Chemistry

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Self-assembly of an M_6L_{12} coordination cube

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Introduction

Self-assembly of coordination polyhedra has received attention in recent years. Large discrete assemblies of bridging ligands and metal ions often have high symmetry corresponding to Platonic and Archimedean solids. Modulation of the ligand structure and the coordination geometry of the metal ion can control the possible polyhedra. For example, square planar metals and bent bidentate bridging ligands assemble into three dimensional, closed, M_nL_{2n} coordination spheres (n = 6, 12, 24, 30, and 60).

Recently, we demonstrated that the bent bridging ligand 1,3-bis(4-pyridyl)benzene and square planar Pd^{2+} ions self-assemble into an $M_{12}L_{24}$ coordination sphere with cubooctahedral symmetry. We report here that ligand **1** assembles into an M_6L_{12} molecular cube upon complexation with Pd^{2+} (Scheme 1). The six palladium ions exist in the center of each face of the cube and have octahedral symmetry.

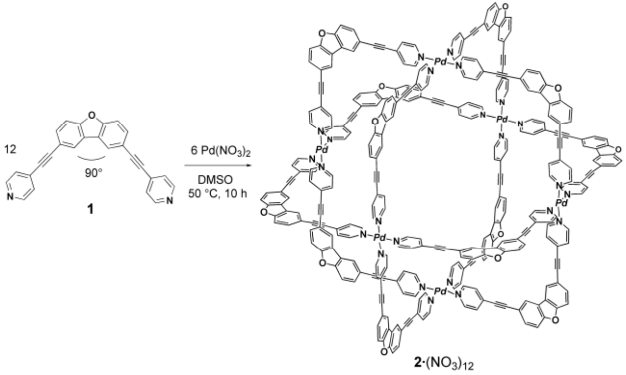

Figure 1 Self-assembly of $M_{12}L_{24}$ cubic **2**.

Results

We designed a molecular cube in which Pd^{2+} ions are located in each face and ligand **1** acts as the corner pieces. When ligand **1** (10 μmol) was treated with $Pd(NO_3)_2$ (5.0 μmol) in DMSO-d_6 (1.0 mL) at 50 °C for 10 h, the quantitative self-assembly of a single product was shown by ^{1}H NMR spectroscopy. The down field shift of the signals compared to ligand **1**, particularly for the pyridyl α- and β-hydrogen atoms ($\Delta\delta$ = 0.62 and 0.33 ppm, respectively), is characteristic of the metal–ligand complexation.

After anion exchange from NO_3^- to $CF_3SO_3^-$ ions, cold-spray ionization mass spectrometry (CSI-MS) confirmed the M_6L_{12} complex with a molecular weight of 6872.2 Da. Intense peaks at m/z 1569.6, 1225.5, 996.7, 844.1 and 729.9 were assigned to $[M-(CF_3SO_3)_4]^{4+}$, $[M-(CF_3SO_3)_5]^{5+}$, $[M-(CF_3SO_3)_6]^{6+}$, $[M-(CF_3SO_3)_7+(DMSO)]^{7+}$ and $[M-(CF_3SO_3)_8+(DMSO)_2]^{8+}$, respectively (Fig. 2). The cube **2** is remarkably stable and only counter ion dissociation was observed.

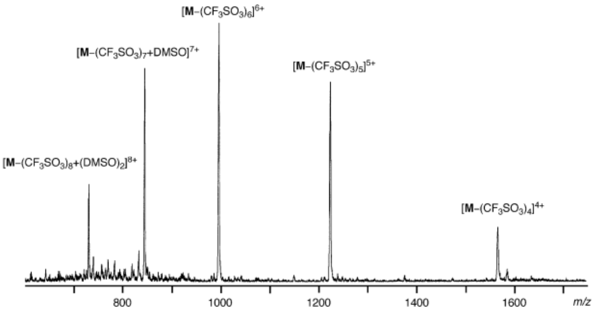

Figure 2 CSI-MS spectrum of **2**. (CH_3CN : DMSO = 10 : 1, $CF_3SO_3^-$ salt).

The structure of complex $\mathbf{2}\cdot(CF_3SO_3)_{12}$ was determined by X-ray diffraction analysis (Fig. 3). By the slow diffusion of THF into a DMSO solution of complex **2** over three weeks, we successfully obtained single crystals which were suitable for crystallographic analysis. Although the severe disorder of solvent molecules and anions in the cavity of $\mathbf{2}\cdot(CF_3SO_3)_{12}$ made it difficult to obtain high quality data, synchrotron X-ray irradiation with high flux and low divergence provided diffraction data capable of structure determination, which confirmed the cubic type M_6L_{12} structure. The dimensions of nanoscale cube **2** are approximately 3 x 3 x 3 nm (27 nm^3).

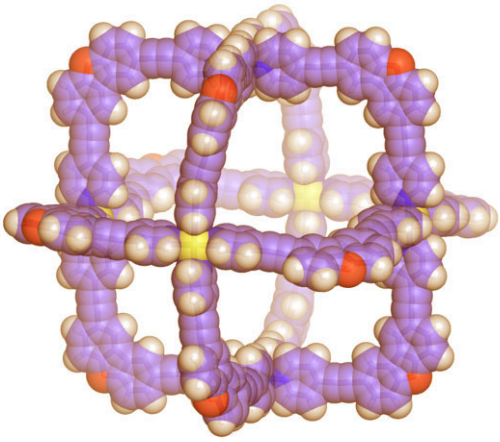

Figure 3 The X-ray crystal structure of **2**. Counter ions and solvent molecules are omitted for clarity.

References

[1] K. Suzuki *et al.*, *Chem. Commun.*, 1638 (2009).

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