Coordination Networks

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A "Compartmental" Borromean Weave Coordination Polymer Exhibiting Saturated Hydrogen Bonding to Anions and Water Cluster Inclusion**

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The Borromean linkage (Figure 1) represents a kind of topological connectivity in which three rings are interlinked without being interpenetrated. Historically, Borromean rings have been used extensively to represent unity. There have been several recent reports of Borromean coordination polymers,[1–7] with previously unrecognised examples being correctly classified by Carlucci et al.[1] while Stoddart and co-workers have synthesized a discrete Borromeate complex.[8,9] Much of the interest in coordination polymer chemistry stems from the creation of robust porous frameworks capable of containing guest molecules.[10–14] Topological connectivity such as interpenetration and the formation of Borromean linkages potentially represents a way of increasing the mechanical strength of these materials since the rings cannot be separated without breaking generally strong chemical bonds. While Borromean linkages or interpenetration can reduce the available free space within a coordination polymer or metal–organic framework (MOF),[15] it increases the surface area of the framework thereby promoting the surface adsorption of gases, for example.[12] Considerable effort has been expended to prevent interpenetration in MOFs, with the use of the bulky secondary building unit (SBU) concept borrowed from zeolite chemistry being particularly effective.[10,11,16,17] The tendency to fill space either by guest inclusion or interpenetration/interlinking arises from the nondirectional stabilizing influence of van der Waals forces. We have been working on a concept of "compartmentalized" coordination polymers in which van der Waals interactions between components of the coordination polymer framework are replaced by a cascade of more specific, directional interactions that limit the ways in which the coordination polymer strands can interact.[18,19] More generally, we have shown that such a strategy can be used to engineer the formation of discrete water clusters.[20,21] In the particular case of coordination polymers, we aim to engineer the creation of materials with a high surface area that contain void space for guest inclusion.

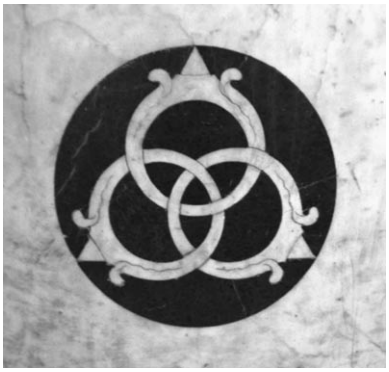
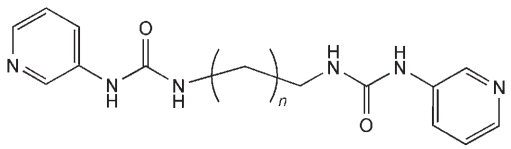


Figure 1. A Borromean symbol in the Cappella Rucellai in the Church of San Pancrazio, now the Marino Marini Museum, in Florence (photograph courtesy of Prof. L. J. Barbour, Stellenbosch University).

We now report such a compartmental coordination polymer in which a Borromean structure forms. The rings are held strictly in register by coordination interactions, argentophilic interactions,[8] and saturated hydrogen bonding[9] to nitrate counterions.

We (and others[22]) have designed ligands of type L (Scheme 1) to contain well-defined, divergent cation-binding, anion-binding, and hydrophobic regions that allow the formation of a coordination polymer structure linked by metal–pyridyl functionalities which are held in register by hydrogen bonding from the urea groups to the metal counterions. The urea group is a well-recognized anion-binding unit that forms particularly stable eight-membered hydrogen-bonded rings with oxyanions.[23–28] In the case of complexes of ligands of type L, this arrangement is expected to leave space for the inclusion of guest species in the pocket created by the hydrophobic oligomethylene spacer. Examples with $n = 1$–7 are readily available by the Curtius rearrangement of nicotinoyl azide to give pyridyl-3-isocyanate, followed by the addition of diaminoalkanes, thus allowing extensive



Scheme 1. Structure of L^n ($n = 1$–7).

