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Coordination Polymers

Ternary Nets formed by Self-Assembly of Triangles, Squares, and Tetrahedra**

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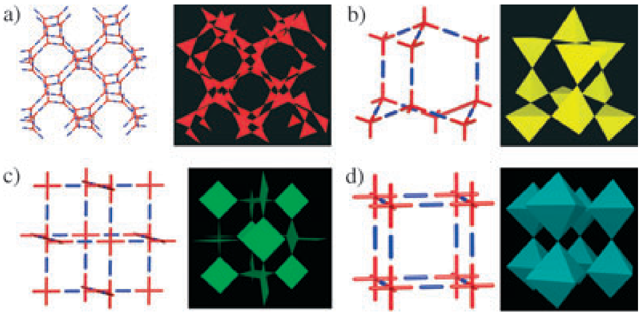
It has now been almost thirty years since Wells catalogued network structures in crystals[1] in a manner that has facilitated the crystal engineering[2] of a wide range of infinite 2D and 3D nets. That crystal engineered nets invoke geometric design principles means that a chemically diverse range of molecular building blocks (MBBs) are available for study as exemplified by coordination polymers (i.e. metal–organic networks),[3] polymers sustained by organometallic linkages[4] and hydrogen-bonded organic networks.[5] Coordination polymers are particularly attractive targets for study: metal coordination and cluster geometries are diverse but they are controllable in a manner that facilitates the design of nets with predictable topology and dimensions; metal moieties can be pre-selected so as to impart functional properties, such as magnetism,[6] luminescence[7] or, in the case of open-framework nets, permanent porosity;[3c,e,8] multifunctional organic ligands can also be selected for their geometric attributes. Coordination polymers can be rationalized and designed using the "node-and-spacer" approach,[3a,b] which simplifies molecular building blocks into topological points and lines. Aesthetically pleasing and potentially functional coordination polymers that have been isolated in recent years are exemplified by (10,3)-a,[9] NbO,[10] diamondoid,[11] and primitive cubic nets.[12] An alternative strategy for the interpretation and design of nets takes into account the shape of the MBBs and represents nets as being sustained by vertex-linked polygons or polyhedra (VLPP).[6a,13] As revealed by Scheme 1, the aforementioned four net types can be visualized as being either "node-and-spacer" or VLPP networks. From the VLPP perspective, the four nets shown in Scheme 1 are all examples of unitary nets in that they are built entirely from one type of polygon or polyhedron. The VLPP approach comes into its own for binary nets, that is, nets sustained by pairs of polygonal or polyhedral MBBs. The structural diversity possible from even the simplest of MBBs is exemplified by (3,4)-connected nets. If squares are connected exclusively to triangles and vice versa, two distinct (3,4)-connected binary nets have been isolated: the Pt_3O_4[14] and twisted boracite nets.[13a,15] Likewise, if tetrahedra are linked exclusively to triangles and vice versa, two additional (3,4)-connected binary nets are accessible, the boracite[16] and cubic C_3N_4 nets[17] (Scheme 2). Herein we address how the VLPP approach can be extended to ternary nets, that is, those sustained by a combination of three polygons or polyhedra.



Scheme 1. Four unitary nets represented in both node-and-spacer and VLPP format: a) (10,3)-a net, b) diamondoid net, c) NbO net, d) primitive cubic net.

We report the synthesis and crystal structures of two compounds that represent prototypal examples of ternary VLPP nets sustained by three distinct MBBs: $[\{[Zn_6(btc)_4(isoquinoline)_6(MeOH)]H_2O(benzene)_2\}_n]$ (USF-3; btc = 1,3,5-benzenetricarboxylate), and $[\{[Zn_6(btc)_4(isoquinoline)_4(MeOH)_2](MeOH)_8(chlorobenzene)\}_n]$ (USF-4). USF-3 and USF-4 are sustained by vertex linkage of triangular, square, and tetrahedral MBBs and represent to our knowledge the first reported examples of ternary nets. The

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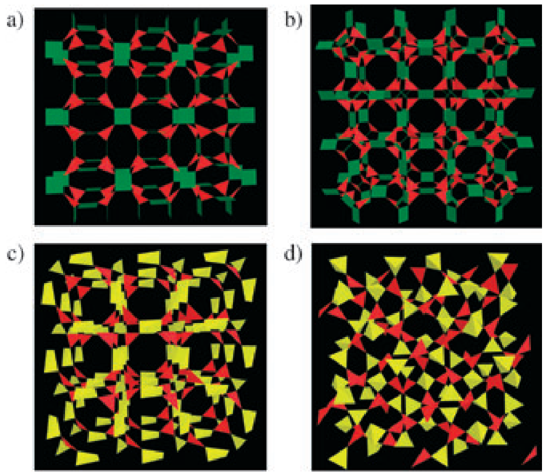
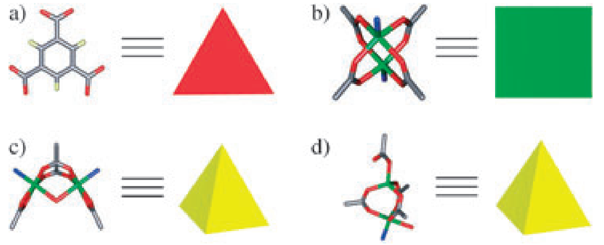


