

1-1-2010

## Dipyridyl beta-diketonate complexes: versatile polydentate metalloligands for metal-organic frameworks and hydrogen-bonded networks

Andrew D. Burrows  
*University of Bath*

Christopher G. Frost  
*University of Bath*

Mary F. Mahon  
*University of Bath*

Paul R. Raithby  
*University of Bath*

Catherine L. Renouf  
*University of Bath*

*See next page for additional authors*

Follow this and additional works at: <https://ro.uow.edu.au/scipapers>



Part of the [Life Sciences Commons](#), [Physical Sciences and Mathematics Commons](#), and the [Social and Behavioral Sciences Commons](#)

---

### Recommended Citation

Burrows, Andrew D.; Frost, Christopher G.; Mahon, Mary F.; Raithby, Paul R.; Renouf, Catherine L.; Richardson, Christopher; and Stevenson, Anna J.: Dipyridyl beta-diketonate complexes: versatile polydentate metalloligands for metal-organic frameworks and hydrogen-bonded networks 2010, 5067-5069.  
<https://ro.uow.edu.au/scipapers/423>

---

## Dipyridyl beta-diketonate complexes: versatile polydentate metalloligands for metal-organic frameworks and hydrogen-bonded networks

### Abstract

The Group 13 metal complexes  $[M(L-2)(3)]$ , where M is Al or Ga and L-2 is 1,3-di(4-pyridyl)-1,3-propanedionato, are hexatopic metalloligands that have been used to prepare mixed-metalorganic frameworks containing interpenetrated primitive cubic networks. In contrast, the europium complex  $[Eu(HL2)(3)-(H2L2)]Cl \cdot 4 \text{ EtOH}$  forms a hydrogen-bonded network following partial protonation of the pyridyl groups.

### Keywords

complexes, diketonate, dipyridyl, hydrogen, frameworks, networks, organic, bonded, metal, metalloligands, polydentate, versatile, beta, CMMB

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

### Publication Details

Burrows, A. D., Frost, C., Mahon, M. F., Raithby, P. R., Renouf, C., Richardson, C. & Stevenson, A. (2010). Dipyridyl beta-diketonate complexes: versatile polydentate metalloligands for metal-organic frameworks and hydrogen-bonded networks. *Chemical Communications*, 46 (28), 5067-5069.

### Authors

Andrew D. Burrows, Christopher G. Frost, Mary F. Mahon, Paul R. Raithby, Catherine L. Renouf, Christopher Richardson, and Anna J. Stevenson

# Dipyridyl $\beta$ -diketonate complexes: versatile polydentate metalloligands for metal–organic frameworks and hydrogen-bonded networks†

Andrew D. Burrows,<sup>\*a</sup> Christopher G. Frost,<sup>a</sup> Mary F. Mahon,<sup>a</sup> Paul R. Raithby,<sup>a</sup> Catherine L. Renouf,<sup>a</sup> Christopher Richardson<sup>ab</sup> and Anna J. Stevenson<sup>a</sup>

Received 29th March 2010, Accepted 21st May 2010

First published as an Advance Article on the web 8th June 2010

DOI: 10.1039/c0cc00646g

**The Group 13 metal complexes  $[M(L^2)_3]$ , where M is Al or Ga and  $L^2$  is 1,3-di(4-pyridyl)-1,3-propanedionato, are hexatopic metalloligands that have been used to prepare mixed-metal–organic frameworks containing interpenetrated primitive cubic networks. In contrast, the europium complex  $[Eu(HL^1)_3 \cdot (H_2L^2)]Cl_4 \cdot EtOH$  forms a hydrogen-bonded network following partial protonation of the pyridyl groups.**

Metal–organic frameworks (MOFs) have attracted considerable attention recently, largely as a consequence of their porosity and subsequent use as materials for applications such as gas storage, separations and catalysis.<sup>1</sup> Mixed–metal–organic frameworks (MMOFs) are an interesting sub-class of these materials, and given that two types of metal ions may have different structural and/or functional roles within a network structure, these are likely to attract increasing attention. While it is possible to prepare MMOFs in a one-pot reaction, it is often difficult to control the nature of the products in this way. This has led to the development of a stepwise synthetic approach to these materials. Thus, a metal centre is reacted with a bifunctional ligand to give an isolable intermediate complex, which itself can act as a building block in network formation.<sup>2</sup> The reaction of this metalloligand with a second metal centre can then be used to form the desired MMOF.

