Borromean sheets assembled by self-supporting argentophilic interactions

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An infinite two-dimensional Borromean coordination framework, stabilized by argentophilic interactions, was obtained by the reaction of a flexible ligand with $AgBF_4$.

In recent years interest in coordination polymers has increased exponentially because of their vast structural diversity and potentially interesting properties.[1] The variety of molecular building blocks, together with the many types of noncovalent interactions that occur between them, facilitates the construction of an infinite number of topologically fascinating systems. In the solid state, 'aurophilic' interactions,[2] *i.e.* attractive interactions between two gold(I) ions with "bond" energies ranging from 20 to 60 kJ mol^{-1},[3] are comparable in strength to, and even somewhat stronger than O–H···O hydrogen bonds (typically 4 to 40 kJ mol^{-1}). Therefore it seems inevitable that the deployment of Au···Au interactions would eventually become recognised as a viable stratagem for crystal design.[4] In their d^{10} electronic configuration silver and copper, the other two coinage metals, have also been shown to exhibit ligand-unsupported 'metallophilic' phenomena (termed 'argentophilic'[5] and 'cuprophilic'[6] interactions, respectively). Relativistic effects in these elements are much less pronounced than for gold and thus argentophilic interactions are weaker than aurophilic interactions, while cuprophilic interactions are weaker still. However, despite the paucity of quantitative data, it is thought that argentophilic interactions are similar in strength to O–H···O hydrogen bonds.[7] It is therefore surprising that, to the best of our knowledge, argentophilic interactions have not yet been implicated as the major facilitator of infinite crystalline frameworks.

Among a number of reports of novel entanglements of individual motifs, the Borromean system represents one of the most intriguing patterns because of its complexity, structural integrity and aesthetic beauty.[8] A set of Borromean rings[9] consists of three interlinked circles. Taken together, the three rings are inseparable but, if one ring is removed, the remaining two rings fall apart. Owing to the interdependence of the three rings for their collective structural integrity, the Borromean motif has been used throughout history to symbolise strength and unity (*e.g.* Fig. 1). Although a total of ten unique interlaced patterns incorporating five distinct link types are possible, the Hopf link with a trivial knot[9b] has been most commonly used.

To date, only a handful of structures comprised of three-fold entangled (6,3) layers exhibiting Borromean links have been reported.[4b,10] However, none of these structures were recognized as

Fig. 1 The alternating rings (top, centre panel—enlarged at bottom) appear in the Cappella Rucellai in the Church of San Pancrazio, now the Marino Marini Museum, in Florence. The rings, in black on white marble, are said to be a symbol of the de Medici family (photographs by LJB).

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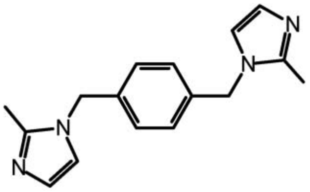
having this kind of topology until they were correctly classified by Carlucci *et al.* in a recent review on coordination networks.[11] We now report the first example of an infinite two-dimensional coordination polymeric system possessing the Borromean entanglement, and which is stabilised by ligand unsupported Ag···Ag interactions.

The complex $\{[Ag_2L_3](BF_4)_2\}$ was obtained by reacting the flexible, *exo*-bidentate ligand L (Scheme 1) with $AgBF_4$ in CH_3CN in a 4 : 1 molar ratio.† Single crystals suitable for X-ray structural analysis‡ were deposited over a period of one week. The asymmetric unit consists of a silver ion (site occupancy = ⅓), one half of ligand L and two disordered BF_4 ions (total site occupancy = ⅓). The silver ion is situated on a threefold axis along [001] and at a distance of 1.531 Å from the $\bar{3}$ symmetry centre at 0,0,½. The coordination environment about the metal ion is trigonal planar and the three imidazole rings are oriented in a propeller-like arrangement with their 2-methyl groups located on the same side of the plane defined by the coordinating nitrogen atoms (Fig. 2). Fig. 2 also shows that each $[AgL_3]$ motif, as described above, is associated with an identical symmetry-related motif across the $\bar{3}$ site by means of an argentophilic interaction (Ag···Ag = 3.0619(4) Å).