Scheme 2. Four (3,4)-connected binary nets represented in VLPP format: a) Pt_3O_4 net, b) twisted boracite net, c) boracite net, and d) cubic C_3N_4 net.

triangular MBB utilized in this study is the 1,3,5-benzenetricarboxylate anion (**A**). The square MBB is the previously reported $Zn_2(RCO_2)_4$ (**B**) and the tetrahedral MBBs are $Zn_2(RCO_2)_2(RCO_2)_2$ (**C**) or $Zn_2(RCO_2)_3(RCO_2)$ (**C′**), for USF-3 and USF-4, respectively, Scheme 3. Zinc(II)-based MBBs were selected because such a wide variety of zinc(II) carboxylate chromophores have been documented.[3d] The formation of the two new ternary nets and the relative ratio of **B** and **C** (2:1) in USF-3 or **B** and **C′** (1:2) in USF-4 appear to be controlled by template molecules and reaction conditions. It is of note that the Zn^{II} and btc can generate other supramolecular isomers[3a] in the presence of other solvents or templates.[9b,13a] Zinc nitrate, 1,3,5-benzenetricarboxylic acid, and isoquinoline in methanol templated by benzene affords USF-3 whereas similar reaction conditions give rise to USF-4 if chlorobenzene is employed as a template. This difference in products obtained is presumably a reflection of the relative size of the template molecules.



Scheme 3. Molecular building blocks (MBBs) employed in the ternary nets USF-3 and USF-4: a) **A**, b) **B**, c) **C**, d) **C′**.

The structures of USF-3 and USF-4 were determined by X-ray single-crystal diffraction[18] and they are depicted in Figure 1 and Figure 2, respectively. There are two different Zn^{II} chromophores present in USF-3: square “paddle-wheel” MBBs, **B**, and pseudo-tetrahedral **C**, in a ratio of 2:1. **B** is perhaps the most frequently used MBB and is present in over 1200 crystal structures that have been deposited in the Cambridge Structural Database (CSD).[19] MBB **C** is far less common than **B** and comprises a binuclear Zn^{II} unit, two bridging carboxylate groups, one bridging oxygen atom, and two chelating carboxylate groups. Methanol and/or isoquinoline serve as axial ligands. As revealed by Figure 1, USF-3 is generated from vertex linking of **A**, **B**, and **C** in the ratio 4:2:1, thereby retaining the 4:3 ratio necessary for sustaining a (3,4)-

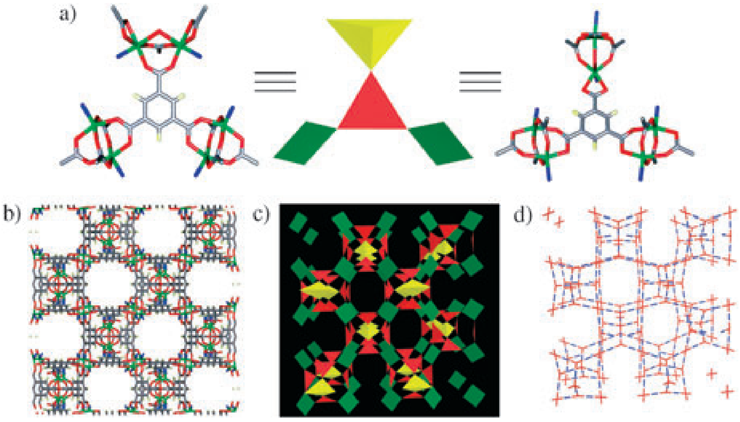


Figure 1. a) Representation of btc units linked to two square MBBs and one pseudo-tetrahedral MBB (two different orientations of the MBBs are shown). b) Crystal structure of USF-3 in stick representation (isoquinoline, benzene, and water are deleted for clarity). Selected bond lengths [Å]: Zn-O 1.985(5)–2.295(5), average 2.082; Zn-N 2.003(7)–2.104(3), average 2.063. c) Schematic representation of USF-3 in VLPP format. d) Schematic representation of USF-3 in node-and-spacer format.