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tuning of the size of the guest inclusion region.[29] Reaction of L^1 with $AgNO_3$ in aqueous dimethylformamide solution results in the reproducible formation of a Borromean weave coordination polymer $[Ag_2(L^1)_3](NO_3)_2 \cdot 7H_2O$ (**1**). Interestingly, the compound may also be obtained from a supramolecular metallogel[30,31] that forms upon the addition of L^1 to a solution of $AgNO_3$ in tetrahydrofuran/water (2:3). Compound **1** was characterized by X-ray crystallography, thermogravimetric analysis (TGA), IR spectroscopy, and elemental analysis. The X-ray crystal structure of **1** shows that it is based on a series of trigonal Ag^I nodes linked into a sheet of large hexanuclear rings by the doubly connected, curved dipyridyl ligands. The hexanuclear rings are noncrystallographically threefold symmetric with Ag···Ag separations of 15.75, 16.20 and 16.48 Å and a diameter of about 31.5 Å (Figure 2). The largest circle that will fit in the hexanuclear ring has a radius of 8.65 Å, as defined by the shortest contact from a centroid of the ring to a neighboring atom.

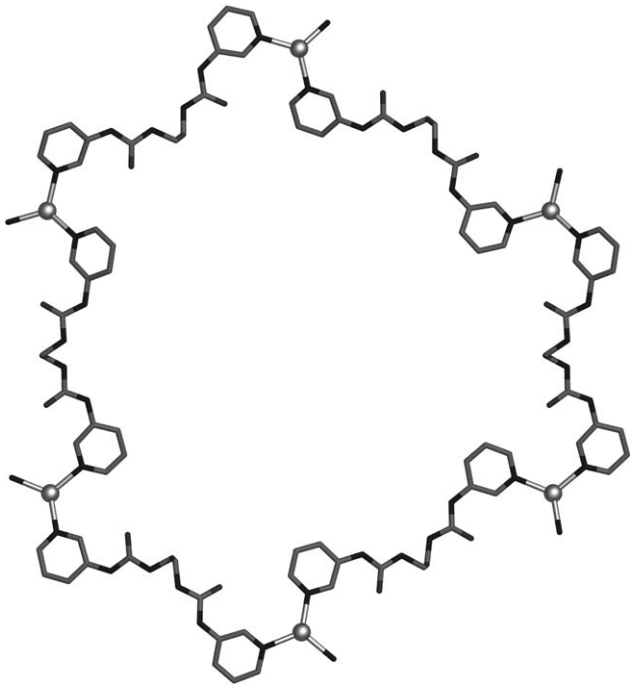

Figure 2. The macrocyclic ring in **1** (approximately 31.5 Å diameter) comprising six Ag^I ions and six ligands. Three ligands have their NH groups pointing into the macrocycle and three point outside to give an approximately threefold symmetry.

The bis-(urea) groups on three of the six ligands point into the macrocycle cavity and interact with the nitrate anions. The nitrate anions form infinite stacks throughout the structure. Each anion is surrounded by a total of three urea groups from three different ligands, with each ligand belonging to a separate coordination network joined into a 2D, three-network slab by hydrogen bonding. Every urea···nitrate interaction takes the form of an eight-membered hydrogen-bonded ring of graph set $R_2^2(8)$, and hence each anion is surrounded by six NH donors and results in the formation of a saturated hydrogen-bonding arrangement in which every nitrate lone pair and every NH proton is involved in a hydrogen bond (Figure 3). The hydrogen bonding to the NO_3^- ions is evidently weaker than in the free ligand (which engages in strong NH···pyridyl interactions[29]) as shown by the shift in ν(NH) from 3301 in L^1 to 3337 cm^{-1} in **1**.

