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Supramolecular Isomerism in Coordination Compounds: Nanoscale Molecular Hexagons and Chains

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Received June 19, 2002

Self-assembly of pre-selected molecular components,[1] supramolecular synthesis,[2,3] represents a paradigm for “bottom-up”[4] one-pot generation of nanoscale structures from readily available molecular moieties. Thus far, geometric considerations have been exploited to guide the selection of nanoscale molecular targets, as exemplified by polygons[5−8] and polyhedra.[9−13] However, more than one superstructure can result from the assembly of identical components, affording supramolecular isomers.[14−16] Figure 1 illustrates three supramolecular isomers that can be generated from a single 120° molecular component or complementary angular and linear components: hexagons, helices, and zigzag chains. Additional supramolecular isomers include larger ring systems (nonplanar) and catenane supramolecular isomers,[17] and other discrete polyhedra may also be possible.[18]

The hexagon represents a discrete planar species of which only a few examples have been reported.[8,19] The zigzag polymer has been widely encountered, whereas the helix remains quite rare in the context of coordination polymers.[20,21] A suitable molecular component that might serve as a building block in this context is 1,3-benzenedicarboxylic acid,[22] H_2bdc, 5-substituted forms of which can self-assemble into molecular hexagons[8a,19,23] or bdc, which can serve as a bifunctional ligand.[24] In this contribution, we report the synthesis and structural characterization of a nanoscale, neutral, planar hexagon, **1**,[25] and its supramolecular isomeric zigzag chain, **2**,[26] each resulting from modular self-assembly of 5-NO_2-bdc and Cu(II) (Figure 2).[27] The known chromophore[28] is square pyramidal Cu(II) with two monodentate carboxylate ligands and three coordinated solvent molecules.

1 results from the modular self-assembly of thirty molecular components: six 5-NO_2-bdc moieties, six Cu(II) cations, and eighteen coordinated solvent molecules. The hexagons are uncharged and have been refined as having six dimethyl sulfoxides, three methanols, and nine waters coordinated to the metals, with six uncoordinated methanols in the cavity. The effective outer diameter of the hexagon is 3.14 nm (measured from opposite nitro groups). The distance from the center of the hexagon to the closest contacts, coordinated solvent molecules, is 0.58 nm, affording an internal cavity with an effective diameter of ca. 0.8 nm (Figure 3). The effective inner diameter of a desolvated hexagon (measured from opposite phthaloyl 2-H sites) is 1.5 nm, compared to 1.2 nm observed for the hexagons formed by H_2bdc-5-$OC_{10}H_{21}$.[8a]

Molecules of **1** pack into sheets with large voids (Figure 3a). The intralayer centroid−centroid separation is 3.5 nm. The sheets stack in an ABCABC fashion (Figure 3b,c) creating hourglass-shaped channels along [001] with an effective diameter of ca. 0.8 nm at the narrowest point. This packing arrangement is contrary to the eclipsed stacking of the hexagons of H_2bdc-5-$OC_{10}H_{21}$.[8a] There are hydrogen-bonding interactions between carbonyl oxygen atoms of the 5-NO_2-bdc moieties in one sheet and coordinated water molecules in adjacent sheets (Figure 4). The interlayer separation is 3.34 Å, which is consistent with $\pi-\pi$ stacking.[29] The solvent-accessible voids in the crystal structure amount to ca. 10% of the total volume; however, this would be increased to 57% upon replacing the coordinated DMSO and MeOH molecules with water molecules. The most intense peaks observed in the X-ray powder diffraction (XPD) patterns from the bulk sample are consistent with those calculated from single-crystal diffraction data.

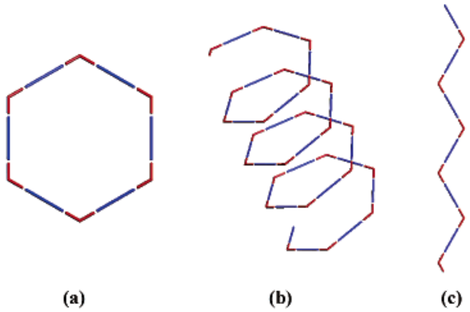

Figure 1. Schematic representation of three structural supramolecular isomers possible for a 120° angular ligand and a linear spacer: (a) 0D hexagon, (b) 1D helix, (c) 1D zigzag chain.

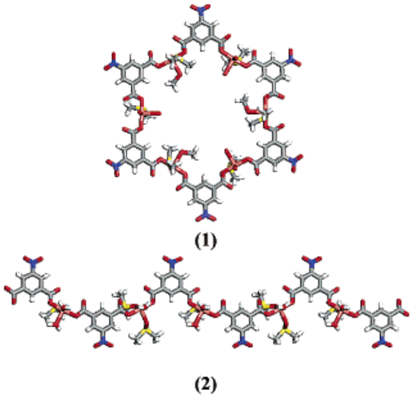

Figure 2. Crystal structure of the two supramolecular isomers: hexagon **1** and zigzag chain **2**. There are two crystallographically independent copper atoms in the hexagon. Oxygen atoms from two 5-NO_2-bdc moieties, DMSO, and H_2O occupy the basal positions. The apical position of the copper atoms points inside the ring and is occupied by MeOH (Cu1) and H_2O (Cu2). Coordinated DMSO molecules point above and below the plane of the ring in an alternating fashion. Outer (measured from opposite nitro groups) and inner (measured from opposite phthaloyl 2-H sites) diameters are 3.1 and 1.5 nm, respectively.

