

# [NiL]<sub>3</sub>[BTC]<sub>2</sub>·14H<sub>2</sub>O [L = 3,10-bis(2-ethyl)-1,3,5,8,10,12-hexaazacyclotetradecane, BTC = 1,3,5-benzenetricarboxylate]: synthesis, structure and unique selective guest molecule absorption properties†

Tong-Bu Lu,<sup>\*a</sup> Hua Xiang,<sup>a</sup> Rudy L. Luck,<sup>\*b</sup> Long Jiang,<sup>a</sup> Zong-Wan Mao<sup>a</sup> and Liang-Nian Ji<sup>a</sup>

<sup>a</sup> Department of Chemistry, Zhongshan University, Guangzhou 510275, China.

E-mail: cesltb@zsu.edu.cn

<sup>b</sup> Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton MI 49931, USA

Received (in Montpellier, France) 4th March 2002, Accepted 16th May 2002

First published as an Advance Article on the web 17th July 2002

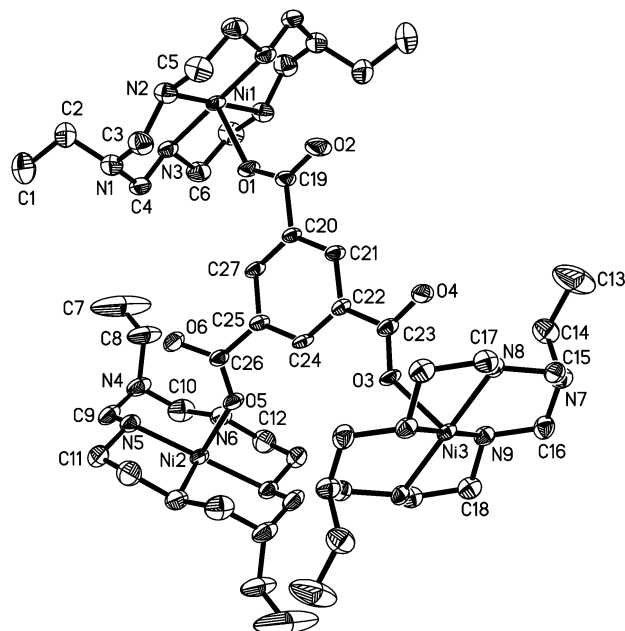
**Reaction of 1,3,5-benzenetricarboxylate with a macrocyclic Ni(II) complex leads to a porous metal-organic framework, which displays a high selectivity for ethanol sorption.**

Recently, much attention has focused on nano-structural metal-organic frameworks (MOFs) constructed by metal-ligand coordination interactions,<sup>1</sup> and their electronic,<sup>2</sup> magnetic,<sup>3</sup> optical<sup>4</sup> and absorption<sup>5</sup> properties have been investigated. Although many MOFs have been investigated for guest molecule absorption,<sup>5,6</sup> few of them show selective absorption properties for small guest molecules.<sup>5c,g,6b</sup> Here, we report on the synthesis of a 2D brick-wall-like MOF, [NiL]<sub>3</sub>[BTC]<sub>2</sub>·14H<sub>2</sub>O (**1**) with 1D open channels, constructed by using a macrocyclic complex [NiL]<sup>2+</sup> [L = 3,10-bis(2-ethyl)-1,3,5,8,10,12-hexaazacyclo-tetradecane] with a 1,3,5-benzenetricarboxylate bridging ligand (BTC). **1** is not soluble in most common solvents (*e.g.*, DMF and DMSO), however, it is soluble in water and decomposes to [NiL]<sup>2+</sup> and BTC<sup>3-</sup>. This limited solubility allows for studies of selective guest solvent absorption by using <sup>1</sup>H NMR spectra, and the results indicate that **1** has a high selectivity to bind ethanol molecules.

Compound **1** is synthesized by reacting a macrocyclic nickel(II) complex [NiL](ClO<sub>4</sub>)<sub>2</sub> with BTC<sup>3-</sup>. The results of an X-ray diffraction analysis indicate that the complex contains a 2D brick-wall structure. In **1**, each Ni(II) ion lies on an inversion center and is six-coordinate. Four nitrogen atoms from the macrocyclic ligand are in the equatorial plane and two carboxylate oxygen atoms from two BTC<sup>3-</sup> anions occupy the axial positions, forming a slightly distorted octahedral geometry (Fig. 1). The Ni–N bond distances [2.040(4)–2.069(4) Å] are slightly shorter than the Ni–O bond distances [2.105(3)–2.136(3) Å]. Each BTC<sup>3-</sup> anion binds to three metal ions resulting in C<sub>1</sub> symmetry and a 2D brick-wall-like network along the *bc* plane and 1D channels along the *a* axis (Fig. 2). The size of the channel is 8.3 × 7.6 Å. The channel volume per unit is estimated to be 481 Å<sup>3</sup> (24.3% of the total) by using the PLATON program (VOID).<sup>7</sup> The voids of the channels are filled with water guest molecules, and these water molecules are linked each other and with the free carbonyl oxygen atom of the BTC<sup>3-</sup> ligand through hydrogen bonding interactions (Ow1...Ow5 = 2.607, Ow1...Ow6 = 2.897, Ow2...Ow4 =