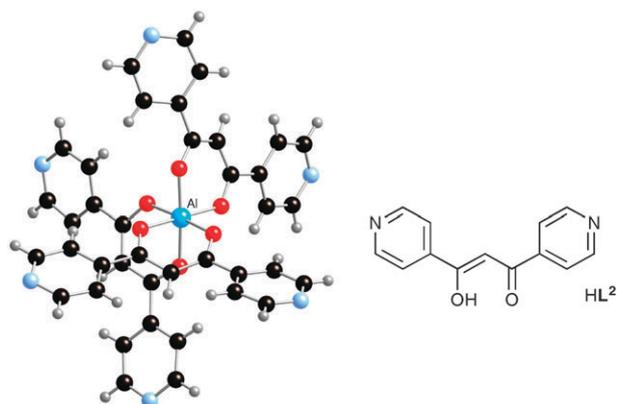
A number of metalloligands have been used in this way, including complexes of pyridinedicarboxylates,<sup>3</sup> Schiff bases<sup>4</sup> and bis(oxamato) ligands,<sup>5</sup> that function as ditopic *O*-donors, and pyridyl-functionalised porphyrins,<sup>6</sup> dipyrinato ligands,<sup>7</sup> terpyridines<sup>8</sup> and tris(triazolyl)borates,<sup>9</sup> that function as polytopic *N*-donors.

Bifunctional ligands based on acetylacetonates are attractive for use in construction of mixed-metal networks. The chelating nature of the bidentate *O,O*-donor ensures relatively low lability, and the negative charge on the ligand allows access to neutral complexes. We have recently reported MMOFs based on 3-cyanoacetylacetonate,<sup>10</sup> whereas the Domasevitch<sup>11,12</sup> and Maverick<sup>13</sup> groups have prepared MMOFs based on 3-(4-pyridyl)acetylacetonate ( $L^1$ ).

A limitation of functionalising at the central carbon of a  $\beta$ -diketonate is the inherent restriction on the number of exotopic donor groups per ligand. Thus, an octahedral complex of the general formula  $[M(L^1)_3]$  functions as a tritopic ligand. In addition, there is an issue with the stability of  $HL^1$ , since it decomposes *via* a reverse-Claisen condensation.<sup>14</sup> We reasoned that by functionalising with 4-pyridyl groups at both ends of the  $\beta$ -diketonate, we could remove the stability limitation, whilst at the same time increasing the number of exotopic donor sites. This would be expected to lead to an increase in the connectivity of the resultant MMOFs. 1,3-Di(4-pyridyl)propane-1,3-dione ( $HL^2$ ) seemed an ideal candidate for this, with octahedral complexes of the form  $[M(L^2)_3]$  expected to contain six remote *N*-donor sites, approximately orientated at the vertices of an octahedron.  $HL^2$  has previously been used to prepare pyrazoles,<sup>15</sup> and shown to exist in solution predominantly as the enol tautomer.<sup>16</sup> Gadolinium and holmium complexes have also been reported very recently.<sup>17</sup>

The reaction of hydrated aluminium or gallium nitrate with  $HL^2$  and NaOH in aqueous solution gave the complexes  $[M(L^2)_3]$  (**1**, M = Al; **2**, M = Ga) in high yield. Following crystallisation from dichloromethane–toluene, crystals of **1** suitable for X-ray single-crystal analysis were obtained. The crystal structure determination† revealed that the crystals were the toluene solvate **1**·1.25C<sub>6</sub>H<sub>5</sub>Me, with the asymmetric unit consisting of one molecule of **1**, one full molecule of toluene, and half of a toluene fragment at 50% occupancy, proximate to the crystallographic inversion centre.

