

### 3,5-Bis{4-[(benzimidazol-1-yl)methyl]phenyl}-4*H*-1,2,4-triazol-4-amine and its one-dimensional polymeric complex with HgCl<sub>2</sub>

Yan-an Li, Qi-Kui Liu, Jian-Ping Ma and Yu-Bin Dong\*

College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, People's Republic of China  
Correspondence e-mail: yubindong@sdu.edu.cn

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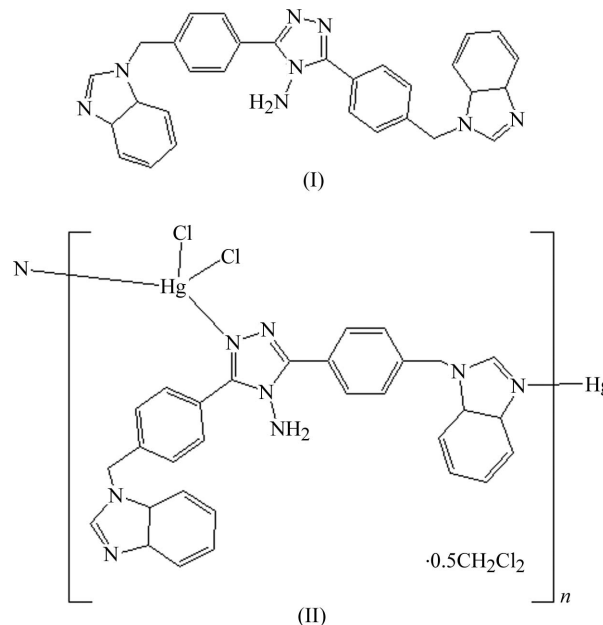
The molecule of 3,5-bis{4-[(benzimidazol-1-yl)methyl]phenyl}-4*H*-1,2,4-triazol-4-amine (*L*), C<sub>30</sub>H<sub>24</sub>N<sub>8</sub>, has an antiperiplanar conformation of the two terminal benzimidazole groups and forms two-dimensional networks along the crystallographic *b* axis *via* two types of intermolecular hydrogen bonds. However, in *catena*-poly[[[dichloridomercury(II)]- $\mu$ -3,5-bis{4-[(benzimidazol-1-yl)methyl]phenyl}-4*H*-1,2,4-triazol-4-amine] dichloromethane hemisolvate], {[HgCl<sub>2</sub>(C<sub>30</sub>H<sub>24</sub>N<sub>8</sub>)]·0.5CH<sub>2</sub>Cl<sub>2</sub>]<sub>*n*</sub>, synthesized by the combination of *L* with HgCl<sub>2</sub>, the *L* ligand adopts a synperiplanar conformation. The Hg<sup>II</sup> cation lies in a distorted tetrahedral environment, which is defined by two N atoms and two Cl atoms to form a one-dimensional zigzag chain. These zigzag chains stack *via* hydrogen bonds which expand the dimensionality of the structure from one to two.

#### Comment

Organometallic complexes have attracted considerable attention because of their fascinating topological structures (Eddaoudi *et al.*, 2002) and potential applications as functional materials in gas storage (Ma & Zhou, 2010), host-guest chemistry (Yoshizawa *et al.*, 2006), catalysis (Kim *et al.*, 2010) and luminescence (Cui *et al.*, 2012). Over the past decade, the design and construction of rigid organic ligands bridged by 1,2,4-triazol-4-amine has been pursued, due to their diversity in coordination chemistry and model applications in functional materials (Wang *et al.*, 2007, 2009; Liu *et al.*, 2009, 2010).

