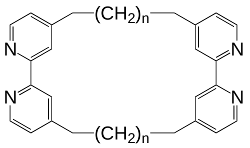
Synthesis and Structural Analysis of a Helical Coordination Polymer Formed by the Self-Assembly of a 2,2′-Bipyridine-Based *exo*-Ditopic Macrocyclic Ligand and Silver Cations**

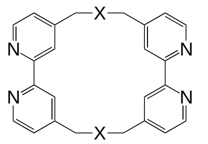
Christian Kaes, Mir Wais Hosseini,* Clifton E. F. Rickard, Brian W. Skelton, and Allan H. White

Because transition metals exhibit numerous oxidation states and coordination geometries as well as a wide range of photochemical and magnetic properties, the design and preparation of coordination polymers, which may be regarded as metalloorganic networks, are topics of current interest.[1] Most of the known coordination polymers contain bis-monodentate ligands.[1, 2] Examples of coordination polymers based on bis-bidentate[3] and bis-tridentate ligands have also been reported.[4] Furthermore, there are numerous discrete polynuclear complexes with helical arrangements,[5] but only a few infinite helical coordination polymers.[6]

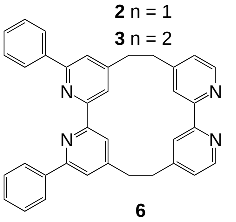
Using the molecular tectonics approach, which involves the self-assembly of complementary molecular building blocks ("tectons"),[7, 8] we have prepared compounds that exist as molecular networks in the solid state. These networks are based on weak van der Waals interactions between convex connectors and concave receptors[9] or on a combination of electrostatic and hydrogen bonding.[10] A further step in our strategy is the use of coordinative bonds for assembling metals and organic ligands into molecular networks. Here we report the design, synthesis, and structural analysis of a helical coordination polymer obtained by self-assembly of the ligand **7** with silver cations.



1 n = 0
2 n = 1
3 n = 2



4 X = SiPh$_2$
5 X = CH$_2$Si(Me)$_2$CH$_2$



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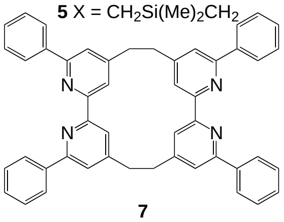

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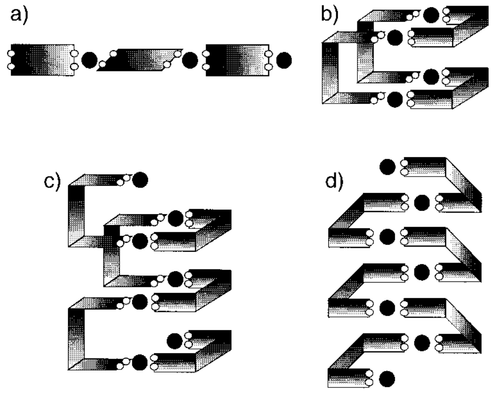

Figure 1. Schematic representation of different types of arrangements that can be obtained by self-assembly of exoditopic ligands and tetrahedrally coordinated metal cations: a) linear, c) "stair-type", d) helical coordination polymer and b) discrete tetranuclear species.

The overall topology of coordination polymers can be controlled by means of the coordination preferences of the metal center and the structure of the bridging ligand. Thus, for bis-bidentate exo ligands and metal cations that adopt a tetrahedral coordination geometry, one can envisage the formation of discrete cyclic or infinite linear polynuclear species. Depending on the structure of the ligand, one of these possibilities may be favored. With bis-bidentate exo ligands that adopt a planar conformation, only one-dimensional linear coordination polymers are conceivable (Figure 1a). With nonplanar bis-bidentate exo ligands that adopt a "roof-shaped" conformation, in addition to discrete cyclic polynuclearspecies such as the tetranuclear complex shown in Figure 1b, infinite one-dimensional networks of the "stair type" (Figure 1c), or single-stranded helical species (Figure 1d) may be formed. However, when constraints such as steric hindrance are imposed, one of the alternative structures may be favored.

The conformational motion can be restricted, and the location of the metal centers and the distance between them controlled by using exo ligands based on macrocyclic frameworks.[11–14] We prepared exo ligands **1**–**7**, in which two 2,2′-bipyridine units are linked at the 4- and 4′-positions by different spacers.[14] Silver(I) was chosen as the metal because it forms kinetically labile complexes with 2,2′-bipyridine and can adopt a tetrahedral coordination geometry. We then attempted to synthesize a one-dimensional coordination polymer by the self-assembly of Ag^I and the *exo*-ditopic bis-chelate ligand **7** (Figure 2).

