

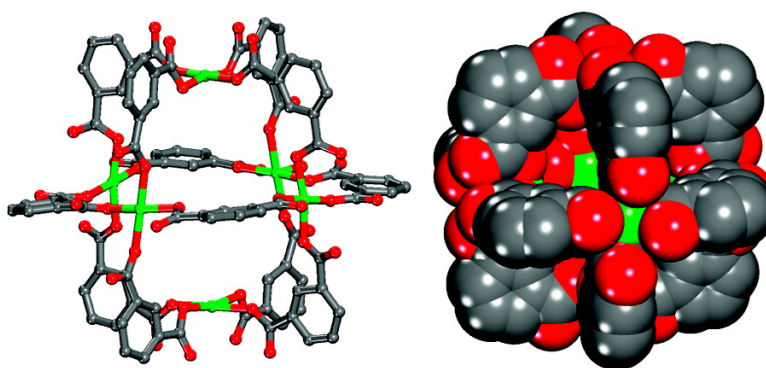
Communication

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## Supramolecular Building Blocks (SBBs) and Crystal Design: 12-Connected Open Frameworks Based on a Molecular Cubohemioctahedron

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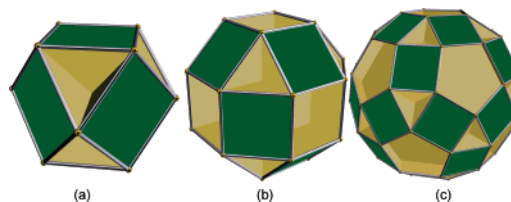
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Molecular building blocks (MBBs) facilitate the design and construction of functional metal–organic materials (MOMs) exemplified by metal–organic frameworks (MOFs), coordination polymers, metallo dendrimers, and metal–organic polyhedra.<sup>1</sup> The MBB approach represents an evolution of the “node-and-spacer” approach,<sup>1g</sup> which exploits the geometric attributes of metal ions and rigid ligands to generate 2D and 3D networks.<sup>2</sup> The relative size of inorganic MBBs (coordination clusters) vs metal ions has afforded unprecedented breakthroughs in terms of scale and porosity.<sup>3</sup> Prior to the assembly process, the inorganic MBBs, typically formed in situ, are targeted for the shape, geometry, and directionality necessary to augment a given anticipated net. The points of extension of the MBBs define the building units, which simultaneously coincide with the vertex figures of the net. Highly symmetrical inorganic MBBs with 3-, 4-, and/or 6-connectivity are readily accessible and are predominately exploited for the generation of MOFs with the respective *n*-connected net.<sup>4</sup> Suitable targets in terms of the nets themselves are the edge transitive nets, a special class of *n*-connected nets with one kind of edge.<sup>5</sup>

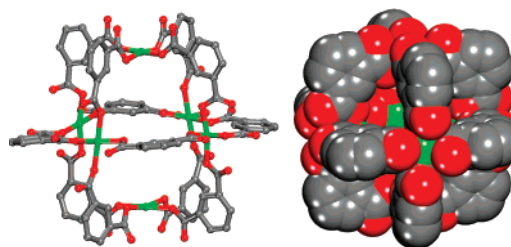
A singular-edge transitive net, the *fcu* net (the only quasi-regular net), is a net that can be targeted as a blueprint for a uninodal (12-connected)-based MOF. The vertex figure of the *fcu* net is the cuboctahedron, a polyhedron that holds the attributes that an SBB would need for the assembly of an MOF having an augmented *fcu*-like net. This relationship between the SBB and a specific net illustrates the potential to derive pathways for the construction of 3D MOFs from SBBs that, when rigidly linked, are *uniquely suited for a particular net*. Furthermore, they offer new horizons in terms of scale and chemical functionality.

A class of SBBs that are potentially accessible in synthetic chemistry are the three metal–organic polyhedra that resemble faceted polyhedra based on square polygons assembled via their vertices (Figure 1).<sup>6</sup> The first examples of such structures are based upon square dicopper tetracarboxylate [Cu<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>] MBBs that link at 120° through 1,3-benzenedicarboxylate (bdc) ligands to form a *small rhombihexahedron* (Figure 1b).<sup>7</sup> They can be “decorated” at their vertices by a range of functional groups, exhibit molecular weights of at least 7 kDa, and serve as SBBs via flexible bdc ligands that facilitate quadruple cross-linking of the 24 vertices of the *small rhombihexahedron*.<sup>8</sup> There exist only two other faceted polyhedra based upon square MBBs, the *cubohemioctahedron* (Figure 1a) and the *small rhombidodecahedron* (Figure 1c), which until now are yet to be explored as potential SBBs for synthesis of 3D MOFs.

