Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Influence of nitrogen-containing chelating ligands on the structures of zinc(II) 4,4′-ethylenedibenzoates

Xiu-Yan Wang,[a]* Jia-Jun Wang[a] and Seik Weng Ng[b]

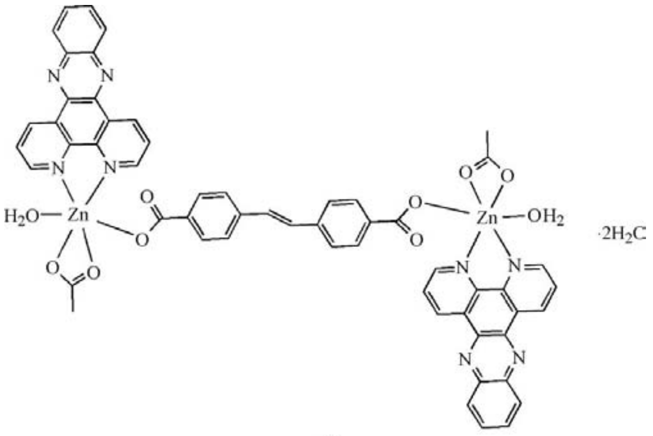
[a]College of Chemistry, Jilin Normal University, Siping 136000, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: wangxiuyan2001@yahoo.com.cn

Received 16 October 2008
Accepted 17 November 2008
Online 26 November 2008

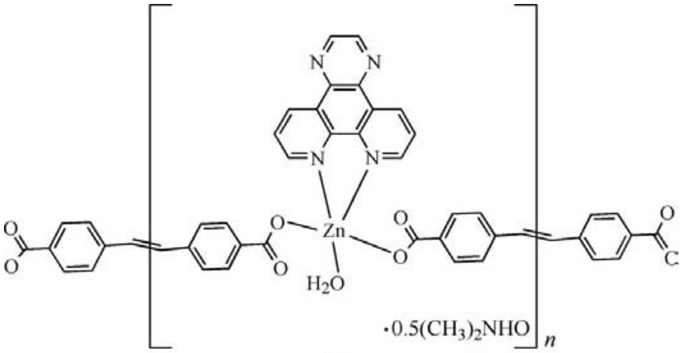
The Zn^{II} compounds, μ-4,4′-ethylenedibenzoato-bis[acetatoaqua(dipyrido[3,2-*a*:2′,3′-*c*]phenazine)zinc(II)] dihydrate, $[Zn_2(C_2H_3O_2)_2(C_{16}H_{10}O_4)(C_{18}H_{10}N_4)_2(H_2O)_2]\cdot 2H_2O$, (I), and *catena*-poly[[[aqua(pyrazino[2,3-*f*][1,10]phenanthroline)zinc(II)]-μ-4,4′-ethylenedibenzoato] *N*,*N*-dimethylformamide hemisolvate], $\{[Zn(C_{16}H_{10}O_4)(C_{14}H_8N_4)(H_2O)]\cdot 0.5C_3H_7NO\}_n$, (II), display very different structures because of the influence of the N-donor chelating ligands. In (I), the coordination geometry of each Zn^{II} centre is distorted octahedral, involving two N atoms from one dipyrido[3,2-*a*:2′,3′-*c*]phenazine (L1) ligand, and four O atoms from one bis-chelating acetate anion, one bridging 4,4′-ethylenedibenzoate (bpea) ligand and one water molecule. Adjacent Zn^{II} atoms are bridged by one bpea ligand to form a dinuclear complex, and the dinuclear species is centrosymmetric. Two types of π–π interactions between neighbouring dinuclear species have been found: one is between the L1 ligands, and the second is between the L1 and bpea ligands. In this way, an interesting two-dimensional supramolecular layer is formed. The layers are further linked by $O-H\cdots O$ and $O-H\cdots N$ hydrogen bonds, generating a three-dimensional supramolecular network. In (II), each Zn^{II} atom is square-pyramidally coordinated by two N atoms from one pyrazino[2,3-*f*][1,10]phenanthroline ligand, three O atoms from two different bpea ligands and one water molecule. The two bpea dianions are situated across inversion centres. The bpea dianions bridge neighbouring Zn^{II} centres, giving a one-dimensional chain structure in the *ab* plane. As in (I), two types of π–π interactions between neighbouring chains complete a three-dimensional supramolecular structure. The results indicate that the structures of the N-donor chelating ligands are the dominant factors determining the final supramolecular structures of the two compounds.

