



Cite this: *Chem. Commun.*, 2015, 51, 8446

Received 10th February 2015,
Accepted 25th February 2015

DOI: 10.1039/c5cc01244a

www.rsc.org/chemcomm

Linearly bridging CO₂ in a metal–organic framework†

Fei-Yan Yi,^a Hai-Long Jiang^b and Zhong-Ming Sun^{*a}

A very rare structurally characterized CO₂-coordinated metal–organic framework was synthesized by a solvothermal reaction. The CO₂ ligand links two open Zn metal centers in a linear and symmetrical $\mu(\text{O},\text{O}')$ coordination mode with a C=O distance of 1.107(4) Å. The new complex reported here is stable under ambient conditions and may provide a new strategy for CO₂ fixation.

Carbon dioxide (CO₂), the primary greenhouse gas emitted through human activities, has caused increasing environmental concerns during the past few decades.¹ To now, some effective strategies have been adopted to capture CO₂ from gaseous waste.² Recently, metal–organic frameworks (MOFs) as a new type of functional materials have attracted intensive attention.³ A large number of porous MOFs as potential CO₂ adsorbents have been reported. These materials exhibit high adsorptive capacities under either low or high pressure due to their extraordinary surface areas, finely tunable pore surface properties, and potential industrial scalability.⁴ From a mechanistic point of view, it is extremely important to model the trapped CO₂ molecules through single-crystal X-ray diffractions within the frameworks, but this is difficult because most CO₂ molecules are disordered in MOFs. Few examples of CO₂ molecules trapped in MOFs have been confirmed by crystallographic analysis⁵ combined with other complementary methods such as IR spectroscopy and computational studies.⁶ Investigation of the manner in which the metal centers coordinate to CO₂ molecules will lay a firm foundation to design new MOF materials for the fixation of CO₂. So far, a few

structurally characterized CO₂-containing organometallic compounds have also been verified.⁷ Usually, CO₂ molecules show four main coordination modes: $\mu_2\text{-}\eta^2\text{C},\text{O}$, $\mu_2\text{-}\eta^3\text{C},\text{O}$, $\mu_2\text{-}\eta^4\text{C},\text{O}$ and $\mu_2\text{-}\eta^2\text{O},\text{O}$. Very recently, Nandi and Goldberg reported a zinc porphyrin-based PrNa-MOF in which one CO₂ molecule bridges two neighboring Zn(II) centers in the $\mu_2\text{-}\eta^2\text{O},\text{O}$ coordination mode with an O–C–O angle of 155.2(10)° and a C=O distance of 1.131(5) Å.⁸ In this communication, we describe an unprecedented ZnMOF complex in which CO₂ molecules are directly fixed by open Zn(II) centers.

The title complex ZnMOF (**1**) was synthesized by typical solvothermal reactions of Zn(NO₃)₂·6H₂O and a semi-rigid polycarboxylic acid hexa[4-(carboxyphenyl)oxamethyl]-3-oxapentane (H₆L) in DMF/H₂O (6 : 1 in volume) after heating at 115 °C for 3 days. Its formula was confirmed as [(CH₃)₂NH₂]₂[Zn₆(OH)(L)]₂(CO₂)·9DMF·3H₂O based on elemental analysis, single-crystal X-ray diffraction, thermogravimetric analysis (TGA) as well as charge balance considerations. The protonated [(CH₃)₂NH₂]⁺ cations are formed *in situ* upon heating DMF.⁹ Single-crystal X-ray diffraction study revealed that compound **1** crystallizes in an orthorhombic space group *Pmna* (Table S1, ESI†). Its asymmetric unit contains two crystallographic-independent Zn²⁺ ions, half ligand L, one μ_3 -OH anion and a quarter of CO₂ molecule (Fig. S1 in ESI†). Other disordered cations and guest molecules are not crystallographically well-defined. As shown in Fig. 1 and Fig. S2a (ESI†), Zn(1) is octahedrally coordinated by six oxygen atoms. Four O atoms in the square plane are from the three carboxylate groups, one vertical O atom is from the CO₂ ligand, and the other

^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CAS), Changchun, Jilin 130022, China. E-mail: szm@ciac.ac.cn; Web: //zhongmingsun.weebly.com/

