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Metal–Organic Polyhedra

Metal–Organic Hendecahedra Assembled from Dinuclear Paddlewheel Nodes and Mixtures of Ditopic Linkers with 120 and 90° Bend Angles**

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Nature has demonstrated the extraordinary ability of biological systems to form large and intricate supramolecular arrays from small and simple building blocks, giving rise to a wide variety of structures and functions. In the past two decades, abiological self-assembly of molecular architectures has evolved into a field of intense investigation in supramolecular chemistry.[1] Besides their aesthetic appeal, some of these assemblies become useful as molecular vessels for selective guest inclusion, protection of sensitive molecules, asymmetric catalysis, and chemical sensing.[2] Among them, coordination polyhedra are one of the fastest-growing families of such supramolecular entities, because coordination-driven assembly allows the selection of metal ions or clusters with different coordination modes and the choice of bridging ligands with a variety of shapes.[3] Most of the coordination polyhedra were assembled from single metal ions and organic bridging ligands, which were mainly pyridine-based.

As a metal cluster node, the dinuclear paddlewheel unit has emerged as a common four-connected building block in the synthesis of highly symmetric coordination polyhedra, also called metal–organic polyhedra (MOPs). It has been used in the design of a number of MOPs structurally controlled by the geometry of the bridging ligand. However, only limited geometric types of polyhedra have been realized with this popular building unit.[3e,4] Typically, the combination of a ditopic bridging ligand with a bend angle of 120° and such a dinuclear paddlewheel unit gave rise to a coordination cuboctahedron.[5] Similarly, a 90° bridging ligand led to a coordination octahedron (Figure 1).[4c,6]

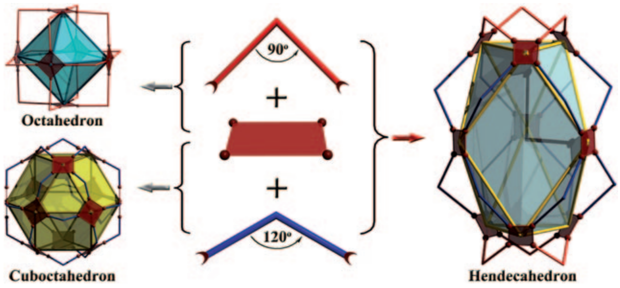
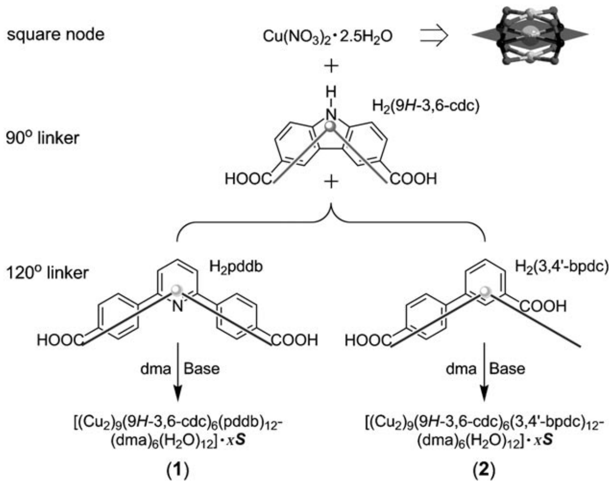


Figure 1. The self-assembly of three metal–organic polyhedra with ditopic angular linkers and four-connected square nodes.

However, almost all of the reported coordination polyhedra contain bridging ligands with a single bend angle, leading to Platonic or Archimedean solids with an even number of edges and an even number of faces. It occurred to us that the application of a mixture of bridging linkers with different bend angles in coordination-driven self-assembly should allow access to novel structural types. With this background in mind, we attempted the assembly of coordination polyhedra using a mixture of ditopic carboxylate ligands with 120 and 90° bend angles and succeeded in obtaining two isostructural metal–organic hendecahedra (Figure 1 and Scheme 1). These coordination hendecahedra have an odd number of faces (eleven) and an odd number of vertices (nine). To the best of our knowledge, compounds **1** and **2** (Scheme 1) represent the first molecular polyhedra with an odd number of faces and an odd number of vertices. Prior to this work, no attempts have been reported in the self-assembly of coordination polyhedra using bridging ligands with different bend angles and metal cluster nodes.[7]



Scheme 1.

