Three-fold parallel interlocking of 2-D brick-wall networks showing ladder-like unsymmetrical Borromean links

Xing-Qiang Lü,[a] Mei Pan,[a] Jian-Rong He,[a] Yue-Peng Cai,[b] Bei-Sheng Kang[a] and Cheng-Yong Su*[a]

Reaction of a semi-rigid ditopic ligand, N,N'-bis(4-pyridylmethyl)pyromellitic diimide (L), with HgI$_2$ afforded the 2-D brick-wall type (6,3) networks, which interlocked in a parallel fashion to give the first example of unsymmetrical Borromean ladder links.

Introduction

As a historic symbol of strength or unity,[1] Borromean rings have raised great interest in chemists not only due to their aesthetic beauty in topological chemistry, but also due to their higher structural complexity[2] compared to well-known catenanes.[3] Unlike Hopf links in catenanes, Borromean links, as shown in Scheme 1, are characteristic of three rings among which no two are interlocked, but taken together they are inseparable. The first example of molecular Borromean rings was realized by Seeman et al in manipulation of the topological properties of DNA sequences in 1997,[4] and very recently, Stoddart et al reported the first chemical synthesis of the smallest Borromean rings with an all-in-one assembly strategy.[2b] The existence of Borromean links in coordination polymers was realized by Ciani et al through a thorough topological analysis and classification of known infinite polymeric networks.[5] This subsequently gave an impetus to topological control of such fascinating entanglement in network engineering.[6]
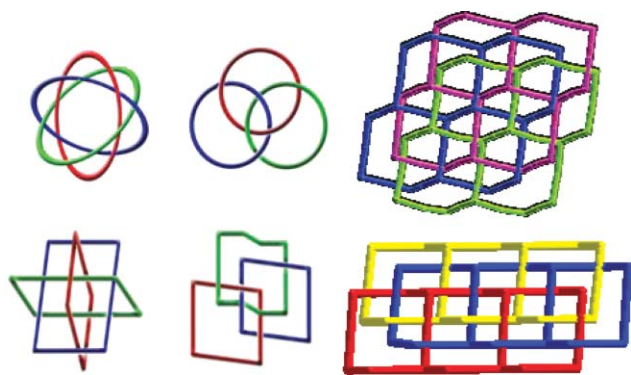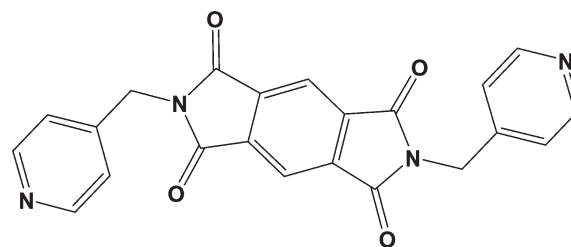

Scheme 1 Presentation of two types of Borromean links. Top: cyclic Borromean rings representing Borromean honeycomb networks; bottom: square Borromean links representing 1-D Borromean ladders.

[a]MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: cesscy@mail.sysu.edu.cn; Fax: 86 20 8411 5178; Tel: 86 20 8411 5178
[b]School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, P. R. China. E-mail: caiyp@scnu.edu.cn

One of the peculiar topological features possessed by Borromean links is that the intrinsic entanglement of three rings prevents separation of the rings just by changing their shapes.[2c] This makes it possible to fabricate a variety of 1-D, 2-D or 3-D networks showing Borromean links with diversified structural geometry,[5a] most of them still waiting to be discovered. A view of two types of Borromean links is shown in Scheme 1. One shows the prototypical ring-like geometry which can be directly related to 2-D honeycomb networks. So far a handful of Borromean networks have been identified,[5,6] all displaying such hexagonal (6,3) net features. A potential geometrical variation may have a square-like form, apparently relating to 1-D Borromean ladders although no actual example has yet been observed.[5a] It is known that extending 1-D ladder structure into two dimensions will result in a brick-wall network, and herein we report the first example of an 2-D brick-wall coordination polymer showing Borromean ladder topology.

