

Syntheses, crystal structures and properties of novel zinc(II) complexes obtained by reactions of zinc(II) malonate with flexible multidentate ligands[☆]

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Abstract

Complex $[\text{Zn}_2(\text{bimb})_2(\text{mal})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**1**) ($\text{mal} = ^-\text{OCOCH}_2\text{COO}^-$) was obtained by reaction of bidentate ligand 4,4'-bis(imidazole-1-ylmethyl)biphenyl (bimb) with zinc(II) salt of malonate, while the reaction of the same metal salt with 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb) gives another novel complex $[\text{Zn}_2(\text{titmb})_2(\text{mal})][\text{mal}] \cdot 12\text{H}_2\text{O}$ (**2**). The structures of these complexes were determined by X-ray crystallography. The results revealed that **1** is a cyclic dinuclear complex in which the malonate groups act as terminators and prevent further aggregation, while **2** is a 2D honeycomb network in which each independent 2D sheet contains two sub-layers bridged by the malonate groups and complex **2** also contains free malonate as a counteranion connected to the 2D layer by C–H...O hydrogen bonds. The entirely different structure and topology of complexes **1** and **2**, on the one hand, indicates that the nature of organic ligands affected the structures of assemblies greatly, and on the other, reveals the versatility of the malonate which can act as a bridging and/or blocking ligand.

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Keywords: Crystal structures; Malonate; Zinc(II) complexes; Flexible ligands

1. Introduction

The use of multidentate organic ligands and suitable metal salts to construct supramolecular architectures has been a major strategy in recent years and construction of discrete supramolecular frameworks, especially with hollow structures has, attracted much attention owing to their ability of encapsulating guest molecules or molecular aggregates [1–4]. Interest in porous metal-organic frameworks (MOFs) has been driven by the prospect of generating a wide range of materials with useful properties for applications such as absorption, ion-exchange and catalysis [5–7]. The stability of porous MOFs is a prerequisite for their use as such materials [8]. Typically, rigid ligands such as 4,4'-bipyridine [9] and benzene-1,3,5-tricarboxylic acid have been deliberately chosen to construct such porous MOFs. Many recent

reports have focused on the synthesis and structural characterization of polymeric transition metal complexes using malonate (mal) as a blocking and bridging ligand [10–12]. The use of malonate as a bridging ligand in metal compounds has shown the versatility of this ligand [10–12]. Malonate is a dicarboxylic ligand and can occupy one or two coordination positions and neutralizes two positive charges of the metal ion. Combining the malonate with other bridging and/or blocking ligands, it is possible to prepare monomers, dimers, trimers, tetramers, infinite 1D chains, and 2D and 3D arrays [13]. For example, Ruiz-Pérez et al. synthesized a series of metal complexes using malonate as a bridging ligand and studied the magnetic properties of these malonate-containing copper(II) complexes [14].

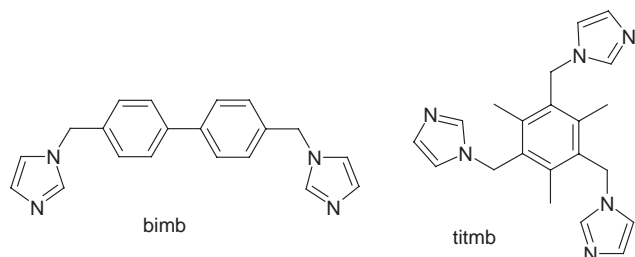
We are interested in the reactions of flexible multidentate ligands with various metal salts to investigate the construction, structure and property of MOFs [15]. Now we have initiated the study of reactions of metal salts with the malonate and other flexible bridging and/or blocking ligands. As shown in Scheme 1, a flexible

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bidentate ligand 4,4'-bis(imidazole-1-ylmethyl)biphenyl (bimb) was adopted in this study, together with the malonate, to construct a novel molecular compound



Scheme 1.

