

A two-dimensional coordination polymer,
 μ -1,3-benzenedicarboxylato- μ -ethylene-
diaminezinc(II) trihydrateYa-Qi Jiang,^{a*} Zhao-Xiong Xie^b
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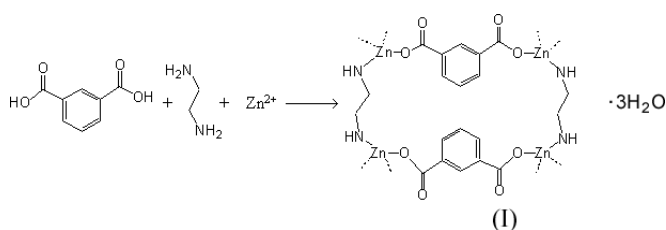
Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.030
 wR factor = 0.068
Data-to-parameter ratio = 14.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

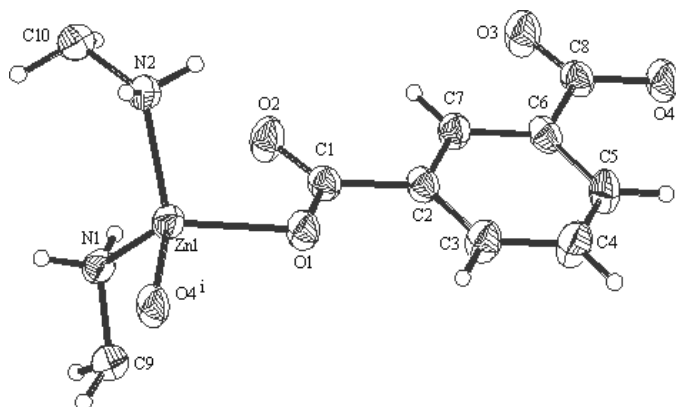
A two-dimensional zinc(II) coordination polymer, $[[\text{Zn}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_2\text{H}_8\text{N}_2)]\cdot 3\text{H}_2\text{O}]_n$, has been constructed from zinc(II), 1,3-benzenedicarboxylic acid and ethylenediamine. Within the polymer, each Zn atom is coordinated by two monodentate 1,3-benzenedicarboxylate ligands and two ethylenediamine ligands which define a distorted tetrahedral geometry. The two-dimensional network is further held together by π - π stacking interactions and hydrogen-bonding interactions, giving two types of extended one-dimensional channels along the a axis with dimensions of $10.207(1) \times 7.286(1)\text{ \AA}$ and $10.207(1) \times 6.240(1)\text{ \AA}$.

Comment

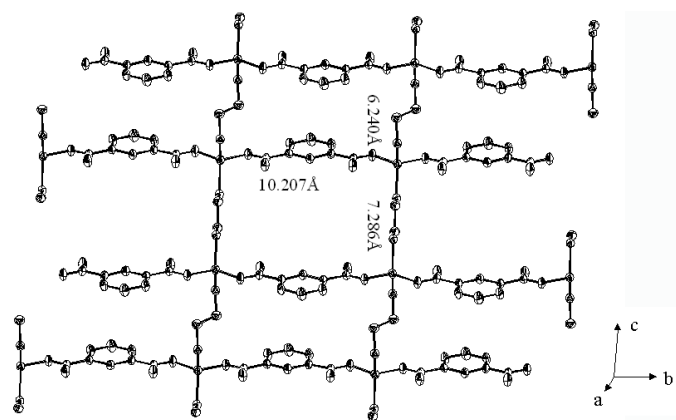
Considerable effort has been devoted to the synthesis and characterization of new crystalline nanosized porous materials, such as coordination polymers and supramolecules, because of their fascinating structures and potential applications in gas separation, molecular recognition, sensors, switches and actuators (Kitaura *et al.*, 2003; Eddaoudi *et al.*, 2002). In constructing coordination polymers, benzenedicarboxylate dianions, due to their versatile bonding mode with metal cations, have been widely used as linkers to bridge metal centres in a number of ways, forming infinite chains or multi-dimensional frameworks (Baca *et al.*, 2001; Wan *et al.*, 2002; Zhang *et al.*, 2000). Many topologically promising architectures have also been constructed from building blocks containing nitrogen donors (Fujita *et al.*, 1994; Ma *et al.*, 2001; Yaghi *et al.*, 1997). Here, we have employed 1,3-benzenedicarboxylic acid (H_2bdc) and ethylenediamine (en) as building blocks, hoping to design a new coordination polymer with a relatively large cavity or channel; the title zinc(II) complex, $[[\text{Zn}(\mu\text{-}O,O'\text{-bdc})(\text{en})]\cdot 3\text{H}_2\text{O}]_n$, (I), with one-dimensional channels in its crystal structure, has been successfully synthesized.



