

Using multimodal ligands to influence network topology in silver(I) coordination polymers

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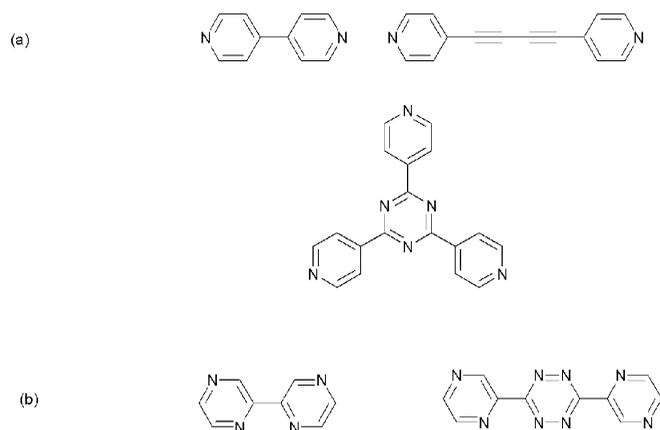
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A range of Ag(I) one- and two-dimensional coordination frameworks has been prepared and structurally characterized by using the multimodal ligand 3,6-di-pyrazin-2-yl-(1,2,4,5)-tetrazine, which offers both monodentate and chelating binding sites. It is demonstrated that multimodal ligands can be used to prepare coordination frameworks with novel and unusual topologies and to influence the precise geometrical arrangement of both ligands and metal centers within such supramolecular arrays.

crystal engineering | supramolecular chemistry | tetrazine

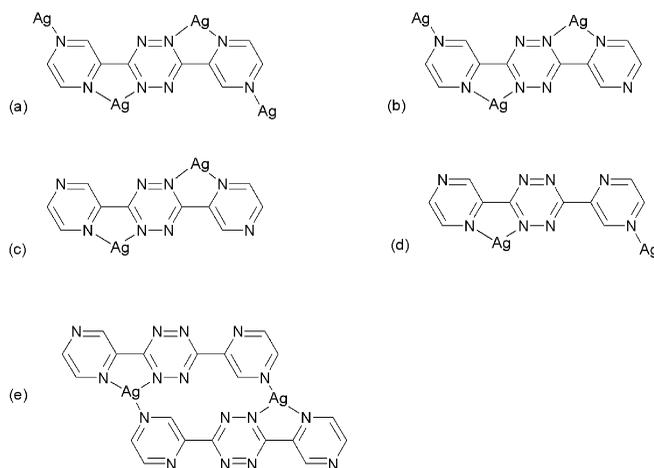
The synthesis of coordination frameworks represents an extremely topical area of research (1–3) that has developed dramatically over recent years with many advances in understanding the control of framework structure and topology. For example, the degree of interpenetration (4), polymeric dimensionality (5), and framework connectivity (6) can be controlled by the design of the constituent building blocks or crystallization conditions. We (7, 8), among others (9–13), have been developing a strategy that uses multimodal bridging ligands that differ from more traditional tri- and tetradentate bridging systems in that they offer chemically distinct binding sites, both chelating and monodentate (Scheme 1). By using such ligands for coordination polymer construction, we aim to introduce further control over network formation by controlling the precise arrangement of metal centers with respect to each other and have recently reported examples of chiral Ag(I) coordination frameworks with diamondoid topology by using 2,2'-bipyrazine as the multimodal bridging ligand (7, 8). We are also interested in the assembly of discrete supramolecular entities, metallacycles, or oligomeric supramolecular arrays into infinite coordination arrays (13). Our recent studies combining coordinatively flexible Cd(II) metal centers with the angular ligand 2,4'-(1,4-phenylene)bispyridine indicate that centrosymmetric metallacyclic units can be readily prepared by using simple ligand design



Scheme 1. (a) Polypyridyl ligands most commonly used for coordination polymer synthesis, which offer a single coordination donor type, and (b) multimodal ligands, which offer both chelating and monodentate donors.

(13). The latter study (13) also demonstrated that the metallacyclic units could be arranged into coordination frameworks by means of bridging of coordinated NO_3^- anions (13). We are now extending this work to use ligands that simultaneously encourage the formation of metallacyclic units and also intermetallacycle bridging.

