DALTON COMMUNICATION

The first four-fold interpenetrating diamondoid framework that traps gaseous molecules: {Zn[*trans*-3-(4-pyridyl)acrylate]$_2$·(*trans*-2-butene)}$_n$

Jing Zhang,[a] Wenbin Lin,*[b] Zhen-Feng Chen,[a] Ren-Gen Xiong,*[a] Brendan F. Abrahams[c] and Hoong-Kun Fun[d]

[a] *Coordination Chemistry Institute, State Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China*
[b] *Department of Chemistry, Brandeis University, Waltham, MA 02454, USA. E-mail: wlin@brandeis.edu*
[c] *School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia*
[d] *X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia*

Received 8th March 2001, Accepted 9th May 2001
First published as an Advance Article on the web 25th May 2001

The first X-ray structurally characterized 3-D diamondoid framework, 1, which can trap gaseous *trans*-2-butene molecules was synthesized; this work suggests that coordination polymers with adjustable porous structures are suitable candidates for advanced gas storage materials.

The research on solid materials for gas storage has recently attracted much attention because gas storage materials find widespread applications in fuel cells,[1] gas-sensors,[2] semiconductor device manufacturing,[3] and catalysts.[4] Up to now most research efforts have been focused on purely inorganic materials such as metal alloys,[5] metal oxides,[4] carbon molecular sieves and carbon nanotubes,[6] fullerenes,[7] and nano-structural materials.[2] Since metal–organic coordination polymers capable of enclathrating organic molecules have been extensively studied and developed, it has recently been shown that some of these new organic zeolite analogues[8,9] may be capable of storing gaseous molecules. In contrast to a large number of coordination polymers that are capable of enclathrating liquid solvent molecules, there are few reports on coordination networks with suitable cavities or channels to trap gas molecules. Seki *et al*.,[10] reported a series of dicarboxylic acid metal complexes as natural gas storage materials and marks the beginning of research on metal–organic coordination polymers as gas storage materials. However, the exact crystal structures of these novel complexes are not available. Two other examples[11,12] of porous coordination polymers: {$CuSiF_6$(4,4′-bipyridine)$_2$}$_n$ and $Zn_4O(BDC)_3$·$(DMF)_8(C_6H_5Cl)$ (BDC = 1,4-benzenedicarboxylate and DMF = *N*,*N*′-dimethylformamide) suggest to us that the rational design of building blocks to form novel porous coordination polymers suitable for trapping the desired gas molecules can be realized. To this end, we have chosen *trans*-3-(4-pyridyl)acrylic acid (4-Hpyac) as the bridging ligand to form neutral coordination frameworks as novel gas storage materials. Neutral coordination frameworks without counter ions existing in the cavity or channel can possess more empty space for entrapping gas molecules than ionic frameworks. Herein, we report the *in-situ* synthesis and detailed crystal structure of {Zn(4-pyac)$_2$·B}$_n$ (B = *trans*-2-butene) **1**, which represents the first diamondoid coordination framework trapping the 2-butene as a gaseous guest molecule. During the period of our research, Cornia *et al*., reported a 3-D crystallographically characterized framework that traps carbon dioxide molecules,[13] and Ozeki and co-workers[14] reported an interesting molecular oxide bowl trapping the NO^- anion from NO gas.

The use of 4-Hpyac as an asymmetric multidentate anionic ligand to construct acentric coordination polymers as second-order nonlinear optical (NLO) materials has recently been reported.[15] In this work, we used ethyl *trans*-3-(4-pyridyl)-acrylate to react with zinc(II) perchlorate in 1-butanol under hydro(solvo)thermal conditions and successfully obtained a novel four-fold interpenetrating diamondoid-like zinc coordination polymer trapping *trans*-2-butene molecules, {Zn(4-pyac)$_2$·B}$_n$ **1**.† The presence of carboxylate groups in **1** was confirmed by the strong peaks at 1611, 1585 and 1370 cm^{-1} (C=O stretching mode) in the infrared spectrum. Moreover, there are no strong peaks at about 1100 cm^{-1}, suggesting no perchlorate anions exist in **1**. Only the thermodynamically more stable *trans*-2-butene molecules were found in **1**, as independently confirmed using GC-MS techniques.

