Anion Template Effect and the Polymerization Degree – Diversity through Flexibility

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Two 2D (**M1** and **M2**) and one 1D (**M3**) metal-organic frameworks (MOFs) have been prepared from pyridine functionalized tetradentate ligand tetrakis(nicotinoxymethyl)methane **TNM** with silver tetrafluoroborate, nickel chloride, and copper hexafluorophosphate. **M1** manifests a previously unpresented mode of 4,4 threefold parallel interpenetration for 2D MOFs. Large channels (vdW diameter 9.4 Å) through eclipsed 2D layers of **M2** were observed. While the open space percentage in the noninterpenetrated **M2** was 38.0 %, the triple interpenetration of the sheets of **M1** reduced the void to 10.8 %. With the same ligand and a similar, weakly coordinating anion as that in **M1**, the structure **M3** was rendered one-dimensional. The result is explained partly by the flexibility of the **TNM** ligand and partly by the lack of a suitable bridging solvent.

Introduction

Since the beginning of crystal engineering,[1] there has been a search for reliable methods to predict and control the product of crystal syntheses. The study of the crystal structures has a dual focus: the analysis of the obtained structures and the prediction of yet to be formed crystals. Meticulous analysis of the crystal structures together with the growing understanding of weak intermolecular interactions such as the CH···O and π-interactions have made it possible to have some control over the outcome of the crystallizations. With yet another compound, some properties of the crystal – centrosymmetricity and porosity being good examples – can be dictated, although complete control still escapes the chemist in many cases. The efforts made to accumulate this knowledge have been documented to general crystal structure databases such as IUCR[2] for inorganic and CSD[3] for organic structures, as well as more specific databases including the metal-organic framework database of interpenetrated frameworks by S. R. Batten,[4] and the topological analysis of the CSD database of Prosperio et al.[5] etc. Our interests lie within the creation of noninterpenetrated metal-organic structures, MOFs,[6–8] their properties and the control of their dimensionality. The prevention of interpenetration can be achieved by using templates (e.g. solvents), bulky ligands, or as in our case, bulky, weakly coordinating anions such as PF_6^-, BF_4^-, or ClO_4^-.[9] The use of these anions indeed seems to block the formation of interpenetrated 3D frameworks,[10,11] but also often results in a network with lower dimensionality. The lowered dimensionality renders the results less useful for applications since the covalent bonding throughout the framework in 3D structures principally stands for higher thermal stability. In this work we examine the reasons behind the lowered dimensionality and the role of the bulky anions as templates for the frameworks.

Results and Discussion

The tetradentate ligand **TNM** is by nature more chelating than the **TINM** (tetrakis(isonicotinoxymethyl)methane): the pyridyl nitrogens are sterically more hindered, thereby rendering the formation of 3D MOFs more difficult (Scheme 1). We have previously shown the synthesis of 3D MOFs possible using the **TNM** ligand. However, this requires an additional bridging element, the methanol molecules, in order to create the 3D connectivity. The frameworks with lower dimensionality are predominantly achieved when using the **TNM** ligand and the bulky anions BF_4^- and PF_6^-, and also in structures with smaller coordinative anions.[12]

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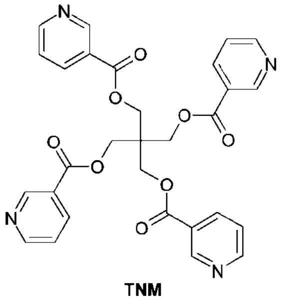
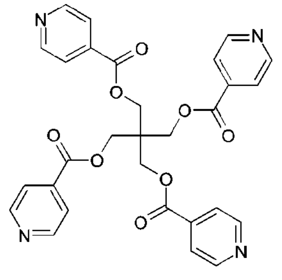