^b Hefei National Laboratory for Physical Sciences at the Microscale, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic files in CIF format, ORTEP representation of the asymmetric unit of **1**, tables of crystal data and structure results, tables of selected bond lengths and bond angles, TGA diagram, simulated and measured XRD patterns, IR spectra of **1**. CCDC 898424. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc01244a

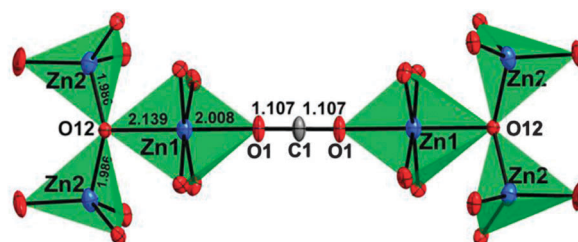


Fig. 1 ORTEP representation of Zn(II) ions and their coordination environments. Thermal ellipsoids are drawn at the 30% probability level. O and C atoms are drawn as red and grey circles, respectively.

one is from μ_3 -OH. The Zn(1)–O bond lengths are in the range of 2.008(4)–2.139(3) Å. In comparison, Zn(2) is tetrahedrally coordinated by four oxygen atoms, three of which come from three different carboxylate ligands and the last one is from the μ_3 -OH ligand shared with Zn(1) (Fig. 1 and Fig. S2a, ESI†). The Zn(2)–O distances vary from 1.943(2) to 1.986(1) Å, which are slightly shorter than those with Zn(1). A Zn(1) ion and two Zn(2) ions are held together by the vertex-sharing μ_3 -OH ligand, resulting in a trinuclear Zn_3^{II} cluster in the shape of an isosceles triangle. It is interesting that the carbon dioxide molecule (O(1)C(1)O(1)) links two Zn_3 clusters in a linear $\mu(\text{O},\text{O}')$ bonding mode to form a $\text{Zn}_3\text{--O=C=O--Zn}_3$ dimer with a Zn(1)–O(1)–C(1) angle of 162.1(3)°. Herein, C(1) locates at an inversion center with 25% occupancy, and O(1) lies at 2-fold axis with 50% occupancy, thus the bond angle of O=C=O is exactly 180° and different from other bent CO_2 molecules in previously documented metal– CO_2 complexes.^{7,8} The C=O bond length of 1.107(4) Å is comparable to that in free carbon dioxide (1.163 Å)¹⁰ and falls within the range of 1.06–1.23 Å observed in other crystal structures containing coordinated CO_2 .^{7,8}

In **1**, each L^{6-} anion connects nine Zn^{II} ions from four trinuclear Zn_3 clusters, in which two carboxylate groups adopt the $\mu_1\text{-}\eta^1\eta^0$ coordination mode and the other four adopt the $\mu_2\text{-}\eta^1\eta^1$ mode (Fig. S2b, ESI†). Meanwhile, each trinuclear Zn_3 secondary building unit (SBU) is linked by four L^{6-} ligands (Fig. S2c, ESI†), and was further extended into a two-fold interpenetrating three-dimensional (3D) network (Fig. S3a, ESI†). In each single net, mesoporous hexagonal channels can be observed approximately $17.8 \times 17.8 \text{ \AA}^2$ (the length of the *b*-axis) along the *a*-axis and $22.3 \times 11.7 \text{ \AA}^2$ along the *b*-axis (including van der Waals radii) (Fig. S3b and c, ESI†). From the topological point of view, each independent framework can be reviewed as a $\{6^6\}$ 4-connected uninodal **dia** net (Fig. S3d–f, ESI†).¹¹ Then the linearly coordinated CO_2 ligand bridged two Zn^{II} SBUs of adjacent independent nets into total 3D frameworks with interconnected channels in a staggered fashion, thus the hexagonal window along the [100] direction is divided into three parts (Fig. 2 and Fig. S4a, ESI† type A: $13.1 \times 9.4 \text{ \AA}^2$, type B: $14.5 \times 9.6 \text{ \AA}^2$, and type C: $16.4 \times 6.1 \text{ \AA}^2$). The coordinated CO_2 molecules reside in channel C and link two open Zn sites. A large-size channel of