Table 1
Crystallographic data for complexes **1** and **2**

Complex	1	2
Empirical formula	C ₂₃ H ₂₆ ZnN ₄ O ₇	C ₄₈ H ₇₆ Zn ₂ N ₁₂ O ₂₀
Formula weight	535.85	1271.95
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁
<i>a</i> (Å)	13.031(15)	13.921(7)
<i>b</i> (Å)	24.717(18)	12.129(7)
<i>c</i> (Å)	7.458(7)	17.426(9)
α (deg)	90.00	90.00
β (deg)	104.05(3)	93.24(4)
γ (deg)	90.00	90.00
<i>V</i> (Å ³)	2330(4)	2938(3)
<i>Z</i>	4	2
<i>D_c</i> (g cm ⁻³)	1.527	1.438
μ (mm ⁻¹)	1.107	0.899
2 θ max (deg)	54.96	54.96
Reflns. Collected	22918	29125
Independent reflns	5330	12399
<i>R</i> _{int}	0.1661	0.1119
Obsd. Reflns. (<i>I</i> > 2 σ (<i>I</i>))	1936	5059
Parameters refined	334	792
<i>R</i> (obsd. data)	0.0631	0.0530
<i>wR</i> (obsd. data)	0.0790 ^a	0.0632 ^b
<i>R</i> (all data)	0.1692	0.1450
<i>wR</i> ₂ (all data)	0.0853	0.0728
Goodness of fit	0.979	0.775
Residual electron density (e Å ⁻³)	0.856; -0.674	0.478; -0.445

^a $w = 1/[\sigma^2(F_o)^2 + (0.0065P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

^b $w = 1/[\sigma^2(F_o)^2 + (0.0746P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

[Zn₂(bimb)₂(mal)₂(H₂O)₂] · 4H₂O (**1**) which is a cyclic dinuclear complex, with the malonate functioning as a terminator, preventing further aggregation. In order to further investigate the effect of malonate as a bridging ligand, another coordination polymer [Zn₂(titmb)₂(mal)][mal] · 12H₂O (**2**) with a 2D honeycomb network was generated, which was obtained from the reaction of a tridentate ligand 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb, Scheme 1) and zinc(II) oxide together with malonate acid. The synthesized complexes were characterized by X-ray single-crystal structure determination and powder X-ray diffraction.

2. Experimental

All commercially available chemicals were of reagent grade and used as received without further purification.

Table 2
Selected bond distances (Å) and angles (deg) for **1** and **2**

[Zn ₂ (bimb) ₂ (mal) ₂ (H ₂ O) ₂] · 4H ₂ O (1)			
Zn1–O1	1.985(4)	Zn1–N22	2.037(5)
Zn1–N12	2.044(4)	Zn1–O3	2.060(4)
Zn1–O5	2.122(4)	O1–Zn1–N22	120.87(15)
O1–Zn1–N12	123.66(17)	N22–Zn1–N12	115.44(18)
O1–Zn1–O3	88.39(16)	N22–Zn1–O3	91.35(19)
N12–Zn1–O3	92.17(18)	O1–Zn1–O5	83.32(15)
N22–Zn1–O5	93.46(17)	N12–Zn1–O5	91.88(18)
O3–Zn1–O5	171.68(15)		
[Zn ₂ (titmb) ₂ (mal)][mal] · 12H ₂ O (2)			
Zn1–O1	1.931(4)	Zn1–N12	1.970(7)
Zn1–N32	1.979(7)	Zn1–N112	1.983(3)
Zn2–O3 ^a	1.923(4)	Zn2–N152	1.986(7)
Zn2–N52	1.987(4)	Zn2–N132 ^b	2.019(8)
O1–Zn1–N12	102.9(3)	O1–Zn1–N32	101.6(3)
N12–Zn1–N32	108.5(2)	O1–Zn1–N112	118.48(14)
N12–Zn1–N112	109.3(3)	N32–Zn1–N112	115.0(3)
O3 ^a –Zn2–N152	109.5(4)	O3 ^a –Zn2–N52	110.86(16)
N152–Zn2–N52	112.9(3)	O3 ^a –Zn2–N132 ^b	107.0(4)
N152–Zn2–N132 ^b	103.37(16)	N52–Zn2–N132 ^b	112.7(4)

^a Equivalent atoms generated by 1–*x*, 1/2 + *y*, 1–*z*.

^b Equivalent atoms generated by *x*, 1 + *y*, *z*.