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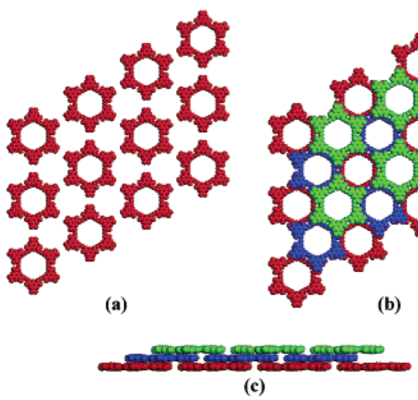

Figure 3. Space-filling model of: (a) Crystal packing of **1** into a sheet with centroid−centroid separations of 3.5 nm. (b) Sheets stacked in an ABCABC fashion creating hourglass channels. (c) Side-view of the stacked sheets of **1**. Coordinated solvent molecules have been removed for clarity.

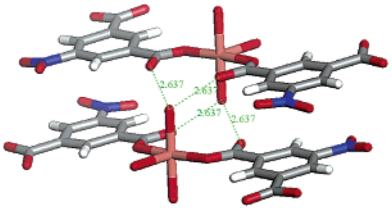

Figure 4. Interlayer hydrogen-bonding between carbonyl oxygen atoms of 5-NO_2-bdc and coordinated water molecules in adjacent sheets results in 24 hydrogen-bonding interactions per hexagon.

Electrospray mass spectroscopy indicates that **1** exists in methanol with 4-coordinated DMSO molecules and 14-coordinated MeOH molecules ($M^+ = 2396$ m/z). **1** is readily soluble in MeOH and sparingly soluble in hot DMSO and DMF. Thermogravimetric analysis of **1** shows a weight loss consistent with loss of guest and coordinated solvent: 9.1% at 48.2 °C (calcd 7.5%) and 31% at 91.0 °C (calcd 28.5%).

Supramolecular isomeric zigzag chains of **2** are obtained under similar reaction conditions.[27] The chains pack efficiently and eschew open cavities. The structure is sustained by hydrogen bonding between the chains and $\pi-\pi$ stacking between the phenyl rings. There are no significant geometrical differences between the chromophores in **1** and **2**.

We present herein what to our knowledge is the largest, neutral molecular hexagon characterized by single-crystal X-ray crystallography and one of its supramolecular isomers, a zigzag chain. Our results indicate that, as might have been expected, the closed discrete structure is thermodynamically favored over the open polymeric supramolecular isomer.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (DMR 0101641) and the CRDF/MRDA (MP2-3021) (V.K. travel and collaboration).

Supporting Information Available: X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 188212 and 188213 contain the supplementary crystallographic data for 1 and 2, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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(25) Crystal data for **1** at 200 K: Hexagonal ($R3$), $a = b = 35.023(4)$ Å, $c = 9.9711(13)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, volume = 10592(2) Å^3, $Z = 3$, $\rho = 1.200$ g cm^{-3}, $\mu = 1.054$ mm^{-1}, $F(000) = 3933$, $2\theta_{\max} = 48.00$ ($-40 \leq h \leq 37$, $-26 \leq k \leq 40$, $-11 \leq l \leq 11$). Final residuals (for 439 parameters) were R1 = 0.0951 for 7267 reflections with $I > 2\sigma I$, and R1 = 0.1211, wR2 = 0.2355, GooF = 0.991 for all 14506 data. Residual electron density was 0.989 and 0.495 e Å^{-3}.
(26) Crystal data for **2** at 200 K: Monoclinic, $P2(1)/n$, $a = 14.0608(12)$ Å, $b = 13.8902(12)$ Å, $c = 19.0465(16)$ Å, $\alpha = \gamma = 90°$, $\beta = 98.487(2)°$, volume = 3679.2(5) Å^3, $Z = 4$, $\rho = 1.679$ g cm^{-3}, $\mu = 1.465$ mm^{-1}, $F(000) = 1912$, $2\theta_{\max}= 56.52$ ($-18 \geq h \geq 11$, $-17 \geq k \geq 18$, $-23 \geq l \geq 25$). Final residuals (for 477 parameters) were R1= 0.0534 for 8628 reflections with $I > 2\sigma I$, and R1= 0.0820, wR2 = 0.1272, GooF = 0.981 for all 22351 data. Residual electron density was 1.057 and 0.646 e Å^{-3}.
(27) To a methanolic solution of 5-nitroisophthalic acid (250 mg, 1.184 mmol) and copper nitrate (276 mg, 1.184 mmol) was added 2,6-lutidine (254 mg, 2.368 mmol). The resulting blue precipitate (371 mg) was recrystallized from DMSO to afford **1** and **2**. Alternatively, **1** was exclusively obtained by heating a solution of the crude precipitate (197 mg) in DMSO (15 mL) for 24 h and allowing the solution to sit for 3−4 weeks to yield 128.3 mg (ca. 27%) of deep blue precipitate, XPD of which confirmed that it was the same as the structure obtained from the single crystal.
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JA027371V