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# Synthesis, crystal structures, luminescent and thermal properties of two new metal–organic coordination polymers based on zinc(II) carboxylates†‡

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Two new metal–organic coordination polymers, $[NH_2(CH_3)_2]_2[Zn_3(bdc)_4]\cdot DMF\cdot H_2O$ (**1**) ($H_2bdc$ = 1,4-benzenedicarboxylic acid) and $[NH_2(CH_3)_2]_2[Zn_3(bpdc)_4]\cdot 5DMF$ (**2**) ($H_2bpdc$ = 4,4′-biphenyldicarboxylic acid), were synthesized by heating a DMF solution of $Zn(NO_3)_2\cdot 6H_2O$, $[NH_2(CH_3)_2]Cl$ and organic carboxylic acids. Single-crystal X-ray structure analysis reveals that these compounds have 3D anionic framework structures built from zinc(II) carboxylate layers linked by carboxylate anions. Compounds **1** and **2** were characterized by IR, TGA and XRPD, and their luminescent properties were also investigated.

## Introduction

Metal–organic coordination polymers constructed from metal ions and organic bridging ligands have attracted considerable attention in recent years.[1] The wide variety of organic ligands and the practically infinite number of ways of uniting metal coordination complexes into extended metal–organic frameworks has lead to a vast number of novel compounds with unique functional properties.[2,3] One approach to assembling such compounds is the binding of 2D sheets through bifunctional rigid ligands to obtain a 3D porous framework.[4] Varying the length or functionalization of linker molecules can change both the geometric parameters of the metal–organic framework and the functional environment within its pores, which affects the sorption properties of the porous coordination polymer.[5]

Among metal–organic frameworks, coordination polymers based on zinc carboxylates play a special role because of the large number of possible building units, varying from Zn(II) monomers to small di-, tri- or tetranuclear clusters, or even infinite chains, assembled into robust porous frameworks. In such structures, zinc atoms adopt coordination numbers 4 (tetrahedron), 5 (tetragonal pyramid) or 6 (octahedron).[6] Among all the open architectures, charge-neutral porous frameworks usually attract the most attention, since there are no non-compliant counterions occupying the interstitial voids. However, recently, it was demonstrated that some ionic species could significantly enhance the framework affinity towards gas molecules, particularly $H_2$, due to stronger interactions between the charges and the induced dipoles.[7] Charged porous frameworks, therefore, could also be valuable synthetic targets, although the corresponding synthetic strategies remain mostly undeveloped.

MOF materials offer a unique platform for the development of solid-state luminescent materials as they have a degree of structural predictability, in addition to well-defined environments for luminophores in their crystalline forms.

Herein, we describe the synthesis, structure, TG, IR and XRPD data, as well as the luminescent properties, of two novel metal–organic coordination polymers, $[NH_2(CH_3)_2]_2[Zn_3bdc_4]\cdot DMF\cdot H_2O$ (**1**) and $[NH_2(CH_3)_2]_2[Zn_3bpdc_4]\cdot 5DMF$ (**2**), which have 3D anionic frameworks built from similar 8-connected linear $Zn_3$ carboxylate complexes, with dimethylammonium cations and solvent molecules within the channels. Such structures could be valuable examples for gas storage sorption property investigations because of the ionic nature of both the framework and the guest species. We also believe that the addition of soluble ionic salts to the reaction medium promotes the formation of charged compounds, and could also be generalised for the synthesis of other porous coordination polymers of ionic nature.

## Results and discussion

Compounds **1** and **2** were obtained by solvothermal reactions of zinc(II) nitrate hexahydrate, dimethylammonium chloride and carboxylic acids in DMF.