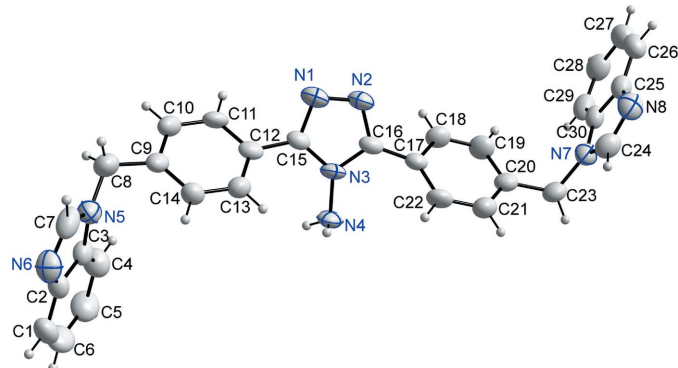
To date, various organic ligands have been used as molecular building blocks, but the use of 1,2,4-triazol-4-amine-based bent organic ligands as semi-rigid components has remained rare until recently. In order to investigate how the semi-rigid organic ligands bridged by 1,2,4-triazol-4-amine affect the arrangement of molecular complexes in self-assembled aggregates, we synthesized a new 1,2,4-triazol-4-amine bridging ligand, namely 3,5-bis{4-[(benzimidazol-1-yl)-

methyl]phenyl}-4*H*-1,2,4-triazol-4-amine, denoted *L* or (I). This compound introduces two large aromatic benzimidazole groups to the ligand. The combination of (I) with HgCl<sub>2</sub> afforded {[HgCl<sub>2</sub>*L*·CH<sub>2</sub>Cl<sub>2</sub>]<sub>*n*</sub>, (II), which features hydrogen-bonded stacking-driven two-dimensional networks.



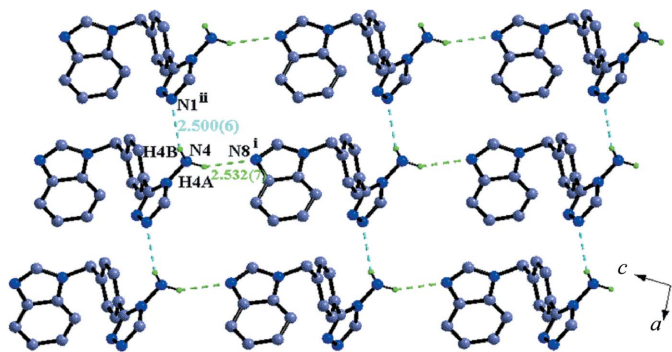
Within the free ligand, (I) (Fig. 1), the terminal benzimidazole groups adopt an antiperiplanar conformation across the central bridging 1,2,4-triazol-4-amine group. The dihedral angles between the planes of the benzimidazole and triazole rings are 58.1 (2) and 88.06 (18)° for the benzimidazole rings containing atoms N5 and N7, respectively, and the dihedral angles between the benzimidazole and adjacent benzene rings are 78.64 (18) and 80.37 (18)°, respectively. The two benzene rings of (I) are almost coplanar, with a dihedral angle of 7.3 (2)°.

In the crystal structure, molecules of (I) are arranged in chains *via* N4—H4A···N8<sup>i</sup> hydrogen bonds along the [101] direction (details and symmetry codes are given in Table 1). The chains stack *via* a second hydrogen-bond interaction (N4—H4B···N1<sup>ii</sup>) to form a two-dimensional network which



**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**

The two-dimensional structure of (I), constructed by hydrogen bonds (dashed lines). Uninvolved H atoms have been omitted for clarity. [Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $x - 1, y, z$ .]

lies parallel to the (010) plane (Fig. 2). This is in contrast with 3,5-bis(2-chlorophenyl)-1*H*-1,2,4-triazol-4-amine (Zachara *et al.*, 2004), the molecules of which are linked by hydrogen bonds to form a one-dimensional chain.