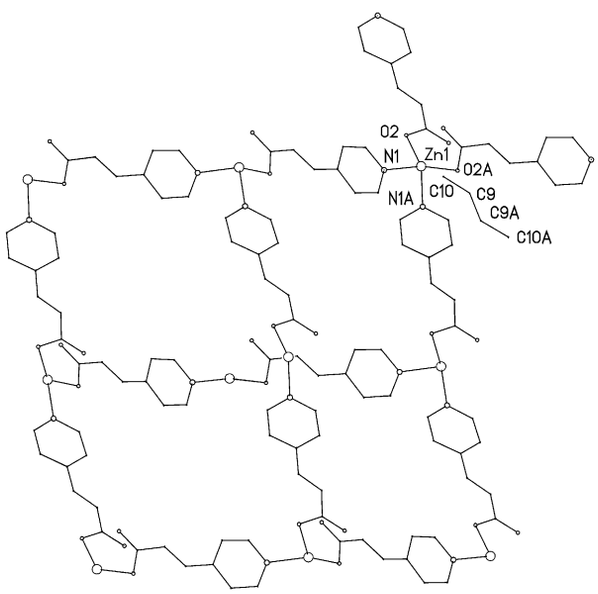

Fig. 1 A diamondoid-like net representation of the coordination polymer {Zn(4-pyac)$_2$·B}$_n$ (**1**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zn(1)–O(2) 1.968(3), Zn(1)–N(1) 2.066(3), C(9)–C(9A)′ 1.143(6), C(9)–C(10) 1.382(2); O(2)–Zn(1)–O(2A) 132.28(18), O(2)–Zn(1)–N(1B) 95.62(12), O(2)–Zn(1)–N(1C) 114.70(13), N(1C)–Zn(1)–N(1B) 100.77(18), C(10)–C(9)–C(9A) 171.8(4).

The three-dimensional diamondoid structure of **1** was revealed by a single crystal X-ray diffraction study in which the coordination environment around the Zn(II) center is a slightly distorted tetrahedron.‡ Every Zn(II) center is coordinated to

 DOI: 10.1039/b102210p

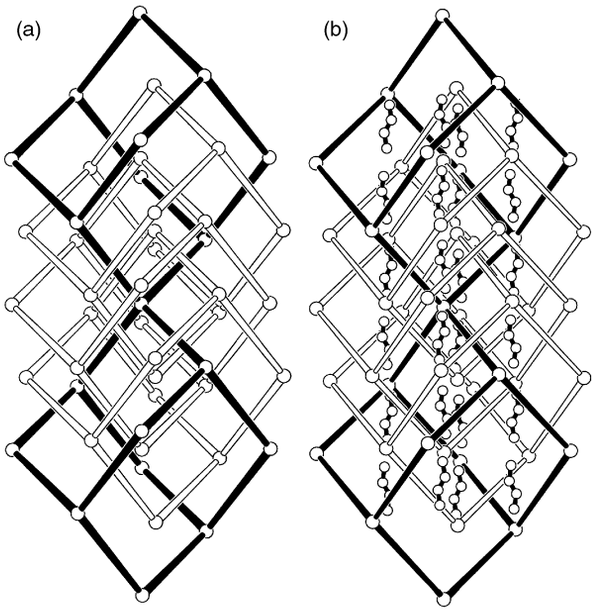

Fig. 2 The diamondoid structure of **1** showing the four-fold interpenetrating network (straight lines and circles represent the 4-pyac ligands and Zn atoms, respectively). (a) Without and (b) with the gaseous *trans*-2-butene molecules.

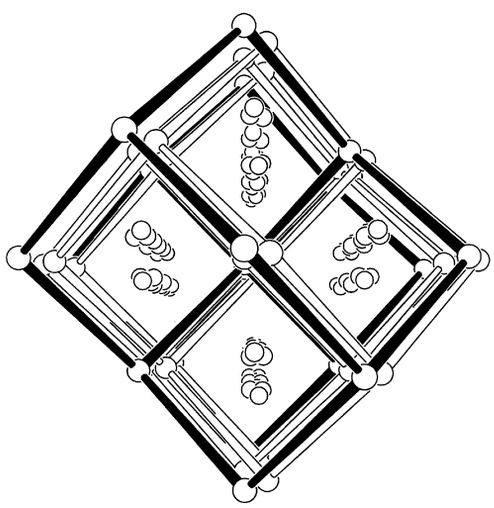

Fig. 3 A view of **1** along the *b*-axis showing trapped *trans*-2-butene molecules in square channels.