TNM



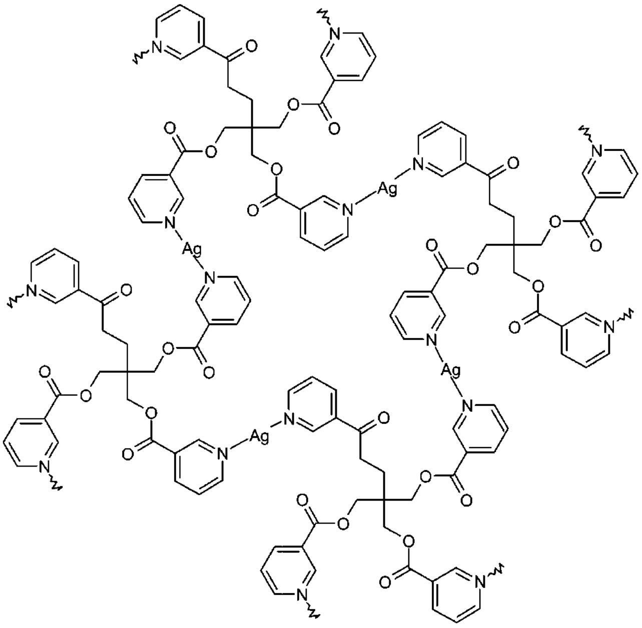
TINM

Scheme 1.

The flexibility of the **TNM** ligand allows the enveloping of the anions within the frameworks and the formation of MOFs with anions of different sizes. The result is a variety of topologies differing from those obtained by the small coordinative anions. The use of the Ag^I cation resulted in a 2D structure, which was also the case with the use of the Ni^{II} cation. The use of Cu^I without the presence of methanol prevented the formation of the Cu–MeOH–Cu bridged structure[12] – a 1D structure was formed instead.

The Threefold Interpenetrated 2D Layer Structure M1

The ligands are located in two sheets, forming the top and bottom of the polymeric layer (Scheme 2). The Ag^I cations, being located in the top, bottom, and middle of the layer, bridge the ligand sheets together, resulting in a 1.5 nm layer (Scheme 2 and Figure 1). There are two Ag^I cations with different coordination environments. The Ag1 cations bridging the **TNM** ligands in the top and bottom of the layers have a distorted square-planar coordination with the two pyridyl ligands [Ag–N distances of 2.167(1) and 2.174(2) Å] coordinated to opposite sides of the Ag^I and two BF_4^- anions [Ag–F distances 2.883(2) and 2.947(2) Å] on the sides of the axis formed by the py-Ag-py coordination. The distortion of the coordination sphere manifests itself by the fluorides of the BF_4^- being positioned above the plane of the Ag^I cation and the pyridyl nitrogens. This is explained by the steric repulsion of the layer of threefold interpenetrated frameworks which pushes the anions above the optimum arrangement. Interestingly, the pyridyl ligands are not eclipsed but arranged nearly perpendicularly. The square-planar coordination sphere of the Ag2 cations in the middle of the layer in **M1** is arranged in a similar way to the Ag1 in the top and bottom of the layer: two pyridyl nitrogens [Ag–N distances of 2.101(1) and 2.146(2) Å] and two loosely bound fluorides of the neighboring BF_4^- anions [Ag–F distances 3.029(1) and 3.370(2) Å]. The coordination sphere is nondistorted. The pyridyl ligand conformation is eclipsed, as usual for opposing pyridyl ligands (Figure 2).[12] The Ag2 is "sandwiched" between two neighboring pyridyl rings which are positioned so that an octahedral environment for Ag2 is formed. The Ag2–C distances to the carbons of these pyridyl rings are 3.164 and 3.218 Å. On the basis of molecular modeling calculations (energy minimization)[13] comparing the coordination environments of Ag1 and Ag2 (two pyridyl rings and two BF_4^-) the environment of Ag2 is more stable, even without the added stability of the "sandwich" pyridyl rings. This result is backed up by the obvious distortion from the optimum square-planar geometry of Ag1 and the results of CSD[3] searches showing the predominance of the eclipsed geometry. However, the conformation of the pyridyl ligands around the Ag^I cations is primarily dictated by the connectivity of the framework.



Scheme 2. A schematic presentation of **M1** without the BF_4^- anions.