Comment

The rational design and synthesis of novel discrete and polymeric metal–organic compounds have attracted increasing interest due to their fascinating structural topologies and their potential applications as functional materials in catalysis, separation and nonlinear optics (Batten & Robson, 1998; Carlucci *et al.*, 2003; Eddaoudi *et al.*, 2001; Ockwig *et al.*, 2005). Considerable progress has been made in controlling the synthesis of networks with interesting topologies (Yang *et al.*, 2008; Batten, 2001) by varying the factors that affect framework formation; however, it is not possible to predict with complete accuracy the exact structure of the resulting framework. It is therefore important to gain a full understanding of the roles of the factors that influence the formation of metal–organic coordination frameworks (Hagrman *et al.*, 1999).



(I)



(II)

In general, there are several factors that can influence the network structures of compounds, such as the coordination environments of metal nodes, and the structural characteristics of the ligands, solvents, templates and counter-ions (Hu *et al.*, 2006). Among these, the selection of an N-containing ligand is extremely important because by changing the structures of the N-containing ligands it is possible to adjust the topologies of coordination frameworks, even for structures containing the same spacer ligand and metal cation (Wang *et al.*, 2005). So far, although the effect of an N-containing ligand on the structures of complexes has been studied, few systematic investigations on the influence of N-containing ligands on their complex structures have been carried out (Tong *et al.*, 2000; Zheng *et al.*, 2001). In particular, the influence of N-containing chelating ligands on network construction through π–π interactions has rarely been documented (Yang, Ma *et al.*,

doi:10.1107/S0108270108038328

2007). To the best of our knowlege, the influence of different 1,10-phenanthroline derivatives on the structures of metal–dicarboxylates has not been studied to date (Yang, Li *et al.*, 2007). In this work, we chose 4,4′-ethylenedibenzoic acid (H_2bpea) as the bridging ligand, dipyrido[3,2-*a*:2′,3′-*c*]-phenazine (L1) and pyrazino[2,3-*f*][1,10]phenanthroline (L2) as the different N-donor chelating ligands, yielding a centrosymmetric dinuclear complex for $[Zn_2(bpea)(L1)_2(H_2O)_2]\cdot 2H_2O$, (I), and a chain structure for $[Zn(bpea)(L2)(H_2O)]\cdot 0.5DMF$ (DMF is dimethylformamide), (II).

Selected bond lengths and angles for (I) are given in Table 1. In compound (I), the coordination geometry of each Zn^{II} centre is distorted octahedral, involving two N atoms from one L1 ligand, and four O atoms from one bis-chelating acetate anion, one bridging bpea and one water molecule (Fig. 1). Adjacent Zn^{II} atoms are bridged by one bpea ligand to form a dinuclear complex with a long Zn$\cdots$Zn distance of 17.405 (3) Å (Fig. 1). The dinuclear species is centrosymmetric, with a crystallographic inversion centre midway between the two Zn^{II} atoms. Notably, the L1 ligands are arranged in a parallel fashion at both sides of a dinuclear species, leading to a structure suitable for aromatic intercalation. Two types of π–π interactions between neighbouring dinuclear species have been found: one is between the L1 ligands [centroid-to-centroid distance of 3.555 (2) Å, vertical face-to-face distance of 3.483 (1) Å and a dihedral angle of 2.212 (1)°], and the second is between the L1 and bpea ligands [centroid-to-centroid distance of 4.027 (2) Å, vertical face-to-face distance of 3.505 (1) Å and a dihedral angle of 2.720 (2)°] (Fig. 2). In this way, a two-dimensional supramolecular layer is formed (Fig. 2). The layers are further linked by O—H$\cdots$O and O—H$\cdots$N hydrogen bonds, generating a three-dimensional supramolecular network (Table 2).

