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Nanoballs: nanoscale faceted polyhedra with large windows and cavities

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Self-assembly of molecular polygons by linking their vertices provides nanosized faceted polyhedra that are porous, contain chemically accessible sites on their facets, are chemically robust, neutral and soluble in common laboratory solvents.

In recent years chemists have developed synthetic design strategies that are based upon the concepts of self-assembly. This supramolecular approach to synthesis, a 'bottom-up'[1] approach to nanoscience, has afforded a new generation of discrete, high molecular weight compounds. These compounds are exemplified by nanoscale spheroid architectures that are based upon Platonic (regular) and Archimedean (semi-regular) solids.[2–9]

Nanoscale versions of Platonic and Archimedean solids have been prepared by one of two approaches: edge-sharing of molecular polygons,[7] or connection of appropriately designed molecular vertices by linear bifunctional rod-like ligands.[10] Edge-sharing of molecular polygons affords closed convex polyhedra whereas connection of vertices generates open structures that are the edge-skeletons of polyhedra. However, there exist other examples of uniform polyhedra[11,12] that to our knowledge remain unexplored in the context of synthetic chemistry. Uniform polyhedra include prisms and antiprisms, polyhedra having star faces and vertices, and polyhedra with both concave and convex faces.[13] In particular, there are nine uniform polyhedra that are closely related to Platonic and Archimedean solids but differ in that their convex faces can be constructed by linking the vertices of regular polygons. Such structures are termed faceted polyhedra[14] since they must contain both open (concave) and closed (convex) faces (*i.e.* faceting).

As revealed by Fig. 1 there are three faceted uniform polyhedra that can be generated by linking the vertices of squares and which one occurs will be strongly influenced by the angle subtended by the 'spacer' moiety that links the vertices: *cubohemioctahedron* (90°) $<$ *small rhombihexahedron* (120°) $<$ *small rhombidodecahedron* (144°). Therefore, judicious control of the angle subtended by the vertices of the squares should afford control over which polyhedron will result. The molecular squares that we have targeted for study are the previously reported metal-organic secondary building units[15] (SBUs) $M_2(RCO_2)_4$ **A**. **A** is illustrated in Fig. 2 and represents a ubiquitous SBU that is present in nearly 900 crystal structures in the Cambridge Structural Database (CSD).[16] It should be noted that it has already been demonstrated that use of polycarboxylate ligands in $M_2(RCO_2)_4$ (*e.g.* benzene-1,4-dicarboxylate[17] or benzene-1,3,5-tricarboxylate[18]) affords self-assembled infinite structures with predictable topology and relatively high thermal stability. It occurred to us that the angular bifunctional ligand benzene-1,3-dicarboxylate, bdc, which subtends an angle of 120°, offers the possibility of generating discrete nanoscale *small rhombihexahedra* or supramolecular isomers[19] in the form of novel infinite coordination polymers.

Nanoscale *small rhombihexahedra* **1**, are formed by layering methanolic $Cu(NO_3)_2$ and H_2bdc onto a solution of pyridine that contains templates such as nitrobenzene or 1,2-dichlorobenzene. Single crystals of $[(L)(S)Cu_2(bdc)_2]_{12}$, L = pyridine, S = methanol, **1a**, form within hours. Alternatively, microcrystals of **1a** can be obtained quantitatively by direct mixing of the above reagents. The crystal structure of **1a**† is illustrated in Fig. 3 and reveals that it can be described as being composed of vertex linked molecular squares (green) that self-assemble into *small rhombihexahedra*. **1a** contains pyridine ligands that are axially bonded to the metal ions that lie at the exterior surface and MeOH ligands at the interior surface metal binding sites. The internal cavity has a volume of *ca.* 1 nm^3 that is easily large enough to encapsulate C_{60}. To our knowledge, **1a** represents the largest spheroid structure that has yet been crystallographically characterized. It has a molecular volume of >10 nm^3 and a molecular weight of 6.80 kDa. **1** can also be formed for L = S = methanol, **1b**. Thus far we have isolated two crystalline phases that contain **1b**, a monoclinic and a cubic phase.†

An isomer of the *small rhombihexahedron* $[(MeOH)_2Cu_2(bdc)_2]_{12}$ **2** crystallizes under similar conditions with 2,6-dimethylpyridine, a non-coordinating base, present instead of pyridine. **2** is illustrated in Fig. 4 and the connectivity of the SBUs is different. **2** has a molecular weight of 6.23 kDa, a molecular volume of *ca.* 10 nm^3 and exhibits textbook hexagonal close packing. Molecular modelling indicates insignificant difference in terms of torsional strain between **1** and **2** (calculated using MSIs Cerius^2 Minimizer module).

