3812 *Inorg. Chem.* **1997,** *36,* 3812−3813

Self-Assembly of Infinite Double Helical and Tubular Coordination Polymers from Ag(CF$_3$SO$_3$) and 1,3-Bis(4-pyridyl)propane

Lucia Carlucci, Gianfranco Ciani,* Dorothea W. v. Gudenberg, and Davide M. Proserpio

Dipartimento di Chimica Strutturale e Stereochimica Inorganica and Centro CNR, Via G. Venezian 21, 20133 Milano, Italy

Received June 26, 1997

Metal-directed supramolecular self-assembly[1] has produced in the last years fascinating results in two topical areas dealing respectively with (i) the deliberate construction of molecular interlocked/intertwined species, like rotaxanes, catenanes, knots, and helicates,[2,3] and (ii) the crystal engineering of extended 2D and 3D networks.[4,5] Conformationally flexible ligands are typical building elements in the former area, while in the latter essentially rigid rodlike organic units are usually employed to connect the metal centers. However, one of the first examples of diamondoid coordination networks (6-fold interpenetrated), reported many years ago, was based on Cu(I) ions and the flexible bidentate adiponitrile,[6] and some interesting interwoven frames incorporating metal ions and flexible-chain linkers have been recently described.[7]

Extending our previous work on the self-assembly of coordination networks based on Ag(I) salts of noncoordinating anions and bidentate aromatic N-donor bases,[8] we are now studying the reactivity of the flexible 1,3-bis(4-pyridyl)propane ligand (bpp), which can assume different conformations (*TT*, *GT*, *GG*, and *GG′*). We have already observed that bpp reacts with AgBF$_4$ and AgClO$_4$ in the ratio 2:1 to give 2-fold interpenetrated diamondoid networks, which will be reported elsewhere.[9] Unexpectedly, the same reaction performed with Ag(CF$_3$SO$_3$) leads to completely different and noteworthy products, including an infinite double helix and a 1D tubular species, comprised of rings threaded with free bpp molecules in a pseudorotaxane-like fashion,[10] which are here described.

The reaction of Ag(CF$_3$SO$_3$) with bpp was carried out by carefully layering over a CH$_2$Cl$_2$ solution (4 mL) of the ligand (0.0725 g, 0.366 mmol) an ethanolic solution (5 mL) of the silver salt (0.047 g, 0.183 mmol). The fast formation of crystals of a polymeric species, [Ag(bpp)](CF$_3$SO$_3$)·EtOH (**1**), was observed at the interface. This is unstable when removed from the mother liquor, and its nature has been established thanks to a fast X-ray data collection on a coated crystal.[11] It consists of parallel 1D sinusoidal chains (period 24.6 Å), with the ligand in a *TT* conformation (see Figure 1, top). The chains are well separated and intercalated by the anions and by solvated ethanol molecules.

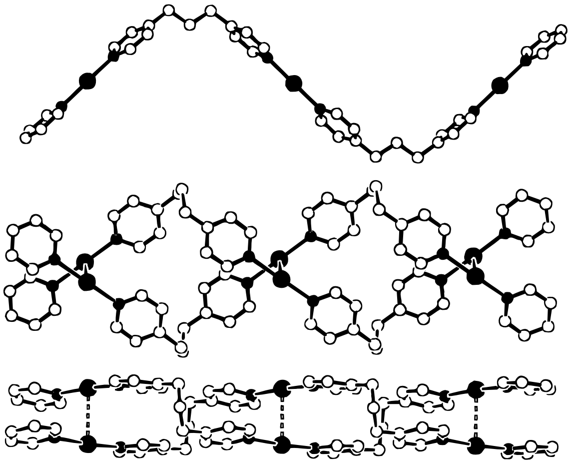

Figure 1. The wavelike polymer of **1** (top) and two views of the double helix of **2** down two normal directions, [010] (middle) and [001] (bottom).

Slow evaporation of the above reaction mixture produced novel species. After some days crystals, more stable in the air than those of **1**, were observed on the walls of the reaction vessel, corresponding to [Ag(bpp)](CF$_3$SO$_3$) (**2**). Further evaporation left a crystalline crust on the bottom, of composition [Ag$_2$(bpp)$_4$](CF$_3$SO$_3$)$_2$·bpp (**3**). Both compounds **2** and **3** have been characterized by single-crystal X-ray analysis.[11]

The structure of **2** shows the balanced packing of left-handed and right-handed double helices of cationic −Ag−bpp−Ag−bpp− chains, extending in direction of the *a* axis. The period of the helices, 21.1 Å (2*a*), is shorter than that of the polymer in **1** since the conformation of the ligand is different, of the *GG′* type (see Figure 1, middle and bottom, and Figure 2). Though the presence of intertwined helical chains as components

---

(1) *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon Press: Oxford, U.K., 1996.

