

A new infinite inorganic [*n*]catenane from silver and bis(2-methylimidazolyl)methane ligand

Chuan-Ming Jin,* Huan Lu, Ling-Yan Wu and Jing Huang

Received (in Cambridge, UK) 6th September 2006, Accepted 25th September 2006

First published as an Advance Article on the web 12th October 2006

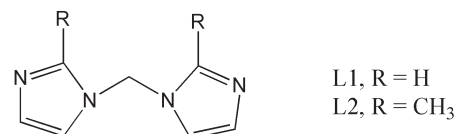
DOI: 10.1039/b612885h

A new type of 1D infinite inorganic [*n*]catenane framework was self-assembled by silver nitrate and bis(2-methylimidazolyl)methane, while a comparatively one-dimensional zigzag cationic chain was generated by AgNO₃ and bis(imidazol-1-yl)methane

Self-assembled supramolecular architectures are currently of great interest due to their intriguing network topologies and their potential applications in microelectronics, nonlinear optics, porous materials, and other technologies.^{1–7} Although the self-assembly of these architectures is mainly controlled by the coordination nature of the metal ions and the ligand's structure, it is also influenced by other factors such as solvent system, templates and counterions.^{8–10} Silver ion is a favorable and fashionable building block or connecting node for coordination polymers, not only due to that it is easy to coordinate to N- or S-containing ligands, but also because the closed-shell d¹⁰ Ag–Ag interaction can often give rise to intriguing supramolecular motifs. Many interesting structures with various geometrical features based on the self-assembled networks of silver are well documented.^{11,12}

Catenanes are an interesting class of compounds with intertwined rings. They have attracted considerable attention from supramolecular chemists due to their novel topological structures, intricate self-assembled process and potential applications in molecular devices. Especially, there is a big challenge for synthetic chemists using classical synthetic routes and methods.¹³ Although a diversity of interlocked catenanes have been prepared using various synthetic strategies with their physical and/or chemical properties examined in recent years,^{14–16} most of them are based on organic skeletons,¹⁷ and only a few examples of inorganic [2]catenanes containing metals have been reported.^{18–20} To the best of our knowledge, no infinite inorganic [*n*]catenane frameworks with silver have been documented so far. In this contribution, we report the preparation and X-ray crystal structure of a new example of inorganic [*n*]catenanes formed through the self-assembly of Ag^I and bis(2-methylimidazolyl)methane ligand, namely, [Ag₄L₂4(NO₃)₄(H₂O)₃]_n (**2**), L₂ = bis(2-methylimidazol-1-yl)methane.

Jung's group has demonstrated that a series of (*n*-Py)₂X (*n* = 2, 3; X = O, S, Si) linkers are useful tectonics for various functional structures.²¹ Encouraged by their elegant work, we prepared two ligands L₁ (BIM, bis(imidazol-1-yl)methane) and L₂ [mBIM, bis(2-methylimidazol-1-yl)methane], both bearing two imidazole moieties bridged by a single methylene group.



The slow diffusion of AgNO₃ with L₁ in water and ethanol produced colorless crystals **1**, which are air-stable and insoluble in water and common organic solvents.† Single-crystal X-ray diffraction analysis reveals that Ag^I in complex **1** is bound by two N-donors from imidazolyl rings of two independent BIM ligands which act as bridges between silver(I) centers, thus generating one-dimensional zigzag chain polymeric propagation as shown in Fig. 1(a). Ag^I ion is in a slightly distorted linear coordination mode with the bond angle of N(2A)–Ag(1A)–N(10B) being 174.23(6)°. The bond lengths Ag(1A)–N(2A) and Ag(1A)–N(10B) are 2.1038(16) and 2.1050(16) Å, respectively. The dihedral angle of the two imidazole rings in the same ligand is 69.7°. Meanwhile, the coordination 2D layer networks were formed through two nitrate anions bridging two Ag^I with bond lengths Ag(1A)–O(3B), Ag(1A)–O(2A) and Ag(1A)–O(2B) of 3.059, 3.382 and 2.955 Å, respectively. (Fig. 1(b)) The closest Ag(1A)⋯Ag(1G) separation in the proximal zigzag chains is 3.859 Å, which is longer than the summed van der Waals radius of two silver atoms (3.44 Å), indicating there is no direct interaction between two Ag^I ions in different cationic chains. The thermogravimetric analysis (TGA) of **1** under nitrogen atmosphere demonstrated a two-step weight loss process. The former step occurs in the range 94–144 °C

