

A new 6^{5.8} topology and a distorted 6^{5.8} CdSO₄ topology: two new supramolecular isomers of [M₂(bdc)₂(L)₂]_n coordination polymers†

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We report the crystal structures of two new coordination polymers that have similar composition but, despite having the same circuit symbol and Schläfli notation, different topologies: a novel 3D topology (USF-1) and a CdSO₄-like topology.

The reduction of supramolecular networks to node-and-spacer representations that illustrate their connectivity has facilitated the analysis and understanding of seemingly complex topologies that have been generated *via* crystal engineering.¹ In particular, circuit symbols and Schläfli (vertex) notations can be used to describe topologies and facilitate comparison of networks of different composition and metrics. Perhaps the most common application of topological notation in crystal engineering has been for the description of interpenetrated networks based upon complementary topologies,² while the description of individual networks has generally focused more on descriptive nomenclature based upon structures of known materials and minerals (*i.e.* NbO, PtS, CdSO₄). In this contribution, we describe two materials that have similar composition, {[M₂(bdc)₂(L)₂]_n} (M = transition metal dication, bdc = 1,3-benzenedicarboxylate, L = coordinated solvent/base), and the same circuit symbol (6^{5.8}) and Schläfli notation (6.6.6.6.6₂.∞), yet have fundamentally different architectures.

The crystal structure of 1‡, {[M₂(bdc)₂(Q)₂]_n} (M = Co, **1a**, Cu, **1b**, Zn, **1c**, Q = quinoline) is illustrated in Figures 1 and 2. **1a–c** are isostructural and composed of dimetal tetracarboxylate paddlewheel clusters,³ secondary building units (SBUs),⁴ bridged by bdc moieties. To our knowledge, these materials represent the first examples of a class of compounds that possess a new 6^{5.8} topology. We have recently published several accounts illustrating other supramolecular isomers⁵ that can be formed by bridging the ubiquitous dicopper tetracarboxylate cluster by bdc.⁶ These structures can be reduced to schematics rationalizing the structures as assembly of molecular squares, [M₂(RCO₂)₄], at their vertices. Although **1** can be analysed in the same manner, such a schematic does little to simplify our understanding of the topology although it can provide insight into the origin of bulk physical properties such as magnetism and porosity. **1** does not possess notable pores or cavities (the hexagonal channel seen in Fig. 1 has an effective diameter of *ca.* 0.25 nm); however, the magnetic behaviour

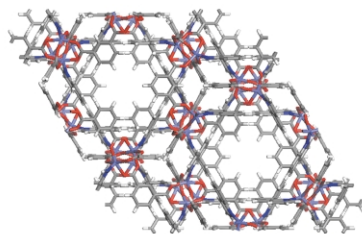


Fig. 1 The crystal structure of [M₂(bdc)₂(Q)₂]_n (M = Co, **1a**, Cu, **1b**, Zn, **1c**, Q = quinoline) viewed along [001]. The hexagonal channels have an effective diameter of only *ca.* 2.5 Å.

† Electronic supplementary information (ESI) available: schematic illustrations of some common 4-connected 3D networks. See <http://www.rsc.org/suppdata/cc/b3/b301221b/>

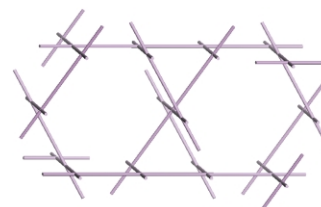


Fig. 2 Schematic illustrating the connectivity of the "paddlewheel" clusters in **1**, the so-called USF-1 net.

exhibited by **1** differs from its supramolecular isomers or its discrete analogues. That [M₂(RCO₂)₄] clusters exhibit magnetism is unsurprising⁷ and the temperature-dependant magnetic susceptibility of **1a** shows a maximum at *ca.* 130 K and a minimum at *ca.* 20 K followed by an upturn at lower temperature. These values are considerably less than those exhibited by related structures. The magnetic phenomena exhibited by **1** are beyond the scope of this communication and will form the basis of a future contribution.

Fig. 2 was derived by treating the dimetal cluster as a single node located between the two metal ions, and connecting the nodes according to the connectivity defined by the bdc bridging ligands. This yields a 6^{5.8} 3D network that is sustained by distorted square planar nodes.

Another 3-D supramolecular isomer is formed when the same reactants are crystallized from a different solvent system and in the presence of a different base. The crystal structure of 2‡, {[M₂(bdc)₂(L)₂]_n} (M = Cu, L = 1.5 pyridine/0.5 water) is illustrated in Fig. 3. Reduction of the crystal structure to a schematic by treating the [M₂(RCO₂)₄] moieties as nodes and connecting them according to the connectivity defined by the bdc bridging ligands yields a different 6^{5.8} 3D network. This network has a topology similar to CdSO₄ (Fig. 4). Interestingly, the connections parallel to [120] are not collinear, which corresponds to a distorted CdSO₄ network with only four geometric nearest neighbours⁸ (an ideal CdSO₄ network has six).

