Synthesis and structural determination of new multidimensional coordination polymers with 4,4′-oxybis(benzoate) building ligands: Construction of coordination polymers with heteroorganic bridges

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Abstract

We report on the synthesis and crystal structures of two new zinc coordination polymers with 4,4′-oxybis(benzoate) (oba) ligands. Single crystals of $[Zn_2(oba)_2(azpy)(dmf)_2] \cdot 6DMF$ (azpy = 4,4′-azopyridine) and $[Zn_2(oba)_2(bpe)] \cdot 2DMF \cdot 4H_2O$ (bpe = *trans*-1,2-bis(4-pyridyl)ethylene) were prepared by treatment of $Zn(CH_3COO)_2 \cdot 2H_2O$ with the H_2oba and bis-pyridine type ligands, azpy and bpe, respectively, in DMF. Compound $[Zn_2(oba)_2(azpy)(dmf)_2] \cdot 6DMF$ has a unique ladder structure comprising of heteroorganic bridges, in which the Zn–oba chains construct the side rails, while the Zn–azpy–Zn parts construct the rungs of the ladder framework. Despite the large size of the cavities, these ladder chains stack without interpenetration, and the cavities in the ladder framework are partially connected to create one-dimensional channel-like cavities. Compound $[Zn_2(oba)_2(bpe)] \cdot 2DMF \cdot 4H_2O$ exhibits a three-dimensional coordination framework that is comprised of heteroorganic bridges. The framework is interwoven by two-dimensional layers of $[Zn_2(oba)_2]$ and the Zn_2–bpe chains. The three-dimensional framework, which contains large cavities, about 13×11 Å^2 in area, has a high porosity and a density of only 0.53 g cm^{-3}.
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Keywords: Coordination polymers; Three-dimensional framework; High porous material; Crystal engineering

1. Introduction

The construction of coordination polymers with new network motifs is of current interest for the development of new functional materials and in fundamental studies of crystal engineering and supramolecular chemistry [1–8]. In the synthesis of new network structures, coordination polymers constructed from heteroorganic bridges are challenging subjects because any synthetic method used needs to take into account the designed construction involving versatile coordination frameworks [9–12]. Nevertheless, coordination networks constructed from heteroorganic

bridges are rare because of the difficulty in achieving the rational incorporation of different organic ligands.

Bis-benzoate-type bridges have been exploited in the synthesis of many coordination networks [7,13–18]. For example, $[M_2(1,4-benzenedicarboxylate)_2]$-type frameworks have been prepared and characterized [17]. The unique feature of this type of network structure is the presence of square cavities, which are retained without collapsing and exhibit porous functionalities such as gas adsorption and heterogeneous catalysts. Although it has been shown that the two-dimensional layers can be connected by additional neutral ligands, structural characterization from X-ray single crystal analysis has not been carried out.