Single-crystal structural analysis shows that complex **1** crystallizes in the $C2/c$ space group and has a 3D network.‡ As shown in Fig. 1, structure **1** comprises two crystallographically-independent Zn(II) atoms forming a trinuclear zinc carboxylate (the distance $Zn(1)\cdots Zn(2)$ is 3.228 Å). Zn(1) lies in a general position. Zn(2) lies on an inversion center. In the asymmetric unit, one bdc moiety lies in

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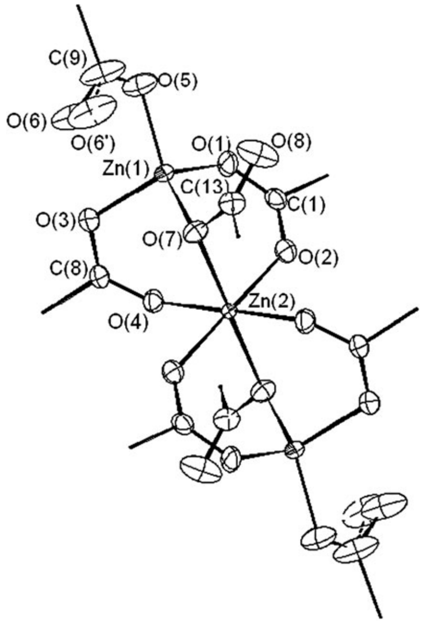

**Fig. 1** A fragment of the crystal structure of **1** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

a general position, and there are also two half bdc moieties, each lying about independent inversion centers. The distorted tetrahedral Zn(1) center is coordinated by four oxygen atoms, which associate with four bdc ligands. The Zn(1)–O bond lengths fall within normal values, ranging from 1.926(3) to 1.973(3) Å. The distorted octahedral Zn(2) centers are coordinated by six oxygen atoms, which associate with six terephthalates. Two Zn(2)–O distances are 2.205(3) Å, the others ranging from 2.041(3) to 2.052(3) Å, and have typical values for octahedral zinc(II) complexes. Each Zn(2) atom is connected to Zn(1) atoms *via* two bridged bidentate $\mu_2$-RCOO-$O,O'$ groups and bridged monodentate $\mu_2$-ROO-$O$ groups to form trinuclear building blocks. Linked together by terephthalates in the *bc* plane, these fragments make up the 3D anionic framework, with 2D channels characterised by dimensions of 4 × 6 Å (Fig. 2). A space within the channels is occupied by disordered dimethylammonium cations, DMF guest and water molecules.

Based on a PLATON[8] analysis (filling of the cavities with probe spheres of radius 1.2 Å), the free volume in the absence of guest solvent molecules was found to be 40%.

Compound **2** crystallizes in the orthorhombic space group $Pna2_1$.‡ As shown in Fig. 3, the structure of **2** is similar to that of the trinuclear building unit of **1**, but the Zn carboxylate complexes in **2** contain three crystallographically-independent zinc atoms. The shortest distance Zn$\cdots$Zn is 3.575 Å. The tetrahedral Zn(1) and Zn(3) centers are coordinated by four oxygen atoms, which associate with four bpdc ligands. The Zn(1)–O and Zn(2)–O bond lengths fall within normal values, ranging from 1.944(3) to 1.959(2) Å. The distorted octahedral Zn(2) centers are coordinated by six oxygen atoms, which associate with six bpdc ligands. All the Zn(2)–O bond lengths fall within normal values, ranging from 2.053(2) to 2.131(2) Å. Unlike in compound **1**, octahedral Zn(2) connects with two tetrahedral zinc atoms only *via* the bidentate bridged $\mu_2$-COO-$O,O'$ group. Similarly to **1**, the 3D anionic framework of **2** is built from 2D sheets of $\{Zn_3(bpdc)_3\}_\infty$ lying in the *ab* plane and connected through bpdc bridged ligands oriented along the *c*-axis (Fig. 4).

From a topological point of view, the carboxylate building units $\{Zn_3(RCOO)_8\}$ in **1** and **2** can be rationalised as hexagonal bipyramids. The connection of such 8-connected nodes results in interlinked trigonal layers stacked one exactly upon another. Both frameworks are therefore isoreticular and have the