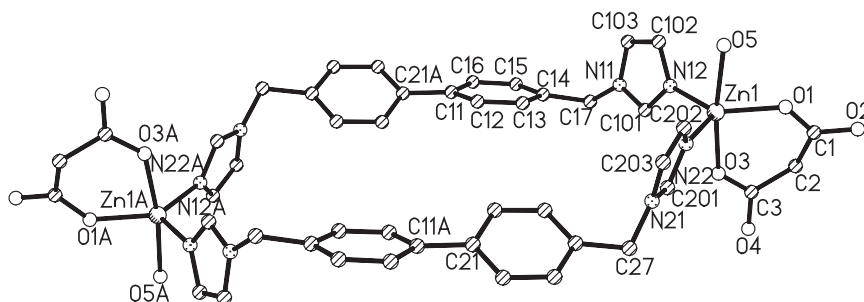
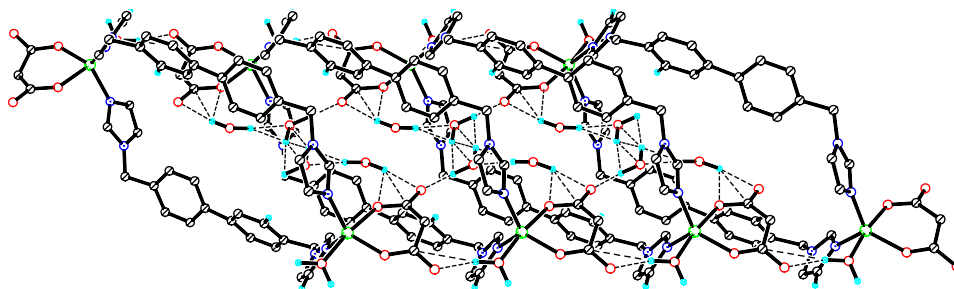


Fig. 1. Molecular structure of [Zn₂(bimb)₂(mal)₂(H₂O)₂] · 4H₂O (**1**) with the lattice water molecules and hydrogen atoms omitted for clarity.

Fig. 2. Side view of 1D tube-like structure of **1** with hydrogen bonds indicated by dashed lines.Table 3
Distances (Å) and angles (deg) of hydrogen bonding for complexes **1** and **2**

$D-H \cdots A^a$	Distance ($D \cdots A$)	$D-H-A$	Angle ($D-H-A$)
[Zn₂(bimb)₂(mal)₂(H₂O)₂] · 4H₂O (1)			
O(5)–H(21)···O(2) ^b	2.763(5)	O(5)–H(21)–O(2) ^b	168
O(5)–H(22)···O(2) ^a	2.730(6)	O(5)–H(22)–O(2) ^a	166
O(6)–H(23)···O(7)	2.694(10)	O(6)–H(23)–O(7)	158
O(6)–H(24)···O(4)	2.996(8)	O(6)–H(24)–O(4)	173
O(7)–H(25)···O(4) ^a	2.829(9)	O(7)–H(25)–O(4) ^a	161
O(7)–H(26)···O(7) ^c	2.729(11)	O(7)–H(26)–O(7) ^c	141
C(23)–H(10)···O(4) ^a	3.423(9)	C(23)–H(10)–O(4) ^a	147
C(202)–H(19)···O(1) ^b	3.451(8)	C(202)–H(19)–O(1) ^b	164
[Zn₂(titmb)₂(mal)][mal] · 12H₂O (2)			
C(11)–H(2)···O(8)	3.236(10)	C(11)–H(2)–O(8)	170
C(12)–H(3)···O(5)	3.143(9)	C(12)–H(3)–O(5)	160
C(14)–H(5)···O(20) ^d	3.217(15)	C(14)–H(5)–O(20) ^d	143
C(21)–H(6)···N(31) ^e	3.117(9)	C(21)–H(6)–N(31) ^e	124
C(32)–H(11)···O(5)	3.424(9)	C(32)–H(11)–O(5)	149
C(51)–H(18)···O(17) ^f	3.442(8)	C(51)–H(18)–O(17) ^f	160
C(61)–H(23)···O(13) ^g	3.459(10)	C(61)–H(23)–O(13) ^g	168
C(112)–H(27)···O(2)	3.108(5)	C(112)–H(27)–O(2)	145
C(113)–H(28)···O(5)	3.155(7)	C(113)–H(28)–O(5)	162
C(131)–H(34)···O(14) ^h	3.471(10)	C(131)–H(34)–O(14) ^h	159
C(132)–H(35)···O(6) ⁱ	3.260(11)	C(132)–H(35)–O(6) ⁱ	168
C(133)–H(36)···O(10B)	3.33(2)	C(133)–H(36)–O(10B)	141
C(134)–H(37)···O(2)	3.388(13)	C(134)–H(37)–O(2)	158
C(151)–H(41)···O(11) ^j	3.370(10)	C(151)–H(41)–O(11) ^j	146
C(152)–H(43)···O(6) ^k	3.150(11)	C(152)–H(43)–O(6) ^k	169
C(153)–H(44)···O(2)	3.285(12)	C(153)–H(44)–O(2)	146