The molecular structure of **1** is shown in Fig. 1. As expected, the complex has distorted octahedral geometry around the



**Fig. 1** The molecular structure of  $[Al(L^2)_3]$  **1**, from the crystal structure of **1**·1.25C<sub>6</sub>H<sub>5</sub>Me.

<sup>a</sup> Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. E-mail: a.d.burrows@bath.ac.uk; Fax: +44 (0)1225 386231; Tel: +44 (0)1225 386529

<sup>b</sup> School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia

† Electronic supplementary information (ESI) available: Syntheses and full crystallographic data for **1** and **3–5**. CCDC 771699–771702. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc00646g

aluminium centre, with ligand bite angles ranging from 88.84(6)° to 91.27(6)°. The AlO<sub>2</sub>C<sub>3</sub> chelate rings are non-planar, with the aluminium atom sitting out of the plane defined by the ligand atoms in the ring. This distortion can be quantified by the angle between the AlO<sub>2</sub> plane and the O<sub>2</sub>C<sub>3</sub> plane defined by the ligand atoms in the chelate ring. These inter-plane ‘fold angles’ are 18°, 16° and 26° for the three ligands.

Together with the constraints imposed by the bidentate nature of L<sup>2</sup>, this folding has a significant impact on the relative orientations of the pyridyl groups. For an ideal octahedral hexatopic metalloligand, the lone pairs on the pyridyl groups would be orientated at 90° and 180° from each other. For [Al(L<sup>2</sup>)<sub>3</sub>], the angles between nitrogen lone pair vectors within the same ligand lie in the range 117° to 122°. The angles between lone pair vectors involving two different ligands range from 69° to 113° for the *cis* positions of the octahedron, and between 155° and 175° for the *trans* positions. The distortions from a regular octahedron can further be quantified by the N···N distances, which range from 7.43 to 11.40 Å for the *cis* positions of the octahedron and from 13.39 to 13.59 Å for the *trans* positions.

Studies on complexes of 3-(4-pyridyl)acetylacetonate (L<sup>1</sup>) have also revealed distortions, which affect the angles between the three exotopic donor groups, and introduce variation from the ‘regular’ angle of 120°. Distortions present in the metalloligands have been shown to be reproduced in M<sup>2+</sup>MOFs derived from them, and the angles between the lone pairs of the pyridyl groups have been used to control the network topology.<sup>12</sup>

Given the distortions from a regular octahedral arrangement of the pyridyl groups in [Al(L<sup>2</sup>)<sub>3</sub>], we reasoned that linking these metalloligands together to produce a regular cubic network would require use of a metal centre with inherent coordinative flexibility. Silver(I) is well known to exhibit a range of coordination numbers and geometries in coordination networks,<sup>18</sup> so appeared the ideal choice as a linker metal.

The reaction of either **1** or **2** with AgNO<sub>3</sub> in hot DMSO gave colourless crystals on cooling to room temperature. These were suitable for a single crystal X-ray analysis, and this revealed the identity of the products as [M(L<sup>2</sup>Ag)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (**3**, M = Al, x = 4; **4** M = Ga, x = 3). The crystallographic analyses‡ revealed the compounds to be isostructural, so the following discussion refers only to **3** for which the X-ray data are better quality. In the structure, silver(I) centres bridge Al(L<sup>2</sup>)<sub>3</sub> metalloligands into

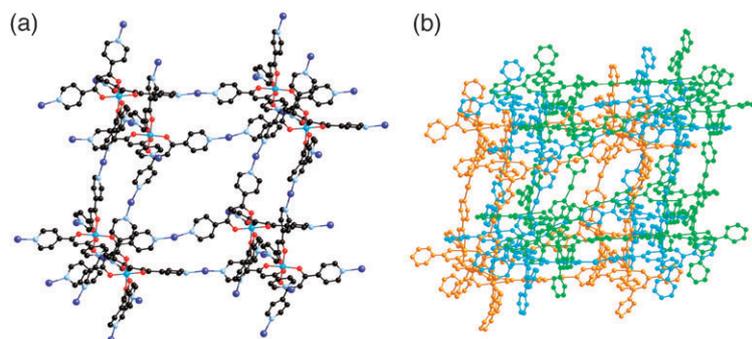
the targetted primitive cubic network, which is triply-interpenetrated (Fig. 2).