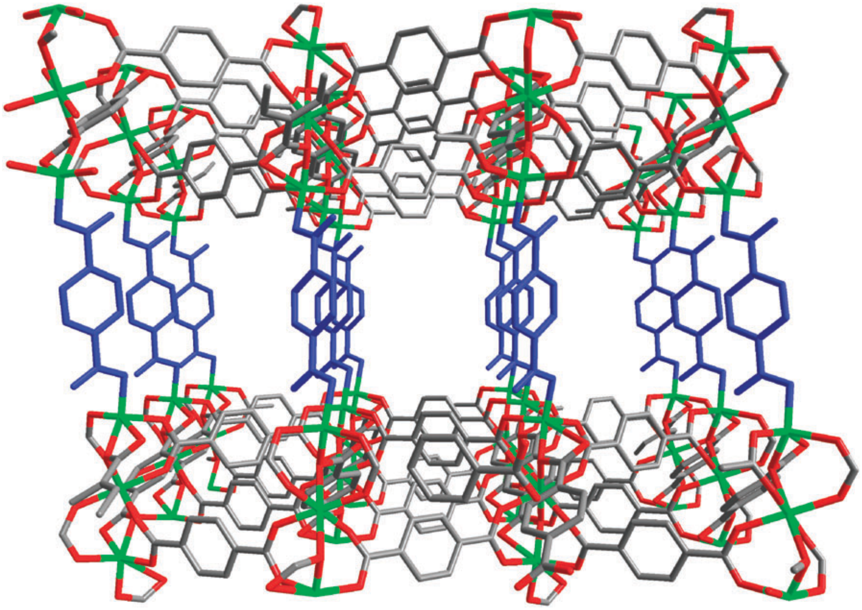

**Fig. 2** A fragment of the framework structure of **1** (wire frame presentation). Hydrogen atoms, guest molecules and dimethylammonium cations within the channels are omitted for clarity. Terephthalate (bdc) linkers, perpendicular to trigonal layers of $\{Zn_3(bdc)_3\}$ in the *bc* plane, are shown blue.

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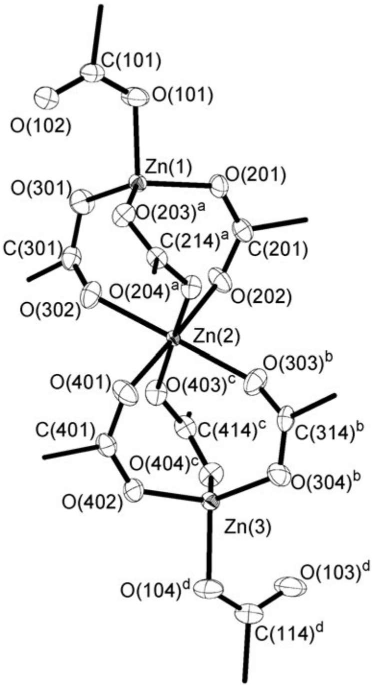

**Fig. 3** A fragment of the crystal structure of **2** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (a) $x + \frac{1}{2}, -y - \frac{1}{2}, z$; (b) $x, y - 1, z$; (c) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (d) $x, y, z + 1$.

connectivity of the Ni subnet in the niccolite mineral (NiAs), which is built from face-shared trigonal prism polyhedrons. The corresponding net is uninodal and has the point symbol $3^6.4^{18}.5^3.6$, also known as **hex**.[9] Contrary to **1**, the overall structure of **2** comprises of two independent interpenetrated networks (Fig. 5), likely to be due to the lengthier bpdc linker in **2** compared to bdc in **1**. Despite the interpenetration, the microporous channels of characteristic dimensions 5 × 8 Å run along the *c* axis of the structure, filled with dimethylammonium cations and DMF guest molecules. The catenation results in a somewhat lower free volume (39%) in **2** compared to **1**. Interpenetration phenomena are quite common for porous metal–organic frameworks, especially when long linkers are used.[10] Strikingly, the interpenetration sometimes increases the sorption capacity compared to non-interpenetrated frameworks.[11] Porous metal–organic frameworks with the same topology have been reported recently.[12] These share the same 8-connected $\{M_3(RCOO)_8\}$ carboxylate building units ($M = Zn^{2+}, Co^{2+}$). However, in the latter compounds, the $\{Zn_3(bpdc)_3\}_\infty$ layers are interlinked by neutral linear 4,4′-bipyridyl ligands, which resulted in charge-neutral $[M_3(bpdc)_3(bipy)]$ porous frameworks. In our experiments, the addition of stoichiometric amounts of a dimethylammonium salt to the reaction mixture plays a critical role in the formation of the charged framework. It apparently promotes the inclusion of these charged cations into the pores of **1** and **2**, shifting the equilibrium towards the formation of charged metal–organic frameworks. It should be pointed out that in similar reaction conditions (solvothermal synthesis from a DMF mixture, but without dimethylammonium), charge-neutral layered Zn(II) carboxylate coordination polymers were isolated from the reaction mixture.[13] We believe that such an

