Chemistry

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Finite, Spherical Coordination Networks that Self-Organize from 36 Small Components

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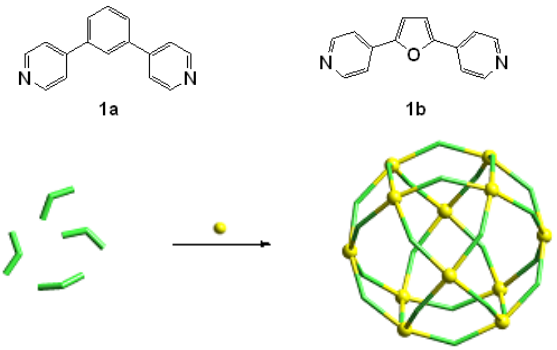
Introduction

Highly symmetric structures often appear in nature as revealed by, for example, the capsids of spherical viruses that possess icosahedral symmetry consisting of 60n identical protein subunits. The reason for the high symmetry lies behind the principle that the increasing symmetry elements reduce the amount of independent structural information, which is directly related to the length of DNA. Thus, the self-organization of tiny subunits into a giant biological molecule can be regarded as the process of not only the structural growth but the amplification of molecular information. We show here that, through metal-ligand interactions, simple banana-shaped organic molecules self-organize into finite, spherical coordination networks with a diameter of up to 7 nm.[1] The spherical coordination networks consist of 36 components (12 equivalent metals and 24 equivalent ligands) and possess cuboctahedron symmetry.

We expect that, if the ligand framework is slightly bent, the coordination network will develop with a constant radius of curvature and a spherical finite network will be obtained (scheme), reminiscent of graphite *vs* fullerene formation from sp^2 carbons. On a basis of this idea, we designed ligands **1a** and **b** and examined their



complexation with naked Pd^{II} ions in a square-planar geometry.

Results

When ligand **1a** (0.02 mmol) was treated with $Pd(NO_3)_2$ (0.01 mmol) in dimethyl sulfoxide (DMSO)-d_6 (1.0 mL) at 70 °C for 4 h, the quantitative self-assembly of a single product was observed by ^1H NMR spectroscopy. Single crystals of **2b** were obtained by very slow vapor diffusion of 1,1,2-trichloroethane into a DMSO solution of **2b**. With a CCD detector, Mo–K_α radiation (55 kV, 30 mA) afforded low resolution data (only 874 unique reflections (>2σ(I))). The poor quality of the data was due to severe disorder of solvents and anions in the extraordinarily large void within the spherical framework of **2b**. However, synchrotron X-ray radiation with high flux and low divergence (NW2 beamline) provided much higher quality of data with 2717 unique reflections (>2σ(I)), from which the spherical $M_{12}L_{24}$ structure of **2b** was solved with all the heavy atoms being refined anisotropically. The crystal system is cubic ($a = b = c = 47.689(4)$ Å) and the cell volume is 108,456(16) $Å^3$. Surprisingly, the framework of **2b** occupies only 20% of the cell volume (as estimated by Platon program), remaining 80% being occupied by disordered solvents and counter ions. The diameter of a sphere in which **2b** is inscribed is 3.4 nm. The closest Pd–Pd distance is 1.3 nm while the furthest one is 2.6 nm.

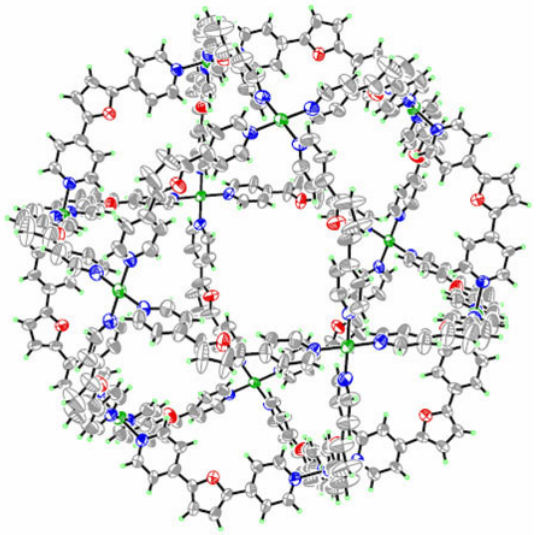


Figure Crystal structure of sphere **2b.** Counterions and solvent are omitted for clarity.

References

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