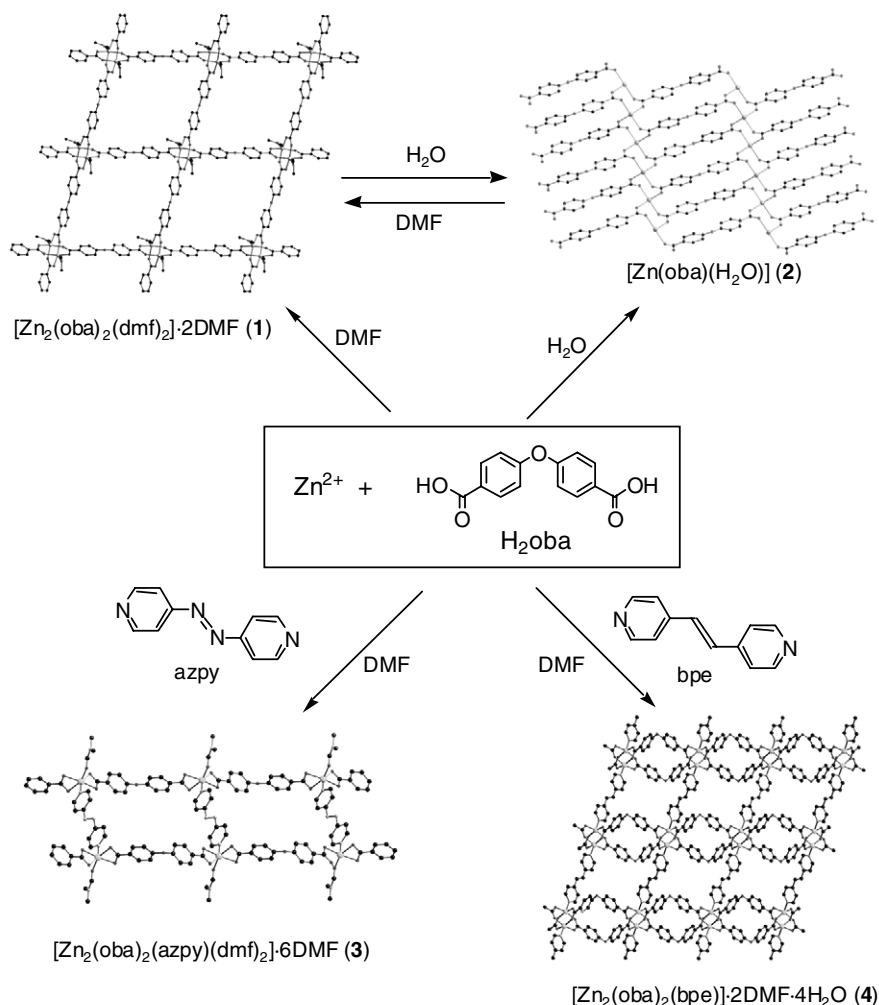We have investigated coordination polymers with chalcogen atoms in the organic bridging ligands [19–21], and

Fig. 1. The summary of Zn–oba network system found in this work.

have reported on two coordination polymers, [Zn$_2$(oba)$_2$-(dmf)$_2$] · 2DMF (oba = 4,4′-oxybis(benzoate)) (**1**) and [Zn(oba)(H$_2$O)] (**2**) in a recent communication. These two compounds show reversible structural transformations depending on the present solvents. In ongoing work, we have successfully created two new zinc coordination polymers constructed from heteroorganic bridges: oba- and bis-pyridine-type ligands, i.e., *trans*-1,2-bis(4-pyridyl)ethylene (bpe) and 4,4′-azopyridine (azpy). Despite the similar structures of the two ancillary ligands, the structures of the resulting compounds, [Zn$_2$(oba)$_2$(azpy)(dmf)$_2$] · 6DMF (azpy = 4,4′-azopyridine) (**3**) and [Zn$_2$(oba)$_2$(bpe)] · 2DMF · 4H$_2$O (**4**), show different network structures. The network motifs of these compounds are illustrated in Fig. 1. This paper describes the synthesis and crystal structures of coordination polymers **3** and **4**.

2. Results and discussion

Diffusion of a DMF solution of H$_2$oba and azpy into a DMF solution of Zn(CH$_3$COO)$_2$ · 2H$_2$O yielded single crystals of Compound **3**. An ORTEP view around the zinc centers is shown in Fig. 2a. The selected bond distances and angles are listed in Table 1. The carboxylate ligands of the oba group bind to the zinc center via a four-membered chelation, in which the two Zn–O bond distances differ significantly: Zn(1)–O(1) = 2.091(3) Å, Zn(1)–O(2) = 2.231(3) Å, Zn(1)–O(3) = 2.283(4) Å, and Zn(1)–O(4) = 2.096(3) Å. In addition to the four carboxylate oxygen atoms, an additional oxygen atom of a dmf molecule and a pyridine nitrogen atom of an azpy group are coordinated to the zinc center. The above coordination center is based on the markedly distorted octahedron observed. This is due to the four-membered carboxylate chelation, in which the N(1) atom of the azpy group and the O(3) atom of the oba group occupy the axial positions at the N(1)–Zn(1)–O(3) group with a bond angle of 151.2(1)°.

