

A novel metal–organic ternary topology constructed from triangular, square and tetrahedral molecular building blocks

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A novel metal–organic network $[\text{Cu}_4(5\text{-NH}_2\text{-1,3-bdc})_4(\text{pyridine})_2(\text{H}_2\text{O})_2]_n$, displaying an unprecedented topology has been constructed utilizing the different coordinating functional groups of 5-NH₂-1,3-bdc to generate a ternary network based upon vertex-linked triangular, square and tetrahedral molecular building blocks (MBBs).

Crystal engineering¹ offers a paradigm for the self-assembly of infinite and discrete nanoscale organic² and metal–organic/coordination³ structures *via* a bottom-up “molecular building block (MBB) approach”.⁴ Structure–function relationships with properties such as magnetism,⁵ luminescence,⁶ and permanent porosity⁷ have thereby been developed in a systematic manner. Wells catalogued network structures in crystals⁸ and spawned the “node-and-spacer” methodology⁹ which simplifies design since it reduces MBBs into topological points and lines. Interpretation and design of nets can also take into account the geometrical shape of the MBBs by representing nets as vertex-linked polygons or polyhedra (VLPP).¹⁰

Topologically the simplest nets are unitary nets comprised of only one type of MBB for which the topology of the net is directed by the geometry and arrangement of the MBBs: (10,3)-a (triangular MBBs), diamondoid (tetrahedral MBBs), NbO (square MBBs), and primitive cubic (octahedral MBBs) nets. The VLPP approach comes into its own for binary nets sustained by pairs of polygonal or polyhedral MBBs and even the simplest combinations of MBBs can result in structural diversity as exemplified by (3,4)-connected nets.¹¹ Nevertheless, the design of novel topologies remains challenging and is a dominant theme in crystal engineering since new topologies can serve as “blueprints” for the design of new classes of materials. We have proposed a design strategy based upon the VLPP approach for the synthesis of ternary nets sustained by a combination of three distinct polygons or polyhedra¹² utilizing zinc(II), which is known to offer structural diversity. In this communication we delineate how 3-connected triangular MBBs with different coordinating functional groups such as, 5-NH₂-1,3-bdc (5-amino-1,3-benzenedicarboxylate)¹³ can promote the formation of two distinct metal centers and a ternary net (Fig. 1) with a new topology, USF-5: $[\text{Cu}_4(5\text{-NH}_2\text{-1,3-bdc})_4(\text{pyridine})_2(\text{H}_2\text{O})_2]_n$, **1**.†

The square MBB utilized in **1** is based upon the ubiquitous dicopper tetracarboxylate, $\text{Cu}_2(\text{RCO}_2)_4\text{L}_2$, or “paddlewheel” which is present in over 600 crystal structures in the Cambridge Structural Database (CSD).¹⁴ The $\text{Cu}(5\text{-NH}_2\text{-1,3-bdc})_4/3(\text{H}_2\text{O})_n$

building block in **1** is a pseudo-tetrahedral MBB. The five-coordinate $\text{Cu}(\text{RCO}_2)_2(\text{RNH}_2)_2\text{L}$ chromophore is present in over 50 crystal structures in the CSD.

USF-5 is closely related to the previously reported USF-4¹² in that each triangular MBB is linked to one square MBB and two pseudo-tetrahedral MBBs which in turn are each linked to four triangular MBBs (Fig. 2). However, USF-5 is significantly different than USF-4 and previously reported (3,4)-connected networks, the long vertex symbols, $(4\cdot 8_2\cdot 8)_4(8\cdot 8\cdot 8_2\cdot 8_2\cdot 12_8\cdot 12_8)$ $(4\cdot 4\cdot 8\cdot 8\cdot 8\cdot 12_{13})_2$ being hitherto unprecedented.¹⁵ Analysis of the physical properties observed in **1** and other ternary nets remains an ongoing study in our laboratory.

When the experimental conditions of **1** were altered to utilize 4-picoline instead of pyridine we obtained two products: green crystals isostructural to **1**,¹⁶ and yellow crystals of $[\text{Cu}(5\text{-NH}_2\text{-1,3-bdc})(4\text{-picoline})]_n$, **2**. The 2-D honeycomb framework of **2** is composed of 3-connected 5-NH₂-1,3-bdc ligands and five-coordinate Cu(II) metal centers which also serve as 3-connected nodes. A series of Zn(II) analogues of this structure has recently been reported.¹⁷

In summary, we have demonstrated a second simple strategy for the design of ternary nets, *i.e.* triangular MBBs containing different coordinating functional groups (*i.e.* carboxylates and amines) which promote the formation of geometrically and chemically distinct metal centers. Further studies will investigate the design of ternary nets from a wider range of geometrical and chemical MBBs, including preformed MBBs.