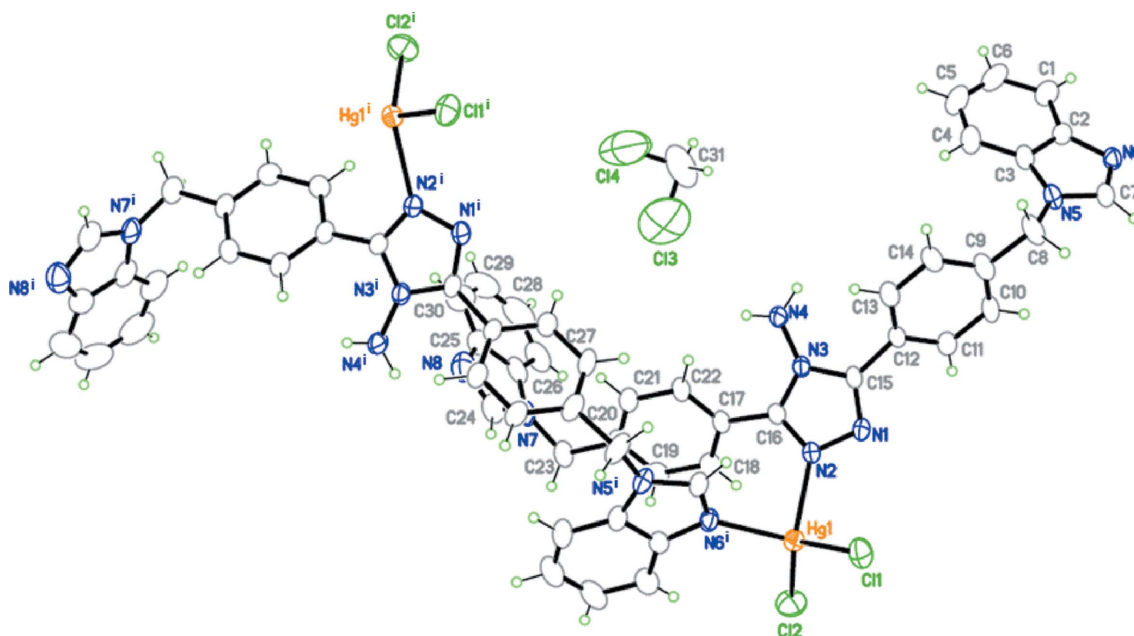
Compound (II) crystallizes with one unique four-coordinated Hg<sup>II</sup> centre in a distorted tetrahedral [HgCl<sub>2</sub>N<sub>2</sub>] environment involving two Cl atoms (Cl1 and Cl2) and two N atoms [N2 and N6<sup>i</sup>; symmetry code: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ] from two different ligands (Fig. 3 and Table 2). Neighbouring Hg<sup>II</sup> cations are bound together by triazole atom N2 and the terminal benzimidazole N6 atom of the *L* ligand to form an {HgCl<sub>2</sub>*L*}<sub>*n*</sub> one-dimensional zigzag chain. The coordination behaviour of the Hg<sup>II</sup> cation is similar to that observed in Hg[1-(pyridin-2-ylmethyl)-1*H*-benzotriazole]Cl<sub>2</sub> (Liu *et al.*, 2008), where the 1-(pyridin-2-ylmethyl)-1*H*-benzotriazole lig-

and (*L*2) is also coordinated to two Hg<sup>II</sup> centres to form a single chain. Similarly, in [Hg(*L*2)Cl<sub>2</sub>], there are no bonding interactions observed between adjacent chains.

The ligand *L* adopts different conformations under different conditions. In the solid state, the benzimidazole moieties adopt a synperiplanar orientation about the triazole core in the free ligand, whereas after coordination to Hg<sup>II</sup> the benzimidazole groups adopt a *cis* conformation. Compared with those given above for (I), the dihedral angles in (II) between the planes of the benzimidazole groups and the adjacent benzene rings change to 87.9 (3) and 75.8 (3)° for the benzimidazole rings containing atoms N5 and N7, respectively. These are nearly perpendicular, clearly as a result of coordination to Hg<sup>II</sup>. Additionally, the dihedral angle formed by the two benzene rings changes from 7.3 (2)° in the free ligand to 18.9 (3)° in (II).