Each zinc center is bridged by an oba group to yield a one-dimensional chain directed along the *b*-axis. The chains are further connected by azpy bridges to yield a ladder-type one-dimensional structure, as shown in Fig. 2b, in which the Zn–oba chains construct the "side rails", and the Zn–azpy–Zn parts construct the "rungs" of the ladder framework. The Zn···Zn distances bridged by the oba and azpy groups
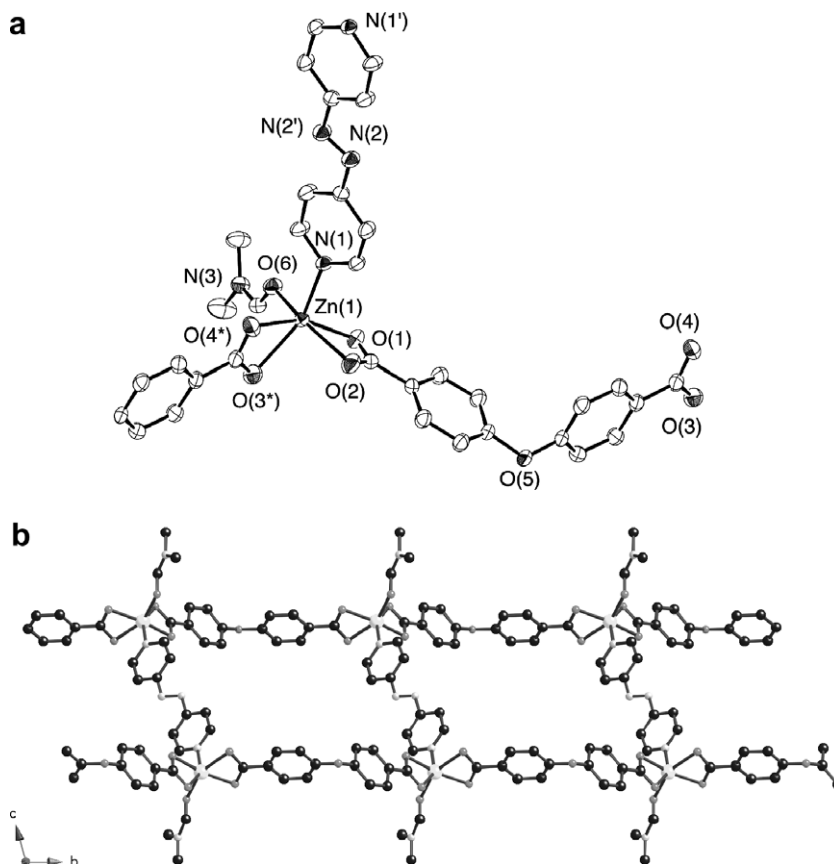
Fig. 2. View of Compound **3**. ORTEP diagram around the zinc center at 30% probability (a) and the ladder-type one-dimensional structure (b).

Table 1
Selected bond distances (Å) and angles (°) for Compound **3**

Zn(1)–O(1)	2.091(3)	Zn(1)–O(2)	2.231(3)
Zn(1)–O(3*)	2.283(4)	Zn(1)–O(4*)	2.096(3)
Zn(1)–O(6)	2.042(3)		
O(1)–Zn(1)–O(2)	60.5(1)	O(1)–Zn(1)–O(3*)	105.5(1)
O(1)–Zn(1)–O(4*)	156.4(1)	O(1)–Zn(1)–O(6)	95.3(1)
O(1)–Zn(1)–N(1)	102.6(1)	O(2)–Zn(1)–O(3*)	92.3(1)
O(2)–Zn(1)–O(4*)	99.7(1)	O(2)–Zn(1)–O(6)	155.5(1)
O(2)–Zn(1)–N(1)	96.0(1)	O(3*)–Zn(1)–O(4*)	59.6(1)
O(3*)–Zn(1)–O(6*)	90.6(1)	O(3*)–Zn(1)–N(1)	151.2(1)
O(4*)–Zn(1)–O(6)	102.7(1)	O(4*)–Zn(1)–N(1)	91.7(1)
O(6)–Zn(1)–N(1)	93.2(1)		