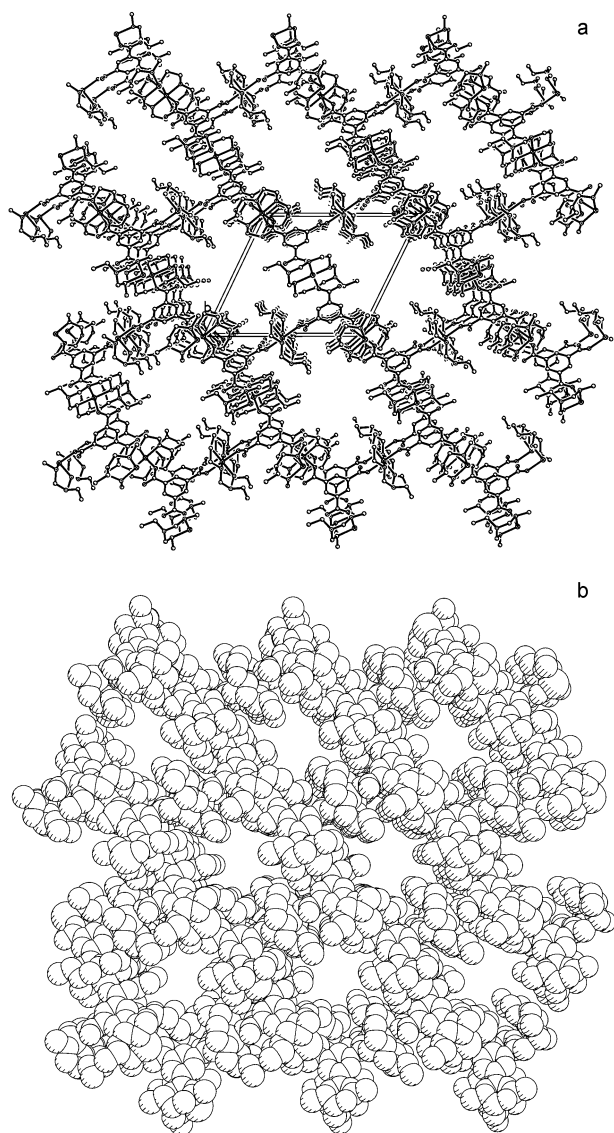
2.735, Ow2...Ow5<sup>a</sup> = 2.880, Ow3...Ow4<sup>a</sup> = 2.797, Ow3...Ow5 = 2.801, Ow1...O4 = 2.831, Ow5...O2<sup>b</sup> = 2.676, Ow6...O4<sup>b</sup> = 2.899, Ow7...O6<sup>c</sup> = 2.795 Å; *a* = −*x* + 1, −*y* + 1, −*z*; *b* = −*x* + 1, −*y*, −*z*; *c* = −*x* + 2, −*y* + 1, −*z* + 1).

The water guest molecules in **1** are easily lost even at room temperature, resulting in pale pink powders. The departure of the guest water molecules is probably facilitated by the hydrophobic environment of the channels induced by the pendant ethyl groups of the macrocycles. TG analysis indicates that all the water molecules can be removed from the channel at less than 70 °C, and the 2D framework is stable up to 200 °C. The solvent absorption experiments were done by suspending the dried solids [the <sup>1</sup>H NMR spectrum is shown in Fig. S1 of the Electronic supplementary information (ESI)] in solvent mixtures of acetone–CH<sub>3</sub>CN–CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH (1 : 1 : 1 : 1) and benzene–toluene–THF–C<sub>2</sub>H<sub>5</sub>OH (1 : 1 : 1 : 1) and allowing them to stand overnight. After filtration and drying in air, the solids were dissolved in D<sub>2</sub>O (former mixture) and D<sub>2</sub>O–acetone-*d*<sub>6</sub> (4 : 1, latter mixture). The <sup>1</sup>H NMR