Owing to its two flexible methylene groups, L is capable of assuming conformations ranging from 'C' to 'S' in shape. The latter is exclusively present in the current structure. Each ligand bridges two silver ions which, in turn, each coordinate to three separate ligands. This coordination mode results in the formation of large hexagonal rings (Fig. 3) with a van der Waals inner-diameter of approximately 16.3 Å. Each hexagon is defined by six silver ions as its vertices and six ligands as its edges, and adjacent rings share edges and vertices to form a 2D honeycomb lattice. The six metal ions are non-coplanar and the overall conformation of each ring is approximately that of a chair. However, it is perhaps more useful to describe the six silver ions as forming the vertices of two triangles: one triangle is defined by ions at positions 1, 3 and 5 while the second triangle is defined by ions at positions 2, 4 and 6 (Fig. 3). These two triangles are parallel to one another and approximately 3.06 Å apart.



Scheme 1 1,4-Bis(2-methylimidazol-1-ylmethyl)benzene.

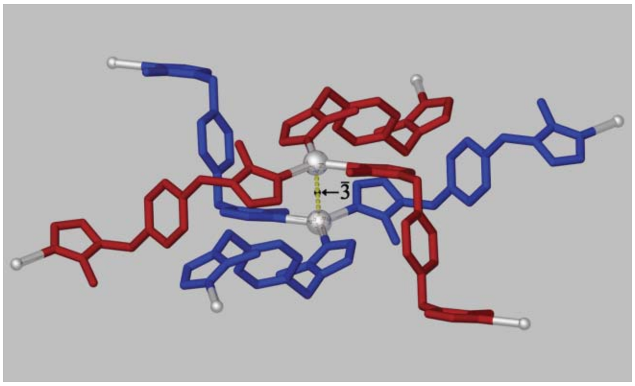


Fig. 2 Perspective view showing that each ligand (capped sticks) bridges two silver ions (metallic spheres) and that each silver ion is coordinated to three ligands. The coordination geometry about each silver ion is trigonal planar. The two "infinite" complexes (shown in red and blue) are attracted to one another by means of Ag···Ag interactions (fragmented yellow cylinder).

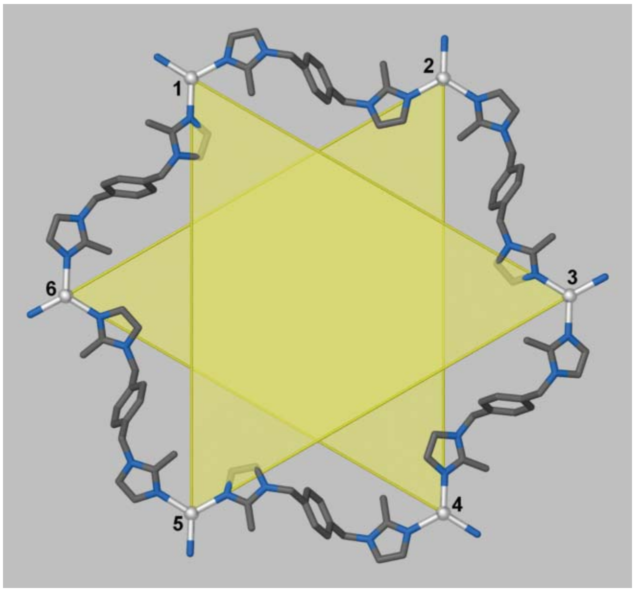


Fig. 3 Projection along [001] showing the formation of a hexagonal ring consisting of six silver ions (metallic spheres) and six ligands (capped sticks; N blue; C grey; H omitted). The ring forms part of an "infinite" 2D lattice of fused rings. Semitransparent yellow triangles indicate that alternate metal ions are situated at different levels with respect to the mean plane of the hexagon.

It is well-known that, when coordination polymeric complexes form large two- or three-dimensional holes, the structures usually interpenetrate in order to satisfy close-packing. It is interesting to note that true interpenetration does not occur in the present structure. Instead, three separate honeycomb lattices, as described above, are entangled to form a Borromean weave. In Fig. 4 it can be seen that the blue honeycomb layer is always above the red layer which is always above the green layer which, in turn, is above the blue layer. Thus, although no two layers are mutually interpenetrated, the entanglement of the three layers cannot be unraveled without breaking covalent or coordination bonds. In order to form a Borromean weave, either with three discrete rings or with three honeycomb lattices, it is essential for the rings to buckle (*i.e.* the weave cannot be formed using flat rings). This geometrical requirement is easily satisfied by the flexible conformation of the ligand L which places alternate silver ions within each ring at one of two different levels with respect to the mean plane of the ring. Small gaps formed in the Borromean weave system are occupied by the BF_4 anions and the overall structure is thus efficiently packed. The silver ions of all three components of the Borromean weave are situated on threefold rotation axes as pairs interacting across a site of $\bar{3}$ symmetry, and can thus be considered to be the nodes of the framework. Thus,