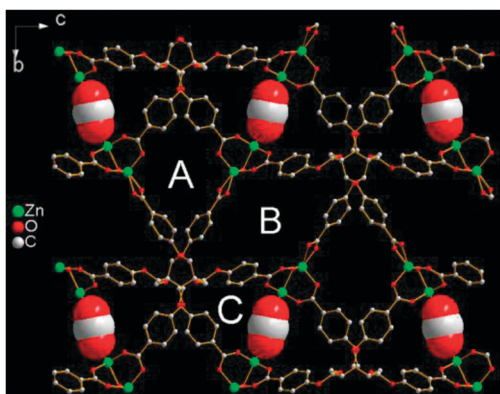


Fig. 2 View of compound **1** along the *a*-axis. Zn, O, and C atoms are drawn as bright green, red, and gray balls, respectively. The bridging CO_2 ligands are shown in the space-filling mode. A, B and C represent three types of channels in **1**.

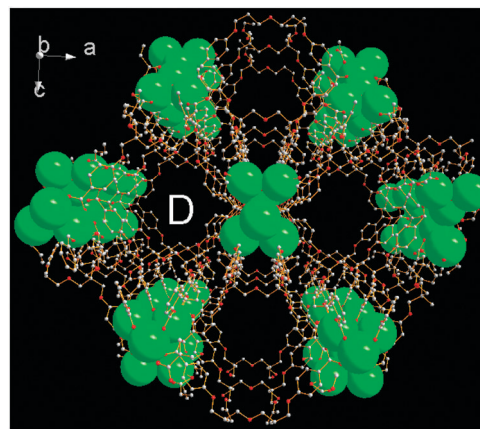


Fig. 3 3D porous framework of compound **1** projected along the *b*-axis with D type of the channel. Zinc atoms are represented as bright green balls in the space-filling mode. Hydrogen atoms and free solvent molecules are omitted for clarity.

$12.5 \times 10.5 \text{ \AA}^2$ (type D) can still be observed perpendicular to the *ac* plane (Fig. 3 and Fig. S4b, ESI†). The channels B and D mentioned above intersect each other, forming two-dimensional intersecting channels in this compound (Fig. S4c, ESI†). Free solvent molecules are located in the channels. TOPOS analysis reveals that the whole structure can be simplified as a 4,8-connected **alb** net (Fig. S4d, ESI†) with a solvent-accessible volume of approximately 5715.2 \AA^3 per unit cell, and a pore volume ratio calculated to be 57.0% using the PLATON program.¹²

In order to confirm the CO_2 molecule was indeed fixed successfully in the ZnMOF (**1**), several verifiable methods are adopted. Firstly, four randomly selected crystals were used for single-crystal X-ray diffraction analyses on different CCD diffractometers and the experimental details are depicted in the ESI† as shown in Tables S1 and S2. All results display that a linear coordinated CO_2 ligand appears obviously in position and strongly binds two metal sites. Secondly, to gain more insight into the CO_2 bonded in the ZnMOF (**1**), IR spectroscopy was used as a complementary method to study the interaction of carbon dioxide with the metal site and provides further evidence for the existence of CO_2 in **1**. As depicted in Fig. S5 (ESI†), an absorption band at 2456 cm^{-1} can be assigned to the stretching vibration of the C–O bond from the bridging CO_2 ligand. In comparison to free linear carbon dioxide ($\nu_{\text{asym}} = 2348 \text{ cm}^{-1}$),¹³ the value is at a higher frequency, but consistent with experimentally observed shorter bond length in other materials reported to date.^{5,7,8} Thirdly, the solid sample (80 mg) of complex **1** was placed in a 1.5 mL centrifugal tube with 1 mL of H_2O , then concentrated H_2SO_4 (40 μL) was added and sealed. Some small bubbles could be observed immediately, due to the destruction of the framework of **1** by H_2SO_4 thereby releasing the coordinated CO_2 molecules. After 5 h, the small bubbles were gathered into a big bubble. In order to observe the phenomenon more clearly, a similar experiment was done in glass vials (5 mL), then capped and kept still, as shown in Fig. S6 (ESI†). As a comparison, concentrated H_2SO_4 with the same volume was added into a pure DMF solution as well as the DMF solution with Zn^{2+} salt, respectively, but no change was observed. Then the