The first combination of ligands adopted for the assembly of a molecular hendecahedron was 9*H*-carbazole-3,6-dicar-

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boxylate (9*H*-3,6-cdc^{2-}) and 4,4′-pyridine-2,6-diyldibenzoate (pddb^{2-}), which we designed and synthesized. The former has a bend angle of about 90°, the latter of 120°. The reaction of H_2(9*H*-3,6-cdc), H_2pddb, and $\mathrm{Cu(NO_3)_2\cdot 2.5\,H_2O}$ in the presence of base (2,6-dimethylpyridine) in *N,N*-dimethylacetamide (dma) at room temperature produced the first hendecahedral cage compound, $[(\mathrm{Cu}_2)_9(9H\text{-3,6-cdc})_6(\mathrm{pddb})_{12}(\mathrm{dma})_6(\mathrm{H_2O})_{12}]\cdot x\boldsymbol{S}$ (**1**, $\boldsymbol{S}$ = non-coordinated solvent molecule, Scheme 1), isolated as blue-green plate-like crystals suitable for single-crystal X-ray diffraction studies. The identity of the bulk sample was confirmed by powder X-ray diffraction (PXRD, see the Supporting Information).

The structure of **1** was determined by single-crystal X-ray diffraction studies. Compound **1** crystallizes in the $R\bar{3}c$ space group. The molecule of **1** has crystallographically imposed D_3 symmetry, although the idealized point group symmetry is D_{3h}. As shown in Figure 2 a, c, the molecular structure of **1** consists of nine $\mathrm{Cu_2}$ units, six 9*H*-3,6-cdc^{2-} ligands, and twelve pddb^{2-} ligands. Three 9*H*-3,6-cdc^{2-} ligands link three $\mathrm{Cu_2}$ units to form a triangular moiety. Two of these moieties are connected through three additional $\mathrm{Cu_2}$ paddlewheel units and twelve pddb^{2-} entities, six on each triangular moiety. The compound contains 2 + 6 triangular and three quadrilateral windows of sizes (atom-to-atom distance along an edge after considering van der Waals' radii) 7.0 × 7.0 × 7.0, 7.0 × 11.8 × 12.3, and 11.8 × 12.3 × 11.8 × 12.3 Å, respectively. The bend angles of 9*H*-3,6-cdc^{2-} and pddb^{2-} linkers in **1** are 88 and 115°, respectively, slightly deviated from the ideal 90 and 120° angles. The dimensions of **1** are approximately 3.7 nm in height and 3.0 nm in diameter. It is noteworthy that the ligand pddb^{2-} also results in a unique nitrogen-rich interior of the polyhedron. In crystals, these molecules are held together by π···π interactions between pddb^{2-} ligands from adjacent molecular polyhedra to form a porous material (Figure 2 d) with an overall 75 % solvent-accessible volume calculated using the PLATON routine.[8]

When the square $\mathrm{Cu_2}$ units are viewed as vertices and the ligands as edges, **1** can be described as a hendecahedron (Figure 2 e, top) with 2 + 6 triangular and three quadrilateral faces. It can also be viewed as two tapered face-sharing octahedra, as shown in Figure 2 e, bottom. The hendecahedron possesses a $[3^8.4^3]$ (face symbol) pattern of polygonal composition and a $(3^3.4)_6(3.4.3.4)_3$ topology (vertex symbol).[9] Such a hendecahedral framework is unprecedented and interesting not only in synthetic chemistry but also in geometry. It is also remarkable to notice how well the two angular linkers and the square nodes fit together. Alternatively, when each bridging ligand is viewed as a vertex, **1** can be described as an elongated triangular orthobicupola, a Johnson solid, which can also be viewed as an anticuboctahedron with the two triangular-cupola moieties separated by a hexagonal prism (Figure 2 f). It has idealized D_{3h} symmetry with twenty faces: twelve quadrilateral faces and eight triangular faces. Only nine quadrilateral faces are occupied by $\mathrm{Cu_2}$ units; three of the six quadrilateral faces of the hexagonal prism are empty.