The asymmetric unit of (I) is depicted in Fig. 1 and selected bond distances are listed in Table 1. Complex (I) consists of approximately tetrahedral Zn^{2+} centres, linked by two N atoms of two en ligands and two O atoms of two bdc^{2-} ligands. Each bdc carboxylate group is essentially monodentate, with


Figure 1

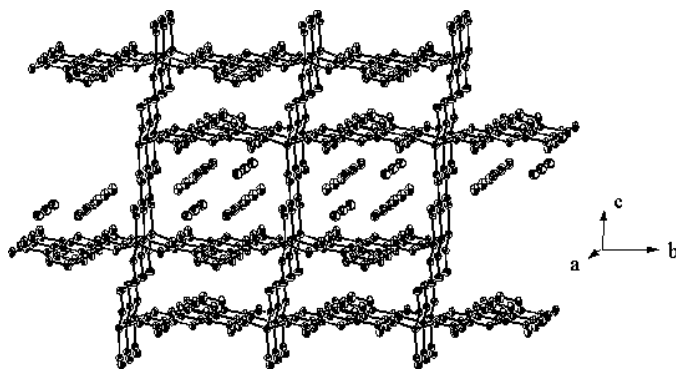
A molecular view of (I), showing the coordination environment of the Zn atom and with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii and the water molecules have been omitted for clarity [symmetry code: (i) $x, y + 1, z$].


Figure 2

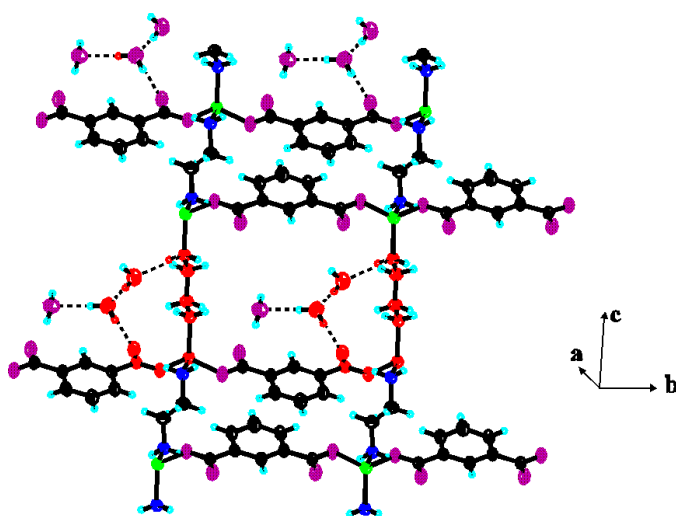
The layered network of (I), viewed along the a axis. Adjacent Zn···Zn separations are 10.207 (1) Å along the b axis, and 6.240 (1) and 7.286 (1) Å along the c axis. Water molecules and H atoms have been omitted for clarity.

