

## A design strategy for four-connected coordination frameworks†

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Reactions of tetrahedral Cu(I) and Ag(I) cations with 2,3,4,5-tetra(4-pyridyl)thiophene allows targeted construction of coordination frameworks with zeolite-like, 4<sup>2</sup>.8<sup>4</sup>, topologies.

Synthetic strategies for the construction of coordination frameworks have developed rapidly over recent years.<sup>1</sup> A building-block methodology is used to generate framework structures in which the geometries of the constituent metal cation and bridging ligands can be used to design networks of specific topology.

One of the distinctive features of zeolitic topologies, a family of four-connected frameworks that are particularly under represented amongst coordination frameworks, is the incorporation of tetrahedral nodes into three-dimensional frameworks that are built from four-membered rings and, six-, or larger-membered rings.<sup>2</sup> Large numbers of potential four-connected nets have been identified.<sup>3</sup> Many nets which include more than one type of node are possible, such as the PtS net,<sup>4</sup> but a more limited number have been described with a single type of node.<sup>5</sup> By far the most common of these are the diamondoid net<sup>6</sup> and to a lesser extent the CdSO<sub>4</sub> net.<sup>7</sup> Other nets such as the NbO net<sup>8</sup> are significantly rarer.

All of the more common four-connected nets contain six-membered and larger rings and examples of four-membered rings are comparatively rare in three-dimensional coordination frameworks. One example of a three-dimensional coordination framework that includes four-membered rings is a supramolecular isomer of [Zn(nicotinate)]<sub>2</sub>∞ which exhibits a 4<sup>2</sup>.8<sup>4</sup> topology and is constructed from square-planar nodes.<sup>9</sup> Another distinctive feature of zeolitic topologies is their resistance to interpenetration despite the porous natures of their frameworks. Recent studies have examined the relationship between interpenetration and porosity and have had startling success at creating large free volumes in metal-organic frameworks.<sup>10</sup>

Although the building-block strategy can be highly successful there are some significant limitations due to the requirement for single crystals that allow complete characterisation of the product material. Single crystal formation of coordination framework materials is synthetically challenging, requiring reversible *intra*-framework interactions for the self-assembly of the coordination framework to take place. This necessity often limits the building-block methodology to suitable metals, first row transition metals and d<sup>10</sup> cations, and hence specific metal geometries. As a result certain network topologies are difficult targets and new strategies are required for combining tetrahedral metal nodes with appropriate subtending donor groups of bridging ligands.

We have developed a strategy that uses a tetradentate ligand to act as a four-connecting framework node that encourages the formation of four-membered rings when bound to tetrahedral metal cations. Topologically the presence of four-membered rings discourages interpenetration as the free volume in any given ring is usually not sufficient to accommodate a further penetrating net.

This strategy is achieved by using a ligand that imparts a nodular angle of ca. 72°. The latter can be achieved by using a tetra-substituted five-membered ring such as that observed in 2,3,4,5-tetra(4-pyridyl)thiophene (**L**) (Fig. 1).<sup>11</sup>

Reaction of **L** with [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (for **1**) or Ag(I) salts (for **2–5**) affords yellow (**1**) or colourless (**2–5**) precipitates of formula {[M(L)]X}<sub>∞</sub> [M = Cu (**1**), Ag (**2–5**); X = BF<sub>4</sub><sup>-</sup> (**1–2**), SbF<sub>6</sub><sup>-</sup> (**3**), CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (**4**), PF<sub>6</sub><sup>-</sup> (**5**)]. Single crystals of **1–5** were grown by slow diffusion of an MeCN solution of the metal salt into a CHCl<sub>3</sub> (**1,2a,3,4**) or CH<sub>2</sub>Cl<sub>2</sub> (**2b,4,5**) solution of the ligand over a 24 h period.†

Single crystal X-ray structural determinations‡ reveal that all six compounds form isotopological three-dimensional frameworks (Fig. 2), crystallising in the highly symmetrical tetragonal space group *I*<sub>4</sub>/*amd*. In each case the metal cations adopt distorted tetrahedral geometries and are coordinated by four separate planar tetradentate ligands (Fig. 1), with each ligand coordinated to four separate metal centres. The framework generates large (10 × 14 Å) and medium (18 × 7 Å) octagonal pores and smaller (8 × 5 Å) tetragonal ones running along the crystallographic *a* and *b* axes

