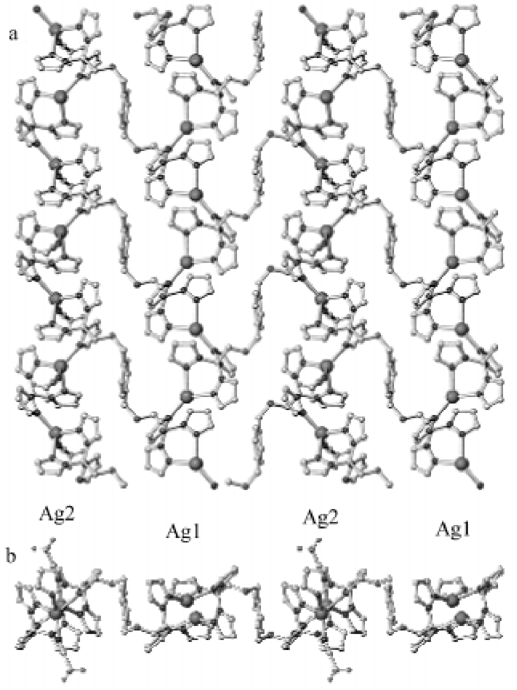


Figure 3. View perpendicular (a) and parallel (b) to the sheets formed by the alternating silver chains

Figure 4 shows that the 2D network (viewed as in Figure 3b) formed by the helical chains and the connecting organic bridges is arranged into a 3D supramolecular structure by weak C−H···F hydrogen bonds. One of the two nonequivalent BF_4^- ions makes four hydrogen bonds with two of the 2D sheets forming the 3D architecture. Two of the bonds, one to each sheet, are very short at 2.262 and 2.290 Å. The average C−H···F bond length of 2.326 Å is significantly shorter than the sum of the van der Waals radii for H and F atoms (2.54 Å)[9] and other known cases of this type of interaction,[10] where the reported values are close to 2.5 Å. The second BF_4^- ion makes two hydrogen bonds, one to each of two sheets, at a distance of 2.302 and 2.353 Å.

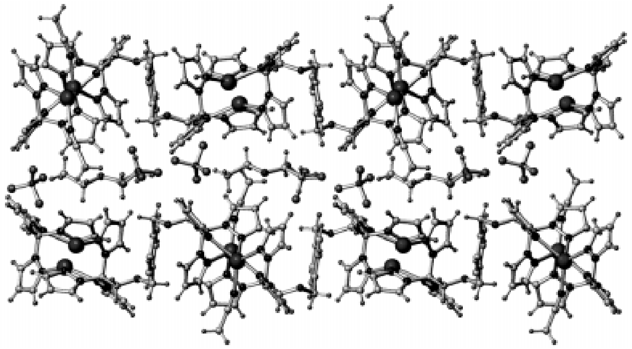


Figure 4. Two sheets held together through C−H···F bonds, forming a 3D architecture

An additional important structural feature is that the solvent molecules are held between the helical layers in a very ordered fashion by weak hydrogen bonds, an unusual observation for helical superstructures.[1a] As pictured in Figure 4, each diethyl ether molecule is bonded through one terminal methyl group to the BF_4 counter-ion that makes four hydrogen bonds (C−H···F separation is 2.362 Å, with the corresponding angle of 142.48°) and also through the ether oxygen atom to a coordinated acetonitrile (C−H···O separation is 2.557 Å with corresponding angle = 150.05°).

We plan to develop these chiral polymers as useful materials in the field of stereospecific synthesis or asymmetric catalysis.[11] The dual chiral material reported here is made using inexpensive and readily available materials. The potential applications of our compounds are increased by the observation of the ordered solvent molecules. Future work will determine the influence of the solvent and the counterion on the overall structure. We are also studying the diversity of the supramolecular structures that arise from small changes in the structure of the ligand (for example, by using *ortho*-xylene in the bridge instead of *para*-xylene).