We have targeted 3,6-di-pyrazin-2-yl-(1,2,4,5)-tetrazine (dpztz), which has the potential to control the relative displacement of up to four coordinated metal centers in a zigzag fashion (Scheme 2). Although bis-2-pyridyl substituted 1,2,4,5-tetrazine units in principle allow coordination of two metal centers in *cis*-bidentate sites, in practice this coordination mode has never been observed and the *trans*-arrangement is always adopted (14–16). Dpztz also has the potential to form metallacyclic units with a suitably flexible transition metal, such as Ag(I), using both chelating and monodentate donors (Scheme 2e). It is our experience that Ag(I) exhibits a marked tendency to adopt both chelating and monodentate donors with coordination frameworks when offered this possibility by a multimodal ligand (7, 8). This coordination preference may be attributed to the drive of the system to adopt what may be termed a “homogeneous” metal coordination environment throughout the coordination polymer (9–12). We now report the reaction of dpztz with Ag(I) and the structural characterization of a range of two-dimensional coordination frameworks with unusual network topologies and an



Scheme 2. (a–d) Coordination modes of the dpztz ligand observed in this study [mode (a) 1, 3; (b) 2; (c) 4; (d) 1] and (e) metallacyclic “Ag₂(dpztz)₂” unit observed in 1–3.

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Abbreviation: dpztz, 3,6-di-pyrazin-2-yl-(1,2,4,5)-tetrazine.

Data deposition: The atomic coordinates have been deposited in the Cambridge Structural Database, Cambridge Crystallographic Data Centre, Cambridge CB2 1EZ, United Kingdom (CSD reference nos. 179200–179203).

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unprecedented one-dimensional tubular ribbon constructed with metallacyclic units. We show that by identifying potential structural subunits, such as metallacycles, multimodal ligands can be used to influence network topologies.

Experimental Procedures

All chemicals were purchased from Aldrich and used without further purification.

3,6-Di-pyrazin-2-yl-[1,2,4,5] Tetrazine (dpztz). A solution of pyrazine-2-carbonitrile (12.63 g, 0.12 mol) in tetrahydrofuran (75 cm³) was treated with conc. HCl (15 cm³) and stirred for 30 min. Hydrazine monohydrate (35 cm³, 0.72 mol) was added dropwise and the resulting solution was refluxed for 14 h. The reaction solution was diluted with water (≈80 cm³), cooled to -10°C, and conc. acetic acid (25 cm³) was added. A saturated aqueous solution of sodium nitrite (30 g, 0.44 mol) was added dropwise, forming a pink solution. The solution was extracted with CH₂Cl₂, the organic layer was dried over anhydrous MgSO₄, and the solvent was removed *in vacuo*. The product was recrystallized from EtOH to give a purple microcrystalline solid (Yield: 3.55 g, 25%). For spectroscopic and analytical data see the supporting information, which is published on the PNAS web site, www.pnas.org.

[Ag₂(dpztz)₃(PF₆)₂]_∞ 1. AgPF₆ (7.6 mg, 0.030 mmol) and dpztz (3.7 mg, 0.015 mol) were dissolved in MeCN (5 cm³) to give a homogeneous solution. Dropwise addition of diethyl ether affords a dark pink microcrystalline product. Crystals suitable for single-crystal x-ray diffraction studies were grown by vapor diffusion of diethyl ether into an analogous reaction solution. For spectroscopic and analytical data see supporting information.

Compounds 2-4 were prepared, and single crystals were grown, analogously to 1 but with a 4:1 AgX (X = PF₆ 2, BF₄ 3, SbF₆ 4) to dpztz reactant ratio.

Crystal Data for {[Ag₂(dpztz)₃(PF₆)₂·2MeCN]_∞ 1. C₃₄H₂₄Ag₂F₁₂N₂₆P₂, *M* = 1302.48, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 8.0650(5), *b* = 16.2966(11), *c* = 17.0513(11) Å, β = 96.631(1)°, *U* = 2226.1(2) Å³, *Z* = 2, *D_c* = 1.943 g cm⁻³, μ(Mo-Kα) = 1.067 mm⁻¹, *T* = 150(2)K; 5,579 unique reflections [*R*_{int} = 0.040] [3,858 with *I* > 2σ(*I*)]. Final *R* = 0.0382, *wR*₂(all data) = 0.0851.

Crystal Data for {[Ag(dpztz)]PF₆]_∞ 2. C₁₀H₆AgF₆N₈P, *M* = 491.07, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 10.663(2), *b* = 11.566(3), *c* = 11.972(3) Å, β = 99.303(4)°, *U* = 1457.1(9) Å³, *Z* = 4, *D_c* = 2.239 g cm⁻³, μ(Mo-Kα) = 1.580 mm⁻¹, *T* = 150(2)K; 3,565 unique reflections [*R*_{int} = 0.039] [2,307 with *I* > 2σ(*I*)]. Final *R* = 0.0428, *wR*₂(all data) = 0.1024.