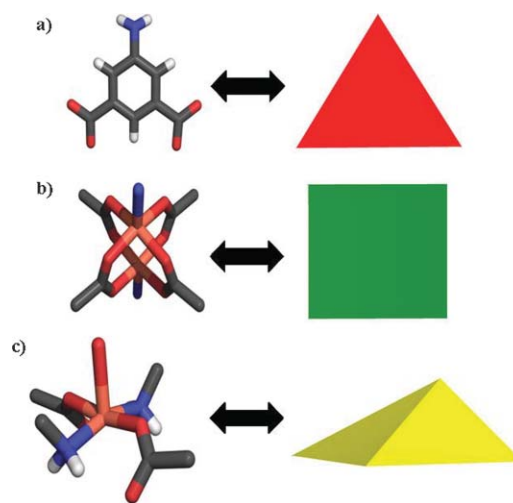


Fig. 1 Molecular building blocks (MBBs) employed in the ternary net USF-5: (a) 5-NH₂-1,3-bdc – triangular MBB; (b) $\text{Cu}_2(\text{RCO}_2)_4\text{L}_2$ – square MBB; (c) $\text{Cu}(\text{RCO}_2)_2(\text{RNH}_2)_2\text{L}$ – pseudo-tetrahedral MBB.

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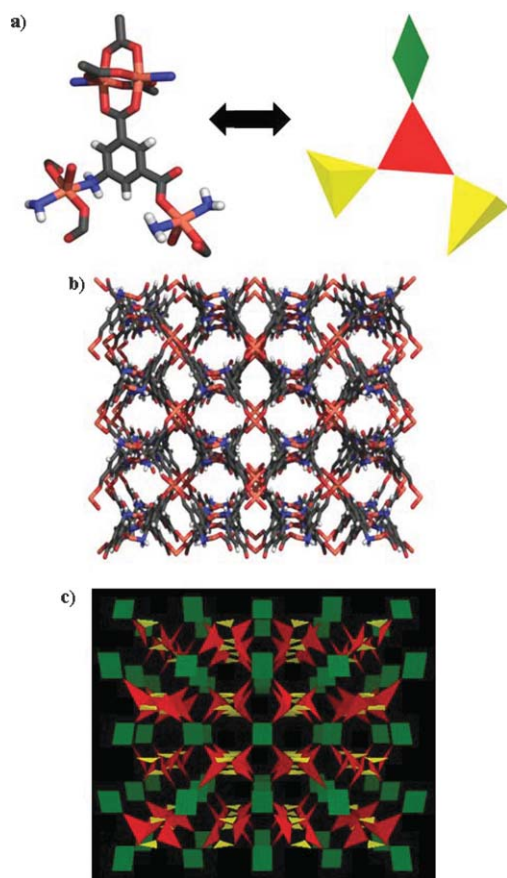


Fig. 2 (a) Triangular 5-NH₂-1,3-bdc units linked to one square MBB and two pseudo-tetrahedral MBBs. (b) Crystal structure of **1** viewed down the [100] axis in stick representation (pyridine and H₂O ligands have been deleted for clarity). (c) Schematic representation of **1** in VLPF format viewed down the [100] axis.

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Notes and references

† *Experimental data for 1*: Green crystals form in 38% yield within one day of layering a 10.0 mL methanolic solution of Cu(NO₃)₂·2.5H₂O (116 mg, 0.499 mmol) through a 10.0 mL methanol buffer layer onto a 10.0 mL methanolic solution containing 5-amino-1,3-benzenedicarboxylic acid (91 mg, 0.50 mmol) and pyridine (0.12 mL, 1.5 mmol). *Experimental data for 2*: Green (compound **1**) and yellow (compound **2**) crystals form within one day of layering a 10.0 mL methanolic solution of Cu(NO₃)₂·2.5H₂O (116 mg, 0.499 mmol) through a 10.0 mL methanol buffer layer onto a 10.0 mL methanolic solution containing 5-amino-1,3-benzenedicarboxylic acid (91 mg, 0.50 mmol) and 4-picoline (0.15 mL, 1.5 mmol).

Crystallographic data for 1: C₂₁H₃₀Cu₂N₃O_{15.50}, *M_r* = 699.56, orthorhombic, space group *Ibam*, *a* = 14.669(7), *b* = 16.833(8), *c* = 24.743(11) Å, *V* = 6109(5) Å³, *Z* = 8, *D_c* = 1.521 g cm⁻³, *μ* = 1.464 mm⁻¹, *F*(000) = 2872, *2θ*_{max} = 50.22° (−17 ≤ *h* ≤ 16, −8 ≤ *k* ≤ 20, −29 ≤ *l* ≤ 29), *T* = 298(2) K, 14695 measured reflections, *R*₁ = 0.0671 for 1283 reflections (*I* > 2σ(*I*)), *wR*₂ = 0.1883 for 2787 independent reflections (all data) and 201 parameters, *GOF* = 0.882. *Crystallographic data for 2*: C₁₄H₁₂Cu₂N₂O₄, *M_r* = 335.80, monoclinic, space group *P2₁/n*, *a* = 12.7210(18), *b* = 7.7387(11), *c* = 14.005(2) Å, β = 108.106(2)°, *V* = 1310.4(3) Å³, *Z* = 4, *D_c* = 1.702 g cm⁻³, *μ* = 1.684 mm⁻¹, *F*(000) = 684, *2θ*_{max} = 50.28° (−13 ≤ *h* ≤ 15, −9 ≤ *k* ≤ 9, −16 ≤ *l* ≤ 16), *T* = 298(2) K, 6452 measured reflections, *R*₁ = 0.0447 for 1776 reflections (*I* > 2σ(*I*)), *wR*₂ = 0.1139 for 2316 independent reflections (all data) and 191 parameters, *GOF* = 1.041.

Data were collected on a Bruker SMART-APEX CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). 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 solution and refinement was 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 658210 and 658211. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712905j

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