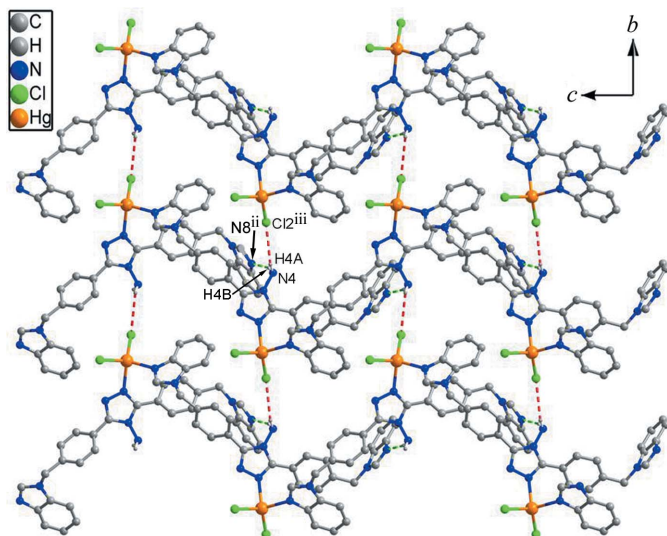
In the solid state, the zigzag chains in (II) are arranged along the *c* axis, where they interact *via* N4–H4A⋯Cl2<sup>iii</sup> hydrogen-bond interactions, as shown in Fig. 4 (details in Table 3; symmetry code given in Table 3). The result is that a two-dimensional sheet is generated in the *bc* plane. The dichloromethane solvent molecules are located within the cavities formed by the layered stacking of (II) (Fig. 5), although it appears that only about half of the solvent molecule sites are occupied.

In summary, a new compound with a common zigzag chain motif has been successfully obtained based on a new 1,2,4-triazol-4-amine bridging bent organic ligand, (I), and HgCl<sub>2</sub>. The chains assemble through hydrogen bonds to form a two-dimensional network. The hydrogen-bond interactions play an important role in constructing high-dimensional supramolecular compounds.



**Figure 3**

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .]



**Figure 4**  
The two-dimensional structure of (II), constructed by hydrogen bonds (dashed lines). Uninvolved H atoms have been omitted for clarity. [Symmetry codes: (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (iii)  $x, y - 1, z$ .]

### Experimental

For the preparation of (I), 80% hydrazine hydrate (2.8 g, 45 mmol) was added with stirring to a solution of 3,5-bis[4-[(benzimidazol-1-yl)methyl]phenyl]-1,3,4-oxadiazole (1.49 g, 3.0 mmol) in *N,N*-dimethylformamide (DMF; 20 ml). The mixture was stirred for 4 h at 423 K, then cooled to room temperature and poured into water (100 ml). The product was obtained as a white solid and purified on a silica-gel column using tetrahydrofuran as the eluent to afford (I) as a white crystalline solid (yield 1.00 g, 67%). A solution of (I) (5.00 mg, 0.010 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was left for about 2 d at room temperature, after which time colourless crystals were obtained (yield 3.24 mg, 65%). IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 3442 (s), 1633 (s), 1496 (s), 1385 (s), 1295 (m), 1200 (w), 1123 (w), 974 (w), 765 (s), 619 (m);  $^1\text{H}$  NMR (300 MHz, DMSO, 298 K, TMS):  $\delta$  8.44 (s, 2H,  $-\text{C}_3\text{H}_2\text{N}_2-$ ), 7.96–7.94, 7.47–7.44 (*aabb*, 8H,  $-\text{C}_6\text{H}_4-$ ), 7.67–7.64 (*d*, 2H,  $-\text{C}_3\text{H}_2\text{N}_2-$ ), 7.56–7.53 (*d*, 2H,  $-\text{C}_6\text{H}_3-$ ), 7.23–7.18 (*m*, 4H,  $-\text{C}_6\text{H}_3-$ ), 6.17 (s, 2H,  $-\text{NH}_2$ ), 5.57 (s, 4H,  $-\text{CH}_2-$ ). Elemental analysis calculated for  $\text{C}_{30}\text{H}_{24}\text{N}_8$ : C 72.32, H 4.91, N 22.77%; found: C 72.56, H 4.87, N 22.57%.