1 and **2** are distinguished by the following features: they are neutral and soluble in organic solvents; they are chemically robust because of the stability of the square SBU (confirmed by high resolution mass spectrometry); they are likely to be chemically diverse because **A** exists for so many metals,

Fig. 1 The three types of faceted uniform polyhedra that can be generated by linking the vertices of squares only: *cubohemioctahedron*, *small rhombihexahedron* and *small rhombidodecahedron*.

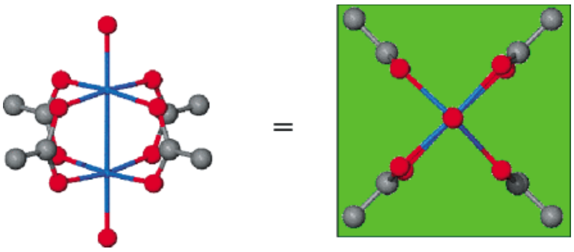

Fig. 2 The square SBU, $M_2(RCO_2)_4$ **A**, employed in this study. In the compounds described herein, **A** is schematically represented as a square (green).

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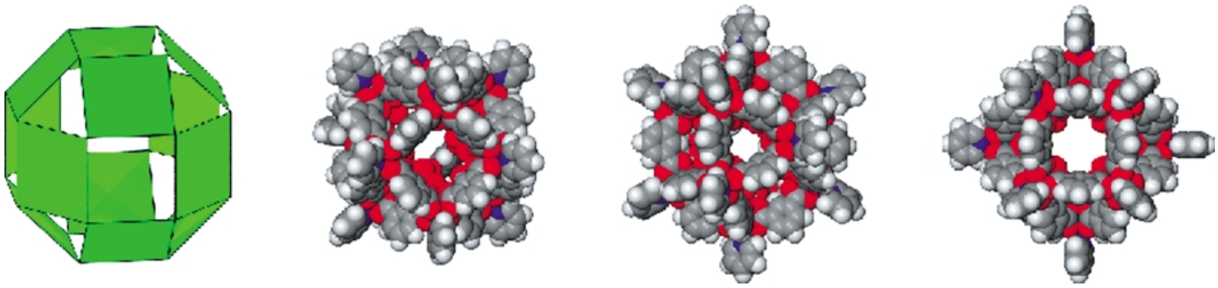

Fig. 3 Crystal structure of $[(L)(S)Cu_2(bdc)_2]_{12}$, L = pyridine, S = methanol, **1**. The schematic illustrates how linking of molecular squares generates the edge-skeleton of **1**. Note how the large bowl-shaped square and triangular windows provide access to the interior of **1**. Disordered solvent is found in these windows and in the 1 nm^3 internal cavity. There is high thermal motion and/or disorder in the ligands and the guest molecules but the structure of the core is well determined and unambiguous.

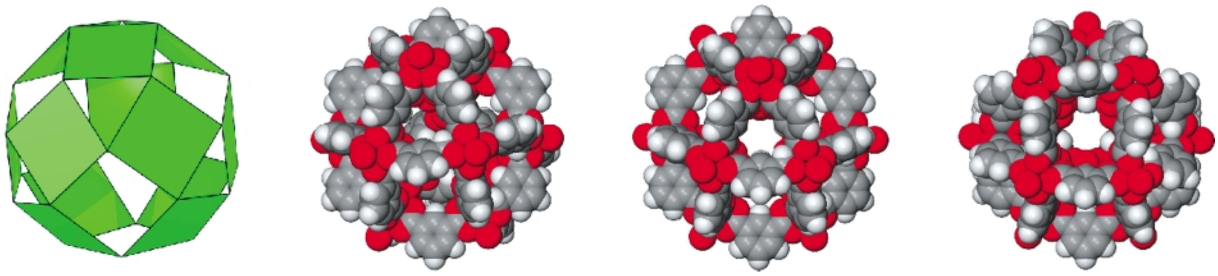

Fig. 4 Crystal structure of $[(S)_2Cu_2(bdc)_2]_{12}$, S = methanol, **2**. The schematic illustrates the subtle differences between the connectivity in **1** and **2**.

including magnetically active and catalytically active metals; they have both internal and external sites that are suitable for further chemical modification. Indeed, it is possible to envisage **1** and **2** as the building blocks for much larger structures by acting as the node of infinite networks[20] or as the core of mesoscale dendritic structures; their interior cavities can be accessed *via* triangular or square windows, which are bowl shaped and contain organic guests. Loss of coordinated molecules occurs at higher temperatures. Furthermore, judicious selection of angular spacers in the presence of molecular polygons should ultimately generate all nine faceted polyhedra and their structural isomers.