**Fig. 1** ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% level.

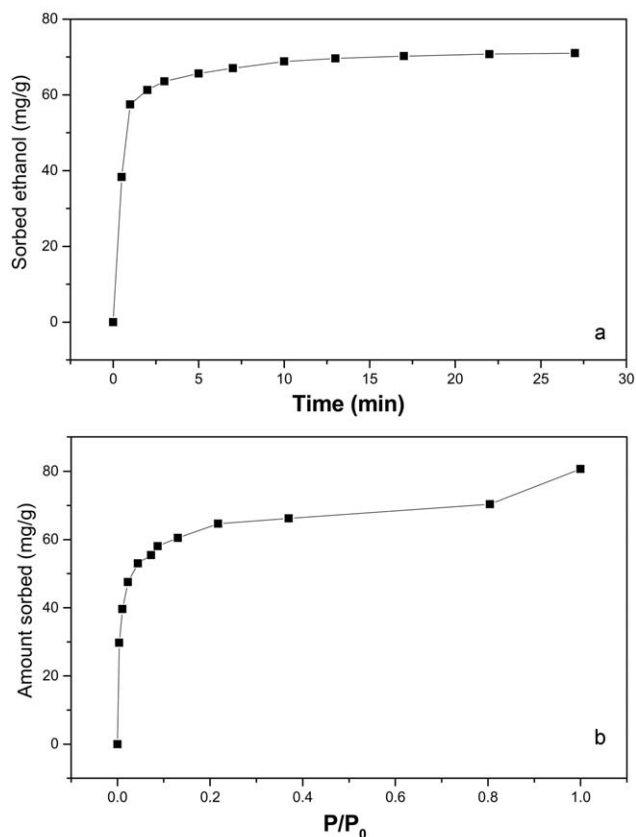
† Electronic supplementary information (ESI) available: <sup>1</sup>H NMR spectra of dried **1**, as prepared and after immersion in different solvent mixtures. See <http://www.rsc.org/suppdata/nj/b2/b202220f/>



**Fig. 2** Structural views of **1** along the *a* axis, showing the 1D channels. (a) The molecular packing arrangement. (b) A space-filling model. Water molecules are omitted for clarity.

spectra revealed that in both solvent mixtures, only ethanol was absorbed by the dried solids (Fig. S2 and S3, ESI). This clearly indicates that dried **1** has a high affinity for ethanol molecules.

In order to further understand the sorption process of dried **1** for ethanol, the weight gain monitored as a function of time [Fig. 3(a)] at the saturation vapor pressure of ethanol (about 44 Torr) at room temperature (24 °C) was measured using an electromicrobalance (CAHN 2000). As shown in Fig. 3(a), ethanol molecules were absorbed very quickly and almost reached equilibrium within 1 min. After that, there is no further absorption, indicating that the 1D channels are completely filled with ethanol molecules. A weight gain of about 70 mg g<sup>-1</sup> corresponds to the sorption of two ethanol molecules per formula unit at equilibrium pressure. The ethanol vapor sorption isotherm measurement of dried **1** revealed a type I isotherm [Fig. 3(b)], different from that of Zn<sub>2</sub>(BTC)(NO<sub>3</sub>), which shows a type V isotherm.<sup>5c</sup> The sorption reached equilibrium at very low ethanol vapor pressure ( $P/P_0 < 0.2$ ). This rapid and lower vapor pressure sorption indicates a strong sorbate-sorbant interaction, and this strong interaction is a factor in the high selectivity of dried **1** for ethanol molecules. We believe that this high selectivity is due to the



**Fig. 3** (a) Weight gain measured as a function of time for dried **1** exposed to ethanol vapor. (b) Ethanol vapor sorption isotherm for dried **1**.

size selectivity of the pores in dried **1** for ethanol molecules and hydrogen bonding interactions between the ethanol molecules and the free carbonyl oxygen atoms of the BTC<sup>3-</sup> ligand. We are currently crystallizing the complex from water in the presence of ethanol in order to obtain crystals with which to conduct a single-crystal X-ray analysis. This should allow us to determine exactly how the ethanol molecules are located within the channels.

In summary, a porous MOF that displays a high selectivity for ethanol sorption was constructed *via* ligand-to-metal ion coordination interactions.

## Experimental

### Materials

Na<sub>3</sub>BTC was prepared by reaction of H<sub>3</sub>BTC (1,3,5-benzenetricarboxylic acid) with an aqueous solution of NaOH. [NiL](ClO<sub>4</sub>)<sub>2</sub> was prepared by using the reported method.<sup>8</sup> All other chemicals were used as purchased without further purification.