For the synthesis of (II), a solution of  $\text{HgCl}_2$  (5.42 mg, 0.020 mmol) in  $\text{CH}_3\text{OH}$  (5 ml) was layered onto a solution of (I) (9.93 mg,

0.020 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 ml). The mixture was left for about a week at room temperature and colourless crystals of (II) were obtained (yield 8.64 mg, 62%). IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 3447 (w), 1636 (s), 1509 (w), 1459 (m), 1384 (w), 1266 (m), 1193 (m), 740 (s). Elemental analysis calculated for  $\text{C}_{61}\text{H}_{50}\text{Cl}_6\text{Hg}_2\text{N}_{16}$ : C 45.34, H 3.23, N 13.66%; found: C 45.20, H 3.11, N 13.82%.

### Compound (I)

#### Crystal data

$\text{C}_{30}\text{H}_{24}\text{N}_8$   
 $M_r = 496.57$   
Monoclinic,  $C_c$   
 $a = 6.141$  (2) Å  
 $b = 19.914$  (6) Å  
 $c = 19.910$  (6) Å  
 $\beta = 96.537$  (6)°

$V = 2418.8$  (13) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.17 \times 0.11 \times 0.09$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)  
 $T_{\min} = 0.986$ ,  $T_{\max} = 0.992$

5790 measured reflections  
2748 independent reflections  
2008 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.063$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.116$   
 $S = 1.00$   
2748 reflections  
343 parameters

2 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.14$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.15$  e Å<sup>-3</sup>

### Compound (II)

#### Crystal data

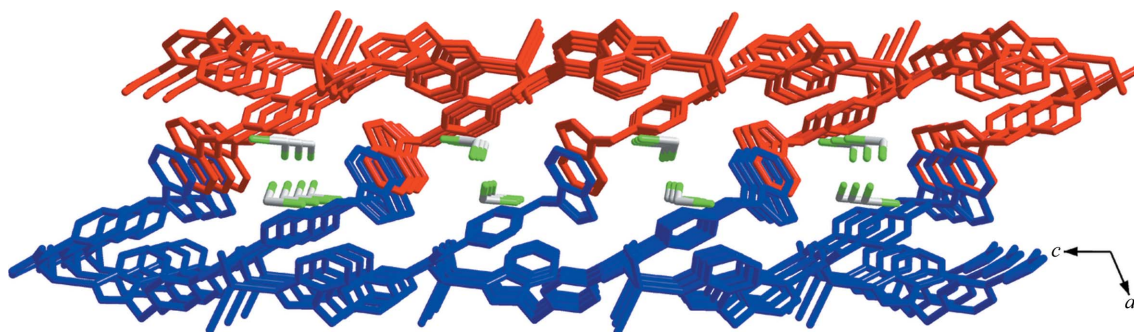
$[\text{HgCl}_2(\text{C}_{30}\text{H}_{24}\text{N}_8)] \cdot 0.5\text{CH}_2\text{Cl}_2$   
 $M_r = 810.53$   
Monoclinic,  $P2_1/c$   
 $a = 16.627$  (3) Å  
 $b = 10.6199$  (18) Å  
 $c = 20.082$  (3) Å  
 $\beta = 113.586$  (2)°

$V = 3249.9$  (10) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 5.02$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.40 \times 0.38 \times 0.34$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)  
 $T_{\min} = 0.239$ ,  $T_{\max} = 0.280$

16724 measured reflections  
6097 independent reflections  
4599 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$



**Figure 5**  
The crystal packing of (II), viewed along the *b* axis. The dichloromethane solvent molecules are located in channels.

**Table 1**

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N4-H4A\cdots N8^i$	0.89	2.53	3.354 (5)	155
$N4-H4B\cdots N1^{ii}$	0.89	2.50	3.222 (6)	138

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $x - 1, y, z$ .**Table 2**

Selected geometric parameters (Å, °) for (II).