Crystal Data for {[Ag₄(dpztz)₃(MeCN)₄](BF₄)₄]_∞ 3. C₃₈H₃₀Ag₄B₄F₁₆N₂₈, *M* = 1657.62, triclinic, space group *P*-1 (no. 2), *a* = 11.4337(13), *b* = 11.7865(14), *c* = 12.6113(14) Å, α = 99.213(2), β = 104.719(2), γ = 118.810(2)°, *U* = 1357.9(3) Å³, *Z* = 1, *D_c* = 2.027 g cm⁻³, μ(Mo-Kα) = 1.539 mm⁻¹, *T* = 150(2)K; 6,134 unique reflections [*R*_{int} = 0.058] [5,052 with *I* > 2σ(*I*)]. Final *R* = 0.0502, *wR*₂(all data) = 0.1407.

Crystal Data for {[Ag₂(dpztz)₃](SbF₆)₂·2MeCN]_∞ 4. C₃₄H₂₄Ag₂F₁₂N₂₆Sb₂, *M* = 1484.04, triclinic, space group *P*-1 (no. 2), *a* = 10.4171(8), *b* = 11.5232(8), *c* = 11.7809(8) Å, α = 102.792(1), β = 98.176(1), γ = 116.099(1)°, *U* = 1191.18(15) Å³, *Z* = 1, *D_c* = 2.069 g cm⁻³, μ(Mo-Kα) = 2.039 mm⁻¹, *T* = 150(2)K; 5,304 unique reflections [*R*_{int} = 0.021] [4,815 with *I* > 2σ(*I*)]. Final *R* = 0.0333, *wR*₂(all data) = 0.0833.

All single-crystal x-ray experiments were performed on either a Bruker AXS SMART1000 CCD detector (1-3) or Bruker AXS

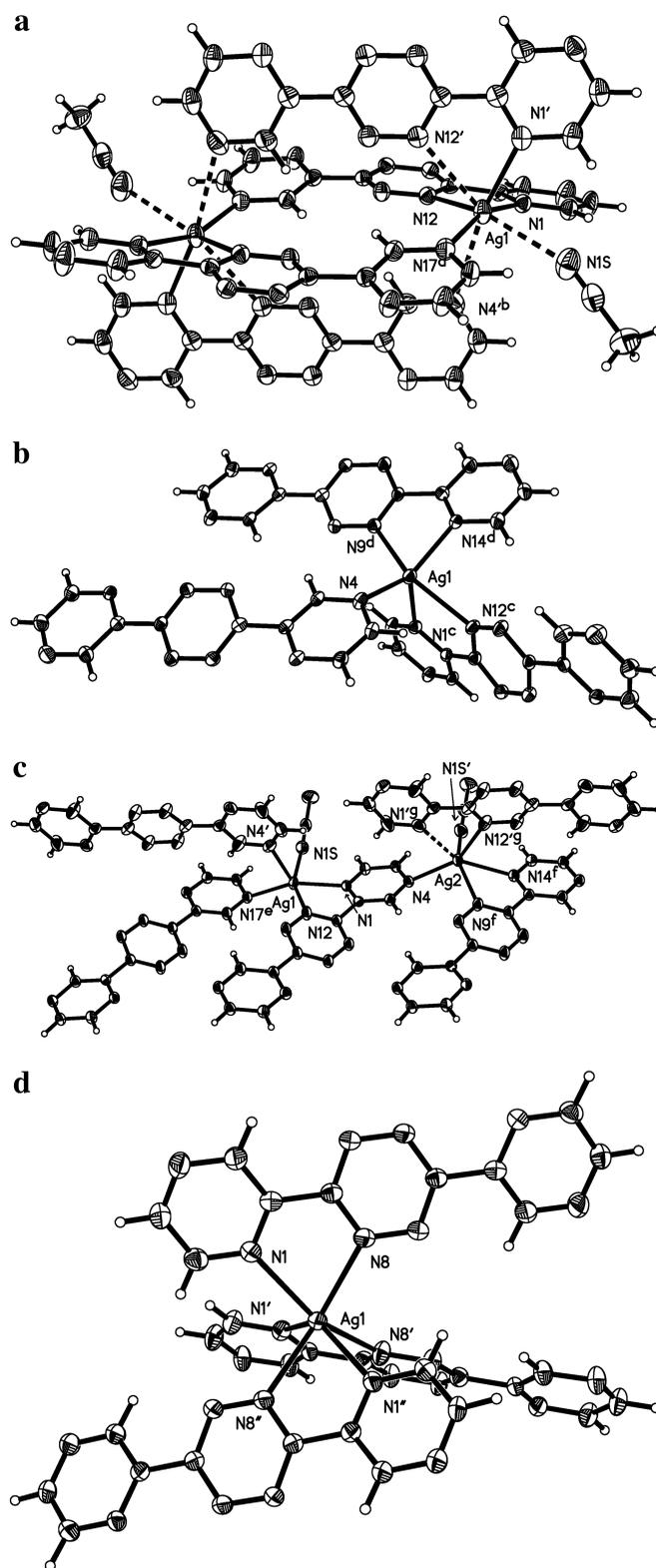


Fig. 1. View of the Ag(I) coordination environments observed in 1-4 (a-d). Bond lengths and symmetry codes are given in Table 1. Displacement ellipsoids are drawn at the 50% probability level.

