

Bis(μ -5-carboxybenzene-1,3-dicarboxylato- $\kappa^2O^1:O^3$)bis[(2,2'-bi-1*H*-imidazole- κ^2N^3,N^3')]zinc

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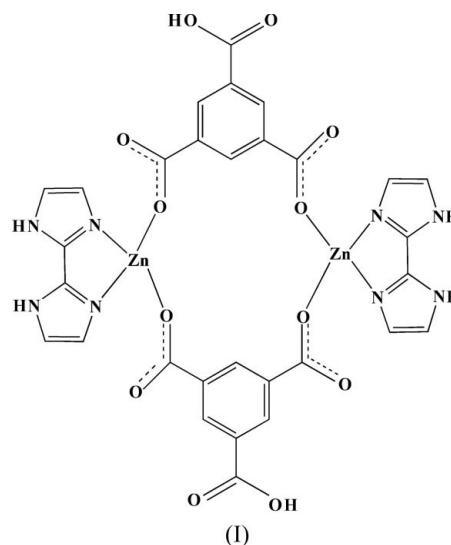
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The title compound, $[\text{Zn}_2(\text{C}_9\text{H}_4\text{O}_6)_2(\text{C}_6\text{H}_6\text{N}_4)_2]$, consists of two Zn^{II} ions, two 5-carboxybenzene-1,3-dicarboxylate (Hbtc^{2-}) dianions and two 2,2'-bi-1*H*-imidazole (bimz) molecules. The Zn^{II} centre is coordinated by two carboxylate O atoms from two Hbtc^{2-} ligands and by two imidazole N atoms of a bimz ligand, in a distorted tetrahedral coordination geometry. Two neighbouring Zn^{II} ions are bridged by a pair of Hbtc^{2-} ligands, forming a discrete binuclear $[\text{Zn}_2(\text{Hbtc})_2(\text{bimz})_2]$ structure lying across an inversion centre. Hydrogen bonds between carboxyl H atoms and carboxylate O atoms and between imidazole H atoms and carboxylate O atoms link the binuclear units. These binuclear units are further extended into a three-dimensional supramolecular structure through extensive O—H...O and N—H...O hydrogen bonds. Moreover, the three-dimensional nature of the crystal packing is reinforced by the π - π stacking. The title compound exhibits photoluminescence in the solid state, with an emission maximum at 415 nm.

Comment

Crystal engineering and supramolecular chemistry have been the most active areas of materials research in recent years, owing to the intriguing structural topologies examined and their potential applications in host-guest chemistry and catalysis (Ma *et al.*, 2009; Mezei *et al.*, 2007). The key to the successful construction of supramolecular architectures is the control and manipulation of coordination bonds and noncovalent interactions by carefully selecting the coordination geometry of the metal centres and the organic ligands containing appropriate functional groups (such as polycarboxylic acids and polypyridines; Tong *et al.*, 1999; Dong *et al.*, 2000). Benzene-1,3,5-tricarboxylic acid is one of the most extensively studied ligands because of its versatile coordinating modes and structural robustness (Yaghi *et al.*, 1997; Lin *et al.*, 2007), and new compounds based on the benzene-1,3,5-tricarboxylic acid (H_3btc) ligand are observed continually (Xu *et al.*, 2007; Jiang *et al.*, 2010). However, almost all reported

compounds with H_3btc are two- or three-dimensional structures because it has six O-atom donors. There are almost 50 reports of zinc complexes involving the H_3btc ligand; however, all but five of these (Jo *et al.*, 2005; Du *et al.*, 2006; Plater *et al.*, 2001; Chen *et al.*, 2006; Braverman *et al.*, 2007) are extended structures. In addition, all five discrete structures are mononuclear zinc compounds. We report herein the synthesis and crystal structure of the title zinc H_3btc complex, (I), with a discrete binuclear structure. To the best of our knowledge, no binuclear zinc structure with H_3btc has been reported previously.



The asymmetric unit of (I) consists of one Zn^{II} centre, one Hbtc^{2-} ligand and one bimz molecule. As depicted in Fig. 1, the Zn1 ion is four-coordinated by two carboxylate O atoms [O1 and O3ⁱ; symmetry code: (i) $-x, -y, -z$] from two Hbtc^{2-} ligands and two imidazole N atoms from one chelating 2,2'-bi-1*H*-imidazole (bimz) ligand in a tetrahedral coordination environment. The $[\text{ZnO}_2\text{N}_2]$ tetrahedron is distorted, with the O/N—Zn—O/N bond angles varying from 82.69 (6) to