It should be noted that, to our knowledge, we herein report the first example of the network topology exhibited by **1**, which we have termed the USF-1 net. The ideal net has *R*3̄*c* symmetry, *a/c* = √(8/3), with vertices at 18 *d*.⁹ The ideal CdSO₄ net has *P*4₂/*mmc* symmetry, *c/a* = 2 with vertices at 2 *a*.⁹ Although both networks are 4-connected, each vertex has six nearest neighbours. The connectivity of USF-1 is generated by connecting the vertices at (1/2,0,0) and (1/2,0,1/2), and (1/2,0,0) and (1/3,1/6,1/6). A 6-connected net can be generated by also

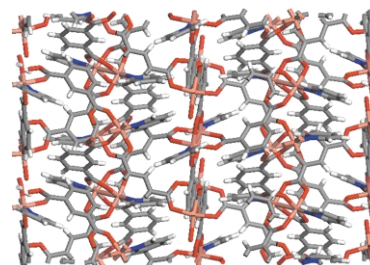


Fig. 3 The crystal structure of [Cu₂(bdc)₂(L)₂]_n (L = 1.5pyridine/0.5H₂O), **2**, viewed along [001].

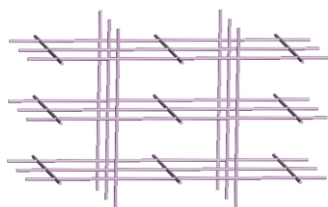


Fig. 4 Schematic illustrating the connectivity of an ideal CdSO₄ network, which has the same basic topology of the network observed for **2**.

connecting (1/2,0,0) and (5/6,1/6,1/6), the USF-2 net, which has six equidistant edges. The connectivity of the CdSO₄ net is generated by connecting (0,0,0) and (0,0,1/2), and (0,0,0) and (1,0,0). The 6-connected cubic lattice can be generated by also connecting (0,0,0) and (0,1,0).

Although visual inspection of projections down various crystallographic vectors indicates that the networks are quite different, a more rigorous comparison was employed. The number of nearest neighbours (nn) was calculated for "shells" of adjacent vertices, such that each shell is a set of vertices equidistant from a particular vertex. These data are presented in Table 1.

Table 1 Number of vertices in nearest neighbour shells

	nn ₁ ^a	nn ₂	nn ₃	nn ₄	nn ₅	nn ₆	nn ₇	nn ₈	nn ₉	nn ₁₀
USF-1	6	4	8	18	8	6	18	16	16	24
CdSO₄	6	12	8	6	24	24	12	30	24	24

^a nn₁ refers to the set of nearest neighbours, nn₂ the set of next nearest neighbours, etc...

These data show that there are 124 total vertices within the nn₁₀ shell for **1**, and 170 vertices within the nn₁₀ shell for **2**. These values can be used to describe a *topological density*, which is not the same as material density because the volume of the nn₁₀ shell for different nets is not the same. In this particular case, the material density (defined as vertices per unit volume) of USF-1 is 2.6% less than a CdSO₄ net with equal edge lengths.

The cubic and hexagonal diamondoid topologies are another set of 4-connected nets that are different but have the same Schläfli notation (6₂.6₂.6₂.6₂.6₂.6₂). In this case, the nets have the same material density, but the hexagonal diamond net has ca. 48% less vertices in its nn₁₀ shell. Another method for comparing topologically similar nets is to calculate the *coordination sequence*.⁹ Hexagonal diamondoid is topologically denser than cubic diamondoid using this method.

A 3-D network related to **1** and **2** has been recently reported, the so-called MOF-112 net.^{†10} This particular network results from the increased torsion angle between the carboxylates imposed by a 4-substituted bromine on the bdc. The net has a different topology which is defined by the circuit symbol (6².8⁴) and Schläfli notation (6₂.6₂.8.8.8.8). This net has *P4/mmm* symmetry, *a/c* = 2, with vertices at 1 *a* and 2 *f*.⁹ The connectivity can be generated by connecting (0,0,0) and (1/2,0,0), and (0,1/2,0) and (0,1/2,1). The authors have also used this torsional strain to synthesize materials that exhibit the CdSO₄¹⁰ and NbO¹¹ topologies from 2-bromo-1,4-benzenedicarboxylates.[†]

Topological analysis of **1** and **2** by examining the schematic representations of their chemical connectivity facilitates the description and comparison of two otherwise complex three-dimensional architectures. Furthermore, it allows definition of a previously unknown topology, USF-1, and prediction of a yet to be isolated topology, USF-2.[†] The identification of new topologies remains an important aspect of crystal engineering, as these serve as "blueprints" for the design of new materials. Efforts toward the enumeration of new topologies and reports of previously unrealized networks therefore represent an essential branch in the evolution of the discipline.