Herein, we report the first examples of MOFs based on the assembly of cubohemioctahedra as SBBs as opposed to discrete molecules or ions.<sup>9</sup> The novel anionic cubohemioctahedron of formula [M<sub>6</sub>(bdc)<sub>12</sub>]<sup>12-</sup>, M = Ni, Co, (Figure 2) sustains a



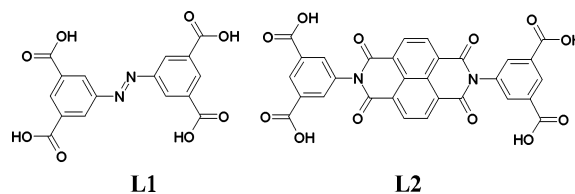
**Figure 1.** Three-faceted polyhedra that can be generated via linking of molecular squares: (a) cubohemioctahedron, (b) small rhombihexahedron, (c) small rhombidodecahedron.



**Figure 2.** Prototypal metal–organic cubohemioctahedron [M<sub>6</sub>(bdc)<sub>12</sub>]<sup>12-</sup>, in stick (left) and space-filling modes (right); hydrogen atoms have been omitted for clarity.

12-connected *fcu* net<sup>10</sup> through rigid cross-linking of the bdc ligands at each of its 12 vertices.

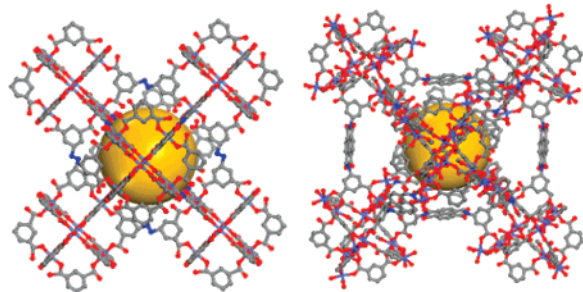
Reaction between 3,5-H<sub>4</sub>ATC, 3,5-dicarboxyl-(3',5'-dicarboxylazophenyl)benzene,<sup>11</sup> **L1**, and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O affords [Ni<sub>2</sub>(**L1**)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>, **1**.<sup>12</sup> The crystal structure of **1** is built from centrosymmetric [Ni<sub>6</sub>(**L1**)<sub>12</sub>]<sup>12-</sup> anions that are connected by **L1**.



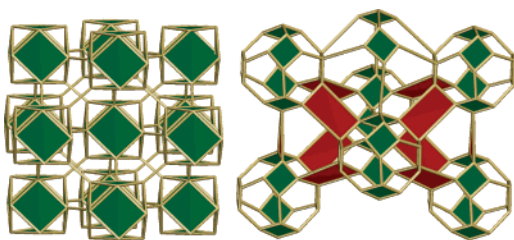
Each Ni cation, Ni1, assumes octahedral geometry: the equatorial plane is occupied by four monodentate carboxylato oxygen atoms from different **L1** ligands (Figure 2); aqua ligands lie in the axial positions. The charge is balanced by a crystallographically disordered Ni(II) cation, Ni2, that bridges the axial aqua ligand and two of the four carboxylato moieties. The disorder of Ni2 means that it appears to symmetrically coordinate to the four carboxylato moieties, facilitating crystallization in space group *Fm* $\bar{3}$ . Large, red, block crystals of [Co<sub>2</sub>(**L2**)(MeOH)(H<sub>2</sub>O)<sub>4</sub>]<sub>n</sub>, **2**, were obtained from H<sub>4</sub>BIPA-TC (**L2**) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.<sup>13</sup> The crystal structure of **2** reveals that the structure is sustained by the same cubohemioctahedron as **1** with each Co moiety, Co1, bonded to ordered

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**Figure 3.** X-ray crystal structures of **1** (left) and **2** (right). Hydrogen atoms omitted for clarity.



**Figure 4.** Schematic representations of **1** and **2** showing the 12-connected augmented *fcu* (left)- and NbO (right)-like topologies.

dicationic  $\text{Co}(\text{H}_2\text{O})_3$  moieties,  $\text{Co}_2$ . The  $\mu_2$ -aqua ligand hydrogen bonds with the two monodentate carboxylates as has been observed in a discrete analogue.<sup>14</sup> The overall symmetry of **2** is therefore reduced, compared to that of **1**, but space group  $Pa\bar{3}$  is a maximal non-isomorphic subgroup (type **IIa**) of space group  $Fm\bar{3}$ . The Ni analogue of **2**, **3**, can also be prepared via solvent layering and forms small cube-shaped, pale-yellow crystals.