^aEquivalent atoms generated by $x, y, -1+z$.^bEquivalent atoms generated by $x, 3/2-y, -1/2+z$.^cEquivalent atoms generated by $1-x, 1-y, 1-z$.^dEquivalent atoms generated by $1-x, -1/2+y, 1-z$.^eEquivalent atoms generated by $x, 1+y, z$.^fEquivalent atoms generated by $1-x, -1/2+y, -z$.^gEquivalent atoms generated by $x, y, 1+z$.^hEquivalent atoms generated by $-1+x, y, z$.ⁱEquivalent atoms generated by $x, -1+y, z$.^jEquivalent atoms generated by $x, y, -1+z$.^kEquivalent atoms generated by $-x, -1/2+y, 1-z$.

Solvents were purified according to the standard methods. The C, H and N analyses were carried out on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Thermogravimetric analysis (TGA) of the crystalline sample was carried out on a simultaneous SDT 2960 thermal

analyzer under flowing N₂ at a heating rate of 10°C min⁻¹ in the 20–600°C temperature range. Powder X-ray diffraction patterns were recorded on a Rigaku D/max-RA rotating anode X-ray diffractometer with graphite-monochromatic CuK α ($\lambda = 1.542 \text{ \AA}$) radiation at room temperature.

2.1. Syntheses of $[Zn_2(bimb)_2(mal)_2(H_2O)_2] \cdot 4H_2O$ **1**

An aqueous solution (10 mL) of ZnO (4.1 mg, 0.05 mmol) and H_2mal (5.2 mg, 0.05 mmol) was refluxed and stirred for about 8 h. The aqueous solution was filtrated and cooled down to room temperature and a solution of bimb (15.7 mg, 0.05 mmol) in ethanol (10 mL) was carefully layered over the aqueous solution at room temperature. Two weeks later, colorless needle crystals suitable for X-ray analysis were obtained in 65% yield. Calcd. elem. anal. for $C_{46}H_{52}Zn_2N_8O_{14}$: C 51.55; H 4.89; N 10.46; and found: C 51.42; H 4.97; N 10.55.

2.2. Syntheses of $[Zn_2(titmb)_2(mal)][mal] \cdot 12H_2O$ **2**

The title complex was also prepared by slow diffusion between two layers of the aqueous solution (10 mL) of zinc(II) salt of malonate, obtained as described above from ZnO (4.1 mg, 0.05 mmol) and H_2mal (5.2 mg, 0.05 mmol), and titmb (18.0 mg, 0.05 mmol) in methanol (10 mL) at room temperature. Single crystals suitable for X-ray analysis were obtained in 50% yield 3 weeks later. Calcd. elem. anal. for $C_{48}H_{76}Zn_2N_{12}O_{20}$: C 45.33; H 6.02; N 13.21; and found: C 45.27; H 6.20; N 13.12.

2.3. X-ray crystal structure determinations

The collections of crystallographic data for complexes **1** and **2** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The structures were solved by direct methods with SIR92

[16] and expanded using the Fourier technique [17]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms, except for those of water molecules, were positioned with idealized geometry. The hydrogen atoms connected to water O were found in the difference Fourier map and the positions were refined using fixed B factor ($1.2B_{eq}$ of the connected atom). The refinements caused unreasonable O–H bond distances; thus, the distances were constrained by SADI. The other hydrogen atoms were located by geometrical calculation using HFIX (AFIX). In complex **2**, two carbon atoms of bridging malonate and three water molecules disordered into two positions with site occupancy factors (SOF) of 0.466(10) for C202, C203, O4, O9, O10 and 0.534(10) for C204, C205, O4B, O9B, O10B, respectively. The refined Flank parameter (BASF) of **2** was 0.310(14), which implies a partially racemic structure. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [18]. Details of the crystal parameters, data collection and refinement are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-225411 (**1**) and CCDC-225412 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; [mailto: deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