Symmetry equivalent positions; $* = x, y, z$.

are 14.1 Å and 13.1 Å, respectively, which form large cavities with an effective area of about 12×11 Å^2. The cavities in the framework exhibit a compressed octahedral structure at the apexes of the four zinc atoms and two ether–oxygen atoms. The coordinating dmf molecules protrude in the same direction as the corresponding side rail.

Despite having large cavities, the ladder frameworks stack along the direction of the $(a + c)$ vector without interpenetration. Although the oba ligands of the chain are located between the two cavities of different adjacent chains, the cavities are large enough to form crevices, which are connected to create one-dimensional channels

directed along the $(a + c)$ vector. The channels are filled with three free dmf molecules per one zinc atom.

The single crystals of Compound **4** were grown using a similar procedure to that used to prepare Compound **3**. An ORTEP view around the zinc centers is shown in Fig. 3a. The selected bond distances and angles are listed in Table 2. The dinuclear zinc centers in Compound **4** are supported by the four carboxylate groups of oba, in which the crystallographic inversion center is located in the central region between the two zinc atoms. The Zn···Zn distance (2.954 (2) Å) is close to that of Compound **1** (2.928 (1) Å). The pyridine nitrogen atom of the bpe group coordinates to the zinc center at the apical position, yielding a square pyramidal geometry. The Zn$_2$ units are connected by oba ligands to form a two-dimensional framework

Table 2
Selected bond distances (Å) and angles (°) for Compound **4**

Zn(1)–O(1)	2.050(5)	Zn(1)–O(2*)	2.032(6)
Zn(1)–O(3′)	2.003(5)	Zn(1)–O(4′)	2.030(4)
Zn(1)–N(1)	2.019(6)		
O(1)–Zn(1)–O(2*)	159.1(2)	O(1)–Zn(1)–O(3′)	88.5(2)
O(1)–Zn(1)–O(4″)	87.7(2)	O(1)–Zn(1)–N(1)	96.1(2)
O(2*)–Zn(1**)–O(3)	88.9(2)	O(2*)–Zn(1*)–O(4)	87.4(2)
O(2*)–Zn(1)–N(1)	104.7(2)	O(3′)–Zn(1*)–O(4)	159.3(2)
O(3′)–Zn(1)–N(1)	102.2(2)	O(4″)–Zn(1)–N(1)	98.5(2)

Symmetry equivalent positions; $* = 1/2 - x$, $1/2 - y$, $-z$, $' = x$, $-y$, $1/2 + z$, $'' = 1/2 - x$, $1/2 + y$, $1/2 - z$.