two pyridyl nitrogen atoms and two carboxylate oxygen atoms from four different 4-pyac anions. Each 4-pyac anion links between two adjacent Zn(II) ions and expands in three-dimensions to form a diamondoid-like structure (Fig. 1). The first view of the structure displays a large cavity in every diamondoid unit (the adjacent Zn···Zn separation is about 11.07 Å). A more careful examination shows that such cavities are reduced by three other identical interpenetrated diamondoid nets (Fig. 2). With the 4-pyridylacrylate groups omitted for clarity, Fig. 3 depicts the interpenetrating structure forming square channels with the dimensions 11.07 Å × 11.07 Å and *trans*-2-butene molecules are trapped in the square channels along the *b*-axis. All of the bond lengths for Zn–O and Zn–N are similar to those previously reported.[16,17]

Compound **1** not only shows the ability to trap gaseous *trans*-2-butene molecules, but also exhibits a strong blue-fluorescent emission (Fig. 4). In comparison to the free Hpyac ligand which shows a fluorescence maximum at 395 nm, a bathochromic shift in **1** (emission at *ca*. 430 nm with an excitation wavelength of 395 nm) was observed. This bathochromic shift is undoubtedly due to the deprotonation of the ligand when forming the 3-D diamondoid network. We believe that the π–π stacking interactions of the pyridyl groups may have also contributed to the bathochromic shift in **1**.

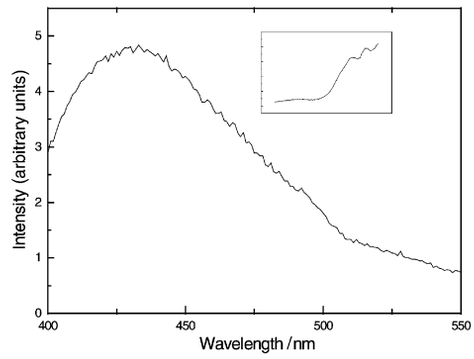

Fig. 4 Fluorescence emission spectrum of **1** in the solid state at room temperature.

Compound **1** is stable at room temperature and insoluble in common solvents such as alcohols, benzene, acetonitrile, chloroform and water. TGA analysis of **1** shows that the complex is stable up to 140 °C, and exhibits a weight loss of 12.6% of the total weight between 140–245 °C, corresponding to the removal of one *trans*-2-butene molecule per formula unit (calc. 13.5%). Powder X-ray diffraction studies on samples before and after the removal of *trans*-2-butene guest molecules indicated that the framework structure of **1** is maintained upon removal of the guest.

The ability of **1** to trap gaseous *trans*-2-butene molecules strongly supports the view that coordination polymers with designable cavities or channels can store appropriate gas molecules and therefore function as novel gas storage materials. Such materials should find a wide range of potential applications in the future.

Acknowledgements

R. G. X. acknowledges the funding support from The Major State Basic Research Development Program (Grant No. G2000077500) and the National Natural Science Foundation of China. W. L. thanks US NSF (DMR-9875544) for financial support and H. K. F. thanks the Malaysian Government R&D Grant 305/pfizik/610942.

Notes and references

† $\{Zn(4\text{-pyac})_2 \cdot B\}_n$ **1** was synthesized by a hydro(solvo)thermal reaction. A typical procedure is as follows: A heavy-walled Pyrex tube containing a mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol), ethyl *trans*-3-(4-pyridyl)acrylate (0.15 g, 1 mmol), 1-butanol (1.5 mL) and H_2O (0.1 mL) was frozen, sealed under vacuum and placed inside an oven at 110 °C. The colorless prismatic crystals were harvested after 48 h of heating. Yield: 0.32 g (76.6%). Calc. for $C_{20}H_{20}N_2O_4Zn$: C, 57.45; H, 4.79; N, 6.70. Found: C, 57.49; H, 4.75; N, 6.77%. IR (KBr, cm^{-1}): 3110 (w), 2900 (w), 2839 (w), 1642 (m), 1611 (s), 1585 (s), 1430 (m), 1370 (s), 1225 (m), 1065 (w), 1020 (w), 865 (w), 837 (m), 747 (m), 610 (m), 520 (w).