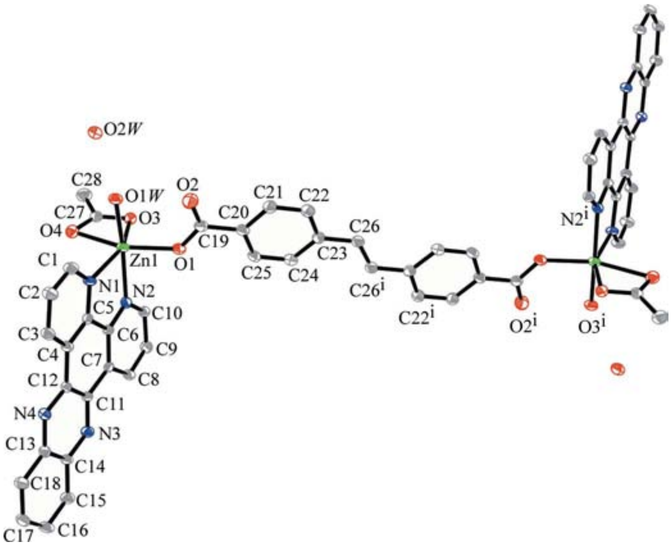


Figure 1
A view of the local coordination of the Zn^{II} cation in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1 - x, 1 - y, 2 - z$.]

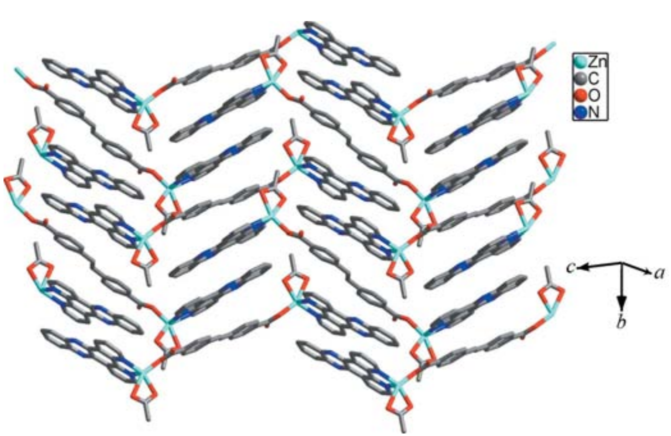


Figure 2
A view of the two-dimensional supramolecular structure of (I).

It is noteworthy that the structure of (I) is different from that of the related dinuclear structure $[Pb(adip)(L1)]_2$ (adip is adipate; Yang, Ma *et al.*, 2007), in which the two adip ligands link two Pb^{II} centres to give a dinuclear species. A two-dimensional supramolecular layer is formed through only one type of π–π interaction between L1 ligands of neighbouring dinuclear species. The structure of (I) is also entirely different from that of the related polymer $[Mn_2(dpdc)_2(L1)]_n$ (dpdc is the biphenyl-2,2′-dicarboxylate dianion; Che *et al.*, 2008). In that structure, four Mn^{II} atoms are bridged by the carboxylate groups of the dpdc ligands to form an unusual tetranuclear Mn^{II} cluster; the clusters are further connected together by the aromatic backbone of the dicarboxylate ligands, forming a one-dimensional chain structure along the *b* axis.

To investigate the influence of N-donor chelating ligands on the complex frameworks, a smaller 1,10-phenanthroline-based ligand (L2) was used under the same reaction conditions as for (I), and a structurally different coordination polymer $[Zn(bpea)(L2)(H_2O)]\cdot 0.5DMF$, (II), was obtained from the reaction system. As shown in Fig. 3, each Zn^{II} atom is square-