Treatment of **7** with 1.2 equivalents of AgPF$_6$ in CH$_3$CN at 25 °C for about 12 h gave a colorless, clear solution, which was evaporated to dryness. The solid thus obtained was redissolved in CH$_3$CN, and slow diffusion of toluene/hexane (1/1) into the solution gave morphologically uniform single crystals. The same type of crystals could also be grown without the evaporation step.

The solid-state structure of the coordination polymer was elucidated by an X-ray structure analysis,[15] which revealed

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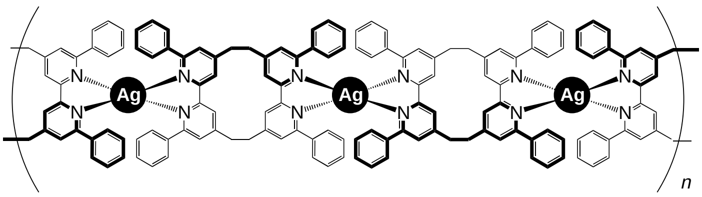

Figure 2. Infinite coordination polymer obtained by the self-assembly of the *exo*-ditopic ligand **7** and silver ions.

that the cationic component of the structure is a single-stranded helical network formed by alternate silver atoms and ligand **7**, which are mutually bridging (Figure 3). The helix extends along the crystallographic *a* axis, and two crystallographic twofold axes pass perpendicularly through the non-crystallographic axis. The fragment that determines the pitch of the single helix is composed of four Ag atoms and four ligand molecules. The interior of the helix is not empty, but occupied by phenyl groups (Figure 3). The interstices in the solid were occupied to different extents by CH_3CN molecules and PF_6^- anions.

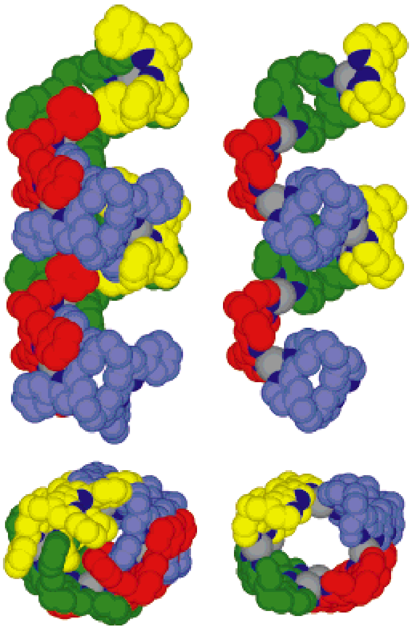

Figure 3. X-ray structure of the infinite single-stranded helical coordination polymer obtained by self-assembly of ligand **7** and silver cation. Projection of the cationic array along (top left) and normal (bottom left) to the polymer axis. For the sake of clarity, the same projections without the Ph groups at the 6 and 6′ positions are also shown on the right. Hydrogen atoms, anions, and CH_3CN molecules are omitted in both representations. The different colors of the ligands are merely intende to more clearly reveal the pitch of the helix.

The observed helical structure is derived from the primary structure of **7**, which adopts a roof-shaped conformation in the complex. However, since **7** is not chiral, a racemic mixture of both the right- and left-handed helical coordination polymers was obtained, as expected. The infinite network crystallized in the centrosymmetric space group *C*2/*c*. The roof-shaped conformation adopted by **7** was previously observed in the solid state for the *exo*-binuclear Ru^{II} complex of the analogous ligand **1**.[14b] This conformation was due to the shortness of the ethylene bridges connecting the two 2,2′-bipyridine units at the 4- and 4′-positions. Indeed, X-ray structural studies on Ru^{II} *exo*-binuclear complexes with ligands **3**[14d] and **5**[14e] showed that when the length of the spacer group is increased, both ligands adopt a planar conformation. In the trinuclear $Ru^{II}-Cu^{I}-Ru^{II}$ complex with two macrocycle **6**, both ligands also adopt a roof-shaped conformation.[14f]

In the one-dimensional network of Ag^+ and **7**, three crystallographically nonequivalent Ag atoms (Ag1, Ag2, Ag3) and two slightly different roof-shaped conformers of the ligands (L1 and L2) were identified (Figure 4), of which Ag2 and Ag3 are located on the crystallographic twofold axes. Ligands L1 and L2 differ in the conformation of the ethylene bridges (CCH_2CH_2C dihedral angles of 40.0 and 68.5° for L1; and −67.7 and −70.0° for L2). Consequently, two different Ag–Ag distances of 8.8 (Ag1–Ag2) and 9.8 Å (Ag1–Ag3) are present. For both L1 and L2, the two pyridine rings of each bipyridine unit were not coplanar. The average tilt angle of L1 is 20.5°, and that of L2 21.4°.