‡ Crystal data for **1**: $C_{20}H_{20}N_2O_4Zn$, $M_r = 417.75$, orthorhombic, space group *Pnna*, $a = 12.471(1)$, $b = 13.804(1)$, $c = 12.005$ Å, $U = 2066.7(3)$ $Å^3$, $Z = 4$, μ(Mo-Kα) = 22.3 cm^{-1}. The intensity data were collected at 293(2) K on a Siemens P4 four circle diffractometer using the ω–2θ scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL[18] software, with 2378 unique absorption-corrected (empirical, $T_{min} = 0.6830$, $T_{max} = 0.7933$) reflections. All non-hydrogen atoms were anisotropically refined. The refinement converged at $R = 0.0447$ and $wR = 0.1210$ for a total of 123 parameters and 1279 observed reflections with $I \geq 2.0\sigma(I)$. CCDC reference number 156501. See http://www.rsc.org/suppdata/dt/b1/b102210p/ for crystallographic data in CIF or other electronic format.

1 B. S. Oh, K. Ozay and T. N. Veziroglu, *Hydrogen Energy Prog. XII, Proc. World Hydrogen Energy Conf., 12th*, 1998, **2**, 1265.
2 V. Provenzano, *NATO ASI Ser., Ser. C*, 1998, **50**, 335.
3 G. M. Tom and J. V. McManus, *US Pat.*, US 5,935,305, 1999.

4 J.-P. Cuif, G. Blanchard, O. Touret, A. Seigneurin, M. Marczi and E. Quemere, *Soc. Automot. Eng.*, *SP*, 1997, **SP-1228**, 35; R. Di Monte, P. Fornasiero, M. Graziani and J. Kaspar, *J. Alloys Compd.*, 1998, **275**–**277**, 877; H. Permana, D. N. Belton, K. M. Rahmoeller, S. J. Schmieg, C. E. Hori, K. Y. S. Ng and A. Berenner, *Soc. Automot. Eng.*, *SP*, 1997, **SP-1288**, 23.
5 I. Yonezu, *Netsu Bussei*, 1999, **13**, 279.
6 C. H. Chang and A. Stella, *Prepr. Symp.-Am. Chem. Soc.*, *Div. Fuel Chem.*, 1998, **43**, 580; C. Natzenadel, A. Zuttel, D. Chartouni and L. Schlapbach, *Electrochem. Solid-State Lett.*, 1999, **2**, 30.
7 B. P. Tarasov, V. N. Fokin, A. P. Moravsky, Y. M. Shul'ga, V. A. Yarys and D. V. Schur, *Hydrogen Energy Prog. XII, Proc. World Hydrogen Energy Conf.*, *12th*, 1998, **2**, 1221.
8 For reviews: T. Iwamoto, in *Inclusion Compounds*, J. L. Atwood, J. E. D. Davies and D. D. MacNicol, eds., Academic Press, London, 1991, vol. 5, ch. 2–4, pp. 177–212; C. Janiak, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1431.
9 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem.*, *Int. Ed.*, 1998, **38**, 2638.
10 K. Seki, S. Nakai, K. Mori and S. Takamizawa, *Jpn. Pat.*, JP 2000 109,485, 2000; K. Seki, K. Mori and S. Takamizawa, *Jpn. Pat.*, JP 2000 63,393, 2000; K. Seki, N. Inoue, K. Mori, M. Sato and A. Tanba, *Jpn. Pat.*, JP 2000 63,385, 2000; K. Seki, K. Mori and S. Takamizawa, *Jpn. Pat.*, JP 10 316,684, 1998.
11 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
12 S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 2082.
13 A. Cornia, A. Caneschi, P. Dapporto, A. C. Fabretti and D. Gatteschi, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1780.
14 N. Kawanami, T. Ozeki and A. Yagasaki, *J. Am. Chem. Soc.*, 2000, **122**, 1239.
15 O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong and W. Lin, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 536.
16 J. A. Dean (Editor), *Lange's Handbook of Chemistry*, McGraw-Hill Book Co. Press, New York, 1999, section 4, pp. 4–36.
17 A. Orpen, A. G. Brammer, F. Allen, O. Kennard, D. G. Watson and R. J. Jayor, *J. Chem. Soc.*, *Dalton Trans*, 1989, S1.
18 G. M. Sheldrick, SHELXTL, Program for Crystal Structure Determination, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1994.