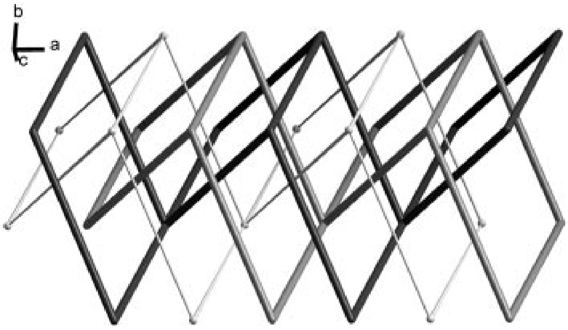


Figure 1. A schematic presentation of the threefold interpenetration of the 4,4 nets of **M1**. Only central carbon atoms and the connections between them are shown.

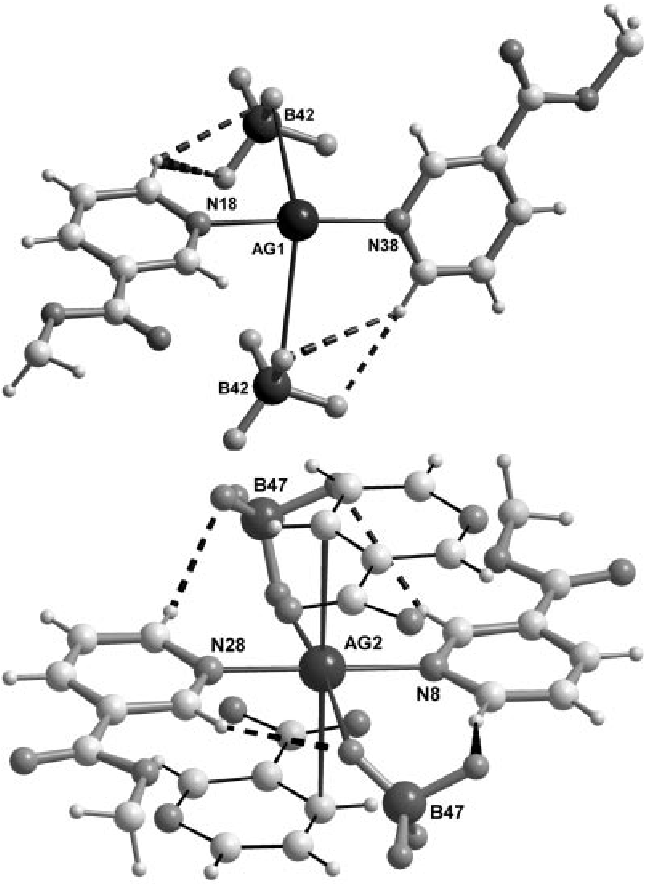


Figure 2. The coordination spheres of Ag1 and Ag2, showing the weak hydrogen bonds between the pyridyl hydrogen atoms and the fluorides of the BF_4^-. The shortest weak CH···F bond for those BF_4^- around the Ag1 is 2.365(2) Å (H39···F44) and for the BF_4^- around the Ag2 2.351(5) Å (H29···F50). The pyridyl rings on top and bottom of the Ag2 and their interactions with the Ag2 are also shown.