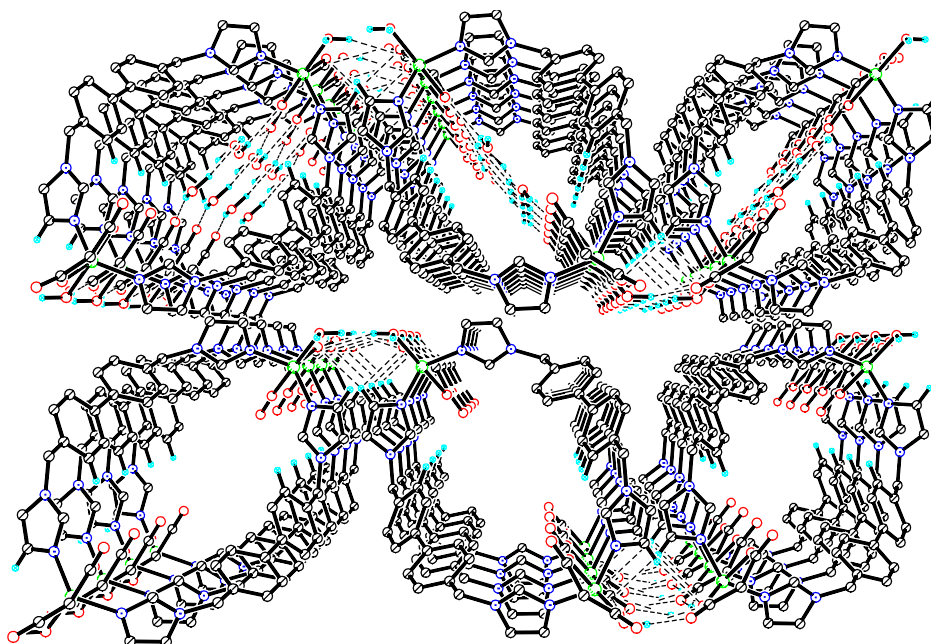


Fig. 3. Crystal packing diagram for complex **1** on bc plane with hydrogen bonds indicated by dashed lines.

3. Results and discussion

3.1. Crystal structure of $[Zn_2(bimb)_2(mal)_2(H_2O)_2] \cdot 4H_2O$ **1**

The structure of **1** was confirmed by X-ray single-crystal structure determination. The complex crystallizes in monoclinic space group $P2_1/c$ and the structure of the complex is displayed in Fig. 1 along with the atom numbering scheme. It is clear that each Zn(II) center is coordinated by two N atoms from two different bimb ligands with N–Zn–N bond angle of $115.44(18)^\circ$ and Zn–N bond distances of 2.037(5) and 2.044(4) Å, respectively (Table 2). The additional positions are occupied by three O atoms, two of which are from one malonate dianion and the other is from a water molecule with Zn–O bond distances ranging from 1.985(4) to 2.122(4) Å and O–Zn–O bond angles varying from $83.32(15)^\circ$ to $171.68(15)^\circ$ as listed in Table 2. Therefore, the local coordination geometry around the Zn1 can be described as a distorted trigonal bipyramid with a N_2O_3 donor set. Each bimb ligand with an extended conformation of “Z” shape in turn connects two metal atoms. The dihedral angle between the two coordinated terminal imidazole groups of each bimb is 59.5° while the dihedral angle between two benzene ring planes of each biphenyl group is 31.9° . Such a coordination mode makes the compound **1** a cyclic dinuclear complex with Zn–Zn distance of 16.35 Å. It is noteworthy that the $^-OCOCH_2COO^-$ and H_2O bound to the metal center by O donor function as terminators and prevent further aggregation.

It is interesting that the macrocyclic rings are further connected by O–H...O hydrogen bonds to give a 1D tube-like chain (Fig. 2). The data of the hydrogen bonds are summarized in Table 3. The inner channel of the 1D tubelike chain is occupied by crystal water molecules, and the distance of C11–C21 is 8.81 Å (atom numbering scheme shown in Fig. 1). A previous reported zinc(II) tubelike MOF containing 1D tubes was obtained by reaction of titmb with zinc(II) acetate [19]. The 1D tubes of **1** were further linked by C–H...O and O–H...O hydrogen bonds to form a 2D framework as illustrated in Fig. 3.

3.2. Crystal structure of $[Zn_2(titmb)_2(mal)][mal] \cdot 12H_2O$ **2**

The title complex crystallizes in the monoclinic form with $P2_1$ space group, and the coordination environment around the zinc(II) center in complex **2** is shown in Fig. 4a. It is obvious that there are two crystallographically independent zinc atoms (Zn1 and Zn2) in the asymmetry unit. Zn1 and Zn2 have similar coordination geometry and each zinc(II) atom is coordinated by three imidazole N atoms from three