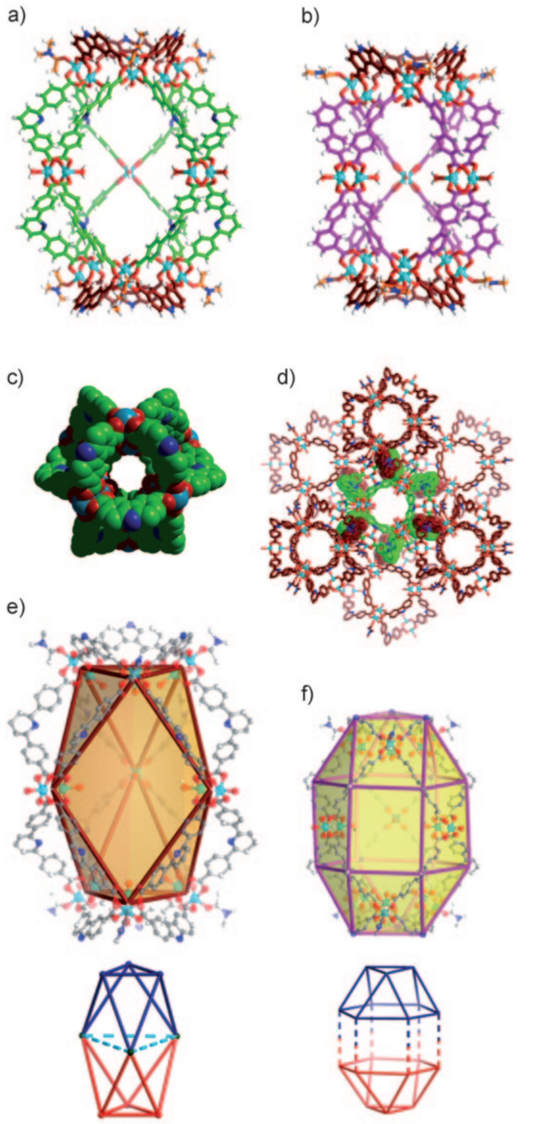

Figure 2. a, b) The molecular structures of **1** and **2**, respectively (Cu cyan; O red; N blue; C maroon, green, orange, or pink; H white). c) Space-filling representation of **1** viewed from the [001] direction. d) Molecular packing of **1** in the crystal structure with space-filling representation highlighting the intermolecular π–π interactions. e, f) Schematic representation of the polyhedra when considering the metal clusters or ligands, respectively, as vertices.

Under synthetic conditions similar to that of **1**, biphenyl-3,4′-dicarboxylate (3,4′-bpdc^{2-}), an unsymmetrically shortened ligand with a bend angle of 120°, gave rise to another metal–organic hendecahedral cage compound, $[(\mathrm{Cu}_2)_9(9H\text{-3,6-cdc})_6(3,4'\text{-bpdc})_{12}(\mathrm{dma})_6(\mathrm{H_2O})_{12}]\cdot x\boldsymbol{S}$ (**2**, Scheme 1), the structure of which was also determined by single-crystal X-ray diffraction. The phase purity of the bulk sample was confirmed by PXRD (see Supporting Information). Compound **2** is isostructural with **1** and also crystallizes in the $R\bar{3}c$ space group, thus indicating that the molecular hendecahedron is likely a common structural type from a combination of suitable bridging ligands with 90 and 120° bend angles and four-connected planar nodes (Figure 2 b). As expected, the 3.2 × 2.4 nm overall dimensions of **2** and the window sizes are consistently smaller than those of **1**, proportional to the size of the ligand.

Preliminary gas sorption studies were also performed with an evacuated sample of **1** (Figure 3). The N_2 sorption isotherm shows type I gas sorption behavior indicative of a microporous material, with a Langmuir surface area of 372 $m^2 g^{-1}$.

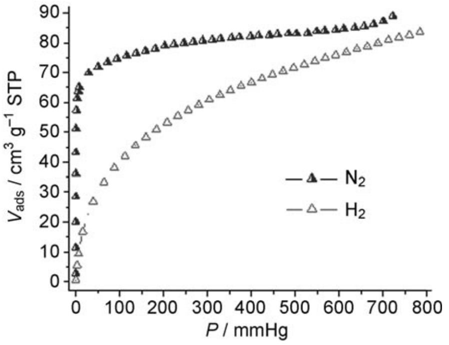

Figure 3. N_2 and H_2 adsorption isotherms of **1** at 77 K.

Both N_2 and H_2 uptakes are relatively low with respect to the calculated accessible surface area, presumably because of the blockage of the cavity windows in the activated sample. Indeed, after activation the sample became almost amorphous, as verified by PXRD. This loss of crystallinity may be attributed to position rearrangement of the molecular cages of **1** with respect to one another upon activation. On the molecular level, the cage structure of **1** and its porosity should be maintained.[4c] However, we cannot rule out the possibility of structural disintegration.