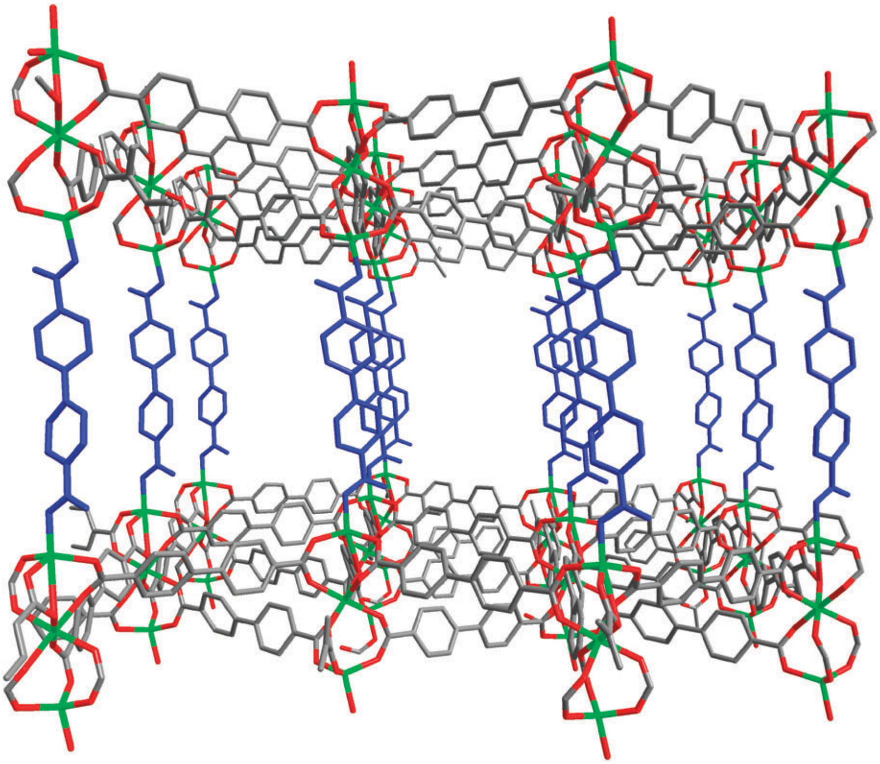

**Fig. 4** A fragment of the framework structure of **2** (wire frame presentation). Hydrogen atoms, guest molecules and dimethylammonium cations within the channels are omitted for clarity. Biphenyldicarboxylate (bpdc) linkers, perpendicular to trigonal layers of $\{Zn_3(bdc)_3\}$ in the *ab* plane are shown blue.

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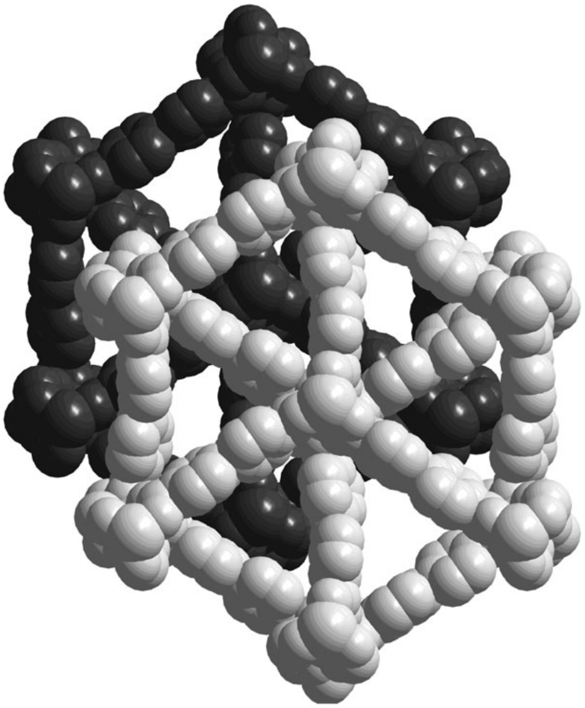

**Fig. 5** Two interpenetrated frameworks in **2** viewed along the *c* axis. Atoms belonged to different frameworks are showed as light- and dark-grey spheres.

increase of the ionic strength of the reaction medium could be generalised and used for the synthesis of other coordination polymers with charged frameworks.