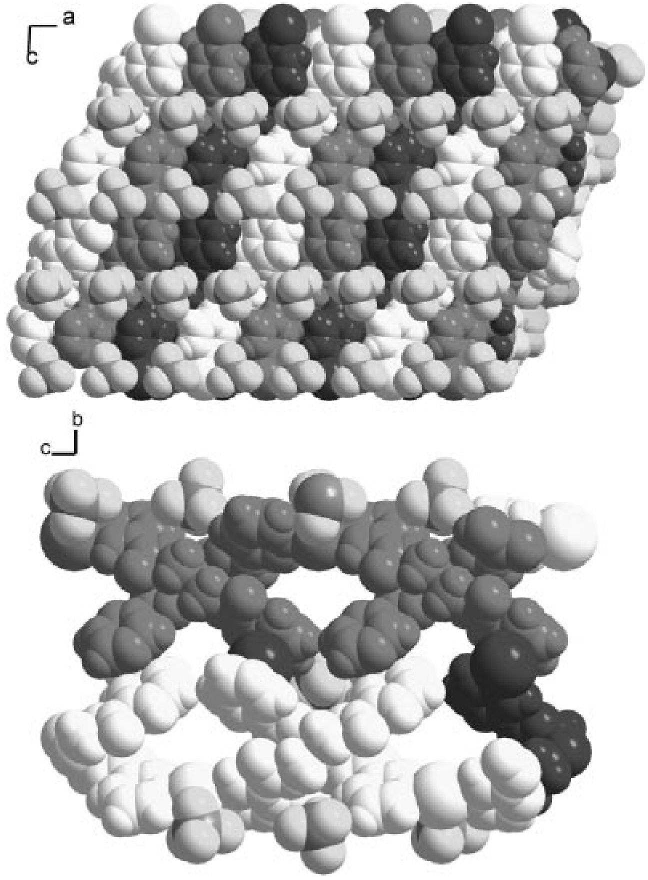


Figure 3. A space-filling presentation of **M1** along the *b* and *a* axis, showing the interpenetration of the layers and the channels along the *a* axis. The BF_4^- anions are shown only in the middle one of the three horizontally adjacent cavities shown in the lower figure. The three separate layers are shown in light, medium, and dark grey.

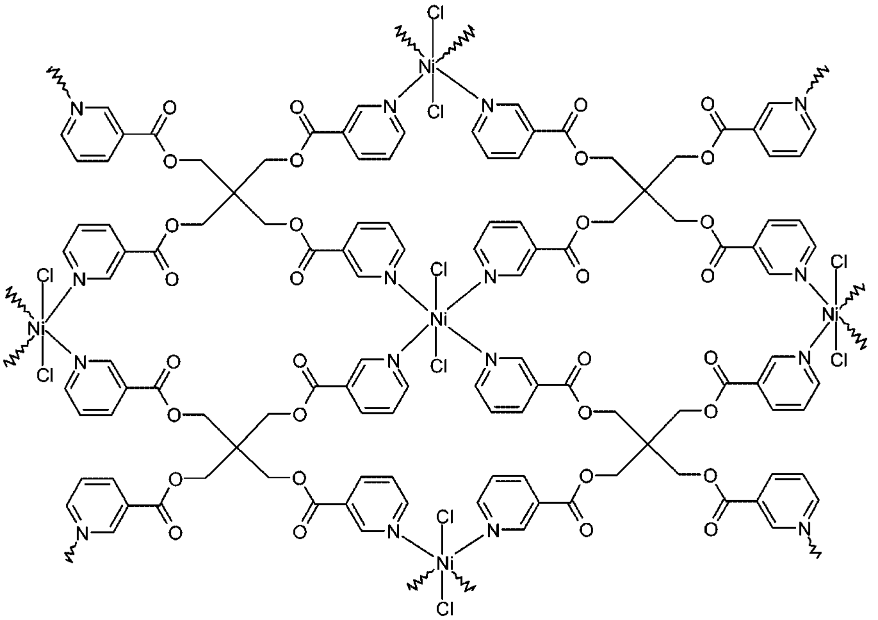
This explains the unfavored coordination geometry of the Ag1.

The BF_4^- anions are in close vicinity to the Ag^I cations, resulting in sparse anion layers between the polymeric frameworks and also channels (filled with anions) inside the layers. The 4,4 topology 2D sheets are threefold parallel interpenetrated (Figure 1), however, not completely consuming the open space of the framework. Besides the channels containing the BF_4^- anions, an additional set of channels remains along the *a* axis (Figure 3). The disordered solvent that could not be localized from the cavities was treated with SQUEEZE/BYPASS.[14]

The threefold parallel interpenetration of two-dimensional 4,4 nets is already known.[15–18] However, the mode of interpenetration of **M1** is previously unpresented. This mode is due to the use of the flexible tetradentate ligand which provides new geometrical possibilities for the network. In our previous work we presented a noninterpenetrated 2D structure with four **TNM** ligands coordinated to each Cu^{II} cation.[12] The use of Ag^I with two coordination sites for the **TNM** ligand makes the network of **M1** looser: the smallest loop in **M1** consists of eight ligand arms plus the metal coordination (56 bonds), whereas in our previous 2D **TNM** structure, the size of the loop (28 bonds) was half that of the **M1**. The amount of counter anions per metal cation is also halved in **M1**. The larger loops and reduced number of anions are the reasons for the threefold interpenetration in **M1**.