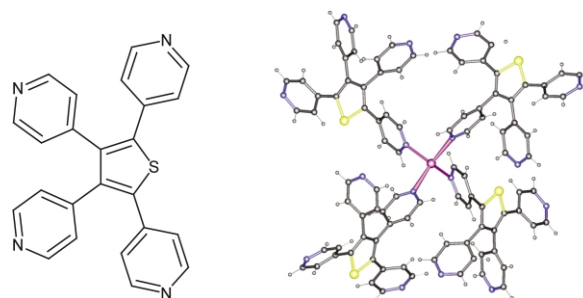


Fig. 1 (left) View of ligand **L**. (right) View of the metal coordination sphere observed in compound **3**. An essentially identical arrangement is observed in compounds **1,2,4** and **5** (Ag – purple; S – yellow; N – blue; C – grey).

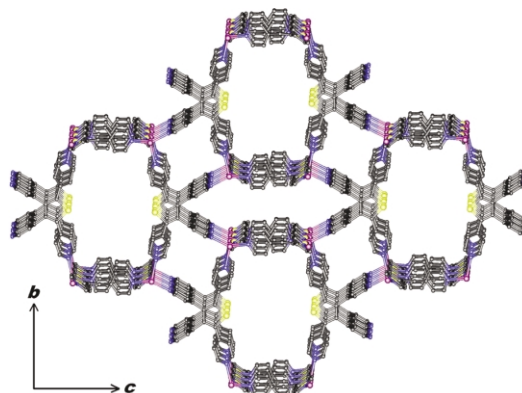
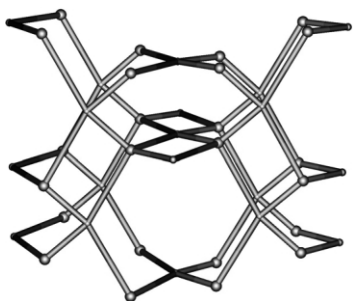


Fig. 2 View along the crystallographic *a*-axis of the cationic {[M(L)]<sup>+</sup>}<sub>∞</sub> coordination framework formed by **1–5**. (M – purple; S – yellow; N – blue; C – grey).

† Electronic supplementary information (ESI) available: experimental details and full topological analysis. See <http://www.rsc.org/suppdata/cc/b3/b315243j/>



**Fig. 3** View of the topological net observed in **1–5** illustrating the four-connected  $4^2.8^4$  network (metal nodes – grey; ligand nodes – black).

(Fig. 2). The pores are filled with disordered counter-anions, which have been completely located only in the case of **3**. For the other structures only partially occupied counter-anions have been located and the SQUEEZE procedure<sup>12a</sup> was used to treat regions of diffuse electron density that could not be appropriately modelled. The large pores within the cationic framework of **1–5** constitute, on average, 63.5% of the unit cell volume,<sup>12b</sup> excluding counter-anions and solvent. In the structure of **3**, where all of the large  $\text{SbF}_6^-$  counter-anions could be located the solvent accessible volume is 42.5%. Interpenetration is normally expected for frameworks which occupy less than 50% of the total crystal volume. For the frameworks in **1–5** interpenetration is prevented both by the topology, as the 4- and 8-membered rings have the wrong shapes and sizes to allow penetration, and by the counter-anions which fill space within the pores.

Variation in incorporated solvent, as in **2** and **4**<sup>†</sup>, or in anion commonly has a significant impact on the resultant coordination framework, particularly for Ag(I) compounds.<sup>1</sup> However, it is important to note that this is not the case here. It is even more remarkable that varying the framework cation from Ag(I) to Cu(I) does not alter the topology of the resultant framework, suggesting that this structure is particularly robust.