Results and discussion

The semi-rigid ligand, N,N'-bis(4-pyridylmethyl)pyromellitic diimide (L, Scheme 2), features in a long rigid basal plane and two freely rotatable pyridyl donor groups which are capable of taking two conformations in either U or Z modes.[7] We have previously used the ligand to react with Cd(NO$_3$)$_2$ to obtain 1-D ladders,[7a] and react with HgI$_2$ in 1 : 1 metal-to-ligand ratio in MeOH-DMF solution to get a 'two-over/two-under' cloth-like 2-D network.[7b] To further investigate the structures diversification shown by this ligand, we reacted L with HgI$_2$ in a 3 : 2 metal-to-ligand ratio in EtOH-CHCl$_3$ mixture and, unexpectedly, obtained a 2-D structure, $[(HgI_2L)(HgI_2L_{1/2})]_n$ (1), which displayed a brick-wall network sustained by Hg···I weak coordinations.


Scheme 2 Molecular structure of ligand L.

Single crystal X-ray diffraction revealed that the asymmetric unit contains three half moieties of the ligand **L**, each one lying about an independent inversion centre. Two independent half-ligand **L** moieties bond to Hg1 and the other half-ligand **L** bonds to Hg2 in the asymmetric unit. There were two crystallographic independent Hg(II) ions in the asymmetric unit: Hg1 was coordinated to two N atoms from two individual **L** (Hg–N, 2.427(6) and 2.554(6) Å) and two I$^-$ anions (Hg–I, 2.623(1) and 2.666(1) Å), giving a distorted tetrahedral geometry as depicted in Fig. 1, while tetrahedral geometry of Hg2 was completed by three I$^-$ anions (Hg–I, 2.604(1), 2.633(1) and 3.158(1) Å) and one N atom from an individual **L** ligand (Hg–N, 2.475(6) Å). A long Hg–I bond was formed between Hg2 and I1 which also coordinated to Hg1, thus connecting Hg1 and Hg2 to offer an unsymmetrical 'T-shaped' building block responsible for the overall 2-D brick-wall network topology (Fig. 1). Since this Hg2–I1 bond distance was significantly longer than the other three Hg–I bonds, it can be regarded as an Hg···I weak coordination. Therefore, the structure can also be described in this way: repeating of –Hg1**L**– units gives rise to 1-D chains. These chains were further connected by –(Hg2)$_2$**L**– motifs *via* Hg···I weak interactions to formed 2-D brick-wall network. All the ligands exhibited a *Z*-mode conformation, and the network was remarkably undulating, leaving voids inside each network.

It is interesting to note that the brick-wall networks in **1**, although each is crystallographically independent, interlock in a specific way to fill in the voids mutually, thus resulting in a three-fold parallel entanglement as shown in Fig. 2. Detailed analysis reveals that true interpenetration does not occur in this close-packing layer. Instead, any two undulating brick-wall networks are not interlocked, but appearance of the third network causes an inherent interwoven fashion which can be schematized to a Borromean ladder links as depicted in
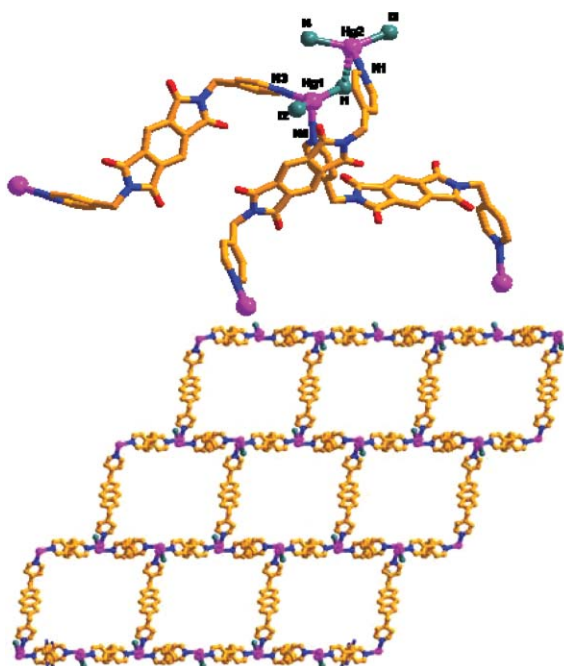
Fig. 1 The independent 2-D brick-wall network (top) formed in **1** with the 'T-shaped' building blocks (bottom).
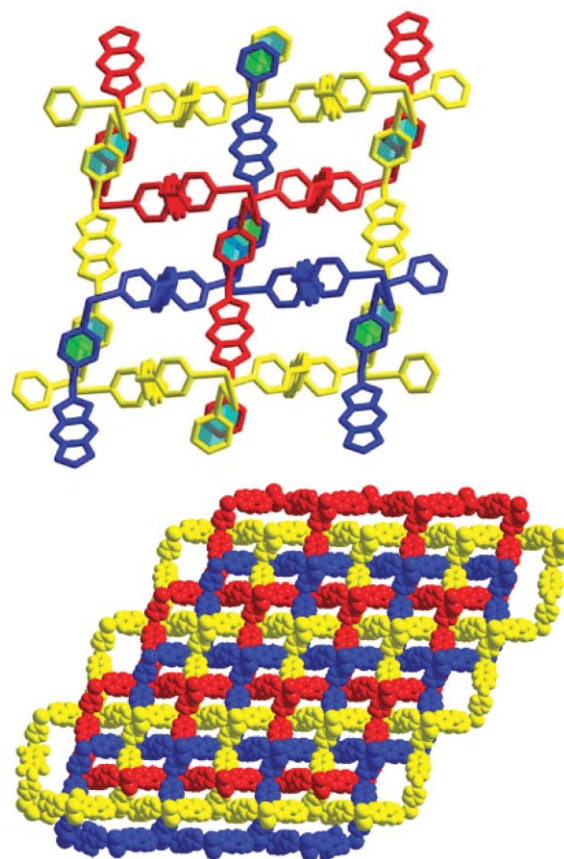
Fig. 2 π···π stackings (highlight, top) formed between 'T-shaped' building blocks stabilizing Borromean brick-wall networks (bottom).