The 2D Layer Structure M2

We have previously synthesized a 3D MOF from **TINM** and $NiCl_2$[12] and respectively shown that the **TNM** ligand is unable to form a 3D MOF with a coordinative anion (and without the aid of an additional bridging component).[12,10] However, the formation of structures with lower dimensionality is possible with these components: 1 and 2D structures have already been obtained.[12,19] Here we present an eclipsed 2D layer structure with large pores (5.0 × 8.1 Å) through the crystal lattice along the *a* axis and smaller pores along the *b* and *c* axes (Scheme 3 and Figure 4). Similarly with the $CoCl_2$ structure reported earlier,[19] the net-



Scheme 3. A schematic presentation of **M2**.

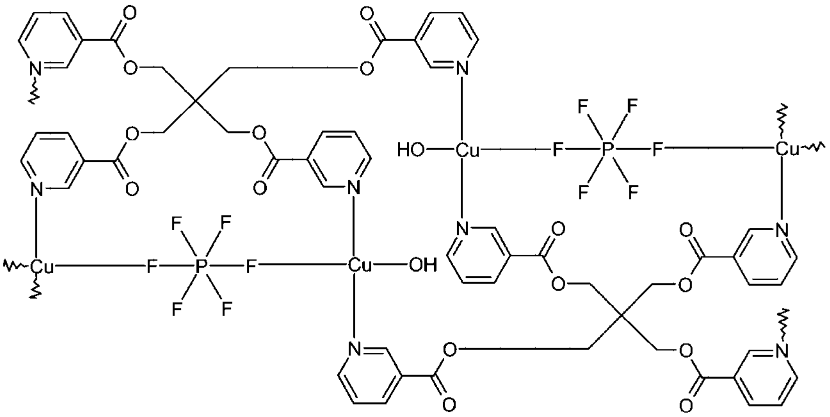
work complies with the 4,4 topology with alternating nodes of the ligand central carbons and the Ni^{II} cations. The angles and distances between the nodes are presented in Figure 5.

The chloride anions are coordinated to the Ni^{II} cations in a 35.6 and 35.8° angle to the normal of the plane formed by the Ni^{II} cations in one layer. The octahedral coordination sphere of the Ni^{II} cations is tilted sideways (see Figure 4 and Figure 5) in order to minimize the repulsion of the chloride anions of neighboring layers. The layers are held together by weak hydrogen bonds between the chloride anions, the carbonyls, and the aromatic hydrogens. The attractive interactions are neither very strong nor numerous, resulting in the disorder of the molecule. The disorder was modeled by splitting the two arms (the carbonyl group and the pyridyl rings) of the independent half of the ligand into two positions. The population parameters of these halves were refined and then fixed to the refined values for the refinement of their temperature factors. The disordered solvent was treated with SQUEEZE/BYPASS.[20] The solvent accessible void for the structure was 30.0%.[20]

The 1D Chain Structure M3

The use of **TNM** together with the $Cu(PF_6)_2/Cu(OH)_2/CuPF_6$ and in the absence of MeOH resulted in a 1D MOF structure. Each chain is composed of two parallel rows of **TNM** ligands with paired, linear conformation. The pyridyl groups of the parallel rows are superimposed and bridged together by the Cu^I cations with the N–Cu–N axis perpendicular to the direction of the polymeric chain (Scheme 4). The PF_6^- and OH^- anions and the coordinated water molecules are enveloped in the wrinkles of the heavily puckered chains. The puckering is due to the linear coordination of the *meta*-isomer pyridyl rings to the Cu^I (Figure 6).

The neighboring chains are held together by the CH···O interactions between the aromatic hydrogens and the car-



Scheme 4. A schematic presentation of **M3**.