The relative scale of **1–3** is determined by the ligands **L1** and **L2**, with **L2** being ca.  $1.5\times$  the length of **L1**. The cubohemioctahedron of **1** possesses cavities with inner dimensions of ca.  $8.7 \text{ \AA}$  if one considers the van der Waals cross section between adjacent metals, while the distorted cubohemioctahedron of **2** and **3** has a corresponding dimension of ca.  $9.08 \text{ \AA}$  (Figure 3). Much larger tetrahedral and octahedral cavities develop between the cubohemioctahedral SBBs as the ligands connect through triangular windows or square faces to generate idealized triangular windows proportional to the length of the ligands. The octahedral cavity is cross-shaped and exhibits internuclear distances of  $23.3 \text{ \AA}$  in **1** and  $32.9 \text{ \AA}$  in **2** and **3** (Figure S5).

The topology of **1–3** can be rationalized in two different but equally acceptable ways as depicted in Figure 4. The spheroid building unit can be interpreted as a 12-connected net in which the squares are assembled by connecting the centroids of the benzene rings. A decorated cubohemioctahedron SBB of formula  $\text{M}_{12}\text{L}_6$  is thereby revealed. The SBBs are connected through **L1** or **L2** to generate the observed face-centered cubic network. On the other hand, if one interprets the carbon bearing the carboxylate groups as a point of extension, then the framework is assembled from two distinct 4-connected nodes: a square MBB and a rectangular ligand. The  $\text{M}_{12}\text{L}_6$  moieties would be regarded as an assembly of squares, rectangles, and hexagons, generating cages resembling those in the zeolite structure *sodalite*. The assembly of such 4-connected nodes can be rationalized as having NbO-like topology.

In summary, we report herein a novel cubohemioctahedron SBB that can be linked by ligands **L1** and **L2** to form nanoscale 12-connected *fcu*-like frameworks. That such SBBs can be exploited to form MOFs via a crystal engineering approach implies that polyhedral SBBs are amenable to crystal design approaches that facilitate the generation of nets that cannot be readily accessed through MBBs, that the limit of scale for metal–organic materials

has not yet been realized, and that a high degree of fine-tunability will be feasible for such MOFs. Future work will focus upon the properties of **1–3**, and preliminary studies show that **1** exhibits hydrogen adsorption, whereas **2** and **3** undergo guest and/or metal exchange.<sup>14</sup>

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**Supporting Information Available:** XRPD, hydrogen adsorption, UV/vis, IR, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Solvothermal: **L1** (9.24 mg, 0.025 mmol),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (15 mg, 0.05 mmol), DMF (1 mL), HMTA (0.1 mL, 1 M in  $\text{H}_2\text{O}$ ), and  $\text{HNO}_3$  (0.400 mL, 2.81 M in DMF) were placed in a 20-mL vial, which was sealed, heated to  $85 \text{ }^\circ\text{C}$  for 12 h, and then cooled to room temperature. Crystallographic data for **1**:  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_{11}$ ,  $M = 549.68$ , cubic,  $Fm\bar{3}$ ,  $a = 31.3400(7) \text{ \AA}$ ,  $V = 30,782.0(12) \text{ \AA}^3$ ,  $Z = 24$ .  $R$  values ( $I > 2\sigma(I)$ ):  $R_1 = 0.1432$ ,  $wR_2 = 0.3462$ . (13) Slow diffusion: Bottom layer **L2** (2.97 mg, 0.005 mmol), 2,6-lutidine (4.64  $\mu\text{L}$ , 0.04 mmol), caffeine (9.00 mg, 0.046 mmol) in 3 mL DMF, middle layer 1 mL MeOH, top layer  $\text{Co}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_6$  (3 mg, 0.0103 mmol) dissolved in 3 mL MeOH. Crystallographic data for **2**:  $\text{C}_{29}\text{H}_{23}\text{Co}_2\text{N}_2\text{O}_{18} \cdot x\text{H}_2\text{O}$ ,  $M = 805.37$ , cubic  $Pa\bar{3}$ ,  $a = 39.288(22) \text{ \AA}$ ,  $V = 60,642(6) \text{ \AA}^3$ ,  $Z = 24$ .  $R$  values ( $I > 2\sigma(I)$ ):  $R_1 = 0.1296$ ,  $wR_2 = 0.2902$ .
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