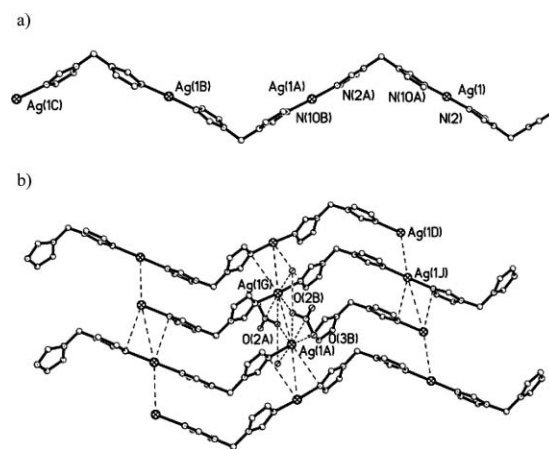


Fig. 1 (a) A part of the 1D cationic chain with zigzag structure in **1**. (b) 2D layer networks in **1**. Symmetry codes: (i) $x - 1/2, 1/2 - y, 1/2 + z$; (ii) $1/2 + x, 1/2 - y, z - 1/2$.

Hubei Key Laboratory of Bioanalytic Technique, Department of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi, Hubei, 435002, P. R. China

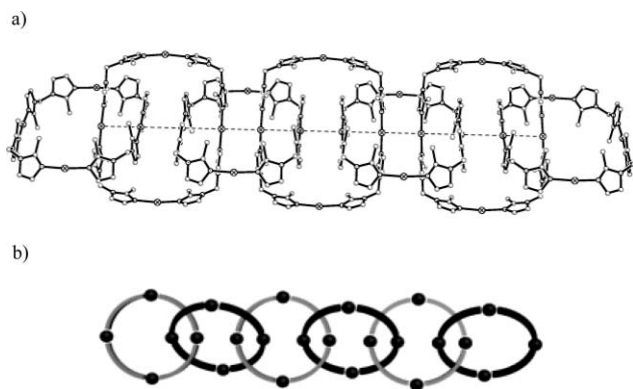


Fig. 2 (a) A part of the 1D infinite inorganic $[n]$ catenane structure in **2**. Anions and hydrogen atoms are omitted for clarity. Symmetry codes: (i) $x, 1 - y, z$; (ii) $1 - x, y, 1 - z$; (iii) $x, z - y, z$. (b) Molecular tectonics of the 1D infinite $[n]$ catenane cationic chain in **2**. Two different types of rings are present with a dihedral angle of 48.3° .

with a weight loss of 23.5% while the latter step occurs in the range $299\text{--}322^\circ\text{C}$ with a weight loss of 44.8%.

Interestingly, when **L2** was used instead of **L1** for the reaction with AgNO_3 under the otherwise identical conditions, a new type of infinite inorganic 1D $[n]$ catenane **2** was obtained.† There are two slightly different types of 32-membered macrometallacycles in the 1D chain (Fig. 2(a)). In one type of 32-membered macrometallacycle, the Ag^{I} ions is coordinated by two imidazole nitrogen atoms from different **L2** ligands in a distorted linear fashion with N–Ag–N bond angles of 164.72 and 176.48° and Ag–N bond lengths of 2.109 and 2.116 \AA , respectively. The dihedral angle of the two imidazole rings in the same ligand is 105.8° . In this way, every four silver ions and four ligands bridge each other alternately to form a 32-membered macrometallacycle with an Ag(3A)–Ag(3B) and Ag(4A)–Ag(4B) separation of $10.958 \times 14.646 \text{ \AA}$ (Fig. 3). Each ring was further bridged by NO_3^- anions weakly coordinated to Ag^{I} ion to form a one-dimensional chain of supramolecular squares with the nearest Ag^{I} separation distance of 3.859 \AA in neighboring rings (Fig. 3). In another type of 32-membered macrometallacycle, each Ag^{I} ion is coordinated by two imidazole nitrogen atoms with N–Ag–N bond angles of 164.75 and 177.91° , and Ag–N bond lengths of 2.077 and 2.094 \AA , and the dihedral angle of the two imidazole rings in the same ligand is 68.7° . Cyclic self-assembly leads to a 32-membered macrometallacycle with an Ag–Ag separation of $11.187 \times 14.025 \text{ \AA}$, with an Ag^{I} separation distance of 3.875 \AA in neighboring rings.