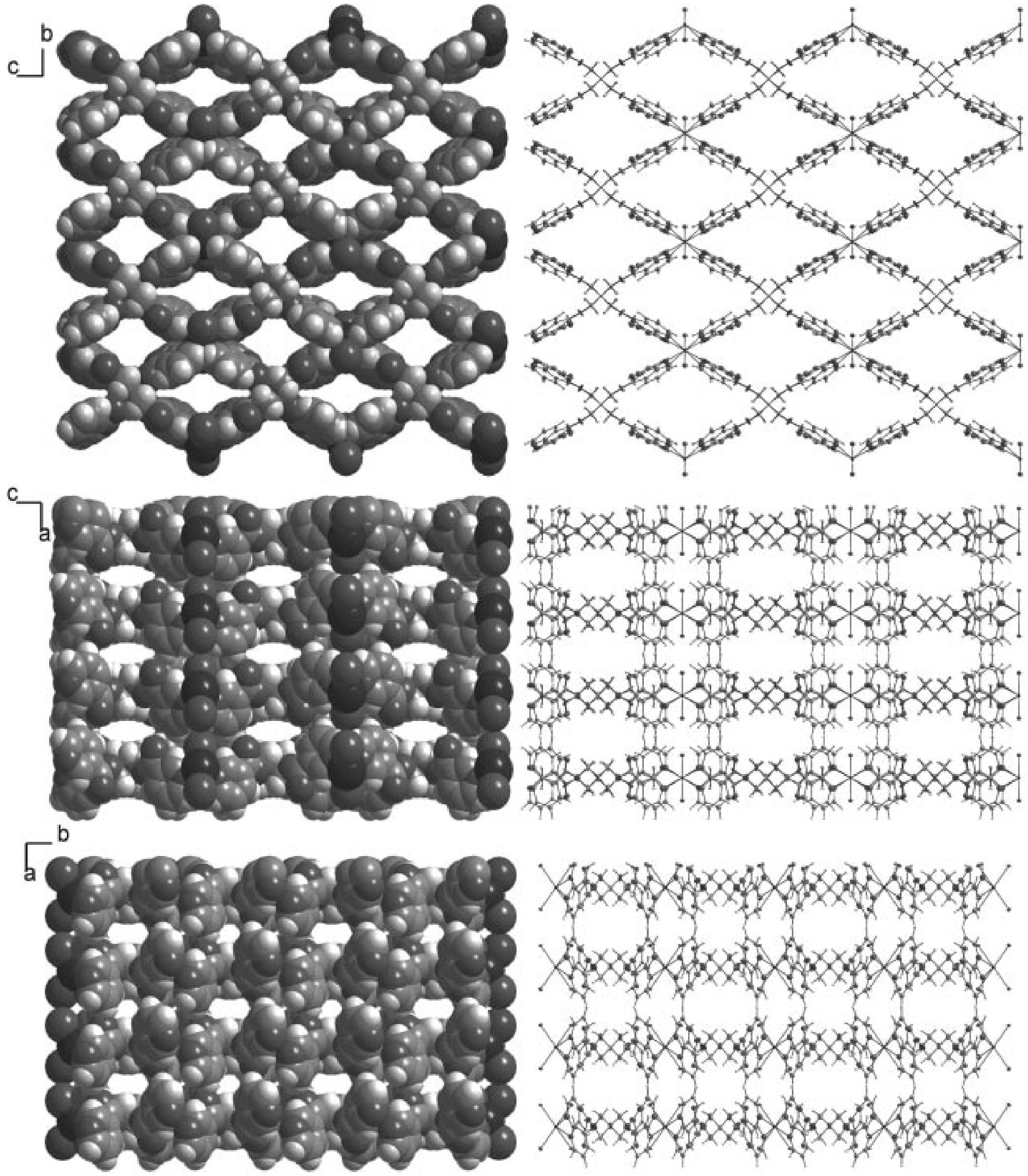


Figure 4. The space-filling and ball and stick plots for **M2**, showing the pores through the lattice along all crystallographic axes.

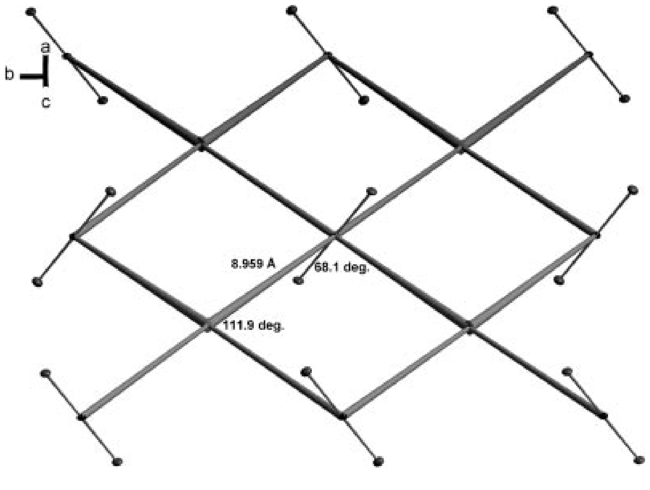


Figure 5. A schematic presentation of **M2**. The angles and distances between the nodes of the network are shown.