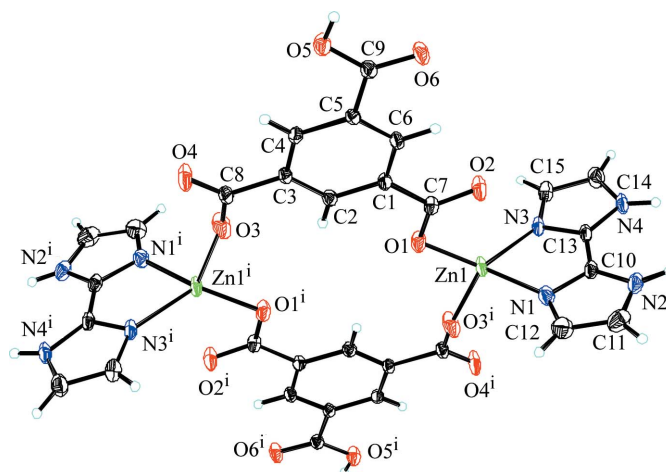


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, -y, -z$.]

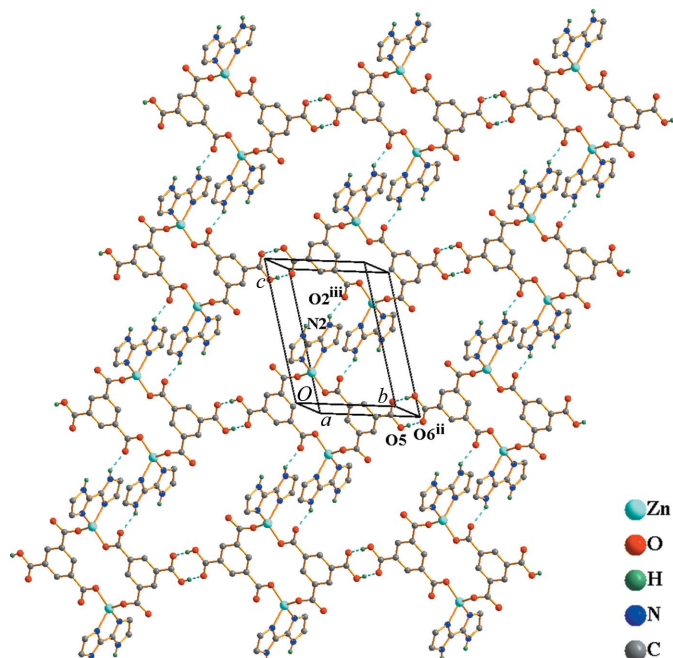


Figure 2
A perspective view of the hydrogen-bonded two-dimensional layer in the crystal structure of (I). Dotted lines between H and O atoms indicate hydrogen bonds. [Symmetry codes: (ii) $-x + 1, -y + 2, -z$; (iii) $x + 1, y, z + 1$.]

130.27 (6) $^\circ$ (Table 1); the narrowest bond angle is associated with the N–Zn–N bond angle, which is due to the restricted bite angle of the bimz ligand. The bond distances involving the Zn1 ion are normal and comparable with the values in related zinc(II) complexes (e.g. Du *et al.*, 2006; Plater *et al.*, 2001). Each Hbtc $^{2-}$ anion bridges two neighbouring Zn II ions through its two monodentate carboxylate groups (Fig. 1). The uncoordinated carboxyl group is protonated for charge balance, as suggested by the strong absorption at 1725 cm $^{-1}$ in the IR spectrum. Two Hbtc $^{2-}$ anions bridge two neighbouring Zn II ions to form a centrosymmetric binuclear structure, as depicted in Fig. 1. The bimz ligands coordinate to Zn II centres in a chelating fashion, precluding the propagation of Zn/Hbtc/Zn linkages to generate a higher-dimensional framework;

however, a three-dimensional structure is achieved *via* hydrogen bonding.

Looking carefully at the crystal packing, it can be seen that the O5–H5 \cdots O6 ii [symmetry code: (ii) $-x + 1, -y + 2, -z$; Table 2] hydrogen bonds give a carboxylic acid inversion-dimer arrangement with an $R_2^2(8)$ motif (Bernstein *et al.*, 1995), which leads to the formation of a one-dimensional chain propagating along the crystallographic *b* axis (Fig. 2). These chains are then linked *via* N–H \cdots O hydrogen bonds involving carboxylate atom O2 and the imidazole H atom on atom N2, again giving an inversion-dimer arrangement, this time of graph-set $R_2^2(16)$ (Fig. 2). These two hydrogen bonds, *viz.* O–H \cdots O and N–H \cdots O, lead to the formation of the two-dimensional network. A second N–H \cdots O hydrogen bond, involving carboxylate atom O4 and the imidazole H atom on atom N4 (Table 2), gives a third inversion-dimer arrangement, also of graph-set $R_2^2(16)$, which links the two-dimensional networks to form a three-dimensional hydrogen-bonded structure (Fig. 3). π – π stacking interactions between inversion-related parallel benzene rings and between inversion-related parallel N1 imidazole rings are arranged in an offset fashion: the centroid–centroid distances are 3.4759 (9) and 3.7985 (13) Å, respectively. Between N1 and N3 imidazole rings, the centroid–centroid distance is 3.7768 (13) Å and the dihedral angle is 3.36 (12) $^\circ$. The three-dimensional nature of the crystal packing is reinforced by the π – π stacking.