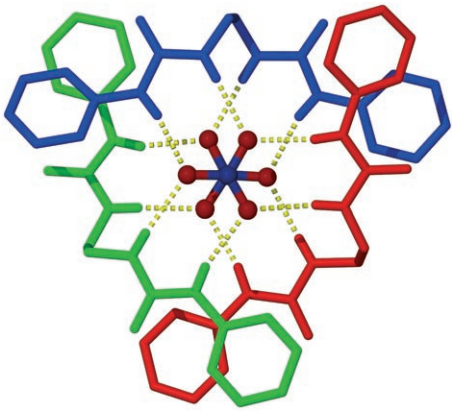

Figure 3. Two nitrate anions surrounded by three bis(urea) ligands in the structure of **1**. The ligands are color coded to show that each belongs to a different independent network within the Borromean structure. Hydrogen-bonding distances: 2.960(6)–2.944(6) Å.

It is this arrangement which defines the relationship between the three independent networks that make up the Borromean structure. Figure 4 shows, for example, that the green network passes over the blue network at every crossing point. Thus, the two networks would be easily separable were it not for the red network, which passes over the green network but under the blue one. The 3.21 Å inter-anion spacing within a Borromean sheet allows the anion stack to be supported by argentophilic interactions between the pairs of Ag^I cations (Ag···Ag 3.54 Å) that surround the anion cavity.[2]

The metal-anion-pyridyl-urea unit may thus be regarded as a kind of supramolecular SBU constrained by strong, charged, hydrogen-bonding interactions. This supramolecular unit defines the nature of the crossing points of the rings, and hence the threefold symmetry of the nitrate anion is amplified into the threefold symmetry of the entire network. The final result is that a cavity with a solvent-accessible volume of 177 $Å^3$ remains once the coordination preference of the Ag^I center and NO_3^- ions have been satisfied. This cavity is occupied by a discrete cluster of seven water molecules (Figure 5). The cluster is bound on one side by a long-range Ag···O interaction of 2.62 Å and on the other by a pair of CH···O hydrogen bonds from two pyridyl groups to an apical water molecule. The cluster also forms strong OH···O interactions with the urea carbonyl groups. The water heptamer is ordered but of an irregular geometry that best fits the available space and hydrogen-bonding motifs.

It was clearly of interest to determine whether the water cluster can be exchanged for other guest molecules. Thermogravimetric analysis (TGA) showed that the water is extremely tightly held by the network, with no weight loss occurring before decomposition with an onset temperature of 172 °C. However, it proved possible to produce no fewer than

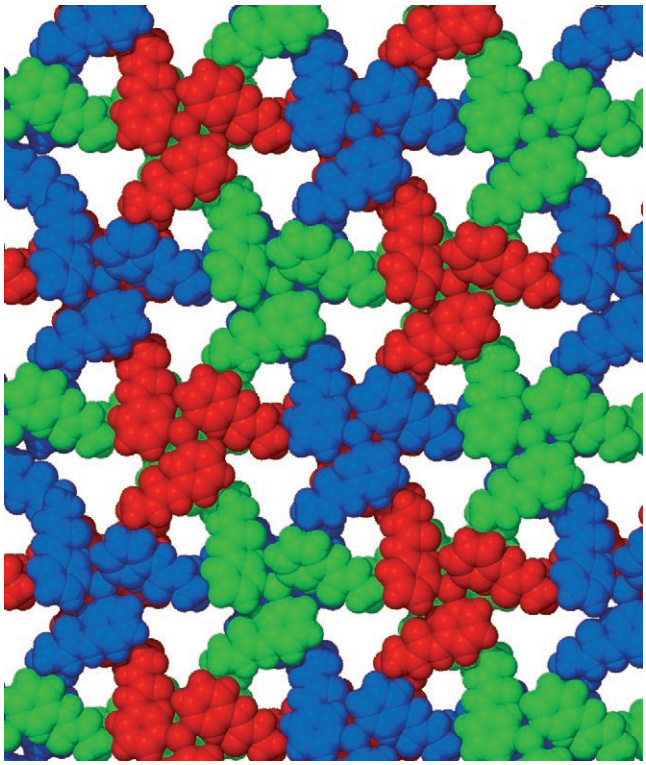

Figure 4. Borromean network structure of **1** with each independent network color coded. The approximately circular cavities contain nitrate anions while the larger cavities of approximately triangular shape contain discrete water heptamers. The anion stacks are continuous throughout the structure while the water-containing cavities are terminated by an Ag^{I} ion on one side and a pair of pyridyl moieties on the other.