SMART APEX (4) diffractometer both equipped with an Oxford Cryosystems (Oxford, U.K.) open-flow cryostat (17) [graphite monochromated Mo-Kα radiation (λ = 0.71073 Å); ω

Table 1. Selected bond lengths (Å) for compounds 1–4

1		2		3		4	
Ag1-N1	2.419 (3)	Ag1-N1 [‡]	2.454 (4)	Ag1-N1	2.370 (4)	Ag1-N1	2.435 (4)
Ag1-N1'	2.473 (3)	Ag1-N4	2.253 (4)	Ag1-N4'	2.436 (5)	Ag1-N8	2.439 (4)
Ag1-N12	2.606 (3)	Ag1-N9 [§]	2.466 (4)	Ag1-N12	2.510 (5)	Ag1-N1'	2.428 (4)
Ag1-N17*	2.390 (3)	Ag1-N12 [‡]	2.512 (4)	Ag1-N17 [¶]	2.352 (5)	Ag1-N8'	2.460 (4)
Ag1...N4' [†]	2.841 (3)	Ag1-N14 [§]	2.338 (4)	Ag1-N15	2.463 (5)	Ag1-N1''	2.456 (4)
Ag1...N12'	2.810 (3)			Ag2-N1''	2.711 (5)	Ag1-N8''	2.463 (4)
Ag1...N15	2.780 (4)			Ag2-N4	2.411 (4)		
				Ag2-N9**	2.460 (5)		
				Ag2-N12''	2.514 (6)		
				Ag2-N14**	2.564 (5)		
				Ag2-N15'	2.376 (5)		

Symmetry codes:

*1 - x, 1 - y, 2 - z.

†1 + x, y, z.

‡1½ - x, y + ½, 1½ - z.

§1 - x, -y, 1 - z.

¶-1 - x, -y, 1 - z.

||-2 - x, -1 - y, -z.

**-2 - x, -y, -z.

scans]. Absorption corrections were applied by a semiempirical approach (18). Other details of crystal data, data collection, and processing are given in supporting information. All of the single-crystal structures were solved by using direct methods (1,4) or by Patterson methods (2,3) with SHELXS-97 (19), and all non-H atoms were located by using subsequent difference-Fourier methods (20). In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, except those of MeCN solvent molecules, which were located in ΔF syntheses and refined as part of rigid rotating groups. Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre.

Powder x-ray diffraction patterns data were collected with a Philips X'PERT θ -2 θ diffractometer with Cu-K α ($\lambda = 1.5406$ Å) radiation. Samples were mounted on flat glass-plate sample holders. Purity was assessed by comparing the experimental powder pattern to a simulated powder pattern taking the single-crystal structural data for compounds 1–4 as a model.

Results and Discussion

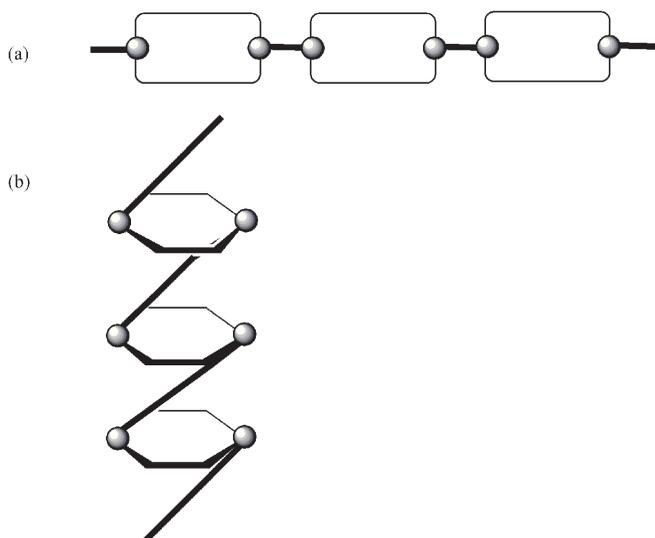
The novel ligand dpztz was prepared by an adaptation of the method reported by Kaim and Fees (21) used for the synthesis of 3,6-di-pyrimidyl-2-yl-[1,2,4,5] tetrazine. 2-Cyanopyrazine was refluxed with concentrated HCl and hydrazine monohydrate in tetrahydrofuran overnight to form 1,4-dihydro-dpztz, and subsequent oxidation with aqueous sodium nitrite solution afforded the product in 25% yield.