Scheme 1. Simply to say, the triply interwoven networks show the essential Borromean feature that no two of them are mutually interpenetrated, but as a whole the three entangled networks can not be unraveled without breaking coordination interactions. Such puzzling interweaving is apparently due to the flexible nature of the ligand. The preference of the ligand adopting *Z*-mode conformation[7] causes undulating arrangement of the network, which is believed the critical requirement for formation of Borromean links in coordination polymers.[5a] On the other hand, The weak Hg···I coordination participates in the 'T-shaped' building block which is also highly distorted from the normal rigid planar 'T-shaped junctions', known as an important connection in the formation of diversified coordination frameworks.[8]

Such distorted unsymmetrical 'T-shaped' connections make the present Borromean networks distinctive compared with other identified Borromean analogues.[5,6] In a topological sense, the brick-wall network has the common (6,3) net topology, equivalent to that of the honeycomb network. Both can be assembled from three metal ions and three ligands to form a six-membered basic unit; however, the latter contains the trigonal 'Y-shaped' nodes (C_3 symmetry) while the former possesses the 'T-shaped' nodes (C_2 symmetry). The geometric difference results in hexagonal or rectangular basic six-membered units, respectively, which subsequently determine the network geometry. In comparison to a handful of known Borromean honeycomb networks containing trigonal C_3

symmetrical Borromean links, the present case offers a new ladder-like C_2 unsymmetrical Borromean topology. Such unsymmetry means, on one hand, a lower C_2 node, and on the other hand, three nonequivalent connectors, implying the possibility of fabricating diversified Borromean networks other than solely hexagonal nets.

It should be borne in mind that predictable engineering of Borromean network is still a significant challenge. However, examination of all available Borromean networks indicates that various supramolecular forces played important roles in the formation and stabilization of Borromean topology. This is evident since hydrogen bonds,[5d] $I^-\cdots I$ halogen bonding,[6b] offset face-to-face $\pi\cdots\pi$ stacking,[5c] argentophilic (Ag⋯Ag)[5b,6a] or aurophilic (Au⋯Au) interactions[5e] were found to make critical contributions to the formation of Borromean networks. In the present case, offset face-to-face $\pi\cdots\pi$ stackings formed between pyridyl rings represent the major factor influencing Borromean interweaving. As shown in Fig. 2, each 'T-junction' involves three $\pi\cdots\pi$ stackings and the Borromean links were stabilized by these multiple intermolecular interactions.

Thermal gravimetric analysis for the crystalline samples of complex **1** indicated that the frameworks collapsed at about 250 °C and a major weight loss was observed in the range of 250 to 410 °C, corresponding to structure decomposition. The final weight loss continued up to 700 °C.

Conclusions

In summary, a new example of Borromean network was obtained which showed an unsymmetrical Borromean ladder links. A few common characters may now be summarized for Borromean networks observed so far: (a) consisting of (6,3) nets with six-membered basic rings, (b) showing obvious network undulating, and (c) assisted by weak intermolecular forces. The present new example is of significance because it indicates that Borromean links may not be necessarily symmetrical and the net form may not be necessarily hexagonal as observed previously. This finding suggests that more diversified Borromean networks await discovery and creation. As more synthetic paradigms of Borromean networks are obtained, the ambitious goal of controlled engineering of coordination polymers, as complex as Borromean links, is foreseen.