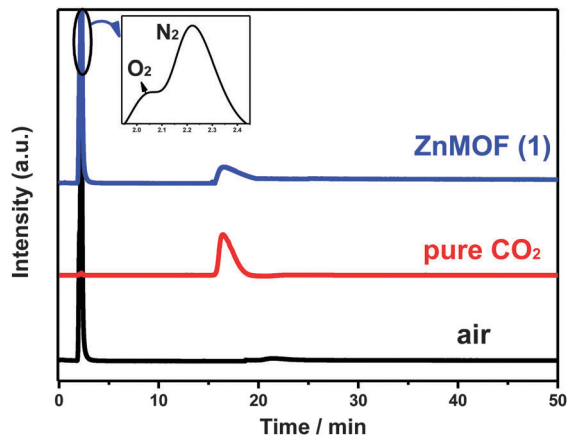


Fig. 4 GC measurements of air, pure CO₂, and released CO₂ gas from the title compound ZnMOF (**1**) destroyed by concentrated H₂SO₄.

generated gases of headspace over the sample was collected by sealing the needle (1 mL), and then used for gas chromatography (GC) analysis (Fig. 4). By comparison, the air and pure CO₂ gas with the same volume were also used for GC measurements, respectively. As shown in Fig. 4, the results indicate that the CO₂ molecules in air are almost negligible, the released CO₂ molecules from compound **1** are very clear and the peak matches well with the one from pure CO₂ gas. The results discussed above strongly demonstrate that the CO₂ ligand is connected to the framework of ZnMOF (**1**).

Another important question also needs to be resolved about the source of the CO₂ molecule in ZnMOF (**1**). The most likely scenario is the *in situ* decomposition of solvent DMF during the solvothermal synthesis under acidic conditions, which is a very common process and has also been verified by this work (Fig. S7, ESI[†]) and others by mass spectrometry (MS) analysis.^{5d,14} To demonstrate the generation of CO₂ from DMF, several solutions containing pure DMF (1 mL), the DMF solution with Zn²⁺, as well as the DMF solution with H₆L and Zn²⁺ for ZnMOF (**1**), have been prepared and heated at 80 °C for 48 h, then the upper gas was used for MS measurements and for detecting the variation of CO₂ gas. It is noteworthy that CO₂ gas was indeed detected from DMF (Fig. S7, ESI[†]).

Thermogravimetric-mass spectrometry (TG-MS) analysis (Fig. 5) was also performed by heating the crystals of compound **1** under a N₂ atmosphere from room temperature to 800 °C. For comparison, analysis with pure H₆L was also carried out under the same experimental settings. The initial release of CO₂ molecules begins even at a relatively low temperature of 70 °C. Then the first CO₂ peak was observed at 115 °C, which may have originated from the coordinated CO₂ molecules and partial decomposition of DMF molecules located in the channel of ZnMOF (**1**). The second stage of CO₂ release was found in the temperature range of 350 to 550 °C, corresponding to the decomposition of carboxylate ligands. These results are in accordance with those of TGA analyses. A further test was performed to investigate whether the ZnMOF (**1**) can release or even refix CO₂ molecules, which is more interesting to us, so that its thermal stability can be examined by PXRD measurements after

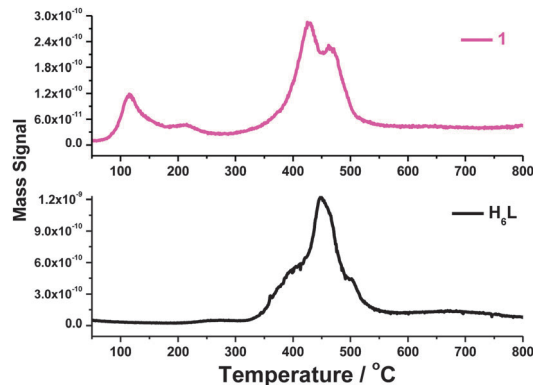


Fig. 5 TG-MS spectroscopy for the detection of CO₂ while heating compound **1** and H₆L under N₂ from RT to 800 °C.

heat treatment at 120 °C first. It is a pity that a significantly different pattern compared to the simulated one was obtained, implying that the original structure has changed, even collapsed.