The solid-state fluorescent properties of complexes **1** and **2** were measured at room temperature (Fig. 6). Their emission spectra were collected from 300 to 700 nm with excitation wavelengths at about 330 nm for **1**, and from 300 to 600 nm with excitation wavelengths at about 338 nm for **2**. Intense peaks in the emission spectra were observed at 452 nm for **1** and at 400 nm for **2**. The peak in the emission spectrum of **1** at 452 nm can be attributed to ligand-to-metal charge transfer (LMCT).[14–16] The intense emission at 400 nm in the spectrum of **2** can be assigned to LMCT and the intraligand emission of benzenedicarboxylate ligands resulting from the $\pi^* \rightarrow n$ transition.[17,18]

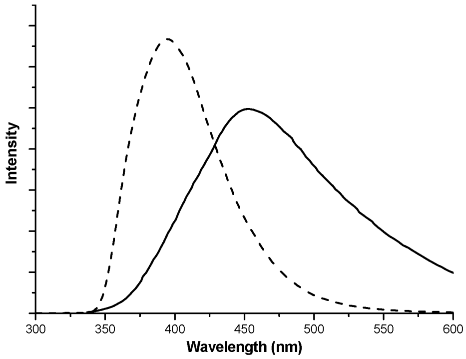

**Fig. 6** The solid-state fluorescent spectra of **1** (—) and **2** (---) recorded at room temperature.

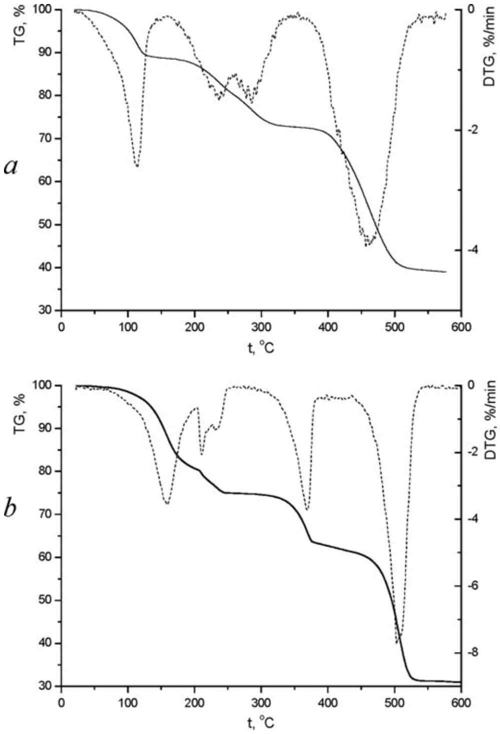

**Fig. 7** TG–DTG curves of compounds (a) **1** and (b) **2** at a heating rate of 10 K min$^{-1}$.

Compounds **1** and **2** were analyzed by thermogravimetric analysis (TGA) in He. As shown in Fig. 7(a), compound **1** exhibited a gradual weight loss of 10.2% between 20 and 200 °C, corresponding to the release of water and DMF guest molecules (calc. 8.6%). The following decrease of mass below 220 °C can be associated with the destruction of the metal–organic framework. Compound **2** (Fig. 7(b)) exhibited a gradual weight loss of 25.1% between 20 and 250 °C, corresponding to the release of five DMF molecules (calc. 25.2%). The following decrease of mass below 350 °C can be associated with the destruction of the metal–organic framework. It should be noted that compound **2** is more thermally stable than **1**, probably due to the interpenetration effect in **2**.

X-Ray powder diffraction data were recorded to check the crystallinity of the samples. The experimental spectra of compounds **1** and **2** are almost consistent with those simulated based on the structure models derived from the single-crystal X-ray diffraction data (Fig. S1‡).