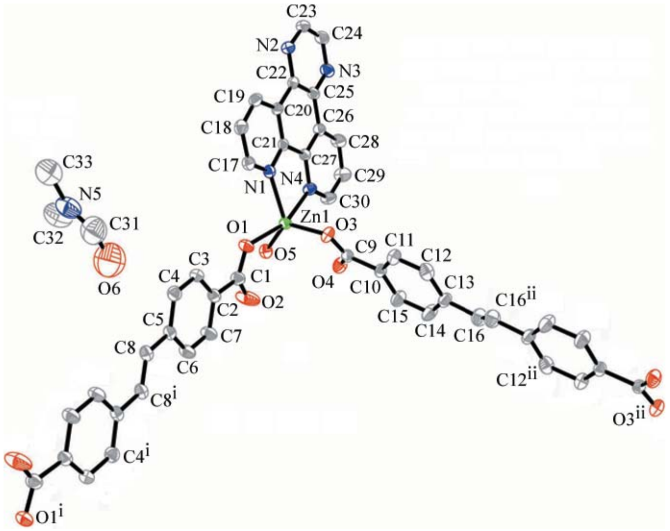


Figure 3
A view of the local coordination of the Zn^{II} cation in (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $3 - x, -y, 1 - z$; (ii) $3 - x, 2 - y, -z$.]

pyramidally coordinated by two N atoms from one L2 ligand, three O atoms from two different bpea ligands and one water molecule. The average Zn—O and Zn—N distances in (II) are comparable with those observed for (I) (Table 3). The two bpea dianions are situated across inversion centres. As depicted in Fig. 4, the bpea dianions bridge two neighbouring Zn^{II} centres, giving a one-dimensional chain structure in the *ab* plane. Clearly, the N-containing chelating ligand L2 plays an important role in the formation of the chain structure. Two N atoms from the secondary L2 ligand occupy two coordination positions of the Zn^{II} atom, while the remaining coordination positions are available for bpea ligands, allowing the formation of the chain structure. As in (I), two types of π–π interactions between neighbouring chains have been found: one is between the centrosymmetrically related L2 ligands [centroid-to-centroid distance of 3.705 (1) Å and vertical face-to-face distance of 3.430 (3) Å], and the second is between L2 and bpea ligands [centroid-to-centroid distance of 3.632 (1) Å, vertical face-to-face distance of 3.424 (1) Å and a dihedral angle of 5.150 (7)°] (Fig. 5). In this way, a three-dimensional supramolecular structure is formed (Fig. 5). O—H···O hydrogen bonds further consolidate the structure of (II) (Table 4).

It is noteworthy that the structure of (II) is entirely different from that of the related structure $[Cd_2(1,4\text{-ndc})_2(L2)_2]$ (1,4-ndc is naphthalene-1,4-dicarboxylate; Qiao *et al.*, 2008), where the tetranuclear cadmium carboxylate clusters are connected together by the aromatic backbone of the dicarboxylate ligands, forming a three-dimensional α-polonium net.

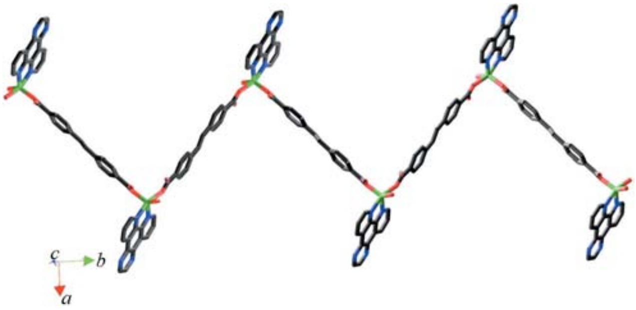


Figure 4
A view of the one-dimensional chain of (II).

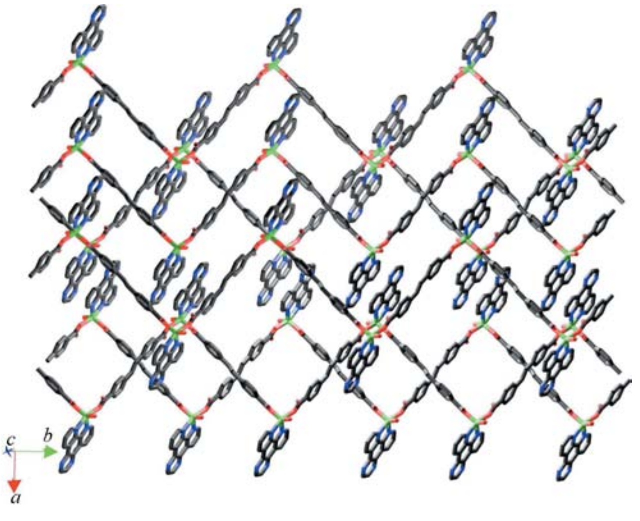


Figure 5
A view of the three-dimensional supramolecular structure of (II).