Zn1—O1 1.991 (1) Å and Zn1—O4ⁱ 1.996 (2) Å [symmetry code: (i) $x, y + 1, z$]. However, the Zn1···O2 and Zn1···O3ⁱ distances of 2.705 (2) and 2.613 (2) Å suggest a non-negligible interaction with atoms O2 and O3ⁱ; this may be described as a semi-chelating coordination mode (Addison *et al.*, 1971). Considering these weak interactions, the coordination polyhedron of Zn is distorted from a tetrahedron towards an octahedron. For example, the O1—Zn—O4 angle is 100°, almost half-way between the tetrahedral (109.5°) and octahedral (90°) values. Likewise, the N1—Zn—N2 angle of 116° is increased from the tetrahedral value of 109.5° towards the octahedral value of 180°.

The assembly of the complex can best be viewed as having the following two components. Firstly, each bdc anion behaves as a bidentate ligand, bridging two adjacent Zn atoms through O atoms of both carboxylate groups to produce a chain along the b axis with a periodicity of 10.207 (1) Å, as shown in Fig. 2. Secondly, neighbouring chains are further connected together by ancillary en ligands linking two adjacent Zn atoms through


Figure 3

The crystal packing generated by stacking of the two-dimensional sheets of (I), forming one-dimensional channels along the a axis.


Figure 4

The crystal packing of (I), viewed along the a axis, clearly showing the 13-membered hydrogen-bonded rings (in red).

their N atoms, generating a two-dimensional architecture running along the c direction. The two-dimensional sheet then propagates in the bc plane (Fig. 2). In these two-dimensional sheets, the bdc benzene rings of neighbouring chains are located on opposite sides and form an S-type architecture. The interchain separations of the metal ions are 7.286 (1) and 6.240 (1) Å, respectively, giving two rectangular frames with dimensions of 10.207 (1) × 7.286 (1) Å and 10.207 (1) × 6.240 (1) Å.

The three-dimensional network is constructed by layer-by-layer stacking of the two-dimensional sheets *via* π – π interactions, resulting in a one-dimensional channel with a size of about 10.207 (1) × 7.286 (1) Å (Fig. 3). All the water molecules are located in the channels. The face-to-face distance of *ca* 3.55 Å between two nearest-neighbour bdc benzene rings indicates the presence of π – π stacking interactions. Finally, hydrogen bonds (Table 2) assist in stabilizing the whole structure. The NH₂ groups and non-coordinated O atoms and water molecules form 13-membered hydrogen-bonded rings (Fig. 4).

Experimental

1,3-Benzenedicarboxylic acid (5 mmol) was dissolved in ethanol (30 ml) in the presence of ethylenediamine (20 ml). Zinc nitrate (10 mmol) in water was added dropwise and the solution was refluxed for 4 h. The mixture was then filtered to remove the white precipitate. The colourless product, (I), which crystallized from the pale-yellow filtrate after 3 d, was collected, washed sequentially with ethanol and water, and dried using diethyl ether (yield *ca* 90%).

Crystal data

| | |
|---|---|
| $[\text{Zn}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_2\text{H}_8\text{N}_2)] \cdot 3\text{H}_2\text{O}$ | $Z = 2$ |
| $M_r = 343.65$ | $D_x = 1.632 \text{ Mg m}^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 5.6038 (4) \text{ \AA}$ | Cell parameters from 3044 reflections |
| $b = 10.2066 (7) \text{ \AA}$ | $\theta = 1.7\text{--}28.3^\circ$ |
| $c = 12.2719 (8) \text{ \AA}$ | $\mu = 1.79 \text{ mm}^{-1}$ |
| $\alpha = 85.549 (1)^\circ$ | $T = 298 (2) \text{ K}$ |
| $\beta = 88.404 (1)^\circ$ | Block, colourless |
| $\gamma = 89.026 (1)^\circ$ | $0.27 \times 0.22 \times 0.19 \text{ mm}$ |
| $V = 699.44 (8) \text{ \AA}^3$ | |