## Conclusions

We have synthesized and structurally characterized two novel compounds, $(NH_2(CH_3)_2)_2[Zn_3(bdc)_4]\cdot DMF\cdot H_2O$ (**1**) and $(NH_2(CH_3)_2)_2[Zn_3(bpdc)_4]\cdot 5DMF$ (**2**), which have anionic metal–organic frameworks based on Zn(II) and aromatic dicarboxylates. Their characteristic channel dimensions are 4 × 6 Å for **1** and 5 × 8 Å for **2**, respectively. An increase of the thermal stability of compound **2** due to the interpenetration effect was observed. The luminescent properties of **1** and **2** were also investigated.

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## Experimental section

### Materials and methods

All chemicals and reagents were used as received from commercial sources without further purification. Elemental analyses (C, H, N) were performed on a Euro EA 3000 CHN elemental analyzer. IR spectra were recorded using KBr pellets on a Scimitar FTS 2000 spectrophotometer in the range 4000–400 $cm^{-1}$. XRPD were performed with a Philips PW 1820/PW 1710 diffraction system ($\lambda_{Cu\text{-}K_\alpha}$ = 1.54056 Å). Thermogravimetric analyses were performed with a NETZSCH TG 209 F1 thermoanalyzer under He (20–600 °C range) at a linear heating rate of 10 °C $min^{-1}$. Room temperature photoluminescence was studied on a Varian Cary Eclipse fluorescence spectrophotometer.

### X-Ray crystallography‡

Data collections of X-ray diffraction intensities for compounds **1** and **2** were performed on a Bruker-Nonius X8Apex CCD diffractometer equipped with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda_{Mo\text{-}K_\alpha}$ = 0.71073 Å). Intensity data were collected at 100 K. Empirical absorption corrections were applied using the SADABS program.[19] The structures were solved by direct methods and refined by the full-matrix least-squares technique on $F^2$ using the SHELX-97[20] package of crystallographic software. All non-hydrogen atoms were refined with anisotropic thermal parameters. In **1**, the DMF of solvation has a half-occupancy, and there are also two water oxygens to which 0.25 occupancies have been assigned. The dimethylammonium cation is disordered around the central N atom so that four half-occupied positions of the $CH_3$ groups emerge. In one of the bdc moieties, an uncoordinated oxygen atom of carboxyl group (see Fig. 1) is disordered over two half-occupied positions, O(6) and O(6′). In order to obtain an appropriate structure model, restraints on the atomic displacement parameters and bond distances for the disordered carboxyl group, dimethylammonium cation and water molecules were applied during the structure refinement of **1**. Restraints on the atomic displacement parameters for the DMF of solvation in **2** were also applied. Hydrogen atoms in $bdc^{2-}$, $bpdc^{2-}$, dimethylformamide and the $CH_3$ groups of the disordered $[NH_2(CH_3)_2]^+$ were located at geometrically-calculated positions and refined using a riding model. For the disordered water of crystallization and dimethylammonium cations in **1**, the hydrogen atoms were not localized. The crystal data, details of the diffraction experiments and the structure refinements for compounds **1** and **2** are shown in Table 1. Selected bond distances and angles for **1** and **2** are listed in Table 2 and Table 3, respectively.

**Table 1** Crystal data and structure refinements for compounds **1** and **2**

| Compound | **1** | **2** |
|---|---|---|
| Formula | $C_{39}H_{41}N_3O_{18}Zn_3$ | $C_{75}H_{83}N_7O_{21}Zn_3$ |
| $M$ | 1035.86 | 1614.59 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $C2/c$ | $Pna2_1$ |
| $a$/Å | 33.1453(16) | 24.6744(5) |
| $b$/Å | 9.5959(4) | 14.5575(5) |
| $c$/Å | 18.4950(8) | 22.4021(6) |
| $\beta$ (°) | 90.467(1) | |
| $V$/Å$^3$ | 5882.3(5) | 8046.8(4) |
| $Z$ | 4 | 4 |
| $D_c$/g $cm^{-3}$ | 1.170 | 1.333 |
| $\mu$/$mm^{-1}$ | 1.271 | 0.960 |
| $F$(000) | 2120 | 3360 |
| Crystal size/mm | 0.50 × 0.35 × 0.10 | 0.40 × 0.24 × 0.16 |
| $\theta$ (°) | 2.20–35.42 | 1.67–28.34 |
| $hkl$ | $-53 \le h \le 53$,<br>$-12 \le k \le 15$,<br>$-30 \le l \le 16$ | $-32 \le h \le 32$,<br>$-12 \le k \le 19$,<br>$-29 \le l \le 27$ |
| $N_{hkl}$ collected/independent/observed | 33788/13263/9279 | 62979/19099/16199 |
| $R_{int}$ | 0.0354 | 0.0298 |
| $T_{max}/T_{min}$ | 0.8834/0.5689 | 0.8615/0.7000 |
| Restraints/parameters | 60/349 | 79/956 |
| Flack parameter | | 0.514(8) |
| Goodness-of-fit on $F^2$ | 1.077 | 1.059 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0782,<br>w$R_2$ = 0.2498 | $R_1$ = 0.0377,<br>w$R_2$ = 0.1060 |
| $R$ indices (all data) | $R_1$ = 0.1093,<br>w$R_2$ = 0.2550 | $R_1$ = 0.0501,<br>w$R_2$ = 0.1127 |
| Largest differential peak/hole/e Å$^{-3}$ | 1.984/−1.173 | 1.381/−0.810 |