An aqueous solution (4 mL) of Na<sub>3</sub>BTC (0.055 g, 0.2 mmol) was layered with a dimethyl formamide solution (4 mL) of [NiL](ClO<sub>4</sub>)<sub>2</sub> (0.20 g, 0.3 mmol) at room temperature. After about three weeks, pink crystals suitable for X-ray analysis formed from the solution; the yield was about 30%.

### X-Ray crystallography

Single-crystal data were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically.

The Ow1, Ow2, Ow4 and Ow5 atoms are disordered (s.o.f. = 0.5). All of the hydrogen atoms bound to carbon were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXL system of computer programs.<sup>9</sup>

CCDC reference number 176796. See <http://www.rsc.org/suppdata/nj/b2/b202220f/> for crystallographic files in CIF or other electronic format.

Crystal data for  $[\text{NiL}]_3[\text{BTC}]_2 \cdot 14\text{H}_2\text{O}$  (**1**).  $\text{C}_{54}\text{H}_{124}\text{N}_{18}\text{O}_{26}\text{Ni}_3$ ,  $M = 1617.9$ , triclinic, space group  $P1$ ,  $a = 8.541(2)$ ,  $b = 14.920(4)$ ,  $c = 17.352(5)$  Å,  $\alpha = 115.233(4)^\circ$ ,  $\beta = 93.117(5)^\circ$ ,  $\gamma = 96.030(5)^\circ$ ,  $U = 1977(1)$  Å<sup>3</sup>,  $Z = 1$ , 9948 independent reflections ( $R_{\text{int}} = 0.0411$ ) with 4745 [ $I > 2\sigma(I)$ ] observed data,  $R_1 = 0.0700$ ,  $wR_2 = 0.1871$ .

## Acknowledgements

This work was supported by the NSFC (29801005), the NSF of CCHE-0079158, and the Ministry of Education of China. The authors thank Prof. M. Mullins for the use of his CAHN 2000 electromicrobalance and B. Oonkhanond for useful discussions.

## References

- (a) F. A. Cotton, C. Lin and C. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; (b) M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (c) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (d) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (e) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (f) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (g) M. Fujita, K. Umamoto, M. Yoshizawa, N. Fujita, T. Kusakawa and K. Biradha, *Chem. Commun.*, 2001, 509.
- (a) Z. Chen, R. J. Wang and J. Li, *Chem. Mater.*, 2000, **12**, 762; (b) L. Pan, X. Y. Huang and J. Li, *J. Solid State Chem.*, 2000, **152**, 236; (c) M. Munakata, C. L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and T. Horino, *Inorg. Chem.*, 1998, **37**, 5651.
- (a) A. K. Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab and J. V. Yakhmi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2606; (b) M. Ohba, N. Usuki, N. Fukita and H. Ōkawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1795; (c) B. Q. Ma, S. Gao, G. Su and G. X. Xu, *Angew. Chem., Int. Ed.*, 2001, **40**, 434; (d) H. Xiang, S. Gao, T. B. Lu, R. L. Luck, Z. W. Mao, X. M. Chen and L. N. Ji, *New J. Chem.*, 2001, **25**, 875; (e) H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10622.
- (a) O. R. Evans, R. G. Xiong, Z. Y. Wang, G. K. Wong and W. Lin, *Angew. Chem., Int. Ed.*, 1999, **38**, 536; (b) W. Lin, Z. Y. Wang and L. Ma, *J. Am. Chem. Soc.*, 1999, **121**, 11249; (c) W. Lin, O. R. Evans, R. G. Xiong and Z. Y. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13272; (d) M. L. Tong, X. M. Chen, B. H. Ye and L. N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237.
- (a) B. L. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021; (b) H. K. Chae, M. Eddaoudi, J. Kim, S. I. Hauck, J. F. Hartwig, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 11482; (c) M. Eddaoudi, H. L. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 1391; (d) A. Laine, M. O'Keeffe and O. M. Yaghi, *Science*, 1999, **283**, 1145; (e) H. L. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; (f) H. L. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571; (g) O. M. Yaghi, *US Pat.*, 5648508, 1997.
- (a) H. J. Choi, T. S. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 1999, **38**, 1405; (b) K. S. Min and M. P. Suh, *Chem. Eur. J.*, 2001, **7**, 303.
- PLATON: A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
- M. P. Suh, B. Y. Shim and T. S. Yoon, *Inorg. Chem.*, 1994, **33**, 5509.
- G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.