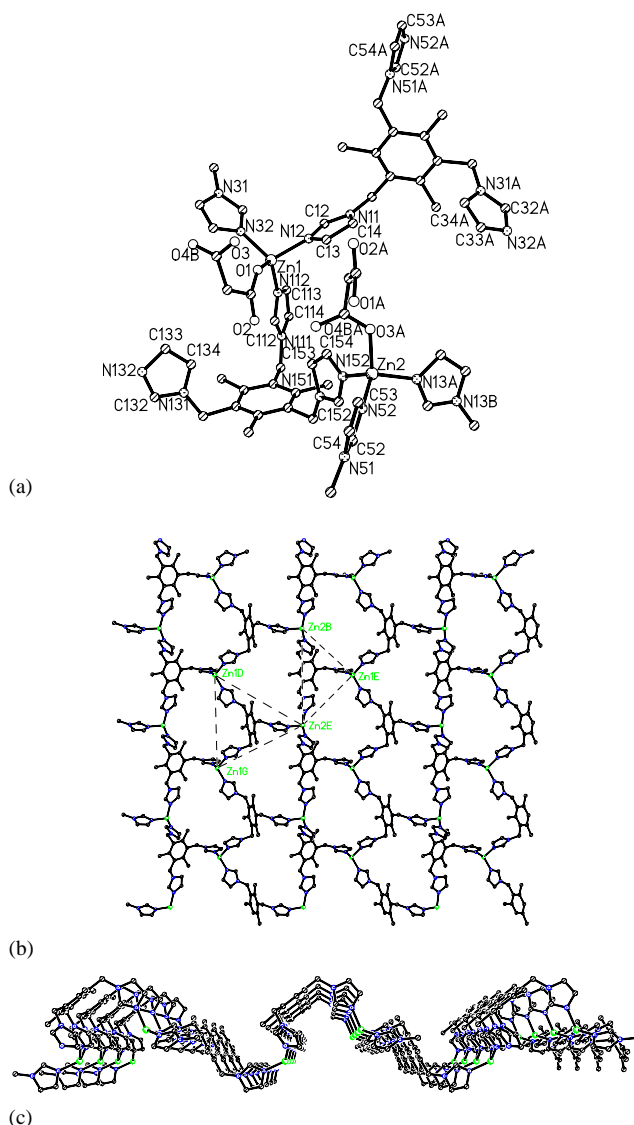
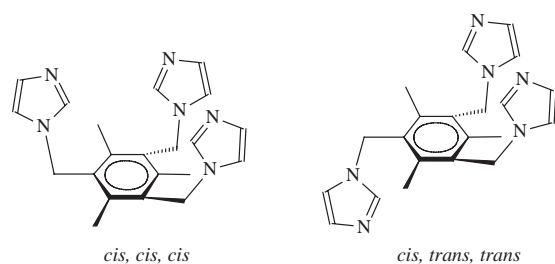


Fig. 4. (a) Coordination environments around Zn1 and Zn2 in complex $[Zn_2(titmb)_2(mal)][mal] \cdot 12H_2O$ (**2**). The free malonate anion, lattice water molecules and hydrogen atoms were omitted for clarity. Top (b) and side (c) views of 2D honeycomb network in **2**.



Scheme 2.

different titmb ligands with N–Zn–N bond angles varying from $103.37(16)^\circ$ to $115.0(3)^\circ$ and Zn–N bond distances ranging from 1.970(7) to 2.019(8) Å (Table 2). The remaining position is occupied by an O atom from