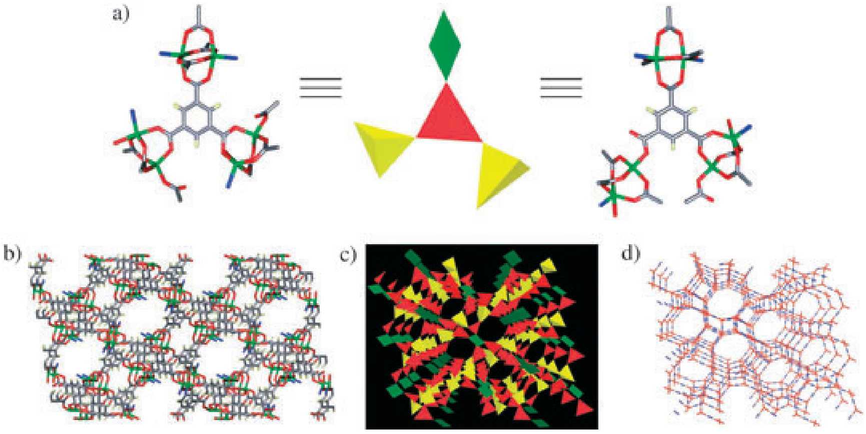


Figure 2. a) Representation of btc units linked to one square MBB and two pseudo-tetrahedral MBBs (two different orientations of the MBBs are shown). b) Crystal structure of USF-4 in stick representation (isoquinoline, methanol, and chlorobenzene are deleted for clarity). Selected bond lengths [Å]: Zn-O 1.912(3)–2.166(4), average 2.005, Zn-N 2.028(5)–2.031(4), average 2.030. c) Schematic representation of USF-4 in VLPP format. d) Schematic representation of USF-4 in node-and-spacer format.

connected net in which 3-connected nodes are exclusively linked to 4-connected nodes and vice versa. Ideally, these three types of MBBs would generate a net structure with large open channels; however, no such channels are observed in USF-3 because isoquinoline, a bulky molecule, is protruding and blocking the possible channels. As a result, there are two different types of cavities within which disordered benzene molecules are trapped (see Supporting Information). One water molecule per asymmetric unit is also present, which engages in hydrogen bonding with the bridging methanol molecules. Thermal gravimetric analysis (TGA) and X-ray powder diffraction data suggest that USF-3 is stable up to at least 130 °C whereas further heating above 180 °C leads to collapse of the framework (see Supporting Information). USF-4 also has two Zn^{II} MBBs: a mixture of **B** and a different pseudo-tetrahedral MBB **C**′. The overall ratio of **A**: **B**: **C**′ is 4:1:2. MBB **C**′ features a binuclear Zn^{II} unit, three bridging carboxylate groups, and one monodentate carboxylate. USF-4 also has cavities but open channels are precluded by the presence of coordinated isoquinoline molecules. However, USF-4 possesses a higher free volume[20] than USF-3, 32.2 % versus 19.3 %, in which methanol and disordered chlorobenzene molecules are located. Thus, USF-3 and USF-4 are the first reported examples of (3,4)-connected ternary nets: triangular, square, and tetrahedral MBBs in the ratios 4:2:1 and 4:1:2, respectively.

That USF-3 and USF-4 might have general implications in the context of designing coordination polymers can be justified by the following considerations. First, although it is established that knowledge of molecular symmetry facilitates the design and synthesis of nets in a systematic manner, until now this has been limited to unitary or binary nets. USF-3 and USF-4 suggest that the use of three or perhaps even more MBBs could represent a facile approach to the construction of VLPP nets with unprecedented topologies. Second, the recently discovered porous metal–organic structures that are capable of guest-induced shape-responsive fitting represent a class of materials that resemble the degree of induced-fit behavior of bioenzymes, such as metalloproteins.[21] That the formation of USF-3 and USF-4 is so dependent upon the presence of guest/template illuminates a possible mechanism for translating structural information from an external medium into the formation of a novel framework. Third, although considerable effort in the field of coordination polymers has been devoted to the pursuit of new structures with unprecedented topologies,[3] discovery and recognition of novel three-periodic nets remains a nontrivial experience. USF-3 and USF-4 are based upon unique connectivity and they represent two examples of hitherto undocumented (3,4)-connected nets.[1] The Schläfli symbols for USF-3 and USF-4 are $(6{\cdot}6{\cdot}6)_4(6_2{\cdot}6_2{\cdot}8_2{\cdot}8_2{\cdot}12_2{\cdot}12_2)_2(6_2{\cdot}6_2{\cdot}8{\cdot}8{\cdot}8{\cdot}8)$ and $(4{\cdot}6{\cdot}8)_2(6{\cdot}6{\cdot}8_2)_2(6{\cdot}6{\cdot}8{\cdot}8{\cdot}10_4{\cdot}{*})$ $(4{\cdot}6{\cdot}6{\cdot}8{\cdot}8{\cdot}10_4)_2$, respectively.[22] Therefore, USF-3 can be regarded as an "intermediate" structure between boracite and twisted boracite, as implied by their vertex symbols. USF-4 represents a more complicated and less symmetric (3,4)-connected net.[1,22] Nevertheless, the new structures are inherently modular and they are sustained by MBBs with shapes that are found throughout molecular chemistry. Therefore, there is every reason to assert that nets with the same topologies as USF-3 and USF-4 will be accessible from a much wider range of MBBs. However, it must be noted that the existence of USF-3 and USF-4 is at least partly a reflection of the tendency for Zn^{II} to exhibit multiple coordination geometries and the one-pot synthetic process employed herein is unlikely to be successful for other metals. In our opinion, as the number of MBBs increases, synthetic strategies will likely have to focus upon preformed MBBs rather than those generated in situ.