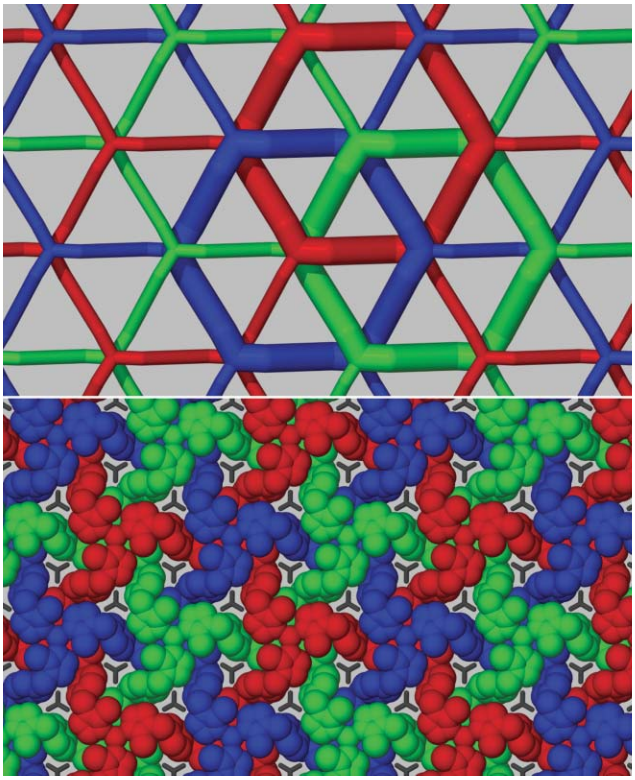


Fig. 4 The topology of an infinite Borromean weave (top) and a projection along [001] (bottom) showing a corresponding weave consisting of three separate honeycomb lattices of $[Ag_2L_3]^{2+}{}_\infty$ (shown as red, green and blue van der Waals surfaces with H atoms omitted). BF_4 anions (grey) are situated in lattice interstices. In the top figure three interlinked rings have been singled out using thicker lines in order to show the Hopf link with a trivial knot of a Borromean ring system.

each two-dimensional weave contains silver ions at two different levels with respect to [001] and the separate components of the weave are held together by argentophilic interactions.

The few Borromean coordination polymeric systems that are currently known to exist are stabilised by, in addition to van der Waals contacts, a variety of supramolecular interactions including hydrogen bonds,[10c] $I^- \cdots I$ halogen bonding,[10b] offset face-to-face $\pi \cdots \pi$ stacking[10a] and Au···Au interactions.[4b] We have presented a structure in which a Borromean framework has been assembled by means of self-supporting argentophilic interactions. The Ag···Ag interactions cooperate with one another to yield a highly stable structure in much the same way that nature uses many weak interactions such as hydrogen bonds in order to stabilise biological systems.

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Notes and references

† It is noteworthy that the described topology was obtained using a 1 : 4 molar ratio of metal salt to L. A molar ratio of 1 : 1 yields a discreet 'molecular box' which is currently the focus of another study.

‡ Crystal data: $C_{24}H_{27}AgB_3F_6N_6$, $M = 653.82$, colourless needle, $0.35 \times 0.15 \times 0.15$ mm^3, trigonal, space group $P\bar{3}$ (No. 147), $a = b = 13.9626(5)$, $c = 7.4577(5)$ Å, $V = 1259.12(11)$ Å^3, $Z = 2$, $D_c = 1.725$ g cm^{-3}, $F_{000} = 658$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 56.5°$, 7945 reflections collected, 1984 unique ($R_{int} = 0.0196$). Final GooF = 1.100, $R1 = 0.0244$, $wR2 = 0.0608$, R indices based on 1904 reflections with $I > 2\sigma(I)$ (refinement on F^2), 126 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.874$ mm^{-1}. The structure was solved and refined using the SHELX-97 suite of programs[12] and the X-Seed[13] interface. Fig. 2–4 were prepared using X-Seed[13] and POV-Ray.[14] CCDC 270010. See http://dx.doi.org/10.1039/b505784a for crystallographic data in CIF or other electronic format.

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