Experimental

All chemicals were commercial products of reagent grade and used without further purification. Infrared spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in the range of 4000–400 cm^{-1} using KBr pellets. ^{1}H NMR measurements were carried out on a Mercury-Plus 300 spectrometer with SiMe$_4$ as internal standard. Thermogravimetric analyses were carried out on a NETZSCH TG 209 Instrument under flowing nitrogen by heating the samples from 25 to 700 °C.

Synthesis

The complex was prepared by layering the solution of HgI$_2$ in EtOH onto the solution of 4-pmpmd in CHCl$_3$ in the M : L

molar ratio of 3 : 2. Yield: 38%. Anal. Calcd. for C$_{33}$H$_{21}$Hg$_2$I$_4$N$_6$O$_6$: C, 26.31, H, 1.41, N, 5.58. Found: C, 26.76, H, 1.78, N, 5.79%. ^{1}H NMR (ppm, DMSO-d$_6$): 8.527 (d, Hpy), 8.276 (s, Hph), 7.400 (d, Hpy), 4.881 (s, –CH$_2$–). IR (KBr pellet, cm^{-1}): 3469 w, 3031 w, 1771 m, 1717 vs, 1609 w, 1425 m, 1390(s), 1365 m, 1341 m, 1302 w, 1218 w, 1115 m, 1083 w, 940 m, 749 w, 724 m, 628 w, 574 w.

X-Ray crystallography

A single crystal of suitable dimensions was mounted onto the end of a thin glass fiber. X-Ray diffraction intensity data were collected at 293 K on a Bruker Smart CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å). The structures were solved by the direct method followed by difference Fourier syntheses, and then refined by full-matrix least squares refinement on F^2 using SHELXL.[9] All the non-hydrogen atoms were refined with anisotropic parameters while H atoms were placed in calculated positions and refined using a riding model.

Crystal data. C$_{33}$H$_{21}$Hg$_2$I$_4$N$_6$O$_6$, M = 1506.34, triclinic, space group $P\bar{1}$, a = 10.882(4), b = 14.319(5), c = 14.827(5) Å, α = 62.896(5)°, β = 89.982(6)°, γ = 69.685(5)°, U = 1893.9(16) Å^3, Z = 2, D_c = 2.641 g cm^{-3}, T = 293(2) K, 7992 unique reflections [R_{int} = 0.0475]. Final $R1$ = 0.0423, $wR2$ = 0.1020. CCDC reference numbers 614290. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613667m

References

1 http://www.liv.ac.uk/~spmr02/rings/.
2 (a) J. S. Siegel, *Science*, 2004, **304**, 1256; (b) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood and J. F. Stoddart, *Science*, 2004, **304**, 1308; (c) C. A. Schalley, *Angew. Chem., Int. Ed.*, 2004, **43**, 4399.
3 J.-P. Sauvage and C. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes, and Knots*, Wiley-VCH, Weinheim, 1999.
4 C. Mao, W. Sun and N. C. Seeman, *Nature*, 1997, **386**, 137.
5 (a) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (b) M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Jiang, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237; (c) M. P. Suh, H. J. Choi, S. M. So and B. M. Kim, *Inorg. Chem.*, 2003, **42**, 676; (d) S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2002, 4561; (e) D. B. Leznoff, B.-Y. Xue, R. J. Batchelor, F. W. B. Einstein and B. O. Patrick, *Inorg. Chem.*, 2001, **40**, 6026.
6 (a) L. Dobrzańska, H. G. Raubenheimer and L. J. Barhour, *Chem. Commun.*, 2005, 5050; (b) R. Liantinio, P. Metrangolo, F. Meyer, T. Pilati, W. Navarrini and G. Resnati, *Chem. Commun.*, 2006, 1819.
7 (a) X.-Q. Lü, J.-J. Jiang, L. Zhang, B.-S. Kang, H.-C. zur Loye and C.-Y. Su, *Inorg. Chem.*, 2005, **44**, 1810; (b) Y.-H. Li, C. Y. Su, A. M. Goforth, K. D. Shimizu, K. D. Gray, M. D. Smith and H.-C. zur Loye, *Chem. Commun.*, 2003, 1630.
8 (a) S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, **246**, 145; (b) H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599.
9 G. M. Sheldrick, SHELX 97, *Program for Crystal Structure Solution and Refinement*, Göttingen University, 1997.