Compounds 1–4 were prepared by reacting dpztz with the appropriate Ag(I)X salt (X = PF₆⁻, BF₄⁻, SbF₆⁻) in MeCN in either a 2:1 (1) or 4:1 (2–4) Ag(I):dpztz ratio. The products were precipitated as dark pink microcrystalline solids by slow addition of diethyl ether. Crystals of suitable quality for single-crystal x-ray diffraction studies were grown by vapor diffusion of diethyl ether into analogous solutions of the ligand and Ag(I) salt in MeCN, and structural determinations were carried out for each compound. It was found that using a high ratio of Ag(I):dpztz in the reaction mixture led to the formation of higher quality single crystals for structural studies (22), and the phase purity of each compound was confirmed by comparison of powder x-ray diffraction (PXD) patterns with simulated powder patterns generated from the single-crystal structures. The reaction between AgBF₄ and dpztz in a 2:1 ratio in MeCN afforded compound 3 only as confirmed by PXD studies. Reaction of AgSbF₆ with

dpztz yielded a predominantly amorphous material that was not of single phase, as shown by PXD, and phase pure frameworks could be isolated only as single crystals by slow diethyl ether vapor diffusion.

The reaction between AgX (X = PF₆⁻, BF₄⁻, SbF₆⁻) and dpztz, in a 4:1 ratio in MeCN, was studied in solution by ¹H NMR and electrospray mass spectrometry. ¹H NMR studies showed a small downfield shift in the ligand protons, relative to the free ligand, indicating an interaction between Ag(I) and the ligand. The electrospray mass spectrum showed only a peak corresponding to [Ag(dpztz)(MeCN)]⁺, no indication of a higher degree of oligomerization. Thus, solution studies show some interaction between Ag(I) and dpztz in solution, but the mononuclear units are the only species definitely present in the solution phase. Although higher degrees of oligomerization, toward polymerization, are not observed, they cannot be ruled out (23).

The structure of 1 reveals each Ag(I) center sitting in a coordination environment with four short Ag-N bond lengths and three longer-range Ag...N interactions (Fig. 1a; Table 1). Thus, each silver cation is linked to two others via the short bond distances to afford a one-dimensional chain composed of Ag₂L₂ metallacycles linked by way of a further dpztz bridging ligand. A related structural motif of alternating loops and rods has been observed for a range of coordination polymers and most pertinently for {[Ag₂(3,3'-dpztz)₃](PF₆)₂]_∞ (3,3'-dpztz = 3,6-dipyridin-3-yl-1,2,4,5-tetrazine) (24). However, a clear distinction is observed for the overall arrangement of 1 in comparison to these other linked-metallacycle species (Scheme 3). Whereas in the previously reported examples of “linked-metallacycles” the plane formed by each metallacyclic unit is approximately parallel to the direction of chain propagation, leading to an “open” chain arrangement (Scheme 3a), in 1 the plane formed by the metallacyclic units are perpendicular to the direction of chain propagation, giving a “concertina” arrangement (Fig. 2, Scheme 3b). Considering the longer-range Ag...N interactions it is apparent that this compacted chain arrangement is adopted because of the interaction between the Ag(I) cation and the pyrazyl N-donor of the cross-linking ligand [Ag...N = 2.841(3) Å]. Taking this longer-range interaction into account, the structure of 1 resembles both a ribbon-type structure and a tubular one-dimensional polymer (25) and thus we term this structure a “tubular ribbon” (Fig. 2). The ribbons run parallel to the *a* axis forming channels that include guest MeCN molecules. Adjacent ribbons interlock and interact via long-range π - π interactions between pyrazyl



Scheme 3. Schematic representation of (a) open-linked metallacycle one-dimensional chains and (b) the concertina chain leading to a tubular ribbon one-dimensional array.

groups of the Ag_2L_2 metallacycles (centroid–centroid separation = 3.83 Å; centroid offset = 1.23 Å) (26).

The structure of $\{[\text{Ag}(\text{dpztz})]\text{PF}_6\}_\infty$ **2** shows each Ag(I) center adopting a five-coordinate geometry (Fig. 1b; Table 1) with two chelating and one monodentate dpztz ligand, and each dpztz ligand coordinating three Ag(I) cations rather than the four anticipated, leaving a pendant, uncoordinated pyrazyl donor. “ $\text{Ag}_2\text{dpztz}_2$ ” metallacyclic units (Scheme 2e) are observed forming four-membered rings, and undulating sheets of 4.8^2 topology are generated with each Ag(I) center and dpztz ligand acting as a three-connected topological node (Fig. 3, Scheme 4a). The sheet is constructed such that chains of alternating Ag(I) centers and tetrazine rings run parallel to the *a* axis and Ag(I)-pyrazine chains run parallel to the *b* axis. The sheet is highly undulating, with a depth of about 13.0 Å, and adjacent sheets are interlocked (without any significant π - π interactions), allowing the formation of channels running parallel to the *c* axis that incorporate the PF_6^- counteranions.