In summary, we have demonstrated that molecular triangles, squares, and tetrahedra are capable of self-assembling at their vertices to generate VLPP ternary nets. Such a ternary approach to generation of VLPPs is inherently modular in nature and consequently we anticipate it to be a strategy that will prove to be feasible for other combinations of molecular polygons and polyhedra.

Experimental Section

USF-3: A solution of 1,3,5-benzenetricarboxylic acid (140 mg, 0.667 mmol) and isoquinoline (0.350 mL, 3.00 mmol) in methanol (20 mL) was heated gently for about 10 min and then carefully layered onto a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (297 mg, 1.00 mmol) in methanol/benzene (3:1, 20 mL). Colorless single crystals formed within 12 h under ambient conditions (217 mg, 59.6 % yield).

USF-4: A solution of 1,3,5-benzenetricarboxylic acid (70 mg, 0.33 mmol) and isoquinoline (0.177 mL, 1.50 mmol) in methanol (20 mL) was carefully layered onto a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.500 mmol) in methanol/chlorobenzene (2:1, 20 mL). Colorless single crystals formed within 12 h under ambient conditions (56 mg, 30.9 % yield).

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[18] Crystal data for USF-3: $M_r = 2201.89$, orthorhombic, $Pmmn$, $a = 19.2471(17)$, $b = 19.9798(18)$, $c = 12.6644(11)$ Å, $V = 4870.1(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.502\,\mathrm{g\,cm^{-3}}$, $2\theta_{max} = 50.08°$ ($-22 \leq h \leq 22$, $-23 \leq k \leq 20$, $-15 \leq l \leq 10$), $T = 100$ K, 25527 measured reflections, $R1 = 0.0796$ and $wR2 = 0.2388$ for 2959 reflections ($I > 2\sigma(I)$), and $R1 = 0.1225$, $wR2 = 0.2669$ for 4570 independent reflections (all data) and 350 parameters, GOF = 1.013. Crystal data for USF-4: $M_r = 2170.27$, monoclinic, $P2_1/n$, $a = 14.5949(14)$, $b = 12.5583(12)$, $c = 25.741(3)$ Å, $\beta = 100.093(2)°$, $V = 4644.9(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.552\,\mathrm{g\,cm^{-3}}$, $2\theta_{max} = 54.00°$ ($-18 \leq h \leq 13$, $-14 \leq k \leq 16$, $-29 \leq l \leq 32$), $T = 100$ K, 21791 measured reflections, $R1 = 0.0644$ and $wR2 = 0.1296$ for 6924 reflections ($I > 2\sigma(I)$), and $R1 = 0.1007$, $wR2 = 0.1418$ for 10044 independent reflections (all data) and 649 parameters, GOF = 1.003. Data were collected on a Bruker SMART-APEX CCD diffractometer using $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), operating in the Ω and ϕ scan mode. All crystal data were corrected for Lorentz and polarization effects, and the SADABS program was used for absorption correction. The structures were solved by direct methods and the structure solutions and refinements were based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were placed in calculated positions and given isotropic U values 20% higher than the atom to which they are bonded. All crystallographic calculations were conducted with the SHELXTL software suite. CCDC-260729 (USF-3) and CCDC-260730 (USF-4) contains 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.

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[22] Vertex symbols for the four (3,4)-connected binary nets discussed herein: Pt_3O_4 net $(8_5{\cdot}8_5{\cdot}8_5)_4(8_2{\cdot}8_2{\cdot}8_4{\cdot}8_4{\cdot}8_4{\cdot}8_4)_3$; twisted boracite net $(6{\cdot}6{\cdot}6)_4(6_2{\cdot}6_2{\cdot}8_2{\cdot}8_2{\cdot}12_2{\cdot}12_2)_3$; boracite net $(6{\cdot}6{\cdot}6)_4(6_2{\cdot}6_2{\cdot}8{\cdot}8{\cdot}8{\cdot}8)_3$; cubic C_3N_4 net $(8_5{\cdot}8_5{\cdot}8_5)_4(8_3{\cdot}8_3{\cdot}8_3{\cdot}8_3{\cdot}8_4{\cdot}8_4)_3$.