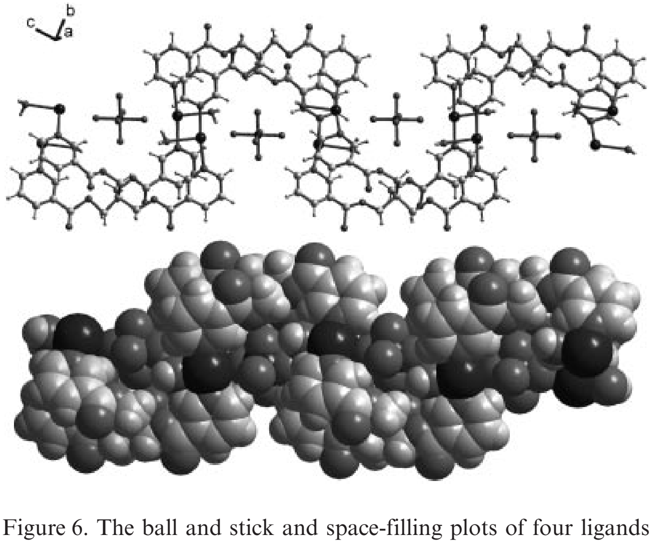


Figure 6. The ball and stick and space-filling plots of four ligands of a chain in **M3** shown along the crystallographic *a* axis.

bonyl oxygens as well as the $\pi\cdots\pi$ and van der Waals interactions. We have previously reported a 3D structure prepared from the same reagents.[10] However, in this previously reported structure the 1D chains were bridged together by the solvent methanol molecules. The absence of an additional bridging component like methanol in the preparation of **M3** prevents the formation of higher dimensionality products. The disorder around the square-planar coordination sphere of the Cu^I cations excludes the detailed discussion of the coordination bond lengths. The disorder was treated by setting geometrical restraints on the ligand. Furthermore, the disordered solvent was treated with SQUEEZE/BYPASS.[20]

Conclusions

The choice of the anions is critical for the topology of the resulting framework. In spite and because of the flexibility of the **TNM** and **TINM** ligands, the frameworks obtained with bulky noncoordinative anions are systematically different from those obtained with small coordinative anions. The flexibility of these ligands allows the tight enveloping of the anions within the forming framework or in other words, the templation of the frameworks by the anions. The use of $AgBF_4$ with **TNM** resulted in the formation of a threefold interpenetrated 2D network **M1**. The use of Ni^{II} instead of Co^{II} did not change the topology of the formed 2D frameworks.[19] However, unlike in the previous Co^{II} structure, the layers were eclipsed, which resulted in large channels (vdW diameter 9.4 Å) through the 2D layers of **M2**. The lack of a suitable bridging solvent (to allow polymerization in the 2nd and 3rd dimension) in the **M3** rendered the structure one-dimensional. As usual, the interpenetration was found to consume the available open space in **M1** resulting in a low value of 10.8%. In the noninterpenetrated structure **M2** the open space percentage was 38.0%.

Experimental Section

Materials and Measurements: All commercially available chemicals are of reagent grade and used as received without further purification. **TNM** and $Cu(PF_6)_2$/$Cu(OH)_2$/$CuPF_6$ were synthesized as previously reported.[10,21] The purity of **M1**–**2** was confirmed by elemental analysis, whereas the EA of **M3** gave inaccurate results due to the decomposition of the structure in air. Transferring the crystals directly from the mother liquid to the perfluorinated oil used in the single-crystal X-ray diffraction experiments, the decomposition was prevented and the diffraction experiment was enabled.

The Threefold Interpenetrated 2D Layer Structure M1: In a solution of **TNM** (22 mg, 39.5 μmol) dissolved in MeOH (3 mL) was added $AgBF_4$ (16 mg, 82.2 μmol) in water (1.5 mL). The solution was slowly allowed to evaporate, and the crystalline solid was collected from the solution before complete evaporation of the solvents and dried in air. Yield: 29%. $C_{29}H_{24}Ag_2B_2F_8N_4O_8$ + 8 H_2O: calcd. C 32.0, H 3.7, N 5.1; found C 31.9, H 2.9, N 5.0.