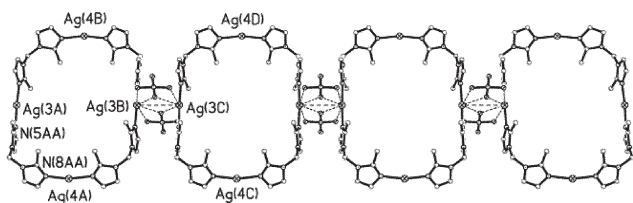


Fig. 3 An unprecedented 1D supramolecular chain of a 32-membered macrometallacycle formed through self-assembly of silver ion and **L2**; the NO_3^- anions are disordered. All hydrogen atoms are removed for clarity. Symmetry codes: (i) $x, 1 - y, z$; (ii) $1 - x, y, 1 - z$; (iii) $x, z - y, z$.

Of most interest is the observation that the two types of macrometallacycle squares are interlocked by each other with a dihedral angle of 48.3° , to form an infinite $[n]$ catenane structure with the Ag–Ag distance being 3.656 \AA between each pair of interpenetrated macrometallacycles (Fig. 2(a)). The Ag(1) and Ag(4) atoms lie on mirror planes and Ag(2) and Ag(3) lie on twofold axes. Although there have been reported in the literature a few examples of discrete supramolecular squares formed through tetranuclear self-assembly of Ag^{I} cations and suitable ligands,²² compound **2** in this work, to the best of our knowledge, is the first example of an infinite inorganic $[n]$ catenane framework. Thermogravimetric analysis (TGA) shows that **2** displayed a weight loss of 19.5% in the range $96\text{--}132^\circ\text{C}$. A further weight loss of 47.2% proceeds in the temperature range $276\text{--}289^\circ\text{C}$.

It is noteworthy that the striking structural difference between compound **1** and **2** is simply caused by a subtle difference in the ligand structure, *i.e.*, the presence of methyl groups in the 2-positions of the imidazole moieties in **L2**. Further work is in progress to evaluate the influences of ligand structure modifications and different anions on the resulting supramolecular structures as well to elucidate the mechanism of inorganic $[n]$ catenane formation, with potential applications in molecular devices.

In summary, the present work has shown that a 1D infinite inorganic $[n]$ catenane framework can be constructed from silver nitrate and the ligand 2-mBIM.

We thank Dr Meng Xiang-Gao, Huazhong Normal University, for structural data, and Dr Zheng Wang, Shanghai Institute of Organic Chemistry, for helpful discussions. This work was supported by the National Science Funds for Distinguished Young Scholars of Hubei Province (2006ABB038), People's Republic of China.

Notes and references

† **1**: An ethanol solution (5 ml) of BIM (**L1**) (74 mg, 0.5 mmol) was slowly diffused into an aqueous solution (5 ml) of AgNO_3 (85 mg, 0.5 mmol) in a test tube. Colorless crystals of $[\text{Ag}(\text{BIM})(\text{NO}_3)(\text{H}_2\text{O})]_n$ (126 mg) were formed at the interface of the solvent in two weeks and were obtained in 75% yield. Elemental analysis. Calc. for $\text{C}_7\text{H}_{10}\text{AgN}_5\text{O}_4$: C 25.02, H 3.00, N 20.84. Found: C 25.31, H 2.94, N 20.63%; IR (KBr, cm^{-1}): $\nu = 3535\text{s}, 3105\text{m}, 3010\text{w}, 1635\text{m}, 1497\text{m}, 1383\text{s}, 1279\text{m}, 1230\text{s}, 1085\text{s}, 1030\text{w}, 831\text{m}, 744\text{s}$ and 652m . *Crystal data for 1* ($\text{C}_7\text{H}_{10}\text{AgN}_5\text{O}_4$, $M_r = 336.07$), monoclinic, $P2_1/n$, $T = 87(2) \text{ K}$, $a = 8.2469(4)$, $b = 7.9889(4)$, $c = 16.3187(9) \text{ \AA}$, $\beta = 97.750(1)^\circ$, $V = 1065.32(9) \text{ \AA}^3$, $Z = 4$, $D_c = 2.095 \text{ Mg m}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 1.905 \text{ mm}^{-1}$, $F(000) = 664$, GOF = 1.046, 11833 reflections 1939 unique ($R_{\text{int}} = 0.0216$), $R = 0.0184$, $wR = 0.0481$. CCDC 614245.

