catena-Poly[[bis[bis(1H-benzimidazole-κN³)-zinc(II)]-μ₄-benzene-1,2,4,5-tetracarboxylato] monohydrate]

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In the title compound, {[Zn₂(C₁₀H₂O₈)(C₇H₆N₂)₄]·H₂O}ₙ, the Znᴵᴵ atom has a distorted tetrahedral geometry, defined by two N atoms from two benzimidazole ligands and two O atoms from two benzene-1,2,4,5-tetracarboxylate (btc) tetra-anions. The complete btc anion is generated by inversion symmetry. The polymeric structure exhibits one-dimensional double chains running along the [100] direction, which further extend into a three-dimensional supramolecular network by way of π–π stacking involving the benzimidazole rings. A non-coordinated water molecule completes the structure.

Comment

The rational design and synthesis of polymeric complexes is of current interest in the field of supramolecular chemistry and crystal engineering. Benzimidazole (C₇H₆N₂; bim) is an attractive choice for a multifunctional linking group and has been investigated in the construction of many metal-organic frameworks (Wang *et al.*, 2006; Yutaka *et al.*, 2004; Rau *et al.*, 2000; Liu *et al.*, 2004). We present here the crystal structure of the title compound, (I), which is a new example in this family with a one-dimensional polymeric structure.

(I)
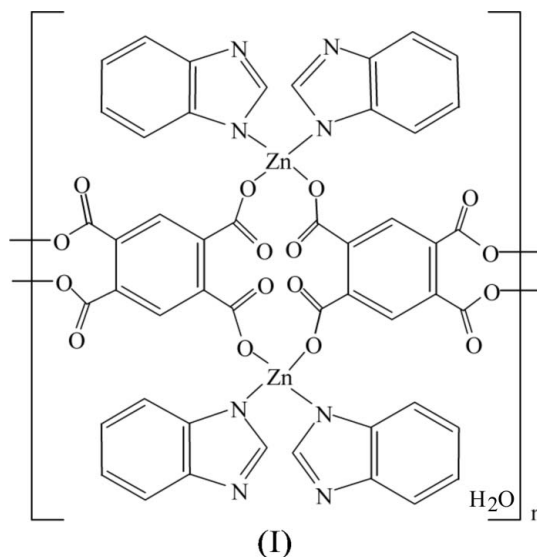
As shown in Fig. 1, the asymmetric unit of (I) contains one Znᴵᴵ atom, two benzimidazole ligands, one-half of a benzene-1,2,4,5-tetracarboxylate (C₁₀H₂O₈⁴⁻; btc) tetra-anionic ligand, and one half-occupancy water molecule. The Znᴵᴵ atom is coordinated by two O atoms from two btc ligands and two N atoms from two bim ligands, resulting in a distorted tetra-hedral geometry (Table 1). Each btc ligand is coordinated to
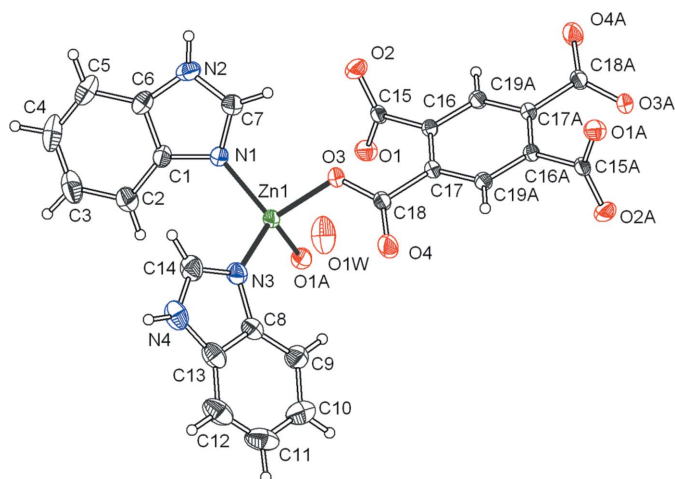
Figure 1
Asymmetric unit of (I), extended to show the Zn coordination, showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms. [Symmetry code: (A) $1 - x, 1 - y, z$.]
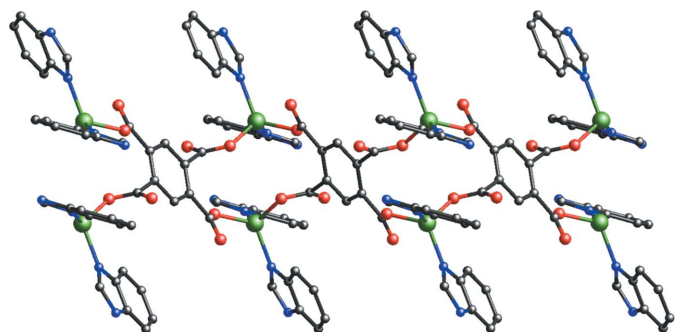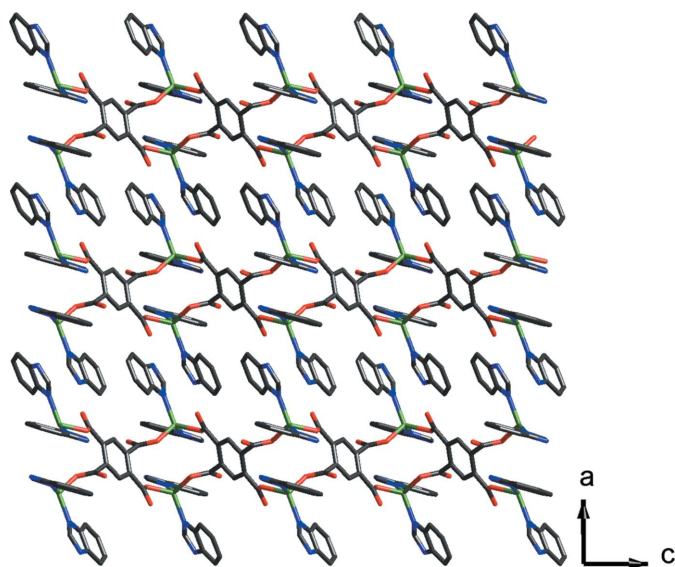