In conclusion, we report a very rare structurally ascertained example of the CO₂-bound metal-organic framework. The successful synthesis of compound **1** provides a definitive pattern to understand CO₂ fixation and may give a promising route to capture CO₂ in MOFs. In addition, the linearly bridging pattern of the CO₂ ligand displays an important structure model for CO₂ coordination chemistry.

We acknowledge the support for this work from the National Nature Science Foundation of China (No. 21171162 and 21201162). We also thank Prof. Zhangquan Peng for his kind help on GC analysis.

Notes and references

- 1 P. Falkowski, R. J. Scholes, E. Boyle, J. Canadell, D. Canfield, J. Elser, N. Gruber, K. Hibbard, P. Höggberg, S. Linder, F. T. Mackenzie, B. Moore, T. Pedersen, Y. Rosenthal, S. Seitzinger, V. Smetacek and W. Steffen, *Science*, 2000, **290**, 291.
- 2 R. Service, *Science*, 2004, **305**, 962.
- 3 (a) N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933; (b) R. B. Getman, Y.-S. Bae, C. E. Wilmer and R. Q. Snurr, *Chem. Rev.*, 2012, **112**, 703; (c) H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.*, 2012, **112**, 836; (d) M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675; (e) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (f) C. M. Doherty, D. Buso, A. J. Hill, S. Furukawa, S. Kitagawa and P. Falcaro, *Acc. Chem. Res.*, 2014, **47**, 396; (g) C. Wang, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222; (h) L.-H. Xie and M. P. Suh, *Chem. – Eur. J.*, 2013, **19**, 11590; (i) H.-M. Zhang, J. Yan, Y.-C. He and J.-F. Ma, *Chem. – Asian J.*, 2013, **8**, 2787.
- 4 (a) K. Sumida, D. L. Rogov, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; (b) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keefe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 11650; (c) Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315; (d) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650; (e) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Angew. Chem., Int. Ed.*, 2012, **51**, 1826; (f) C. Song, Y. He, B. Li, Y. Ling, H. Wang, Y. Feng, R. Krishnac and B. Chen, *Chem. Commun.*, 2014, **50**, 12105; (g) P. Li, J. Chen, J. Zhang and X. Wang, *Sep. Purif. Rev.*, 2015, **44**, 19; (h) Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868; (i) Y.-N. Gong, Y.-L. Huang, L. Jiang and T.-B. Lu, *Inorg. Chem.*, 2014, **53**, 9457; (j) F. Wang, H.-R. Fu, Y. Kang and J. Zhang, *Chem. Commun.*, 2014, **50**, 12065; (k) J.-R. Li, J. Yu, W. Lu,