In summary, by varying the N-containing chelating ligand under the same synthesis conditions, two structurally different Zn^{II} complexes are obtained. In contrast to L2, the bulky phenylene groups in the backbone significantly increase the steric hindrance of the L1 ligand, leading to the formation of (I) and (II) with quite different structures. Therefore, the structures of the N-containing chelating ligands are the dominant factor determining the final supramolecular structures of the two compounds.

Experimental

$Zn(CH_3COO)_2 \cdot 2H_2O$ (0.110 g, 0.5 mmol), H_2bpea (0.133 g, 0.5 mmol) and L1 (0.118 g, 0.5 mmol) were dissolved in a mixture of DMF (9 ml) and distilled water (5 ml). The resulting mixture was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 398 K for 8 d under autogenous pressure. The reaction system was gradually cooled to room temperature at a rate of 5 K h^{-1}. Pale-yellow crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with DMF, and dried in air at ambient temperature (yield 55%, based on Zn^{II}). Compound (II) was prepared in the same way as (I), using L2 as an N-donor chelating ligand. Pale-yellow crystals were obtained (yield 47%, based on Zn^{II}).

Compound (I)

Crystal data

$[Zn_2(C_2H_3O_2)_2(C_{16}H_{10}O_4)$-
$(C_{18}H_{10}N_4)_2(H_2O)_2] \cdot 2H_2O$
M_r = 1151.73
Monoclinic, $P2_1/n$
a = 13.1521 (12) Å
b = 11.9082 (11) Å
c = 15.9668 (15) Å
β = 98.391 (2)°
V = 2473.9 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.05 mm^{-1}
T = 293 (2) K
0.33 × 0.30 × 0.27 mm

Data collection

Bruker APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.701, T_{max} = 0.755
13276 measured reflections
4853 independent reflections
3145 reflections with $I > 2\sigma(I)$
R_{int} = 0.056

Table 1
Selected geometric parameters (Å, °) for (I).

Zn1—N1	2.127 (3)	Zn1—O3	2.111 (3)
Zn1—N2	2.155 (3)	Zn1—O4	2.294 (3)
Zn1—O1	2.009 (2)	Zn1—O1*W*	2.079 (2)
O1—Zn1—O1*W*	91.20 (11)	O3—Zn1—N2	97.25 (10)
O1—Zn1—O3	93.34 (10)	N1—Zn1—N2	76.61 (10)
O1*W*—Zn1—O3	97.04 (10)	O1—Zn1—O4	152.73 (10)
O1—Zn1—N1	111.64 (11)	O1*W*—Zn1—O4	92.66 (11)
O1*W*—Zn1—N1	89.85 (10)	O3—Zn1—O4	59.40 (10)
O3—Zn1—N1	153.98 (11)	N1—Zn1—O4	95.36 (10)
O1—Zn1—N2	89.42 (10)	N2—Zn1—O4	93.35 (10)
O1*W*—Zn1—N2	165.64 (11)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H*W*12···O2*W*	0.856 (18)	1.837 (18)	2.690 (4)	175 (4)
O1*W*—H*W*11···O2	0.854 (18)	1.788 (18)	2.634 (4)	170 (4)
O2*W*—H*W*21···O3^{i}	0.84 (4)	1.97 (2)	2.796 (4)	166 (5)
O2*W*—H*W*22···N4^{ii}	0.84 (2)	2.22 (2)	3.045 (4)	168 (6)

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.116$
$S = 1.01$
4853 reflections
368 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Compound (II)

Crystal data

$[Zn(C_{16}H_{10}O_4)(C_{14}H_8N_4)(H_2O)]\cdot 0.5C_3H_7NO$
$M_r = 618.42$
Triclinic, $P\overline{1}$
$a = 11.2278$ (11) Å
$b = 11.3944$ (11) Å
$c = 11.8165$ (11) Å
$\alpha = 84.345$ (2)°
$\beta = 69.421$ (2)°
$\gamma = 83.982$ (1)°
$V = 1404.4$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.93$ mm^{-1}
$T = 293$ (2) K
0.25 × 0.21 × 0.19 mm