A topological analysis of the networks has been performed using OLEX<sup>13</sup> by considering both the metal and the ligand as topological nodes. A topological representation of the framework structures is shown in Fig. 3 and can be defined as a  $4^2.8^4$  net. Previously reported examples of zeolites containing only four- and eight-membered rings show that the complexes represent new types of zeolite-like structures.<sup>2</sup> The framework seen in **1–5** has the same short vertex symbol (*Schläfli symbol*) as the zeolites EDI and THO,<sup>14</sup> and the same cell symmetry as the NAT structure.<sup>14</sup> The difference between the structures reported here and those exhibited by the zeolites is due primarily to the presence of a planar fourfold node arising from the ligand **L** in the coordination frameworks which precludes the formation of the  $4_2$  rings found in the zeolites.

In conclusion, ligand design can be used to generate specific ring sizes controlling the extended metal coordination sphere and localised framework topology. Long range control over framework structure, that is the extended ordering and orientation of topological nodes, remains an extremely challenging but enticing target for the synthesis of new coordination polymer materials.

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## Notes and references

<sup>†</sup> Crystal data for **1**:  $\text{C}_{30}\text{H}_{23.5}\text{BCl}_9\text{CuF}_4\text{N}_{5.5}\text{S}$ ,  $M = 962.50$ , tetragonal,  $I4_1/amd$ ,  $a = 22.522(3)$ ,  $c = 33.600(4)$  Å,  $U = 17043(3)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 150(2)$  K, 3967 unique reflections. Refinement of 168 parameters converged at final  $R_1 = 0.0662$ ,  $wR_2 = 0.1745$ .

**2a**:  $\text{C}_{29}\text{H}_{21.5}\text{AgBCl}_{12}\text{F}_4\text{N}_{4.5}\text{S}$ ,  $M = 1085.16$ , tetragonal,  $I4_1/amd$ ,  $a = 22.5430(5)$ ,  $c = 35.517(1)$  Å,  $U = 18049.1(8)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 150(2)$  K, 5917 unique reflections. Refinement of 159 parameters converged at final  $R_1 = 0.0466$ ,  $wR_2 = 0.1618$ .

**2b**:  $\text{C}_{31}\text{H}_{27}\text{AgBCl}_2\text{F}_4\text{N}_7\text{S}$ ,  $M = 795.24$ , tetragonal,  $I4_1/amd$ ,  $a = 22.636(5)$ ,  $c = 35.393(5)$  Å,  $U = 18135(6)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 163(2)$  K, 4889 unique reflections. Refinement of 159 parameters converged at final  $R_1 = 0.0418$ ,  $wR_2 = 0.1267$ .

**3**:  $\text{C}_{27}\text{H}_{20}\text{AgCl}_3\text{F}_6\text{N}_5\text{SSb}$ ,  $M = 896.51$ , tetragonal,  $I4_1/amd$ ,  $a = 22.975(5)$ ,  $c = 34.298(7)$  Å,  $U = 18104(11)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 150(2)$  K, 5919 unique reflections. Refinement of 204 parameters converged at final  $R_1 = 0.0665$ ,  $wR_2 = 0.2073$ .

**4**:  $\text{C}_{30}\text{H}_{24}\text{AgCl}_3\text{F}_3\text{N}_6\text{O}_3\text{S}_2$ ,  $M = 816.44$ , tetragonal,  $I4_1/amd$ ,  $a = 23.166(5)$ ,  $c = 34.931(5)$  Å,  $U = 18746(6)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 163(2)$  K, 5047 unique reflections. Refinement of 161 parameters converged at final  $R_1 = 0.0589$ ,  $wR_2 = 0.1908$ .

**5**:  $\text{C}_{27}\text{H}_{21}\text{AgCl}_3\text{F}_6\text{N}_5\text{PS}$ ,  $M = 771.29$ , tetragonal,  $I4_1/amd$ ,  $a = 22.963(5)$ ,  $c = 34.55(1)$  Å,  $U = 18216(9)$  Å<sup>3</sup>,  $Z = 16$ ,  $T = 163(2)$  K, 4980 unique reflections. Refinement of 171 parameters converged at final  $R_1 = 0.0723$ ,  $wR_2 = 0.2173$ .

CCDC 225249–225254. See <http://www.rsc.org/suppdata/cc/b3/b315243j/> for crystallographic data in .cif or other electronic format.

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