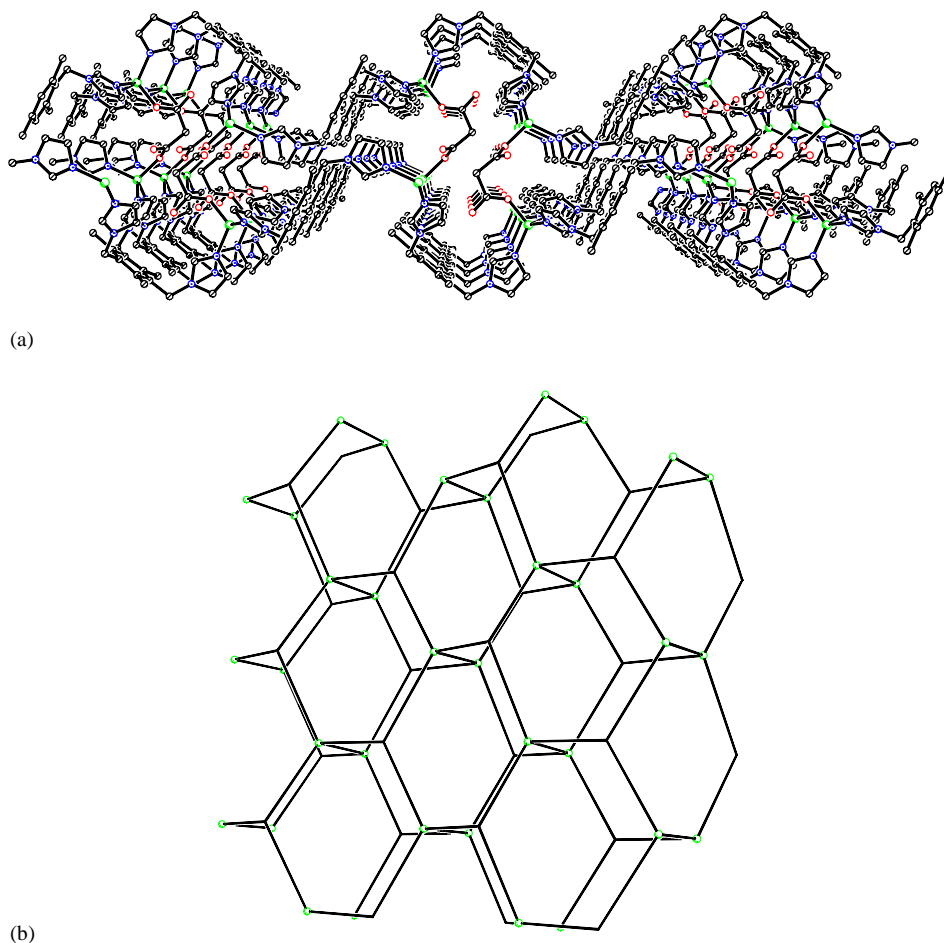


Fig. 5. (a) Side view of the double-layered 2D network of **2**. (b) Schematic illustration of the 2D network of **2**, in which the ligands are represented by three spokes radiating from a point and the zinc center by a green ball.

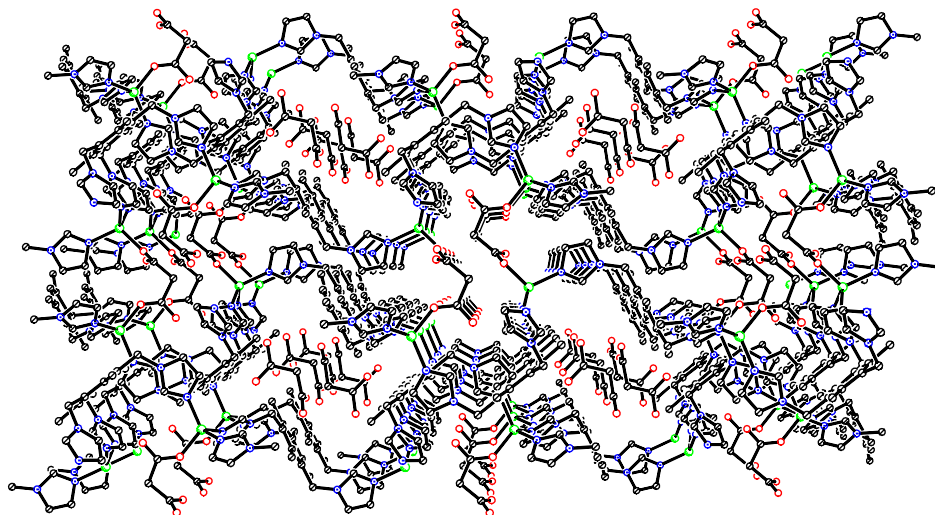


Fig. 6. Crystal packing diagram for complex **2**.

the malonate with Zn–O bond distances of 1.931(4) for Zn1 and 1.923(4) Å for Zn2, respectively, and O–Zn–N bond angles varying from 101.6(3)° to 118.48(14)° as listed in Table 2. Thus the coordination geometry of the

Zn(II) center can be regarded as a distorted tetrahedral with N₃O donor set. On the other hand, the titmb ligand containing N111, N131 and N151 with *cis*, *cis*, *cis*-conformation (Scheme 2) coordinates to three metal