**Table 2** Selected bond lengths (Å) and angles (°) for **1**

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.951(3) | Zn(2)–O(2) | 2.041(3) |
| Zn(1)–O(3)$^a$ | 1.973(3) | Zn(2)–O(4)$^b$ | 2.052(3) |
| Zn(1)–O(5) | 1.926(3) | Zn(2)–O(7) | 2.205(3) |
| Zn(1)–O(7) | 1.964(30) | | |
| O(1)–Zn(1)–O(3)$^a$ | 110.87(15) | O(2)–Zn(2)–O(4)$^a$ | 94.63(12) |
| O(1)–Zn(1)–O(7) | 109.62(12) | O(2)–Zn(2)–O(7)$^c$ | 89.46(11) |
| O(5)–Zn(1)–O(1) | 97.66(17) | O(2)–Zn(2)–O(7) | 90.55(11) |
| O(5)–Zn(1)–O(3)$^a$ | 107.49(16) | O(4)$^b$–Zn(2)–O(4)$^a$ | 180 |
| O(5)–Zn(1)–O(7) | 130.48(17) | O(4)$^b$–Zn(2)–O(7) | 89.58(11) |
| O(7)–Zn(1)–O(3)$^a$ | 100.37(12) | O(4)$^a$–Zn(2)–O(7) | 90.42(11) |
| O(2)–Zn(2)–O(2)$^c$ | 180 | O(7)$^c$–Zn(2)–O(7) | 179.996(1) |
| O(2)–Zn(2)–O(4)$^b$ | 85.37(12) | | |

Symmetry transformations used to generate equivalent atoms: $^a$ $x, -y+2, z-\frac{1}{2}$. $^b$ $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$. $^c$ $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$.

### Synthesis

**$[NH_2(CH_3)_2]_2[Zn_3(bdc)_4]\cdot DMF\cdot H_2O$ (1).** A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.300 g, 1.00 mmol), $H_2bdc$ (0.220 g, 1.30 mmol), $[NH_2(CH_3)_2]Cl$ (0.051 g, 0.60 mmol) and $Et_3N$ (0.101 g, 1 mmol) was dissolved in DMF (25 ml) and heated in a Teflon bomb at 100 °C for 3 d. Colorless crystals were obtained, washed with DMF (2 × 10 ml) and diethyl ether (2 × 10 ml), and dried at 50 °C for 20 min. Yield 23 mg (57%, based on Zn). Anal. calc. for $C_{39}H_{41}N_3O_{18}Zn_3$: C, 45.2; H, 4.0; N, 4.1. Found: C, 44.9; H, 4.0; N, 4.3%. IR (KBr, $cm^{-1}$): 544 m, 663 w, 749 m, 824 m, 889 w, 1018 m, 1062 w, 1095 m, 1134 m, 1387 s, 1438 m, 1503 m, 1603 s, 1668 s, 2491 m, 2806 m, 2933 m, 3051 m, 3443 m.