$Cl1-Hg1$	2.4331 (17)	$Hg1-N6^i$	2.265 (4)
$Cl2-Hg1$	2.3793 (17)	$Hg1-N2$	2.353 (4)
$N6^i-Hg1-N2$	95.32 (15)	$N6^i-Hg1-Cl1$	109.17 (12)
$N6^i-Hg1-Cl2$	112.97 (12)	$N2-Hg1-Cl1$	103.99 (11)
$N2-Hg1-Cl2$	111.62 (13)	$Cl2-Hg1-Cl1$	120.51 (7)

Symmetry code: (i)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .**Table 3**

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N4-H4B\cdots N8^{ii}$	0.89	2.09	2.940 (8)	160
$N4-H4A\cdots Cl2^{iii}$	0.89	2.98	3.473 (5)	117

Symmetry codes: (ii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (iii)  $x, y - 1, z$ .

### Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.038$$

$$wR(F^2) = 0.102$$

$$S = 1.04$$

6097 reflections

397 parameters

6 restraints

H-atom parameters constrained

$$\Delta\rho_{\max} = 1.22 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.64 \text{ e } \text{Å}^{-3}$$

The H atoms on N4 were located in a difference map and their positions were initially refined subject to an N—H distance restraint of 0.89 (2) Å. Subsequently, these H atoms were treated as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . The remaining H atoms were placed in geometrically idealized positions and included as riding atoms, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic H atoms or C—H = 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methylene H atoms.

In noncentrosymmetric (I), Friedel pairs were merged in the final refinement and the absolute structure was chosen arbitrarily. In (II),

the dichloromethane solvent molecule was refined with the C—Cl and Cl $\cdots$ Cl distances restrained to 1.78 (1) and 2.80 (2) Å, respectively, in order to retain reasonable geometry. The solvent sites also appeared to be only partially occupied and a fixed site-occupation factor of 0.5 was employed for chemical and crystallographic rationality. The main directions of movement of covalently bonded atoms C29, C30 and C31 were likewise restrained to be similar, with an s.u. value of 0.005 Å<sup>2</sup> (Müller *et al.*, 2006).

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OV3013). Services for accessing these data are described at the back of the journal.

### References

- Bruker (2003). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cui, Y., Yue, Y., Qian, G. & Chen, B. (2012). *Chem. Rev.* **112**, 1126–1162.
- Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M. & Yaghi, O. M. (2002). *Science*, **295**, 469–472.
- Kim, H. Y., Kim, S. & Oh, K. (2010). *Angew. Chem. Int. Ed.* **49**, 4476–4478.
- Liu, Q.-K., Ma, J.-P. & Dong, Y.-B. (2009). *Chem. Eur. J.* **15**, 10364–10368.
- Liu, Q.-K., Ma, J.-P. & Dong, Y.-B. (2010). *J. Am. Chem. Soc.* **132**, 7005–7017.
- Liu, C.-S., Zhou, L.-M., Guo, L.-Q., Ma, S.-T. & Fang, S.-M. (2008). *Acta Cryst.* **C64**, m394–m397.
- Ma, S. & Zhou, H.-C. (2010). *Chem. Commun.* **46**, 44–53.
- Müller, P., Herbst-Irmer, R., Spek, A. L., Schneider, T. R. & Sawaya, M. R. (2006). *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, edited by P. Müller. Oxford University Press.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Wang, P., Ma, J.-P. & Dong, Y.-B. (2009). *Chem. Eur. J.* **15**, 10432–10445.
- Wang, P., Ma, J.-P., Dong, Y.-B. & Huang, R.-Q. (2007). *J. Am. Chem. Soc.* **129**, 10620–10621.
- Yoshizawa, M., Tamura, M. & Fujita, M. (2006). *Science*, **312**, 251–254.
- Zachara, J., Madura, I. & Włostowski, M. (2004). *Acta Cryst.* **C60**, o57–o59.