directed along the *bc* plane (Fig. 3b). The two-dimensional framework of Zn_2–(oba)$_2$ is similar to that seen in Compound **1**. The oba ligands protrude from the layer plane, forming a significant undulating layer with a thickness of about 11 Å. Each layer contains rhombus cavities with dimensions of about 17 Å × 11 Å.
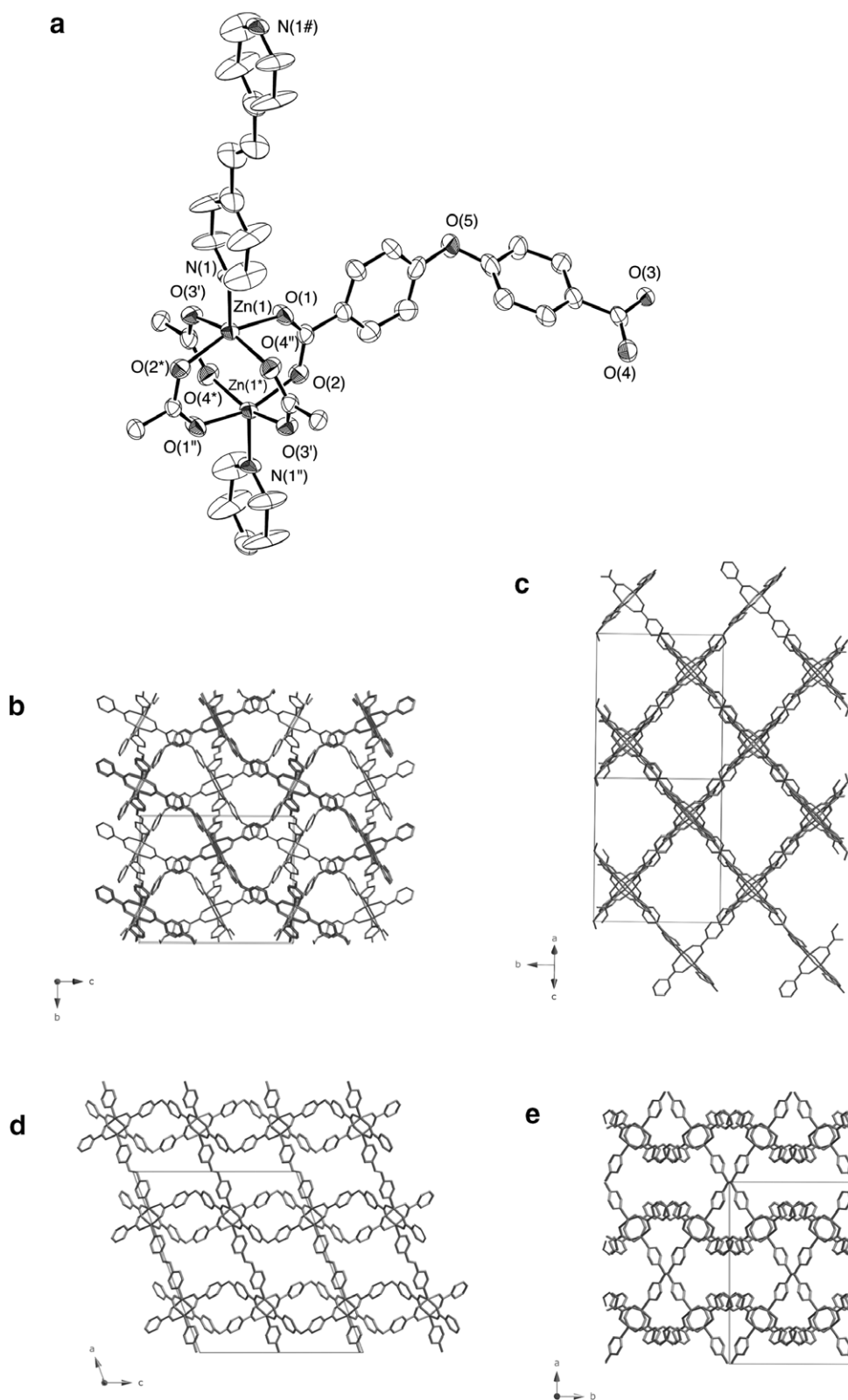

Fig. 3. View of Compound **4**. ORTEP view around the dizinc center at 30% probability (a). View of the coordination framework along the *a*-axis (b), (*a* + *c*) vector (c), *b*-axis (d), and *c*-axis (e).
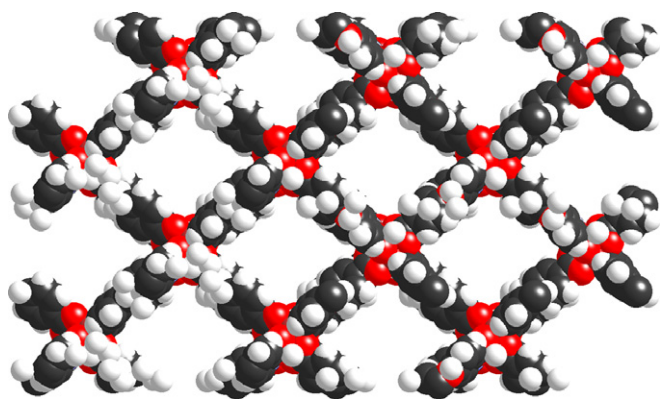
Fig. 4. The aspect of the largest channel structure with van der Waals radii along the $(a + c)$ vector (f).