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Notes and references

† *Crystallographic data* for **1** and **2** were collected on a Bruker SMART-APEX diffractometer using Mo_{Kα} radiation ($\lambda = 0.7107 \text{ \AA}$). 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 $|F|^2$. 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.

Crystals of **1a** were obtained by slow evaporation of an ethanolic solution of cobalt nitrate hexahydrate (297 mg, 1.02 mmol), isophthalic acid (166 mg, 0.999 mmol) and quinoline (0.24 mL, 2.0 mmol) containing nitrobenzene (6 mL). Intensity data were collected at 173 K: Rhombohedral, *R*-3c, *a* = 30.3087(15), *c* = 18.3364(13) Å, *V* = 14587.4(15) Å³, *Z* = 18, $\rho = 1.606 \text{ g cm}^{-3}$, $\mu = 1.096 \text{ mm}^{-1}$, *F*(000) = 7157, $2\theta_{\text{max}} = 56.54^\circ$. Final residuals (for 244 parameters) were *R*1 = 0.0455 for 3985 reflections with *I* > 2σ*I*, and *R*1 = 0.0757, *wR*2 = 0.1153, GooF = 0.939 for all 30199 data.

Crystals of **1b** were obtained by layering an ethanolic solution of isophthalic acid (166 mg, 0.999 mmol) and quinoline (0.30 mL, 2.5 mmol), onto an ethanolic solution of copper nitrate hemipentahydrate (233 mg, 1.00 mmol) containing nitrobenzene (2 mL). Intensity data were collected at 173 K: Rhombohedral, *R*-3c, *a* = 30.337(2), *c* = 18.380(2) Å, *V* = 14649(2) Å³, *Z* = 18, $\rho = 1.456 \text{ g cm}^{-3}$, $\mu = 1.359 \text{ mm}^{-1}$, *F*(000) = 6516, $2\theta_{\text{max}} = 46.52^\circ$. Final residuals (for 243 parameters) were *R*1 = 0.0497 for 2352 reflections with *I* > 2σ*I*, and *R*1 = 0.1205, *wR*2 = 0.1630, GooF = 0.841 for all 18919 data.

Crystals of **1c** were obtained by layering a methanolic solution of zinc nitrate hexahydrate (297 mg, 0.998 mmol), onto a methanolic solution of isophthalic acid (166 mg, 0.999 mmol) and quinoline (0.24 mL, 2.0 mmol) containing nitrobenzene (2 mL). Intensity data were collected at 173 K: Rhombohedral, *R*-3c, *a* = 30.2394(11), *c* = 18.2791(13) Å, *V* = 14475.4(13) Å³, *Z* = 18, $\rho = 1.481 \text{ g cm}^{-3}$, $\mu = 1.545 \text{ mm}^{-1}$, *F*(000) = 6552, $2\theta_{\text{max}} = 57.76^\circ$. Final residuals (for 236 parameters) were *R*1 = 0.0437 for 3916 reflections with *I* > 2σ*I*, and *R*1 = 0.0508, *wR*2 = 0.1192, GooF = 1.608 for all 28023 data.

Green needle-like crystals of **2** were obtained upon the addition of water to a DMF solution (14 mL) of copper nitrate hemipentahydrate (261 mg, 1.12 mmol), isophthalic acid (178 mg, 1.07 mmol) and pyridine (0.24 mL, 3.0 mmol). Intensity data were collected at 200 K: Monoclinic, *P*₂/n, *a* = 10.6661(12), *b* = 30.303(4), *c* = 16.3650(19) Å, $\beta = 95.877(2)^\circ$, *V* = 5261.5(10) Å³, *Z* = 4, $\rho = 1.564 \text{ g cm}^{-3}$, $\mu = 1.670 \text{ mm}^{-1}$, *F*(000) = 2494, $2\theta_{\text{max}} = 56.64^\circ$. Final residuals (for 684 parameters) were *R*1 = 0.0650 for 12275 reflections with *I* > 2σ*I*, and *R*1 = 0.1129, *wR*2 = 0.1722, GooF = 1.038 for all 29732 data.

CCDC 202849–202852. See <http://www.rsc.org/suppdata/cc/b3/b301221b/> for crystallographic data in .cif or other electronic format.

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