The asymmetric unit of **3** contains three Al<sub>1/3</sub>(L<sup>2</sup>Ag) fragments, three disordered nitrate ions and some disordered solvent of crystallisation, which was taken as DMSO. The three networks in **3** are crystallographically independent, and the coordination geometry around the aluminium centres is broadly equivalent to that in **1**. The ‘fold angles’ between the C<sub>3</sub>O<sub>2</sub> planes of the ligands and the AlO<sub>2</sub> angles are 17°, 17° and 4°, so for the [Al(L<sup>2</sup>)<sub>3</sub>] units, the distortions from a regular octahedron are reduced from those in **1**. The 2-coordinate silver centres show some distortion from linearity, with N–Ag–N angles of 166.6(3)°, 168.5(3)° and 168.9(2)°. These distortions compensate for the irregularities in the arrangement of the pyridyl groups in the metalloligands. Despite the interpenetration, the structure has a calculated void volume of 51%, including space occupied by the diffuse solvent molecules.

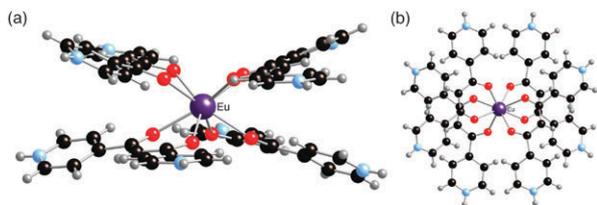
MOFs based on primitive cubic networks have been synthesised previously, though most employed a different strategy to that used to prepare **3** and **4**. In [Zn<sub>4</sub>O(bdc)<sub>3</sub>] (MOF-5; bdc = 1,4-benzenedicarboxylate),<sup>19</sup> for example, the Zn<sub>4</sub>O(O<sub>2</sub>CR) secondary building units (SBUs) form the octahedral vertices of the cube, whereas the benzene rings of the bdc ligands provide the edges of the cube. For **3** and **4**, the roles are reversed, with the metalloligand forming the vertices and the linear silver(I) centres comprising the edges.

Given the success in preparing a network structure based on the [M(L<sup>2</sup>)<sub>3</sub>] hexatopic metalloligand, we reasoned it might be possible to prepare metalloligands with even higher numbers of donor atoms. Accordingly, EuCl<sub>3</sub> was reacted with HL<sup>2</sup> in ethanol in the presence and absence of base. The reactions yielded the same product as yellow crystals suitable for a single crystal X-ray analysis. This analysis enabled the product to be characterised as [Eu(HL<sup>2</sup>)<sub>3</sub>(H<sub>2</sub>L<sup>2</sup>)]Cl<sub>4</sub>·EtOH **5**.‡ In this complex, the β-diketonates remain chelating and anionic, whereas the exodentate pyridine groups of the ligands are in two states of protonation. The HL<sup>2</sup> ligand is zwitterionic, with one of the pyridyl groups protonated, whereas the H<sub>2</sub>L<sup>2</sup> ligand is cationic, due to protonation of both pyridyl groups.

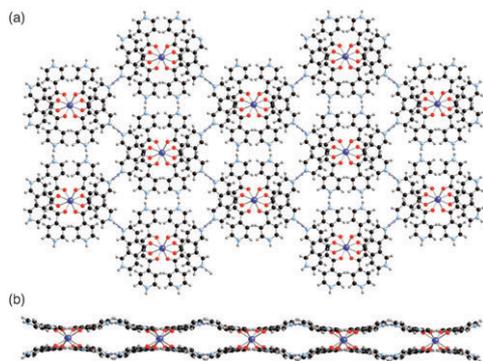
The asymmetric unit of **5** consists of one-quarter of a europium centre (located at a special position in the space group), a partially protonated L<sup>2</sup> ligand, a chloride ion and some diffuse solvent. The europium centre in **5** is 8-coordinate



**Fig. 2** The structure of [Al(L<sup>2</sup>Ag)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>·4DMSO **3**. Part (a) shows a single primitive cubic network, and part (b) shows the triply-interpenetrated networks. Solvent molecules, nitrate ions and hydrogen atoms have been omitted for clarity.