Fig. 5. Thermogravimetric curve of Compound **4**.

These layers are connected by bpe ligands that bridge two zinc centers in the adjacent layers, successfully forming a three-dimensional coordination framework constructed by two organic components. The two-dimensional layer is markedly undulated along the *b*-axis due to the distortion at the ether–oxygen atom of the oba ligands (C–O–C = 118.9(7)°), in which the Zn_2 units are located at the slant of the undulated layer, i.e., the Zn···Zn vectors are not perpendicular, but tilted by about 46° and −46°, respectively, to the *bc* plane. As a result, the Zn_2–bpe chains are not perpendicular to the *bc* plane but are aligned parallel to the $(a + b)$ and $(a − b)$ vectors (Fig. 4).

The basic framework of Compound **3** is constructed by bridges in the two-dimensional layer in the *bc* plane composed of pillars of bpe ligands. The effectively longer Zn···Zn bond distances bridged by oba and bpe groups (about 15 Å and 13.4 Å, respectively) construct the highly porous framework. The density of the $[Zn_2(oba)_2(bpe)]$ framework is only 0.53 g cm^{-3}, reflecting the high porosity of the framework. Compound **4** has channels that are connected in three dimensions. The largest channels are directed along the $(a + c)$ vector, as shown in Fig. 3c, with an effective area of about 13×11 Å^2. In addition, three channels are observed along each axis, with areas of: 4×3, 6×4, and 11×3 Å^2 along the *a*-, *b*-, and *c*-axes, respectively. The channels are filled with two DMF molecules per dinuclear unit.

The thermal stability of the highly porous framework of Compound **4** was estimated using thermogravimetric analysis (Fig. 5). The removal of the guest DMF molecules was observed below about 200 °C (observed 18%, calcd 21%). Any ensuing weight loss due to deformation of the resulting dry sample was not observed until 310 °C, implying a high stability of the guest-free framework of Compound **4**. A similar stability was reported in the three-dimensional coordination polymer $[M_2(1,4\text{-benzenedicarboxylate})L]$ (L = triethylenediamine, 4,4′-bipyridine) [12,22,23], which has similar network motifs to Compound **4**. Characterization of the functionalities based on the highly porous framework of Compound **4** is currently in progress.
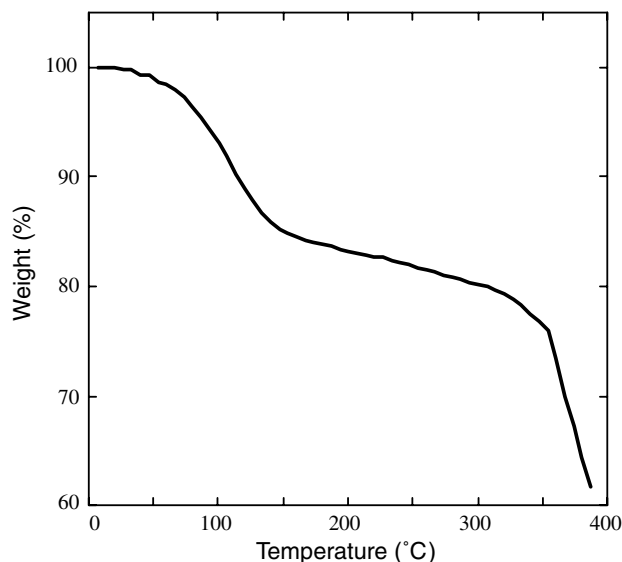
3. Experimental