In contrast to $\{[\text{Ag}(\text{dpztz})]\text{PF}_6\}_\infty$, reaction of AgBF_4 with dpztz in a 4:1 ratio affords $\{[\text{Ag}_4(\text{dpztz})_3(\text{MeCN})_4](\text{BF}_4)_4\}_\infty$ **3**. The structure determination for **3** reveals two distinct Ag(I) centers and two dpztz ligand environments. Both Ag(I) centers adopt a five-coordinate geometry with three dpztz ligands, one chelating and two monodentate, and a coordinated MeCN molecule (Fig. 1c; Table 1), and each dpztz ligand bridges four Ag(I) centers in the manner anticipated (Scheme 2a). One of the Ag(I) cations additionally adopts a further long-range interaction [Ag–N = 2.711(5)Å] to a pyrazine N-donor, but this interaction does not affect the topology of the two-dimensional

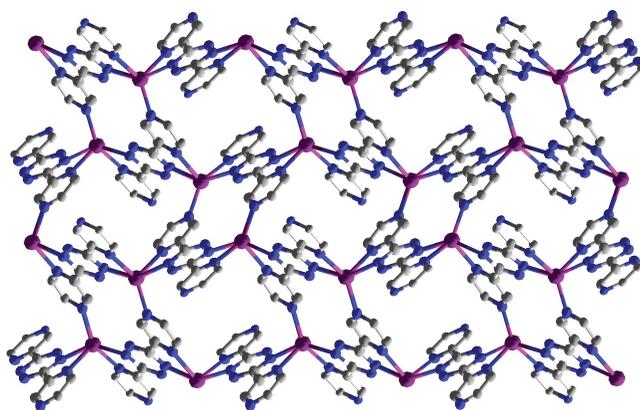


Fig. 3. View perpendicular to the plane of the $\{[\text{Ag}(\text{dpztz})]^+\}_\infty$ sheet in **2** illustrating the 4.8^2 topology of the framework, considering both Ag(I) cations and dpztz ligands as three-connected nodes. Hydrogen atoms and anions are omitted for clarity.

network. The sheet observed contains both three- (Ag) and four-connected nodes (dpztz ligands) (Fig. 4). As in **1** and **2**, four-membered “ $\text{Ag}_2\text{dpztz}_2$ ” metallacyclic units (Scheme 2e) are observed and the sheet also contains further, distinct, four- and eight-membered rings (Scheme 4b) and has a full topological nomenclature of $(4^2.8)_4(4^2.8^2)_1(4^3.8)_2$ [the topological terms refer to the Ag(I) cations and the two different ligand environments, respectively]. To our knowledge, this structural arrangement represents the first example of such a network topology for a coordination polymer. Adjacent sheets interdigitate by means of the coordinated MeCN molecules but no significant interactions between sheets are observed with residual spaces being occupied by the counteranions.

Reaction of AgSbF_6 with dpztz in a 4:1 ratio affords the complex $\{[\text{Ag}_2(\text{dpztz})_3](\text{SbF}_6)_2\}_\infty$. Single-crystal x-ray determination of this complex revealed that, in contrast to **1–3**, each Ag(I) center is coordinated exclusively by chelating groups from three distinct dpztz ligands in a distorted trigonal prismatic geometry (Fig. 1d; Table 1). As all of the monodentate pyrazyl donors remain uncoordinated, each ligand uses only its two chelating pockets in a trans fashion, thereby acting as a simple bridging rod between adjacent Ag(I) centers (Fig. 5). Thus, each Ag(I) center is linked to three others affording a two-dimensional sheet structure that adopts a honeycomb arrangement or 6^3 net (Scheme 4c). No interdigitation between adjacent sheets is observed, and the voids within each sheet are occupied by the SbF_6^- counteranions.

Such 6^3 net structures are well known in coordination frameworks where trigonal nodes, either metal centers or ligands, are linked by means of simple rods to afford the two-dimensional sheet arrangement. However, to our knowledge, this structural type has not been observed previously by using six-coordinate metal centers with three chelating donor groups. Each node is