The 2D Layer Structure M2: A MeOH solution of **TNM** (1.5 mL, 14.4 mM) was carefully layered on top of a THF solution of $NiCl_2\cdot 6H_2O$ (1.5 mL, 15 mM). The solutions were slowly allowed to diffuse and the crystalline solid was collected from the interface of the solvents and dried overnight in air. Yield: 57%. $C_{29}H_{24}Cl_2N_4NiO_8$ + 2 MeOH: calcd. C 49.6, H 4.3, N 7.5; found C 49.2, H 4.2, N 7.4.

The 1D Chain Structure M3: To a solution of **TNM** (6 mg, 10.8 μmol) dissolved in MeCN (1.5 mL) was added a saturated

Table 1. Crystallographic parameters for complexes **M1**–**M3**.

	M1	**M2**	**M3**
Empirical formula	$[Ag_2(C_{29}H_{24}N_4O_8)(BF_4)_2]$	$[Ni(C_{29}H_{24}N_4O_8)Cl_2]$	$[Cu_2(C_{29}H_{24}N_4O_8)(PF_6)(OH)(H_2O)]$
Formula mass	945.88	686.13	863.60
Crystal color, shape	colorless, prisms	green, prisms	colorless, prisms
Crystal dimensions [mm]	0.15×0.20×0.30	0.15×0.20×0.35	0.15×0.15×0.15
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$ (No. 14)	*Cccm* (No. 66)	$P\bar{1}$ (No. 2)
a [Å]	5.5700(3)	14.2220(8)	6.7490(10)
b [Å]	41.5200(3)	20.0730(12)	15.919(3)
c [Å]	15.5158(2)	29.6847(18)	33.874(6)
α [deg.]	90	90	90.361(6)
β [deg.]	92.711(4)	90	89.682(9)
γ [deg.]	90	90	97.801(9)
V [Å^3]	3584.3(2)	8474.3(9)	3605.5(11)
Calculated density [Mg/m^3]	1.753	1.076	1.591
Temperature of collection [K]	123	123	173
Z	4	8	4
R_{obs}	R_1 = 0.0952, wR_2 = 0.2015	R_1 = 0.0626, wR_2 = 0.1911	R_1 = 0.1399, wR_2 = 0.3563
R_{all}	R_1 = 0.2116, wR_2 = 0.2449	R_1 = 0.1274, wR_2 = 0.2178	R_1 = 0.3321, wR_2 = 0.4291
GooF	0.951	1.060	0.871
θ range for data collection [°]	1.0 to 25.2	3.2 to 27.5	3.0 to 24.7
Scan type	phi / omega, 1°	phi / omega, 1°	phi / omega, 1°
Refl. collected / unique / cell refinement	17569 / 5938 / 3788	20148 / 4947 / 1235	17478 / 8999 / 5136
Refined parameters	478	178	668
Res. electron density [e/Å^3]	1.956 / –1.467	0.966 / –0.471	1.513 / –0.776

water solution of $Cu(PF_6)_2/Cu(OH)_2/CuPF_6$ (5 mL). The solution was slowly allowed to evaporate, and the crystalline solid was collected from the solution before complete evaporation of the solvents and dried in air. Yield: 54%.

X-ray Crystallographic Study: The single-crystal X-ray diffraction was done with a Nonius–Kappa CCD diffractometer with graphite-monochromatized Mo-K_α (λ = 0.71073 Å) radiation. The Collect software system was used in the measurement and DENZO-SMN[22] in the processing of the data. The structures were solved and refined by full-matrix least squares on F^2 with the WinGX-software package utilizing SHELXS97 and SHELXL97 modules.[23–25] Hydrogen atoms were refined by a riding model. Absorption correction was not performed for any of the complexes. The graphic presentations of the structures were created with the software Diamond.[26] The crystallographic parameters for the structures **M1**–**M3** are presented in Table 1.

CCDC-256787–256789 contain 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.

Acknowledgments

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