3.1. Preparations of the compounds

The compound $[Zn_2(oba)_2(azpy)(dmf)_2] \cdot 6DMF$ (**3**) was prepared by diffusion of a DMF solution (200 mL) of H_2oba (5.2 g, 20 mmol) and azpy (6.0 g, 20 mmol) into a DMF solution (200 mL) of $Zn(CH_3COO)_2 \cdot 2 H_2O$ (2.2 g, 10 mmol). Red columnar crystals were formed within a period of one week, and these were collected by filtration under a nitrogen atmosphere because of the highly moisture sensitivity. Elemental Anal. Calc. for $C_{44}H_{62}N_6O_{24}Zn_2$ ($[Zn_2(oba)_2(azpy)(dmf)_2] \cdot 12 H_2O$): C, 44.21; H, 5.25; N, 7.06. Found: C, 44.82; H, 5.19; N, 6.69%.

The compound $[Zn_2(oba)_2(bpe)] \cdot 2DMF \cdot 4 H_2O$ (**4**) was prepared using a similar procedure to that used to prepare Compound **3**. A DMF solution (200 mL) of H_2oba (5.2 g, 20 mmol) and bpe (3.6 g, 20 mmol) was allowed to diffuse into a DMF solution (200 mL) of $Zn(CH_3COO)_2 \cdot 2H_2O$ (2.2 g, 10 mmol). Colorless cubic crystals were formed within a period of one week, and these were collected by filtration under a nitrogen atmosphere because of the highly moisture sensitivity. One crystal of each compound was used in the single crystal X-ray analysis, and the residual crystals were used for other measurements. Elemental Anal. Calc. for $C_{52}H_{60}N_6O_{17}Zn_2$ ($[Zn_2(oba)_2(bpe)] \cdot 4DMF \cdot 3H_2O$): C, 53.30; H, 5.16; N, 7.17. Found: C, 53.69; H, 4.79; N, 7.46%.

3.2. Crystal structure determination

For both Compounds **3** and **4**, a suitable single crystal was sealed in a glass capillary tube along with its mother liquid. Data collection was carried out using a Rigaku CCD mercury system fitted with a monochromatic Mo Kα radiation source ($\lambda = 0.71069$ Å) at room temperature for

Table 3
Crystal data for compounds **3** and **4**

	3	**4**
Formula	$C_{31}H_{40}N_6O_9Zn$	$C_{46}H_{50}N_4O_{16}Zn_2$
Fw	706.07	1045.68
Temperature (K)	293	233
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$C2/c$ (#15)
a (Å)	9.792(6)	27.21(2)
b (Å)	14.138(8)	17.77(1)
c (Å)	14.475(8)	22.99(2)
V (Å^3)	1798(1)	10424(14)
α (°)	99.660(6)	90
β (°)	103.095(5)	110.29(1)
γ (°)	107.615(5)	90
Z	2	4
Reflections measured	16,795	34,000
Unique reflections	9839	11,896
Reflections observed	6197 ($I > 2\sigma(I)$)	2748 ($I > 2\sigma(I)$)
No. of variables	424	269
R	0.0821	0.0867
wR	0.0859	0.0974

Compound **3** and at −40 °C for Compound **4**. The X-ray data obtained is shown in Table 3. Six preliminary data frames were measured at increments of $\omega = 0.5°$ to assess the crystal quality and preliminary unit cell parameters. The intensity of the images was also measured at intervals of $\omega = 0.5°$. The intensity of the images was integrated using the Crystal Clear software package, and an empirical absorption correction was applied to the data. The structures were resolved using a direct method (SIR-92). For Compound **3**, all the nonhydrogen atoms were refined anisotropically using the full-matrix least-squares technique except for the crystalline solvent molecules, which were refined isotropically. The geometrical hydrogen atoms were placed in idealized positions, and were included, but not refined. For Compound **4**, the nonhydrogen atoms were refined anisotropically using the full-matrix least-squares technique except for the crystalline solvent DMF molecules, which were not refined, but were included. All calculations were performed using the TEXSAN crystallographic software package (Molecular Structure Corporation, USA).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.048.

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