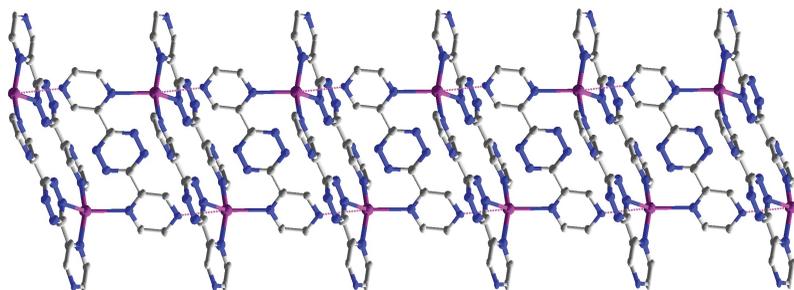
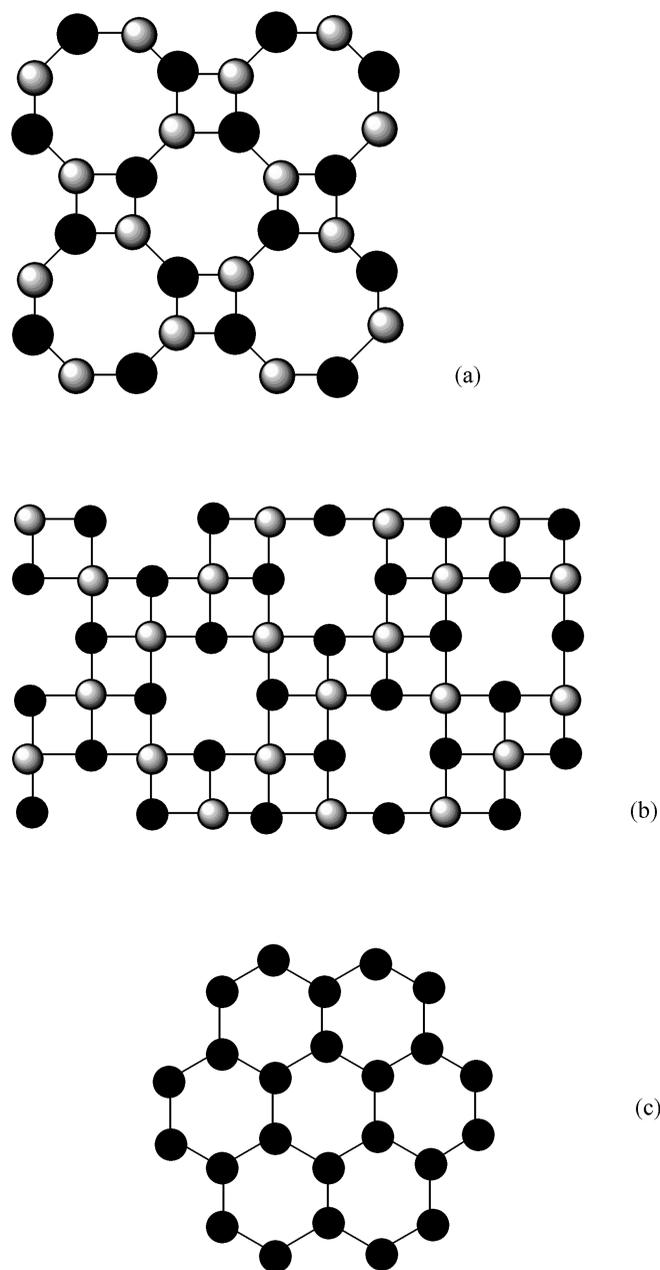


Fig. 2. View of the one-dimensional $\{[\text{Ag}_2(\text{dpztz})_3]^{2+}\}_\infty$ “tubular ribbon” observed for **1** indicating the influence of the long-range Ag...N interactions. Hydrogen atoms, anions, and uncoordinated solvent molecules are omitted for clarity.



Scheme 4. (a) The 4.8^2 topology sheet observed for $\{[\text{Ag}(\text{dpztz})]\text{PF}_6\}_\infty$. (b) The $(4^2.8)_4(4^2.8^2)_1(4^3.8)_2$ topology observed for $\{[\text{Ag}_4(\text{dpztz})_3(\text{MeCN})_4](\text{BF}_4)_4\}_\infty$. Dark circles, Ag(I) centers; gray circles, dpztz ligands. (c) Schematic representation of a 6^3 net observed in 4.

compressed, distorting the angles formed between the intermetallic $\text{Ag}\cdots\text{Ag}\cdots\text{Ag}$ vectors ($\angle\text{Ag}\cdots\text{Ag}\cdots\text{Ag} = 151.4, 102.2, 99.6^\circ$). Thus, each node of the framework is distorted from the ideal value of 120° in a honeycomb structure, and the structure observed more closely resembles a “brick-wall” arrangement. Similar structural arrangements have been identified for some coordination frameworks constructed with T-shaped building blocks such as $\text{Cd}(\text{NO}_3)_2$ (27).