In summary, two metal–organic hendecahedra have been obtained through self-assembly of paddlewheel Cu_2 units and two mixtures of two ditopic linkers with 90 and 120° bend angles. The hendecahedral compounds represent the first examples of molecular polyhedra with an odd number of faces and an odd number of vertices. The work reveals the vast potential of using a mixture of bridging ligands with different bend angles to obtain novel coordination polyhedra that are inaccessible using reported synthetic methods.

Experimental Section

Synthesis of ligands: H_2(9*H*-3,6-cdc) was synthesized according to a reported procedure.[6,10] H_2pddb and H_2(3,4′-bpdc) were synthesized by Suzuki coupling reactions. Details can be found in the Supporting Information.

1: *N,N*-dimethylacetamide (dma, 4 mL) containing H_2(9*H*-3,6-cdc) (25.6 mg, 0.1 mmol) and H_2pddb (32.0 mg, 0.1 mmol) was mixed thoroughly with dma (2 mL) containing $Cu(NO_3)_2 \cdot 2.5\,H_2O$ (48.0 mg, 0.2 mmol). 2,6-dimethylpyridine (44.0 mg, 0.4 mmol) was added to this solution to give a green solution after thorough mixing. The vial was sealed and allowed to stand at room temperature. After 10 days, homogeneous blue-green plate-like crystals of **1** were collected, washed with dma and EtOH, and dried in air (yield: 35 mg). PXRD, thermogravimetric analysis (TGA), and FTIR of as-isolated **1** are shown in Figures S1, S3, and S4, respectively, in the Supporting Information.

2: *N,N*-dimethylacetamide (dma, 3 mL) containing H_2(9*H*-3,6-cdc) (25.6 mg, 0.1 mmol) and H_2(3,4′-bpdc) (24.0 mg, 0.1 mmol) was mixed thoroughly with dma (3 mL) containing $Cu(NO_3)_2 \cdot 2.5\,H_2O$ (48.0 mg, 0.2 mmol). 2,6-dimethylpyridine (219.0 mg, 2.0 mmol, excess) was added to this solution to give a green solution after thorough mixing. The vial was sealed and allowed to stand at room temperature. After 15 days, homogeneous blue-green block crystals of **2** were collected, washed with dma and EtOH, and dried in air (yield: 30 mg). PXRD, TGA, and FTIR of as-isolated **2** are shown in Figures S2, S3, and S5, respectively, in the Supporting Information.

Single-crystal X-ray crystallographic studies: Data were collected on a Bruker-AXS APEXII X-ray diffractometer at 110 K. Raw data collection and reduction were done using APEX2 software.[11] Adsorption corrections were applied using the SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[12] Non-hydrogen atoms (except some in dma molecules) were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of ligands and dma were calculated in ideal positions with isotropic displacement parameters; those of water were originally found from electron density peaks and then refined with restrictions. Free solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. The diffuse electron densities resulting from the these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.[8] The contents of the solvent region are not represented in the unit cell contents in crystal data. Attempts to determine the final formula of such compounds from the SQUEEZE results combined with elemental analysis and TGA data were also unsuccessful because of the volatility of crystallization solvents; therefore, an accurate data set could not be obtained. Crystal data for **1**: $C_{336}H_{252}Cu_{18}N_{24}O_{90}$, $M_r = 7209.34$, hexagonal, space group $R\bar{3}c$, $a = b = 38.289(4)$, $c = 120.10(1)$ Å, $V = 152\,479(30)$ Å^3, $Z = 6$, $d_{calcd} = 0.471\ g\,cm^{-3}$, R_1-$(I > 2\sigma(I)) = 0.0743$, wR_2(all data) $= 0.2375$, GOF $= 0.934$. **2**: $C_{276}H_{216}Cu_{18}N_{12}O_{90}$, $M_r = 6284.33$, hexagonal, space group $R\bar{3}c$, $a = b = 33.423(7)$, $c = 107.88(2)$ Å, $V = 104\,363(36)$ Å^3, $Z = 6$, $d_{calcd} = 0.600\ g\,cm^{-3}$, $R_1(I > 2\sigma(I)) = 0.0774$, wR_2(all data) $= 0.1610$, GOF $= 0.922$; CCDC 745163 (**1**) and 745164 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Adsorption measurements: Gas adsorption measurements were performed using an ASAP 2020 gas adsorption analyzer. The gases used were of ultrapure quality. Before adsorption, the sample was activated by solvent exchange with subsequent pumping under a dynamic vacuum at RT and 50 °C as detailed in the Supporting Information.

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