Data collection

Bruker APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.788$, $T_{max} = 0.837$
7901 measured reflections
5517 independent reflections
4209 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.119$
$S = 1.03$
5517 reflections
416 parameters
39 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

For (I) and (II), all H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$(carrier). The water H atoms were located in a difference Fourier map and refined with distance restraints of O—H = 0.85±0.01 Å and H···H = 1.39±0.01 Å. Their isotropic displacement parameters were freely refined. The DMF molecule of (II) is disordered about a centre of inversion. The C—O bond length was restrained to 1.25±0.01 Å, the N—C(carbonyl) bond length to 1.35±0.01 Å and the other two N—C bond lengths to 1.45±0.01 Å. The atoms were restrained to lie on a plane. The anisotropic displacement parameters were restrained to be nearly isotropic.

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—O3	2.002 (2)	Zn1—N1	2.128 (2)
Zn1—O5	2.043 (2)	Zn1—N4	2.160 (2)
Zn1—O1	2.059 (2)		
O3—Zn1—O5	128.13 (9)	O1—Zn1—N1	89.82 (9)
O3—Zn1—O1	97.25 (9)	O3—Zn1—N4	99.89 (9)
O5—Zn1—O1	87.82 (9)	O5—Zn1—N4	89.00 (10)
O3—Zn1—N1	103.52 (9)	O1—Zn1—N4	160.43 (9)
O5—Zn1—N1	128.18 (9)	N1—Zn1—N4	77.07 (9)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O2	0.842 (10)	1.729 (11)	2.562 (3)	170 (3)
O5—H5*B*···O4^{i}	0.835 (10)	1.868 (11)	2.700 (3)	175 (4)

Symmetry code: (i) $-x+2, -y+1, -z$.

We thank Jilin Normal University and the University of Malaya for generously supporting this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3269). Services for accessing these data are described at the back of the journal.

References

Batten, S. R. (2001). *CrystEngComm*, **3**, 67–73.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bruker (1997). *SMART*. Version 5.622. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Carlucci, L., Ciani, G. & Proserpio, D. M. (2003). *Coord. Chem. Rev.* **246**, 247–289.
Che, G.-B., Wang, J., Liu, C.-B., Li, X.-Y. & Liu, B. (2008). *Acta Cryst.* C**64**, m362–m364.
Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.
Hu, T. L., Li, J. R., Liu, C. S., Shi, X. S., Zhou, J. N., Bu, X. H. & Ribas, J. (2006). *Inorg. Chem.* **45**, 162–173.
Ockwig, N. W., Delgado-Friedrichs, O., O'Keeffe, M. & Yaghi, O. M. (2005). *Acc. Chem. Res.* **38**, 176–182.
Qiao, Q., Zhao, Y.-J. & Tang, T.-D. (2008). *Acta Cryst.* C**64**, m336–m338.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tong, M. L., Chen, H. J. & Chen, X. M. (2000). *Inorg. Chem.* **39**, 2235–2238.
Wang, X. L., Qin, C., Wang, E. B., Su, Z. M., Xu, L. & Batten, S. R. (2005). *Chem. Commun.* pp. 4789–4790.
Yang, J., Li, G.-D., Cao, J.-J., Yue, Q., Li, G.-H. & Chen, J.-S. (2007). *Chem. Eur. J.* **13**, 3248–3261.
Yang, J., Ma, J.-F., Batten, S. R. & Su, Z.-M. (2008). *Chem. Commun.* pp. 2233–2235.
Yang, J., Ma, J.-F., Liu, Y.-Y., Ma, J.-C. & Batten, S. R. (2007). *Inorg. Chem.* **46**, 6542–6555.
Zheng, S. L., Tong, M. L., Fu, R. W., Chen, X. M. & Ng, S. W. (2001). *Inorg. Chem.* **40**, 3562–3569.