atoms to form a hexagon with metal–metal separations (Zn⋯Zn) of 9.03 Å (e.g. Zn1E⋯Zn2E in Fig. 4b), 12.13 Å (e.g. Zn2E⋯Zn2B) and 9.20 Å (e.g. Zn2B⋯Zn1E), respectively. The dihedral angles between each two of three coordinated terminal imidazole groups of the titmb are 57.6° (e.g. C132, C133, C134 and C112, C113, C114), 51.3° (e.g. C112, C113, C114 and C152, C153, C154) and 108.9° (e.g. C152, C153, C154 and C132, C133, C134), while the titmb ligand containing N11, N31A and N51A with *cis*, *trans*, *trans*-conformation (Scheme 2) also coordinates to three metal atoms to form a hexagon with metal–metal distances (Zn⋯Zn) of 12.13 Å (e.g. Zn1D⋯Zn1G in Fig. 4b), 12.99 Å (e.g. Zn1G⋯Zn2E) and 12.86 Å (e.g. Zn1D⋯Zn2E), respectively. The dihedral angles between each two of the three coordinated terminal imidazole groups of the titmb are 59.5° (e.g. C12, C13, C14 and C32A, C33A, C34A), 66.6° (e.g. C32A, C33A, C34A and C52A, C53A, C54A) and 124.5° (e.g. C52A, C53A, C54A and C12, C13, C14). Such a coordination mode generates a 2D honeycomb network with (6,3) topology as shown in Fig. 4b, if the Zn(II) atoms and the centers of titmb ligands are considered as nodes, and the connection of the malonate is ignored. Two 2D sheets shown in Fig. 4b (or Fig. 4c) are connected by malonate groups to produce a double-layered 2D network (Fig. 5a), namely, the malonate groups serve as bridges to connect two sub-layers within an independent sheet as a schematic illustration shows in Fig. 5b which is different from complex 1 in which the $^-OCCH_2COO^-$ acts as terminators. The two metal ions linked by the malonate have a distance of 5.96 Å. The infinite 2D networks are linked together by C–H⋯O hydrogen bonds to give a 3D structure for complex 2 as illustrated in Fig. S1 and the crystal water molecules occupied the voids of the 3D framework. There are large open channels in the complex 2 formed between two neighboring 2D layers; the uncoordinated malonate are located in the channels (Fig. 6) and held there by hydrogen bonds. The distances of C⋯O are in the range of 3.143(9)–3.471(10) Å and the C–H–O angles are in the range from 141° to 170° (Table 3).

3.3. Properties of complexes 1 and 2

The structure analyses revealed that the synthesized complexes contain guest water molecules and the stability of the complexes after removal of guest molecules is important in view of the developing molecular-based materials. TGA and X-ray powder investigations were thus carried out for complexes 1 and 2. TGA data of 1 showed that a weight loss of 9.7% (calculated 10.0%) corresponding to the liberation of the water molecules was observed below 135°C (Fig. S2). The X-ray powder pattern of the crystals after removal of the water molecules exhibited that they did

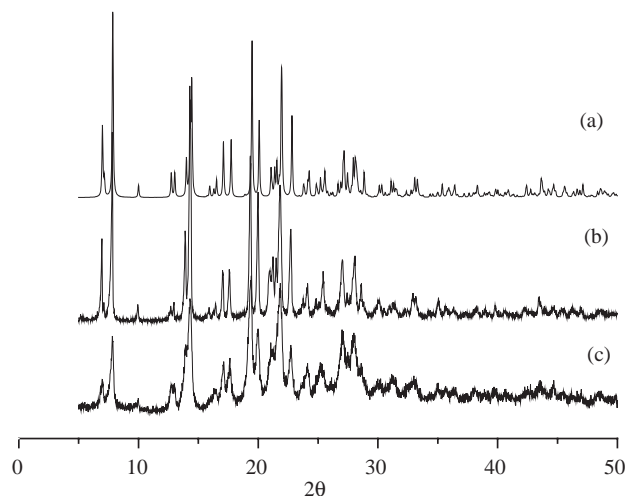


Fig. 7. X-ray powder diffraction diagram of (a) the simulated diagram of 1, (b) of 1 and (c) 1 after immersion in an aqueous solution after removing the water molecules.

not remain identical to those of the original crystals, which may probably be caused by the loss of the coordinated water molecules, which occurred almost at the same time with the guest (uncoordinated) water molecules. However, it is interesting that when complex 1, after removal of the water molecules, was immersed in an aqueous solution for one day, the resulted complex showed the same X-ray powder pattern with complex 1 (Fig. 7). The TGA curve of the crystalline sample of 2 showed the loss of all guest water molecules below 150°C. Unfortunately, the powder X-ray diffraction pattern of the complex without H₂O obtained by heating complex 2 to 150°C for 2 h displayed strong broadening reflections indicating loss of crystallinity. The structure could not be completely recovered after the dehydrated complex immersed in water or flowed by methanol gas.

Acknowledgments

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