- L.-B. Sun, J. Sculley, P. B. Balbuena and H.-C. Zhou, *Nat. Commun.*, 2013, **4**, 1538; (l) J. Park, D. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 99; (m) R. Wang, Q. Meng, L. Zhang, H. Wang, F. Dai, W. Guo, L. Zhao and D. Sun, *Chem. Commun.*, 2014, **50**, 4911; (n) Y. Hu, W. M. Verdegaal, S.-H. Yu and H.-L. Jiang, *ChemSusChem*, 2014, **7**, 734; (o) T.-H. Bae and J. R. Long, *Energy Environ. Sci.*, 2013, **6**, 3565; (p) N. Planas, A. L. Dzubak, R. Poloni, L.-C. Lin, A. McManus, T. M. McDonald, J. B. Neaton, J. R. Long, B. Smit and L. Gagliardi, *J. Am. Chem. Soc.*, 2013, **135**, 7402.
- 5 (a) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650; (b) P.-Q. Liao, D.-D. Zhou, A.-X. Zhu, L. Jiang, R.-B. Lin, J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 17380; (c) J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin and X.-M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5789; (d) J. A. Johnson, S. Chen, T. C. Reeson, Y.-S. Chen, X. C. Zeng and J. Zhang, *Chem. – Eur. J.*, 2014, **20**, 7632; (e) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650.
- 6 (a) R. Poloni, B. Smit and J. B. Neaton, *J. Am. Chem. Soc.*, 2012, **134**, 6714; (b) R. Poloni, B. Smit and J. B. Neaton, *J. Phys. Chem. A*, 2012, **116**, 4957; (c) M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876; (d) K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly and J. R. Long, *Chem. Sci.*, 2010, **1**, 184; (e) W. L. Queen, C. M. Brown, D. K. Britt, P. Zajdel, M. R. Hudson and O. M. Yaghi, *J. Phys. Chem. C*, 2011, **115**, 24915; (f) X. Kong, E. Scott, W. Ding, J. A. Mason, J. R. Long and J. A. Reimer, *J. Am. Chem. Soc.*, 2012, **134**, 14341; (g) P. D. C. Dietzel, R. E. Johnsen, H. Fjellvag, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, 5125; (h) G. B. S. Miller, T. K. Esser, H. Knorke, S. Gewinner, W. Schöllkopf, N. Heine, K. R. Asmis and E. Uggerud, *Angew. Chem., Int. Ed.*, 2014, **53**, 14407.
- 7 (a) D. H. Gibson, *Coord. Chem. Rev.*, 1999, 335; (b) K. K. Pandey, *Coord. Chem. Rev.*, 1995, **140**, 37; (c) A. Cornia, A. Caneschi, P. Dapporto, A. C. Fabretti, D. Gatteschi, W. Malavasi, C. Sangregorio and R. Sessoli, *Angew. Chem., Int. Ed.*, 1999, **38**, 1780; (d) C.-C. Chang, M.-C. Liao, T.-H. Chang, S.-M. Peng and G.-H. Lee, *Angew. Chem., Int. Ed.*, 2005, **44**, 7418; (e) S. Takamizawa, E.-i. Nakata, T. Saito and K. Kojima, *CrystEngComm*, 2003, **72**, 411; (f) P. D. C. Dietzel, R. E. Johnsen, H. Fjellva, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, 5125; (g) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni and M. Manassero, *Chem. Commun.*, 1975, 636; (h) R. Alvarez, E. Carmona, E. Gutierrez-Puebla, J. M. Marin, A. Monge and M. L. Poveda, *Chem. Commun.*, 1984, 1326; (i) S. Komiya, M. Akita, N. Kasuga, M. Hirano and A. Fukuoka, *Chem. Commun.*, 1994, 1115; (j) C. H. Lee, D. S. Laitar, P. Mueller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2007, **129**, 13802; (k) G. Gao, F. Li, L. Xu, X. Liu and Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 10838; (l) I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757.
- 8 G. Nandi and I. Goldberg, *Chem. Commun.*, 2014, **50**, 13612.
- 9 (a) A. D. Burrows, K. Cassar, R. M. W. Friend, M. F. Mahon, S. P. Rigby and J. E. Warren, *CrystEngComm*, 2005, **7**, 548; (b) E. Neofotistou, C. D. Malliakas and P. N. Trikalitis, *CrystEngComm*, 2010, **12**, 1034; (c) J.-S. Qin, S.-R. Zhang, D.-Y. Du, P. Shen, S.-J. Bao, Y.-Q. Lan and Z.-M. Su, *Chem. – Eur. J.*, 2014, **20**, 5625.
- 10 X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
- 11 (a) V. A. Blatov, *Struct. Chem.*, 2012, **23**, 955–963. TOPOS software is available for download at <http://www.topos.samsu.ru>; (b) V. A. Blatov, TOPOS, a Multipurpose Crystallochemical Analysis with the Program Package, Russia, 2004; (c) M. O’Keeffe, Reticular Chemistry Structure Resource, <http://rcsr.anu.edu.au/>; (d) V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576.
- 12 (a) A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194; (b) A. L. Spek, *PLATON99*, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.
- 13 A. K. Brisdon, *Inorganic Spectroscopic Methods*, Oxford, New York, 1998, ch. 2, p. 23.
- 14 J. Zhang, S. M. Chen, R. A. Nieto, T. Wu, P. Y. Feng and X. H. Bu, *Angew. Chem., Int. Ed.*, 2010, **49**, 1267.