**$[NH_2(CH_3)_2]_2[Zn_3bpdc_4]\cdot 5DMF$ (2).** A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.300 g, 1.00 mmol), $H_2bpdc$ (0.480 g, 2.00 mmol) and $[NH_2(CH_3)_2]Cl$ (0.082 g, 1.00 mmol) was dissolved in DMF (30 ml) and heated in a Teflon bomb at 100 °C for 3 d. Colorless crystals were obtained, washed with DMF (2 × 10 ml) and diethyl ether (2 × 10 ml), and dried at 50 °C for 20 min. Yield 183 mg (36%, based on Zn). Anal. calc. for $C_{75}H_{83}N_7O_{21}Zn_3$: C, 55.8; H, 5.2; N, 6.1. Found: C, 55.9; H, 5.0; N, 6.1%. IR (KBr, $cm^{-1}$): 442 m, 537 w, 572 w,

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**Table 3** Selected bond lengths (Å) and angles (°) for **2**

| | | | |
|---|---|---|---|
| Zn(1)–O(101) | 1.944(3) | Zn(2)–O(303)$^b$ | 2.098(2) |
| Zn(1)–O(201) | 1.945(2) | Zn(2)–O(401) | 2.053(2) |
| Zn(1)–O(203)$^a$ | 1.954(2) | Zn(2)–O(403)$^c$ | 2.088(2) |
| Zn(1)–O(301) | 1.951(2) | Zn(3)–O(104)$^d$ | 1.959(2) |
| Zn(2)–O(202) | 2.067(2) | Zn(3)–O(304)$^b$ | 1.956(2) |
| Zn(2)–O(204)$^a$ | 2.109(2) | Zn(3)–O(402) | 1.951(2) |
| Zn(2)–O(302) | 2.131(2) | Zn(3)–O(404)$^c$ | 1.948(2) |
| O(101)–Zn(1)–O(201) | 96.52(10) | O(401)–Zn(2)–O(204)$^a$ | 85.35(9) |
| O(101)–Zn(1)–O(203)$^a$ | 103.14(10) | O(401)–Zn(2)–O(302) | 85.52(10) |
| O(101)–Zn(1)–O(301) | 107.79(11) | O(401)–Zn(2)–O(303)$^b$ | 95.63(10) |
| O(201)–Zn(1)–O(203)$^a$ | 116.98(11) | O(401)–Zn(2)–O(403)$^c$ | 92.34(9) |
| O(201)–Zn(1)–O(301) | 109.40(11) | O(403)$^c$–Zn(2)–O(204)$^a$ | 177.19(9) |
| O(301)–Zn(1)–O(203)$^a$ | 119.65(11) | O(403)$^c$–Zn(2)–O(302) | 87.43(8) |
| O(202)–Zn(2)–O(204)$^a$ | 92.80(9) | O(403)$^c$–Zn(2)–O(303)$^b$ | 90.56(9) |
| O(202)–Zn(2)–O(302) | 92.58(10) | O(304)$^b$–Zn(3)–O(104)$^d$ | 107.55(11) |
| O(202)–Zn(2)–O(303)$^b$ | 86.33(10) | O(402)–Zn(3)–O(104)$^d$ | 95.51(11) |
| O(202)–Zn(2)–O(403)$^c$ | 89.57(9) | O(402)–Zn(3)–O(304)$^b$ | 114.78(11) |
| O(204)$^a$–Zn(2)–O(302) | 93.99(8) | O(404)$^c$–Zn(3)–O(104)$^d$ | 109.32(10) |
| O(303)$^b$–Zn(2)–O(204)$^a$ | 88.07(8) | O(404)$^c$–Zn(3)–O(304)$^b$ | 114.00(10) |
| O(303)$^b$–Zn(2)–O(302) | 177.72(9) | O(404)$^c$–Zn(3)–O(402) | 113.77(10) |
| O(401)–Zn(2)–O(202) | 177.24(10) | | |

Symmetry transformations used to generate equivalent atoms:$^a$ $x + \frac{1}{2}, -y - \frac{1}{2}, z$. $^b$ $x, y - 1, z$. $^c$ $x - \frac{1}{2}, -y + \frac{1}{2}, z$. $^d$ $x, y, z + 1$.

680 m, 703 m, 772 s, 840 m, 1005 m, 1022 m, 1093 m, 1175 m, 1253 m, 1390 s, 1545 m, 1606 s, 1668 s, 1942 w, 2499 w, 2800 m, 3066 m, 3425 m.

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