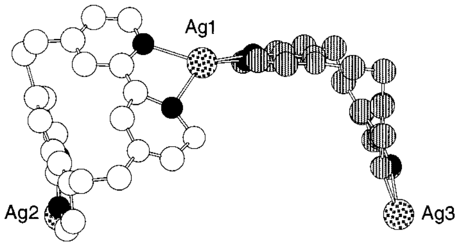

Figure 4. A section of the structure showing the crystallographically nonequivalent L1 (left) and L2 (right) conformers and three silver ions (see text for definition). For the sake of clarity, hydrogen atoms are omitted.

All silver atoms are coordinated to two sets of bipyridine units to give a AgN_4 coordination sphere in which the N-Ag-N angles range from 73.5 to 139.5° for Ag1, from 74.4 to 149.7° for Ag2, and from 73.6 to 153.9° for Ag3. For all three silver atoms, the Ag–N distances range from 2.30 (estimated standard deviation (esd): 0.8) to 2.47 (esd: 0.2) Å, and the bite angles of the ligands from 73.5(9) to 74.4(6)°. The interplanar (N_2Ag/AgN_2) dihedral angles are 70(1), 65.2(7), and 68(1)°.

Inspection of CPK models revealed that the formation of the helical structure with ligand **7** was probably due to the presence of phenyl groups at the 6- and 6′-positions. Indeed, for both discrete cyclic polynuclear species such as the tetranuclear complex (Figure 1b), and the infinite stair-type network (Figure 1c), the substitution of hydrogen atoms at the 6- and 6′-positions in ligand **1** by phenyl groups in ligand **7** could generate severe steric hindrance between phenyl groups of consecutive ligands. This assumption is supported by electrospray mass spectrometric studies on the Cu^I coordination polymer formed with ligand **7**, in which no peak corresponding to the cyclic tetranuclear complex was detected.

In conclusion, we have synthesized a single-stranded helical coordination polymer as a racemic mixture of left- and right-handed helices by self-assembly of an *exo*-ditopic ligand and silver. The structure of the infinite network was established by single-crystal X-ray structure analysis. With the same combination of ligand and metal, the generation of optically pure left- or right-handed helices by using chiral anions is currently under investigation. Furthermore, the formation of linear coordination polymers (Figure 1a) with ligands such as **3** and **5** and silver or copper is also being studied.

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[15] Suitable crystals were obtained from acetonitrile/toluene/hexane. Reflections were measured on an area detector. Crystal dimensions: $0.12 \times 0.10 \times 0.05$ mm (mounted in a capillary). $C_{48}H_{36}AgF_6N_4P \cdot 11/4\,CH_3CN$, $M_r = 1034.6$, monoclinic, space group $C2/c$, $a = 17.7806(8)$, $b = 34.529(2)$, $c = 38.715(2)$ Å, $\beta = 91.915(5)^\circ$, $V = 23756$ Å^3, $Z = 16$, $\rho_{calcd} = 1.15\ \mathrm{g\,cm^{-3}}$, $F(000) = 8456$, $T = 295$ K, monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ cm; 27682 measured reflections ($R_{int} = 0.10$, $2\theta_{max} = 52.6^\circ$), of which 19624 were unique and were corrected for absorption. Final conventional $R = 0.11$ and $Rw = 0.11$ (statistically weighted) for 5092 observed reflections ($I > 3\sigma(I)$). $T_{min}/T_{max} = 0.35/0.86$ (SADABS), Xtal3.4 program system. Phenyl and pyridine rings were refined as rigid bodies, and the geometries of the anions and solvent molecules were constrained to "idealized" values, with isotropic thermal parameters. Ring 24n was modeled as disordered over two sets of sites of equal occupancy. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100747. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Alternating Ethene/Propene Copolymerization with a Metallocene Catalyst**

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Metallocene catalysts have introduced an element of design into the construction of polyolefins of defined architecture.[1] Correlation of the catalyst structure with the structure of the resulting polymers has provided considerable insight into the mechanism of polymerization. For example, the syndiospecific polymerization of propene with $[\{(Cp)(Me_2C)(Flu)\}ZrCl_2]$-based catalysts strongly implicates a Cossee-type mechanism[2] in which the olefin inserts at alternating enantiotopic coordination sites with each insertion (Cp = cyclopentadienyl, Flu = fluorenyl).[3] Differentiation of the coordination sites by methyl substitution on the Cp ring in these systems yields hemiisotactic polypropene,[4–6] in which olefin insertion occurs alternately at an aspecific and isospecific coordination site; substitution of the Cp ring with the larger *tert*-butyl substituent yields isotactic polypropylene.[7,8] The latter result has been interpreted by invoking a "chain-skipping" mechanism in which the polymer chain "skips" out of the more sterically hindered site prior to olefin insertion, resulting in polyinsertions at only one isospecific coordination site.[9]

Metallocene catalysts have also proven useful for olefin copolymerization as copolymers produced with metallocene catalysts tend to have more random comonomer distributions and better compositional homogeneity than copolymers produced with heterogeneous catalysts.[1] However, metallocene catalysts also offer the possibility to design catalyst

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