Figure 2
A view of the one-dimensional double chain running along the [100] direction in (I). H atoms and the water O atom have been omitted.

Figure 3
Packing diagram of the three-dimensional supramolecular network in (I). H atoms and the water O atom have been omitted.

423 K for 48 h under autogenous pressure. After cooling, colorless single crystals of (I) suitable for X-ray analysis were obtained from the reaction mixture.

Crystal data

$[Zn_2(C_{10}H_2O_8)(C_7H_6N_2)_4]\cdot H_2O$	$Z = 4$
$M_r = 871.42$	$D_x = 1.618$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 21.848$ (8) Å	$\mu = 1.41$ mm^{-1}
$b = 11.057$ (5) Å	$T = 295$ (2) K
$c = 14.806$ (6) Å	Block, colorless
$\beta = 90.288$ (15)°	$0.35 \times 0.27 \times 0.22$ mm
$V = 3577$ (2) Å^3	

Data collection

Bruker SMART CCD diffractometer	10890 measured reflections
ω scans	4355 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3911 reflections with $I > 2\sigma(I)$
$T_{min} = 0.639$, $T_{max} = 0.732$	$R_{int} = 0.022$
	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 2.1651P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{max} = 0.039$
$S = 1.04$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
4355 reflections	$\Delta\rho_{min} = -0.52$ e Å^{-3}
262 parameters	
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Zn1—O1^i	1.9325 (11)	C15—O2	1.2356 (18)
Zn1—O3	1.9545 (11)	C15—O1	1.2648 (19)
Zn1—N1	1.9842 (15)	C18—O4	1.2358 (18)
Zn1—N3	2.0049 (14)	C18—O3	1.2726 (18)

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

The non-coordinated water molecule (O1W) was modeled with 50% fractional site occupancy. Its attached H atoms could not be

four Zn^{II} atoms and each bim ligand is coordinated to one Zn atom. The dihedral angle between the planes of the N1- and N3-bim ligands is 49.24 (6)°. The lengths of the C—O bonds in the btc ligand suggest localization of the bonding.

Adjacent [Zn(bim)$_2$] units are linked by the btc ligands to form one-dimensional double chains running along the [100] direction as a molecular ladder (Fig. 2). The two benzimidazole ligands coordinated to one Zn^{II} atom are directed away from the double chains. This orientation plays an important role in defining a three-dimensional network through π–π stacking interactions between nearby bim ligands; firstly, the adjacent double chains are extended into a layer parallel to the (001) plane (Fig. 3), and then a three-dimensional supramolecular network is formed. The face-to-face distances between neighboring parallel benzimidazole planes are 3.364 (2) and 3.377 (2) Å.

Experimental

Compound (I) was prepared by hydrothermal methods. A mixture of Zn(NO$_3$)$_2$·6H$_2$O (0.5 mmol), H$_4$btc (0.6 mmol), benzimidazole (1.0 mmol) and water (12 ml) was stirred for 30 min in air. The mixture was then transferred to a 23 ml Teflon reactor and kept at

located in the present study. The other H atoms were placed in calculated positions with N—H = 0.86 Å and C—H = 0.93 Å and treated as riding atoms with $U_{iso}(H) = 1.2U_{eq}$(carrier).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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