Notes and references

† *Crystallographic data:* intensity data for **1** and **2** were collected at 173 K on a Bruker SMART-APEX diffractometer using Mo-Kα radiation (λ = 0.7107 Å). The data were corrected for Lorentz and polarization effects and for absorption using the SADABS program. Structures were solved using direct methods and refined by full-matrix least squares on $|F|^2$.[11] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions and refined with temperature factors 1.2 times those of their bonded atoms.

Crystal data: for **1a**: triclinic, $P\bar{1}$, a = 26.202(9), b = 27.756(10), c = 28.408(10) Å, α = 92.583(5), β = 96.393(5), γ = 92.643(5)°, V = 20 483(12) Å^3, Z = 2, D_c = 1.279 g cm^{-3}, μ = 1.29 mm^{-1}, $F(000)$ = 7752, $2\theta_{max}$ = 37.88° ($-23 \leqslant h \leqslant 23$, $-25 \leqslant k \leqslant 25$, $-25 \leqslant l \leqslant 20$). Final residuals (for 2529 parameters) were $R1$ = 0.1386 for 10 314 reflections with $I > 2\sigma(I)$, and $R1$ = 0.2849, $wR2$ = 0.4220, GOF = 1.082 for all 31 316 data. Residual electron density: 0.93 and -0.51 e Å^{-3}.

For **1b** (monoclinic phase): monoclinic, $C2/c$, a = 33.933(7), b = 36.925(7), c = 29.577(6) Å, β = 93.4595(28)°, V = 36 991.0 Å^3, Z = 4, D_c = 1.353 g cm^{-3}, μ = 0.76 mm^{-1}, $F(000)$ = 15 582, $2\theta_{max}$ = 34.61° ($-28 \leqslant h \leqslant 28$, $-30 \leqslant k \leqslant 30$, $-24 \leqslant l \leqslant 13$). Final residuals (for 823 parameters) were $R1$ = 0.1353 for 3512 reflections with $I > 2\sigma(I)$, and $R1$ = 0.3056, $wR2$ = 0.4226, GOF = 1.031 for all 11 089 data. Residual electron density: 0.66 and -0.44 e Å^{-3}.

For **1b** (cubic phase): cubic, $Im\bar{3}m$, a = 27.6895(17) Å, V = 21 229.8 Å^3, Z = 2, D_c = 1.016 g cm^{-3}, μ = 1.24 mm^{-1}, $F(000)$ = 6454, $2\theta_{max}$ = 46.50° ($-30 \leqslant h \leqslant 27$, $-26 \leqslant k \leqslant 30$, $-29 \leqslant l \leqslant 30$). Final residuals (for 100 parameters) were $R1$ = 0.0784 for 996 reflections with $I > 2\sigma(I)$, and $R1$ = 0.1069, $wR2$ = 0.2953, GOF = 1.138 for all 1501 data. Residual electron density: 0.83 and -0.44 e Å^{-3}.

For **2**: hexagonal, $P6_3/m$, $a = b$ = 28.6458(19), c = 28.1649(26), V = 20 015.2 Å^3, Z = 2, D_c = 1.222 g cm^{-3}, μ = 1.32 mm^{-1}, $F(000)$ = 7326, $2\theta_{max}$ = 45.11° ($-21 \leqslant h \leqslant 30$, $-27 \leqslant k \leqslant 27$, $-22 \leqslant l \leqslant 30$). Final residuals (for 728 parameters) were $R1$ = 0.1116 for 4003 reflections with $I > 2\sigma(I)$, and $R1$ = 0.1837, $wR2$ = 0.3416, GOF = 1.317 for all 8931 data. Residual electron density: 1.16 and -1.53 e Å^{-3}.

CCDC 161338–161341. See http://www.rsc.org/suppdata/cc/b1/b102714j/ for crystallographic data in .cif or other electronic format.

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