Data collection

| | |
|---|--|
| Bruker SMART CCD area-detector diffractometer | 3078 independent reflections |
| φ and ω scans | 2670 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $R_{\text{int}} = 0.013$ |
| $T_{\text{min}} = 0.630$, $T_{\text{max}} = 0.712$ | $\theta_{\text{max}} = 28.3^\circ$ |
| 4279 measured reflections | $h = -7 \rightarrow 6$ |
| | $k = -13 \rightarrow 13$ |
| | $l = -15 \rightarrow 16$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2]$ |
| $wR(F^2) = 0.068$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.92$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 3078 reflections | $\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$ |
| 215 parameters | $\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|--------------------------------------|-------------|-------------------------|-------------|
| Zn1—O1 | 1.9913 (13) | Zn1—N1 | 2.0364 (18) |
| Zn1—O4 ⁱ | 1.9959 (15) | Zn1—O3 ⁱ | 2.6130 (15) |
| Zn1—N2 | 2.0100 (18) | Zn1—O2 | 2.7049 (15) |
| O1—Zn1—O4 ⁱ | 100.30 (6) | N2—Zn1—O3 ⁱ | 85.11 (6) |
| O1—Zn1—N2 | 105.63 (7) | N1—Zn1—O3 ⁱ | 81.88 (6) |
| O4 ⁱ —Zn1—N2 | 110.00 (7) | O1—Zn1—O2 | 53.33 (5) |
| O1—Zn1—N1 | 111.54 (6) | O4 ⁱ —Zn1—O2 | 153.53 (5) |
| O4 ⁱ —Zn1—N1 | 111.88 (7) | N2—Zn1—O2 | 82.79 (6) |
| N2—Zn1—N1 | 116.17 (7) | N1—Zn1—O2 | 80.38 (6) |
| O1—Zn1—O3 ⁱ | 155.28 (5) | O3 ⁱ —Zn1—O2 | 151.37 (5) |
| O4 ⁱ —Zn1—O3 ⁱ | 54.99 (5) | | |

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

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D\cdots H\cdots A$ | $D\cdots H$ | $H\cdots A$ | $D\cdots A$ | $D\cdots H\cdots A$ |
|-------------------------------------|-------------|-------------|-------------|---------------------|
| N1—H1N1 \cdots O1 ⁱⁱ | 0.85 (2) | 2.41 (2) | 3.093 (2) | 137 (2) |
| N1—H1N2 \cdots O4 ⁱⁱⁱ | 0.85 (1) | 2.39 (2) | 3.147 (2) | 148 (2) |
| N2—H2N1 \cdots O1W ^{iv} | 0.86 (1) | 2.15 (1) | 3.001 (3) | 169 (2) |
| N2—H2N2 \cdots O1W ^v | 0.85 (1) | 2.12 (1) | 2.968 (2) | 171 (2) |
| O1W—H1W2 \cdots O2W | 0.84 (2) | 1.97 (1) | 2.786 (2) | 166 (3) |
| O1W—H1W1 \cdots O3W ^{vi} | 0.84 (2) | 1.95 (1) | 2.787 (3) | 171 (3) |
| O2W—H2W1 \cdots O2 | 0.83 (2) | 1.91 (1) | 2.743 (2) | 174 (2) |
| O2W—H2W2 \cdots O3W | 0.83 (1) | 1.96 (1) | 2.774 (3) | 165 (3) |

Symmetry codes: (ii) $1 + x, y, z$; (iii) $1 + x, 1 + y, z$; (iv) $x - 1, y, z$; (v) $1 - x, 1 - y, 2 - z$; (vi) $2 - x, -y, 2 - z$.

The H atoms of the water molecules and amino groups were located and refined, subject to $\text{O—H} = \text{N—H} = 0.85 (1) \text{ \AA}$ and $\text{H}\cdots\text{H} = 1.39 (1) \text{ \AA}$, and their displacement parameters were set to 1.2 times U_{eq} of their parent atoms. The C-bound H atoms were positioned geometrically and constrained with a riding model ($\text{C—H} = 0.97 \text{ \AA}$).

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2001).

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