Self-Assembly of a Novel Infinite Triple Helices Coordination Polymer {[Co(4,4'-bipyridine)-(4,4'-azobispyridine)$_2$(NCS)$_2$]·H$_2$O}$_n$ via Hydrogen-Bonding Interaction

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The novel complex {[Co(bpy)(azpy)$_2$(NCS)$_2$]·H$_2$O}$_n$ (where bpy = 4,4'-bipyridine, azpy = 4,4'-azobispyridine) comprising unprecedented three parallel interpenetrating two-dimensional (4,4) networks and forming novel infinite triple helices via hydrogen-bonding interaction, has been synthesized and characterized.

Pronounced interests in the crystal engineering of coordination frameworks[1] stem from, not only for their potential applications as zeolite-like materials in molecular selection, ion exchange, and catalysis, but also their intriguing variety of architectures and topologies. Up to now, the most important driving forces in crystal engineering are coordination bonding and hydrogen bonding interactions.[2] The unique directionality, strength, and complementary of non-covalent hydrogen and coordinated bonding play an important role in the construction of a variety of motifs for molecular self-assembly and recognition.[3] Particular interest is supramolecular entanglements, including polymeric catenanes,[4] infinite double helices,[5] polyrotaxanes[6] and other noteworthy supramolecular architectures.[7] Species like these are expected to be of comparable robustness but more flexible than the usual networks entirely based on coordinated bonds with similar ligands.[8] In this work, using two similar ligands 4,4'-bipyridine (bipy) and 4,4'-azobispyridine (azpy) as a mixed ligand system, we have synthesized a novel infinite triple helices coordination polymer {[Co(bpy)(azpy)$_2$(NCS)$_2$]·H$_2$O}$_n$ **1**.[9]

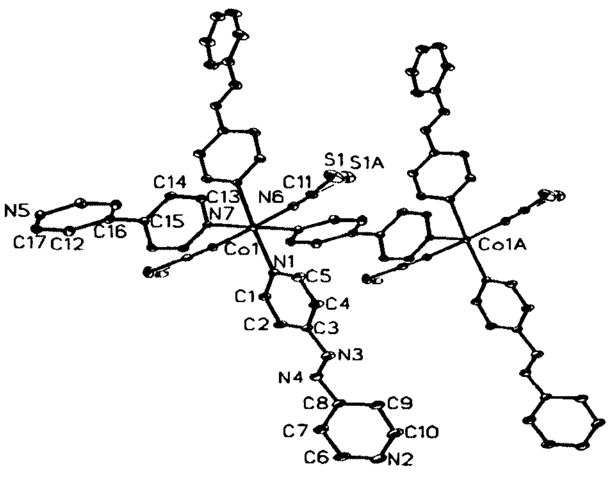

Figure 1. The local coordination of with atom numbers in **1**.

Compound **1** was synthesized by diffusion of a solution of Co(ClO$_4$)$_2$]·6H$_2$O (0.370 g, 1 mmol) and KSCN (0.290 g, 3 mmol) in 20 mL H$_2$O/EtOH (1:1, v/v) into a solution of bpy (0.156 g, 1 mmol) and azpy (0.184 g, 1 mmol) in 20 mL H$_2$O/EtOH (1:1, v/v). Red crystals were obtained after about one month. Yield: 0.196 g (54.6% based on azpy). IR spectrum[10] and elemental analysis confirmed the organic content. (Found: C, 53.34; H, 3.56; N, 23.29%. Calcd for $C_{32}H_{26}CoN_{12}OS_2$: C, 53.55; H, 3.65; N, 23.42%.)

The crystal structure of **1** shows that the C_2-symmetry axis is through the Co(II) atom (Figure 1). The sulfur atom of thiocyanate exhibits twofold positional disorder, and its scattering power is represented by two “half-atoms” S(1) and S(1A) separated by 0.48 Å. The Co(II) atom is, in a distorted octahedral geometry, coordinated by two nitrogen atoms from two bpy (Co(1)–N(7), 2.151(5); Co(1)–N(5)B, 2.196(6) Å), two nitrogen atoms from two azpy (Co(1)–N(1), 2.225(4) Å), and two nitrogen atoms from two thiocyanate groups (Co(1)–N(6), 2.061(4) Å). The Co–N bond length follows the order: azpy > bpy > NCS$^-$. It is surprising that azpy acts as a monodentate ligand coordinating to Co(II) atom with different Co–N bond length.