Experimental Section

p-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (1): α,α′-Dibromo-*p*-xylene, *p*-$(BrCH_2)_2$-C_6H_4, (2.64 g, 0.010 mol) and tris-2,2,2-(1-pyrazoyl)ethanol,[7] HO-CH_2-$C(pz)_3$, (4.88 g, 0.020 mol) were dissolved in dry THF (125 mL). This solution was added dropwise to a suspension of NaH (1.5 g) in dry THF (300 mL) under an inert atmosphere. The mixture was stirred under reflux for 24 h and then allowed to cool at room temperature. Enough water (150 mL) was added dropwise to consume the excess NaH and dissolve the resulting NaBr and NaOH. The THF/water mixture was extracted with ethyl ether (3 × 100 mL), the combined organic extracts were washed with 100 mL saturated $NaHCO_3$ solution, with 100 mL saturated NaCl solution and finally with 100 mL water. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent removed under vacuum to afford the desired compound as a white-yellow powder (5.38 g, 0.0091 mol, 91%). M.p. 128−129 °C. ^1H NMR (300 MHz, [D$_6$]acetone): δ = 7.59, 7.49 (m, 3,3 H, 3,5-H *pz*), 7.18 (s, 2 H, C_6H_4), 6.35 (m, 3 H, 4-H pz), 5.11 (s, 2 H, OCH_2Ph), 4.54 [s, 2 H, OCH_2C(pz)$_3$]. $C_{30}H_{30}N_{12}O_2$ (590.6): calcd. C 60.96, H 5.08; found C 61.06, H 4.98.

$\{p$-$C_6H_4[CH_2OCH_2C(pz)_3]_2Ag_2(BF_4)_2\}_n$ (2) $AgBF_4$ (0.195 g, 1.0 mmol) was dissolved in THF (15 mL) under an inert atmosphere. With vigorous stirring, a solution of *p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (0.295 g, 0.50 mmol) in THF (15 mL) was added dropwise during a 10 min period. A white precipitate appeared as the mixture was stirred for 3 h. The THF was removed by cannula filtration, the white precipitate washed with THF (2 × 10 mL) and then vacuum dried to afford 0.475 g of solid identified as $\{p$-$C_6H_4[CH_2OCH_2C(pz)_3]_2Ag_2(BF_4)_2(THF)\}_n$, m.p. 163−166 °C with decomposition. ^1H NMR ([D$_6$]acetone): δ = 7.82, 7.77 (m, 3,3 H, 3,5-H *pz*), 7.09 (s, 2 H, C_6H_4), 6.57 (m, 3 H, 4-H *pz*), 5.02 (s, 2 H, OCH_2Ph), 4.67 [s, 2 H, OCH_2C(pz)$_3$], 3.62 (m, 2 H, CH_2O THF), 1.92 (m, 2 H, CH_2 THF). $C_{30}H_{30}Ag_2B_2F_8N_{12}O_2\cdot C_4H_8O$ (1051.1): calcd. C 38.81, H 3.64; found C 38.86, H 3.55. ES$^+$/MS: calcd. for $[C_{30}H_{30}N_{12}O_2Ag]^+$ 697.1666; found 697.1683.

Acknowledgments

The authors thank the National Science Foundation (CHE-0110493) for support. The Bruker CCD Single Crystal Diffractometer was purchased using funds provided by the NSF Instrumentation for Materials Research Program through Grant DMR:9975623.

---

[1] [1a] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005−2062. [1b] P. Comba, A. Fath, T. W. Hambley, A. Kühner, D. T. Richens, A. Viefort, *Inorg. Chem.* **1998**, *37*, 4389−4401. [1c] P. N. Prasad, D. J. Williams, *Introduction to Non Linear Optical Effects in Molecules and Polymer*s, John Wiley & Sons, Chichester, **1991**.

[2] [2a] A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson, *Chem. Commun.* **2000**, 665−666. [2b] L. Zhang, P. Cheng, L.-F. Tang, L.-H. Weng, Z.-H. Jiang, D.-Z. Liao, S.-P. Yan, G.-L. Wang, *Chem. Commun.* **2000**, 717−718. [2c] M. Munakata, G. L. Ning, Y. Suenaga, K. Sugimoto, T. Kuroda-Sowa, M. Maekawa, *Chem. Commun.* **1999**, 1545−1546. [2d] C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970−973; *Angew. Chem. Int. Ed.* **1998**, *37*, 920−922.

[3] [3a] Y. Hamuro, S. J. Geib, A. D. Hamilton, *J. Am. Chem. Soc.* **1997**, *119*, 10587−10593. [3b] A. Tanatani, H. Kagechika, I. Azumaya, R. Fukutomi, Y. Ito, K. Yamaguchi, K. Shudo, *Tetrahedron Lett.* **1997**, *38*, 4425−4428. [3c] M. P. Lightfoot, F. S. Mair, R. G. Pritchard, J. E. Warren, *Chem. Commun.* **1999**, 1945−1946.