(2) See *e.g.*: Dietrich-Buchecker, C.; Sauvage, J.-P. *Bull. Soc. Chem. Fr.* **1992**, *129*, 113; Krämer, R.; Lehn, J.-M.; Marquis-Rigault, A. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5394.

(3) For a recent review article see: Fujita, M.; Ogura, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471 and references therein.

(4) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19.

(5) Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13.

(6) Kinoshita, Y.; Matsubara, I.; Higuchi, T.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1221.

(7) See *e.g.*: (a) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878. (b) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 574. (c) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.

(8) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755; **1996**, 1393; *J. Am. Chem. Soc.* **1995**, *117*, 4562; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1985.

(9) Carlucci, L.; Ciani, G.; W. v. Gudenberg, D.; Proserpio, D. M.; Sironi, A. Results to be published.

(10) See *e.g.*: Amabilino, D. B.; Stoddart, J. F.; Williams, D. J. *Chem. Mater.* **1994**, *6*, 1159.

(11) Crystal data: **1**, [Ag(bpp)](CF$_3$SO$_3$)·EtOH, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.263(3)$ Å, $b = 9.303(2)$ Å, $c = 21.346(4)$ Å, $\beta = 95.81(2)°$, $V = 2027.6(8)$ Å^3, $Z = 4$, $D_c = 1.642$ Mg·m^{-3}, final R value 0.0578 for 1405 independent reflections [$F_o > 4\sigma(F_o)$]; **2**, [Ag(bpp)](CF$_3$SO$_3$), orthorhombic, *Pbna* (No. 60), $a = 10.573(2)$ Å, $b = 13.533(2)$ Å, $c = 23.196(6)$ Å, $V = 3319.0(12)$ Å^3, $Z = 8$, $D_c = 1.822$ Mg·m^{-3}, final R value 0.0565 for 1483 independent reflections [$F_o > 4\sigma(F_o)$]; **3**, [Ag$_2$(bpp)$_4$](CF$_3$SO$_3$)$_2$·bpp, triclinic, $P\bar{1}$ (No. 2), $a = 10.745(5)$ Å, $b = 12.039(2)$ Å, $c = 16.469(3)$ Å, $\alpha = 70.04(2)°$, $\beta = 83.31(3)°$, $\gamma = 63.57(2)°$, $V = 1791.6(9)$ Å^3, $Z = 1$, $D_c = 1.395$ Mg·m^{-3}, final R value 0.0965 for 2940 independent reflections [$F_o > 2\sigma(F_o)$]. The data collections were performed at 293 K on a Siemens SMART CCD area-detector diffractometer for **1** and **2** and an Enraf-Nonius CAD4 for **3** (Mo Kα, $\lambda = 0.710\ 73$ Å) by the ω-scan method, within the limits $2 < \theta < 27°$ (**1**), $1 < \theta < 26°$ (**2**), and $3 < \theta < 25°$ (**3**). An empirical absorption correction was applied (SADABS for **1** and **2**, ψ-scan for **3**). The structures were solved by direct methods (SIR92) and refined by full-matrix least-squares (SHELX93). Anisotropic thermal parameters were assigned to all the non-hydrogen atoms but in **3** where the statistically disordered bpp was refined isotropically. All the diagrams were obtained using SCHAKAL program.

S0020-1669(97)00803-3 CCC: $14.00

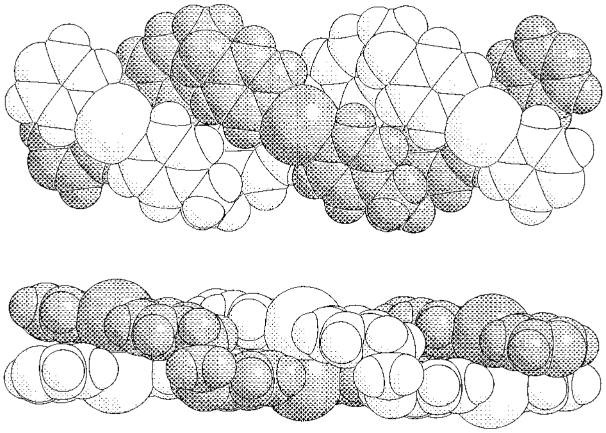

Figure 2. Space-filling representations of the double helix of **2** down two directions normal to the helical axis, [010] (top) and [001] (bottom).