2: The synthesis of **2** was similar to that of **1**, but with ligand mBIM (**L2**) (0.5 mmol) in place of ligand **1**. Colorless crystals were obtained in 67% yield. Elemental analysis. Calc. for $\text{C}_{36}\text{H}_{54}\text{Ag}_4\text{N}_{20}\text{O}_{15}$: C 30.06, H 3.78, N 19.48. Found: C 30.10, H 3.34, N 19.32%; IR (KBr, cm^{-1}): $\nu = 3119.2\text{m}, 2996.3\text{w}, 2402.3\text{w}, 1639.3\text{w}, 1541.9\text{m}, 1506.1\text{m}, 1388.3\text{s}, 1270.6\text{s}, 1142.3\text{w}, 1091.3\text{w}, 1004.3\text{s}, 830.1\text{m}, 748.2\text{s}$ and 661.2m . *Crystal data for 2* ($\text{C}_{36}\text{H}_{54}\text{Ag}_4\text{N}_{20}\text{O}_{15}$, $M_r = 1438.41$), monoclinic, $C2/m$, $T = 292(2) \text{ K}$, $a = 20.913(2)$, $b = 14.8336(15)$, $c = 18.2903(19) \text{ \AA}$, $\beta = 118.808(2)^\circ$, $V = 4971.6(9) \text{ \AA}^3$, $Z = 4$, $D_c = 1.914 \text{ Mg m}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 1.638 \text{ mm}^{-1}$, $F(000) = 2848$, GOF = 1.008, 23676 reflections 4483 unique ($R_{\text{int}} = 0.1191$), $R = 0.0769$, $wR = 0.2123$. CCDC 613418. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612885h

- J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 9.
- J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.
- S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.

- 4 L. Carlucci, G. Ciani and D. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
- 5 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
- 6 J.-C. Bünzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897.
- 7 M. Yoshizawa, M. Nagao, K. Umemoto, K. Biradha, M. Fujita, S. Sakamoto and K. Yamaguchi, *Chem. Commun.*, 2003, 1808.
- 8 C. K. V. Sharma and R. D. Rogers, *Chem. Commun.*, 1999, 83.
- 9 M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.
- 10 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327.
- 11 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
- 12 C. Seward, W.-L. Jia, R.-Y. Wang, G. D. Enright and S. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 2933.
- 13 G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, NY, 1971.
- 14 M. R. Sambrook, P. D. Beer, J. A. Wisner, R. L. Paul and A. R. Cowley, *J. Am. Chem. Soc.*, 2004, **126**, 15364.
- 15 A. L. Hubbard, G. J. E. Davidson, R. H. Patel, J. A. Wisner and S. J. Loeb, *Chem. Commun.*, 2004, 138.
- 16 (a) A. Theil, C. Mauve, M.-T. Adeline, A. Marinetti and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2006, **45**, 2104; (b) J.-P. Collin, V. Heitz, S. Bonnet and J.-P. Sauvage, *Inorg. Chem. Commun.*, 2005, **8**, 1063.
- 17 D. W. Steurman, H.-R. Tseng, A. J. Peters, A. H. Flood, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart and J. R. Heath, *Angew. Chem.*, 2004, **116**, 6648.
- 18 A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin and D. B. Walker, *J. Am. Chem. Soc.*, 2005, **127**, 12612.
- 19 (a) C. P. McArdle, S. Van, M. C. Jennings and R. J. Puddephatt, *J. Am. Chem. Soc.*, 2002, **124**, 3959; (b) D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1894.
- 20 T. S. M. Abedin, L. K. Thompson and D. O. Miller, *Chem. Commun.*, 2005, 5512.
- 21 (a) O.-S. Jung, Y. J. Kim, K. M. Kim and Y.-A. Lee, *J. Am. Chem. Soc.*, 2002, **124**, 7906; (b) O.-S. Jung, Y. J. Kim, Y.-A. Lee, K.-M. Park and S. S. Lee, *Inorg. Chem.*, 2003, **42**, 844; (c) O.-S. Jung, Y. J. Kim, J. Y. Park and S. N. Choi, *J. Mol. Struct.*, 2003, **657**, 207.
- 22 C. V. K. Sharma, S. T. Griffin and R. D. Rogers, *Chem. Commun.*, 1998, 215.



Looking for that **special** chemical science research paper?

TRY this free news service:

Chemical Science

- highlights of newsworthy and significant advances in chemical science from across RSC journals
- free online access
- updated daily
- free access to the original research paper from every online article
- also available as a free print supplement in selected RSC journals.*

*A separately issued print subscription is also available.

Registered Charity Number: 207890

RSCPublishing

www.rsc.org/chemicalscience