[4] [4a] E. C. Constable, M. D. Ward, D. A. Tocher, *J. Am. Chem. Soc.* **1990**, *112*, 1256−1258. [4b] M. J. Hannon, C. L. Painting, N. W. Alcock, *Chem. Commun.* **1999**, 2023−2024. [4c] K. M. Gardinier, R. G. Khoury, J.-M. Lehn, *Chem. Eur. J.* **2000**, *6*, 4124−4131. [4d] P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510−4517. [4e] V. Berl, I. Huc, R. G. Khoury, M. J. Krische, J.-M. Lehn, *Nature* **2000**, *407*, 720−723.

[5] [5a] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584−587; *Angew. Chem. Int. Ed.* **1999**, *38*, 492−495. [5b] M. Hong, W. Su, R. Cao, M. Fujita, J. Lu, *Chem. Eur. J.* **2000**, *6*, 427−431.

[6] [6a] D. L. Reger, *Comm. Inorg. Chem.* **1999**, *21*, 1−28. [6b] D. L. Reger, J. E. Collins, S. M. Myers, A. L. Rheingold, L. M. Liable-Sands, *Inorg. Chem.* **1996**, *35*, 4904−4909. [6c] D. L.

Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands, G. P. A. Yap, *Inorg. Chem.* **1997**, *36*, 345−351. [6d] D. L. Reger, J. E. Collins, D. L. Jameson, R. K. Castellano, *Inorg. Synth.* **1998**, *32*, 63−65. [6e] D. L. Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands, *Organometallics* **1996**, *15*, 2029−2032. [6f] D. L Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands, G. P. A. Yap, *Organometallics* **1997**, *16*, 349−353. [6g] D. L. Reger, J. E. Collins, R. Layland, R. D. Adams, *Inorg. Chem.* **1996**, *35*, 1372−1376. [6h] D. L. Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands, *Inorg. Chem.* **1999**, *38*, 3235−3237. [6i] D. L. Reger, J. E. Collins, M. A. Mathews, A. L. Rheingold, L. M. Liable-Sands, I. A. Guzei, *Inorg. Chem.* **1997**, *36*, 6266−6269. [6j] D. L. Reger, C. A. Little, A. L. Rheingold, K.-C. Lam, T. Concolino, A. Mohan, G. J. Long, *Inorg. Chem.* **2000**, *39*, 4674−4676. [6k] D. L. Reger, C. A. Little, A. L. Rheingold, M. Lam, L. M. Liable-Sands, B. M. Rhagitan, T. Concolino, A. Mohan, G. J. Long, V. Briois, F. Grandjean, *Inorg. Chem.* **2001**, *40*, 1508−1520.

[7] D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold, R. D. Sommer, *J. Organomet. Chem.* **2000**, *607*, 120−128.

[8] *Crystal data* for **2**: $C_{36}H_{43}Ag_2B_2F_8N_{13}O_3$, $M = 1095.19$, orthorhombic, space group $P2_12_12_1$, $a = 10.2820(7)$ Å, $b = 20.2872(14)$ Å, $c = 20.5518(14)$ Å, $V = 4287.0(5)$ Å^3, $T = 173(2)$ K, $Z = 4$, $\rho = 1.697$ Mg^{-3}, Mo-K_α radiation ($\lambda = 0.71073$ Å), $\mu = 1.002$ mm^{-1}, 28911 reflections collected, 8758 independent ($R_{int} = 0.0331$), GOF = 1.010, final R indices [$I > 2\sigma(I)$], $R1 = 0.0388$, $wR2 = 0.0913$, R indices (all data), $R1 = 0.0435$, $wR2 = 0.0933$. Data were collected using $0.54 \times 0.17 \times 0.10$ mm^3 colorless crystal and a Bruker SMART APEX CCD-based diffractometer and the structure was solved and refined using SAINT+ (Version 6.02a) and SHELXTL (Version 5.1). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166558. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[9] [9a] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451. [9b] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384−7391.

[10] [10a] F. Grepioni, G. Cojazzi, S. M. Draper, N. Scully, D. Braga, *Organometallics* **1998**, *17*, 296−307. [10b] K. L. V. Mann, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1998**, 3029−3036. [10c] R. L. Paul, S. M. Couchman, J. C. Jeffery, J. A. McCleverty, Z. R. Reeves, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2000**, 845−851.

[11] [11a] F. A Rampf, M. Spiegler, W A. Herrmann, *J. Organomet. Chem.* **1999**, *582*, 204−210. [11b] M. E. Brown, M. D. Hollingsworth, *Nature* **1995**, *376*, 323−327. [11c] M. Sakamoto, *Chem. Eur. J.* **1997**, *3*, 684−689. [11d] H. Ito, T. Kusukawa, M. Fujita, *Chem. Lett.* **2000**, 598−599.

Received November 5, 2001
[I01389]