Comparison of Structures

The structures observed for compounds 1–4 illustrate the variety of bridging modes that can be observed for dpztz. All four modes illustrated in Scheme 2 *a–d* are observed, mode (a) in 1 and 3,

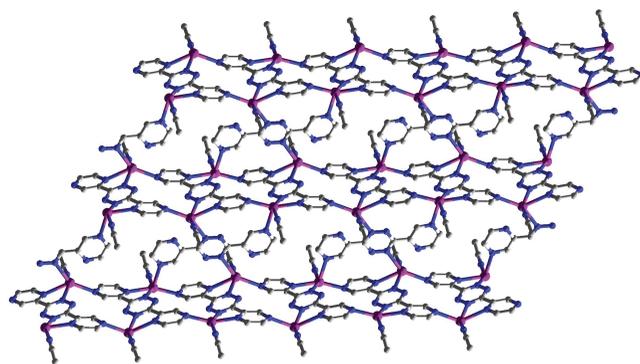


Fig. 4. View perpendicular to the plane of the $\{[\text{Ag}_4(\text{dpztz})_3(\text{MeCN})_4]^{4+}\}_\infty$ sheet in 3 illustrating the different dpztz and Ag(I) environments and the sheet arrangement. Hydrogen atoms, anions, and uncoordinated solvent molecules are omitted for clarity.

mode (b) in 2, mode (c) in 4, and mode (d) in 1. It is interesting to note that despite the wide variety of potential bridging modes the metallacyclic “ Ag_2L_2 ” unit (Scheme 2*e*) is observed in three of the four structures reported here (1–3). Thus, the metallacyclic subunit can be potentially used as a “building block,” a predictable component of the product coordination framework, which can be used to manipulate structural topology. The search for new building blocks is one of the major challenges of coordination polymer chemistry (3, 4).

The topologies observed in 2 and 3 are unusual for coordination polymers and in particular for Ag(I). Both contain three-connected nodes and although such nodes are relatively common within two-dimensional coordination polymers they normally form structures that contain six-membered rings (27–33). In particular, honeycomb sheet arrangements are formed by trigonal planar nodes (28–31), and T-shaped nodes form a range of structural types, including brick-wall (27) and herringbone motifs (30, 31), based on “compressed” honeycomb arrangements. All of these more common types adopt a 6^3 topology, as seen in 4, and larger rings are rarely observed within two-dimensional networks. The 4.8^2 framework is perhaps the next most common arrangement and has been observed for Cd(II) (34) and *f*-block coordination polymers (35), although, to our knowledge, it has not previously been observed for Ag(I) systems. For the complexes reported here the sheet topology relies on the formation of four-membered rings. The combination of Ag(I) and dpztz is ideal for the formation of metallacyclic “ $\text{Ag}_2(\text{dpztz})_2$ ” units (Scheme 2*e*), representing four-membered rings, because of the flexibility of the Ag(I) coordination sphere

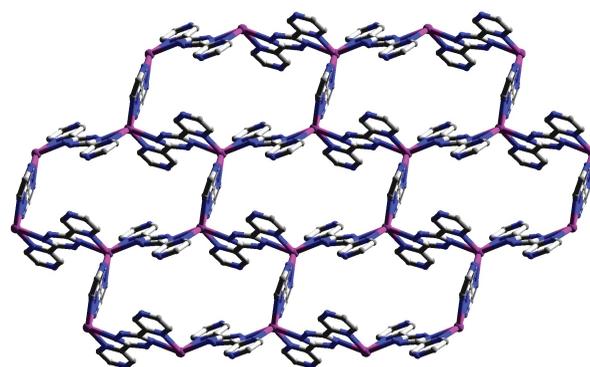


Fig. 5. View perpendicular to the plane of the $\{[\text{Ag}_2(\text{dpztz})_3]^{2+}\}_\infty$ sheet in 4 illustrating the (6,3) topology of the two-dimensional framework. Hydrogen atoms, anions, and uncoordinated solvent molecules are omitted for clarity.

and the relative orientation of chelating and monodentate donor sites on the bridging ligands. By using the multimodal ligand dpztz, the formation of four-membered rings can be encouraged and thus the formation of sheets with unusual topologies is enhanced.

The structure observed for **4** adopts a *tris*-chelate Ag(I) environment, which is surprising for two reasons. Firstly, Ag(I) is well known for its preference for a *bis*-bipyridyl coordination environment and this has been used widely as a design principle for the construction of discrete supramolecular species (36, 37). There is only one previous report of the structural characterization of a Ag(I) cation sitting in a *tris*-bipyridyl environment (38). Secondly, as discussed in more detail above, when using multimodal ligands with Ag(I), we have observed a marked preference for the metal center to adopt a coordination envi-

ronment with both chelating and monodentate ligands (7–12). Compound **4** is also the only structure reported here that does not adopt the “Ag₂(dpztz)₂” subunit within its structure. This example illustrates the complexity of coordination framework design and how challenging it can be to evaluate the influence of the plethora of competing forces involved in the synthesis of solid-state supramolecular architectures.

In summary we have demonstrated that multimodal ligands with multiple binding sites can be used to prepare coordination frameworks with unusual topologies and to influence the precise geometrical arrangement of both ligands and metal centers within one- and two-dimensional arrays.

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