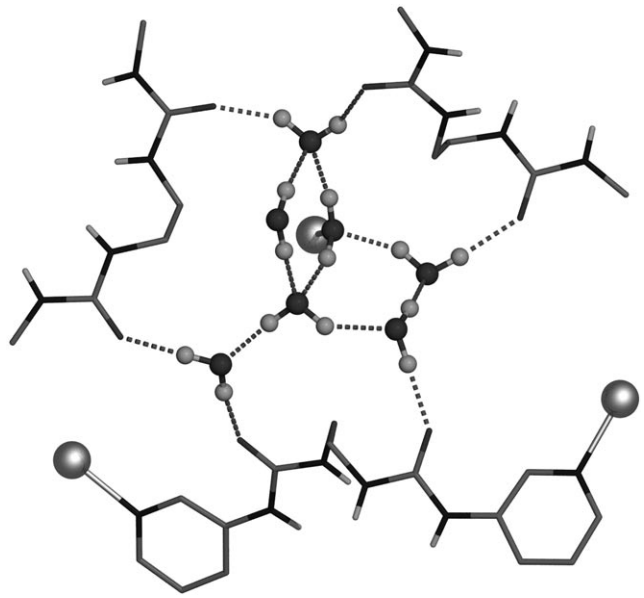

Figure 5. The discrete water heptamer in the structure of **1** showing terminating OH···O=C and Ag—O interactions.

three other pseudopolymorphic Borromean structures by crystallization from solvents such as acetonitrile, methanol, and chloroform. All three structures contain the same 2D Borromean weave motif as **1**, but with different guest species and packing arrangements that differ in the interactions of the guests with the Ag^{I} centers and the mutual offset of the individual 2D Borromean sheets. This finding suggests that the sheets can move fairly readily with respect to one another, perhaps allowing dynamic apertures to open to allow guest exchange.[32] Indeed, DSC analysis of **1** indicates three small phase changes between ambient temperature and 150 °C.

One of the new Borromean pseudopolymorphs is $[Ag_2(L^1)_3](NO_3)_2{\cdot}2\,MeCN{\cdot}x\,S$ (**2**), where S is a disordered mixture of $CHCl_3$/MeOH (2:1). The compound crystallizes with space group $C2/c$ ($P2_1/c$ for **1**). Although the Borromean weave 2D sheet is very similar to that shown in Figure 4, the compound contains two ordered MeCN molecules in the cavity that was previously occupied by water in **1**. The MeCN molecules form long-range N···Ag interactions of 2.82 Å, thereby capping a discrete argentophilically bonded Ag_2 unit. As the guests in the cavity in one sheet interact with Ag^{I} atoms in adjacent sheets, the mutual interactions of the sheets are highly guest-dependent. TGA data for this material shows the very gradual loss of approximately half of the bound solvent over the full temperature range (from ambient to decomposition at 179 °C), which indicates that there is a mechanism for guests to slowly diffuse out.

Other Borromean structures have been reported based on π-stacking, halogen-bonding, argentophilic, and aurophilic interactions;[1–4,6,7,33] however, the present example is the first to incorporate a well-defined anion-binding motif[25] in conjunction with coordination interactions to generate free space even within an interwoven structure and hence allow the inclusion of guest molecules. Work is currently in progress on enlarging the guest-containing cavity in structures of this type with other members of the series L^n.

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