of 3D networks has been sometimes evidenced,[12] discrete infinite polymeric double helices are quite rare in inorganic and coordination chemistry. We have been able to find only one previous example, *i.e.* the silver thiolate [Ag(SCEt$_2$Me)], comprised of chains with sequences of 8 independent alternating Ag(I) cations and SR$^-$ anions.[13] As the two spirals of DNA are connected by hydrogen bond bridges, in **2** the two strands are bridged by weak Ag···Ag aurophilic (d^{10}−d^{10}) interactions[14] of 3.089(1) Å. However, the nature of these interactions is often not clearly understood, and somewhat shorter Ag···Ag contacts of this kind have been considered attractive in some cases, *e.g.* in [Ag(4,4′-bipyridyl)]NO$_3$,[15] but also repulsive, in [Ag(SCEt$_2$Me)].[13] In the direction of these Ag···Ag contacts the two helices in **2** show remarkable compression normal to the spiral axis (see Figure 2, bottom). The silver ions display also an outward weak contact with an anionic oxygen atom [2.663(7) Å].

The peculiar self-organization of the 1D chains in **2** *vs* the more usual situation found in **1** and, possibly, the conversion of **1** into **2** are not simple to rationalize. Probably a major role is played by the *facile* reversible dissociation of the Ag−N bonds in these polymers, which suggests that a concerted ligand scrambling can occur in a pair of parallel chains weakly connected by Ag···Ag interactions. Fujita, Ogura, and coworkers have recently proposed a mechanism for the formation of a [2]-catenane from two molecular rings in terms of ligand exchange between labile Pd−N bonds.[16]

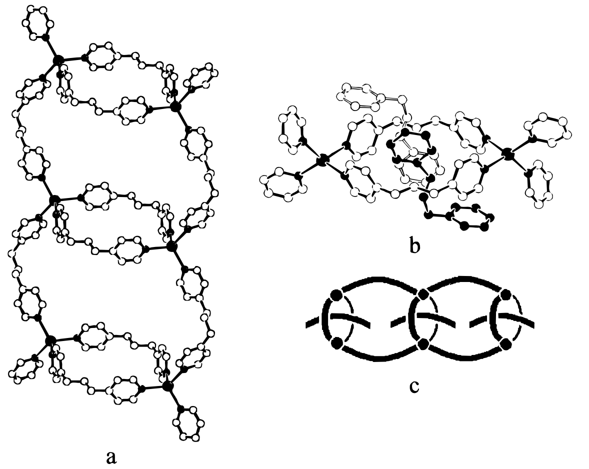

Figure 3. (a) View of the empty tubular polymer of **3**. (b) A single macrocycle showing the threading solvated molecule (two centrosymmetrically related half-molecules, filled and empty circles). (c) Scheme of the polymeric pseudorotaxane motif of **3**.

Compound **3** contains 1D polymers comprised of [Ag$_2$(bpp)$_2$] rings (24-membered macrocycles), which are interlinked by two other bpp ligands, to form tubular-like arrays (see Figure 3a), all running in a parallel direction. The silver ions are 4-connected and display a distorted tetrahedral coordination geometry. The conformation of the bpp molecules changes from *TT* within the rings to *TG* for the inter-ring ones. An unusual feature is the presence of solvated bpp molecules threading the rings of the polymer. This motif (see Figure 3b) is reminescent of the structure of organic pseudorotaxanes,[10] though in **3** only weak interactions can be envisaged between the rings and the guest molecules, which are statistically distributed on two close centrosymmetric locations. This polymeric architecture is, to our knowledge, unprecedented in coordination chemistry. We can consider **3** as an example of a polypseudorotaxane (schematically shown in Figure 3c). Also the anions are contained inside the tubules, in the regions midway between the rings.

Further studies involving other long flexible bidentate ligands are in progress. Though structural control is quite difficult in these systems, very interesting motifs can be isolated, as shown by some recently reported fascinating molecular devices embedded in extended frames,[17] which introduce novel perspective in this area of supramolecular chemistry.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1**−**3** are available on the Internet only. Access information is given on any current masthead page.

IC970803W

---

(12) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubjeta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596. (b) Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Chem. Commun.* **1996**, 1313.

(13) Dance, I. G.; Fitzpatrick, L. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 3785.

(14) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098.

(15) Robinson, F.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2413. Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, *118*, 295.

(16) Fujita, M.; Ibukuro, F.; Seki, H.; Kamo, O.; Imanari, M.; Ogura, K. *J. Am. Chem. Soc.* **1996**, *118*, 899.

(17) Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451. Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Chem. Commun.* **1997**, 339.