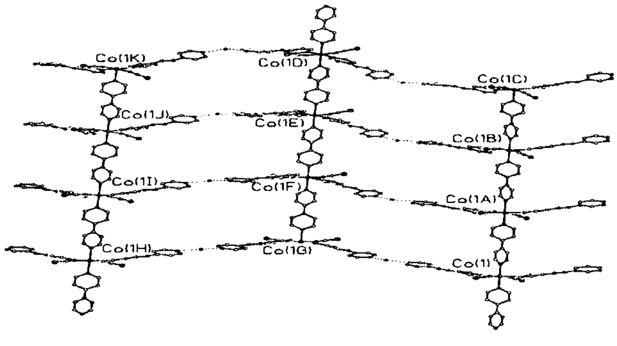

Figure 2. The 2D rhombus network connected via hydrogen-bond interactions.

The bridging ligand bipy links Co(II) atoms to form an infinite “rod with sidearms” (Figure 2). The intermetallic distances through bridging ligand bipy are 11.424 Å. A two-dimensional undulating plane network with large rhombic cavities ca. 21.6 × 11.4 Å, is constructed by uncoordinated water molecule forming hydrogen bonds with two nitrogen atoms from two neighbour “sidearms” (azpy) of the infinitive “rod” (O–N(2), 2.912 Å).

This structure of the complex **1** is composed of layers containing three parallel interpenetrating two-dimensional (4,4) networks (Figure 3). The pyridyl rings of azpy from three interpenetrating layers stack each other with a separation of ca.

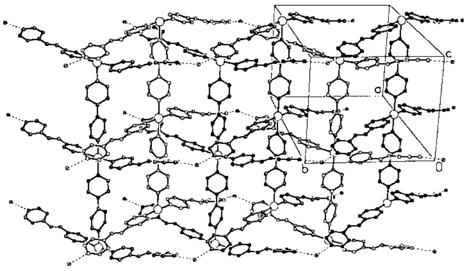

Figure 3. View three parallel interpenetrating 2D (4,4) networks, omitted the NCS$^-$ for clarity.

3.5–4.1 Å, indicating a significant π–π interaction.[11] The least distance of cobalt atom to cobalt atoms of interpenetrating layers is 8.460 Å. The least distance of oxygen atom to cobalt atoms of interpenetrating layers is 10.022 Å. Although some two parallel interpenetrating (4,4) networks have been reported, this topology of interpenetration is unprecedented.[1] This feature is a consequence of the fact the hydrogen-bonding containing chains of the three parallel interpenetrating two-dimensional (4,4) networks form novel infinite triple helices in the [010] direction (Figure 4). The bridging ligand bipy links two triple helices (two cobalt(II) atoms), so infinite triple helices link together via covalent bonds. The helical repeat distance is three times the *b* axis translation.

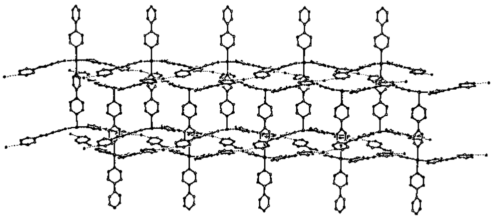

Figure 4. Infinite triple helices in the [010] direction viewing from the [100] direction, omitted the NCS$^-$ for clarity.

Helicates obtained by self-assembly processes have clearly initiated a revolution from classical coordination concepts toward extended supramolecular concepts. The coordination bond has become a tool for the construction of large organized architectures capable of further recognition processes based on various noncovalent interactions such as stacking interactions, hydrogen bonding, or van der Waals interactions.[12] Examples exist for single[13] and double helical infinite chains[5] in which the strands of the helix are independent infinite chains held together by noncovalent forces other than the coordinate bond. To our knowledge, **1** is the first helicates formed by interpenetrating two-dimension network and is the first example in which the adjacent helices link together via covalent bond.

The main limitation of synthetic helices results from the tedious and often complicated preparation of instructed ligand strands suitable for helicate self-assembly. The synthesis of **1** via mixed simple organic ligands opens a new approach of constructing helical molecular frameworks.

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9 Crystal data for **1**: $C_{32}H_{26}CoN_{12}OS_2$, orthorhombic, space group *Pnna*, a = 22.1312(16), b = 14.0403(10), c = 11.4237(8) Å, U = 3549.7(4) Å^3, Z = 4, MW = 717.70, D_c = 1.343 g·cm^{-3}, λ = 0.71073 Å. The data collection was performed at 293(2) K on a Siemens smart diffractometer equipped with CCD area detector. The structure was solved by direct methods and refined by full-matrix least-squares analysis (SHELXTL97), giving a final R_1 value of 0.0691 for 231 parameters and 2947 independent reflections $[I_{obs}>2\sigma(I)]$ and wR_2 of 0.1129.

10 IR Spectra shown the bands as follows: 3395s, 3061s, 2062v, 1678s, 1603s, 1590s, 1567m, 1532w, 1485w, 1406s, 1318w, 1220m, 1071w, 1049w, 1008w, 840s, 815s, 631m, 568m, 521m, and 485w cm^{-1}.

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