**Fig. 3** The structure of the cation in  $[\text{Eu}(\text{HL}^2)_3(\text{H}_2\text{L}^2)]\text{Cl}_4 \cdot \text{EtOH}$  **5**.



**Fig. 4** The sheet structure observed in the crystal structure of  $[\text{Eu}(\text{HL}^2)_3(\text{H}_2\text{L}^2)]\text{Cl}_4 \cdot \text{EtOH}$  **5** shown from (a) the top and (b) the side. Included solvent, anions and hydrogen atoms are omitted for clarity.

and adopts a square anti-prismatic geometry. The four crystallographically identical ligands show a fold angle between the  $\text{C}_3\text{O}_2$  plane and the  $\text{O}_2\text{Eu}$  plane of  $27^\circ$ . As a consequence of these distortions, the nitrogen lone pairs and NH groups lie approximately co-planar, on either side of the europium centre (Fig. 3).

The supramolecular structure of **5** (Fig. 4) reveals that the cations are interlinked into a two-dimensional network by short hydrogen bonds between protonated and neutral pyridine groups [ $\text{N}(1) \cdots \text{N}(1')$  2.730 Å,  $\text{H}(1) \cdots \text{N}(1')$  1.84 Å,  $\text{N}(1) \cdots \text{H}(1)$  172°]. A combination of coordination and hydrogen bonds links the coordinated ligands to one side of the europium centres into chains in two directions, so overall these contacts generate the observed two-dimensional (4,4) network. Additional hydrogen bonds are present with the chloride anions acting as acceptors [ $\text{N}(2) \cdots \text{Cl}(1)$  2.992 Å,  $\text{H}(2) \cdots \text{Cl}(1)$  2.13 Å,  $\text{N}(2) \cdots \text{H}(2)$  161°], but there are no strong interactions between the layers. The structure of **5** contrasts sharply to that reported recently for the gadolinium complex  $[\text{Gd}(\text{L}^2)_3(\text{OH}_2)]$ , which consists of one-dimensional polymers and contains coordinated nitrogen, and suggests that, following deprotonation, **5** can be used as an octatopic metalloligand.

The crystal structures of **3** and **5** reveal that complexes containing  $\text{L}^2$  or its protonated derivatives are versatile components in the formation of network structures, and that use of  $\text{L}^2$  overcomes the stability issues relating to  $\text{L}^1$ . Complexes of  $\text{L}^2$  are metalloligands that can be used to form MMOFs, such as the triply-interpenetrated primitive cubic structures of **3** and **4**. Alternatively, partial protonation affords complexes containing both strong hydrogen bond donors and hydrogen bond acceptors, which assemble to form hydrogen-bonded networks.

We thank the EPSRC, the Leverhulme Trust and the Cambridge Crystallographic Data Centre for funding, the EPSRC for a Senior Fellowship to PRR and Oxford Diffraction for the use of a Nova diffractometer in the data collection for **3**.

## Notes and references

† Selected crystallographic data. **1**,  $\text{C}_{47.75}\text{H}_{37}\text{AlN}_6\text{O}_6$ ,  $M = 817.81$ , triclinic,  $P\bar{1}$ ,  $a = 11.9780(1)$ ,  $b = 12.5850(1)$ ,  $c = 14.3390(2)$  Å,  $\alpha = 87.816(1)^\circ$ ,  $\beta = 84.052(1)^\circ$ ,  $\gamma = 79.823(1)^\circ$ ,  $R_1$ ,  $wR_2$  [ $I > 2\sigma(I)$ ] = 0.0633, 0.1713; **3**,  $\text{C}_{47}\text{H}_{51}\text{Ag}_3\text{AlN}_6\text{O}_{19}\text{S}_4$ ,  $M = 1524.80$ , trigonal,  $R3c$ ,  $a = 22.4562(3)$ ,  $c = 72.1481(4)$  Å,  $R_1$ ,  $wR_2$  [ $I > 2\sigma(I)$ ] = 0.0719, 0.1893; **5**,  $\text{C}_{54}\text{H}_{47}\text{Cl}_4\text{EuN}_8\text{O}_9$ ,  $M = 1245.76$ , orthorhombic,  $Fddd$ ,  $a = 15.1070(4)$ ,  $b = 27.3860(7)$ ,  $c = 29.0380(7)$  Å,  $R_1$ ,  $wR_2$  [ $I > 2\sigma(I)$ ] = 0.0502, 0.1079.

- J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3; S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191; A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284.
- S. Kitagawa, S. Noro and T. Nakamura, *Chem. Commun.*, 2006, 701; S. J. Garibay, J. R. Stork and S. M. Cohen, *Prog. Inorg. Chem.*, 2009, **56**, 335.
- S. Noro, H. Miyasaka, S. Kitagawa, T. Wada, T. Okubo, M. Yamashita and T. Mitani, *Inorg. Chem.*, 2005, **44**, 133; S. M. Humphrey, T. J. P. Angliss, M. Aransay, D. Cave, L. A. Gerrard, G. F. Weldon and P. T. Wood, *Z. Anorg. Chem.*, 2007, **633**, 2342; A. D. Burrows, M. F. Mahon and C. Wong, *CrystEngComm*, 2008, **10**, 487.
- R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. Noro and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2684.
- O. Guillou, C. Daiguebonne, M. Camara and N. Kerbellec, *Inorg. Chem.*, 2006, **45**, 8468.
- B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727.
- S. R. Halper, L. Do, J. R. Stork and S. M. Cohen, *J. Am. Chem. Soc.*, 2006, **128**, 15255; J. R. Stork, V. S. Thoi and S. M. Cohen, *Inorg. Chem.*, 2007, **46**, 11213.
- J. E. Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert and D. J. Price, *CrystEngComm*, 2007, **9**, 456; C. M. Ollagnier, D. Nolan, C. M. Fitchett and S. M. Draper, *Inorg. Chem. Commun.*, 2007, **10**, 1045.
- K.-T. Youm, M. G. Kim, J. Ko and M.-J. Jun, *Angew. Chem., Int. Ed.*, 2006, **45**, 4003.
- A. D. Burrows, K. Cassar, M. F. Mahon and J. E. Warren, *Dalton Trans.*, 2007, 2499.
- V. D. Vreshch, A. N. Chernega, J. A. K. Howard, J. Sieler and K. V. Domasevitch, *Dalton Trans.*, 2003, 1707; V. D. Vreshch, A. B. Lysenko, A. N. Chernega, J. Sieler and K. V. Domasevitch, *Polyhedron*, 2005, **24**, 917.
- V. D. Vreshch, A. B. Lysenko, A. N. Chernega, J. A. K. Howard, H. Krautscheid, J. Sieler and K. V. Domasevitch, *Dalton Trans.*, 2004, 2899.
- B. Chen, F. R. Fronczek and A. W. Maverick, *Inorg. Chem.*, 2004, **43**, 8209; Y. Zhang, B. Chen, F. R. Fronczek and A. W. Maverick, *Inorg. Chem.*, 2008, **47**, 4433.
- L. G. Mackay, H. L. Anderson and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2269.
- M. Ferles, R. Liboska and P. Trška, *Collect. Czech. Chem. Commun.*, 1990, **55**, 1228.
- J. W. Bunting, J. P. Kanter, R. Nelander and Z. Wu, *Can. J. Chem.*, 1995, **73**, 1305.
- P. C. Andrews, G. B. Deacon, R. Frank, B. H. Fraser, P. C. Junk, J. G. MacLellan, M. Massi, B. Moubaraki, K. S. Murray and M. Silberstein, *Eur. J. Inorg. Chem.*, 2009, 744.
- A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; C.-L. Chen, B.-S. Kang and C.-Y. Su, *Aust. J. Chem.*, 2006, **59**, 3.
- M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.