As mentioned above, only five zinc compounds with discrete structures have been reported to date, for example, [Zn(H $_2$ btc) $_2$ (tazcyde)]·DMF (tazcyde = 1,4,8,11-tetraazacyclotetradecane), with an octahedrally coordinated Zn II centre (Jo *et al.*, 2005), and [Zn(H $_2$ btc) $_2$ (L) $_2$] [*L* = 4-amino-3,5-bis-(4-pyridinyl)-1,2,4-triazole or 4-(pyridin-4-ylamino)pyridine], which contains a tetrahedrally coordinated Zn II centre (Du *et al.*, 2006; Braverman *et al.*, 2007). All of them contain a second N-containing ligand, which is similar to that in the title compound. While these reported discrete zinc–H $_3$ btc compounds are all mononuclear, the title compound is a discrete dinuclear structure. It should be noted that the combination of a similar chelating ligand, such as 2,2'-bipyridine or pyridine-2-(1-methyl-1*H*-pyrazol-3-yl), with the H $_3$ btc

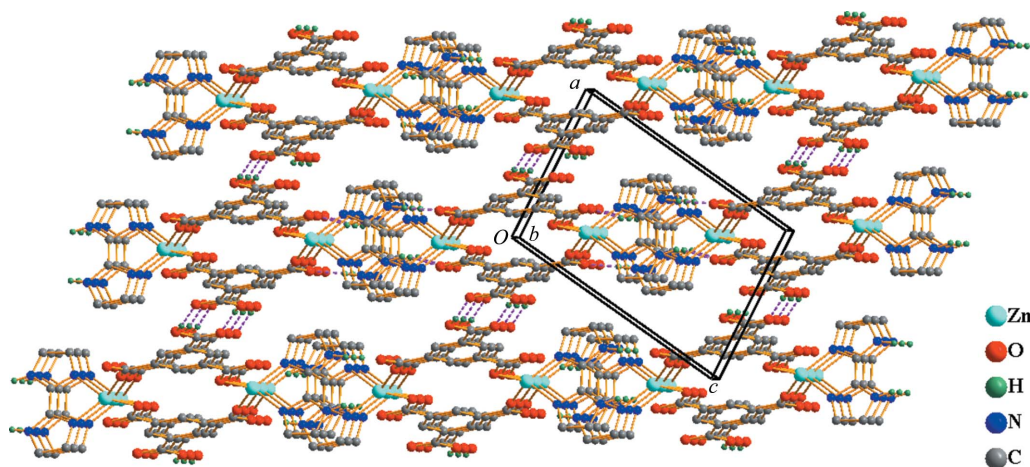


Figure 3
A view, along the *b* axis, of the crystal packing of (I). Dotted lines between H and O atoms indicate hydrogen bonds.

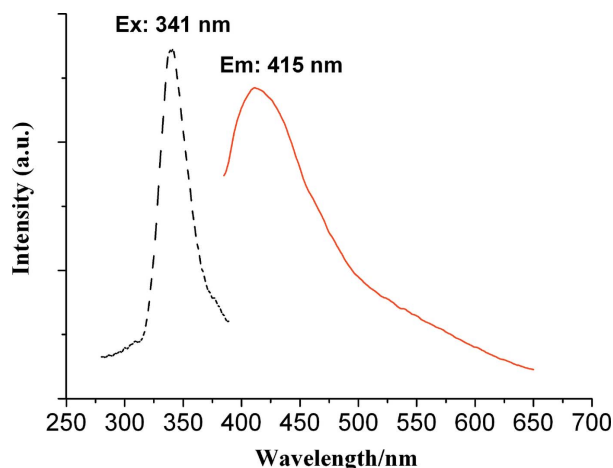


Figure 4

The solid-state photoluminescence spectra of (I) (Ex = excitation and Em = emission).

ligand and Zn^{II} ions produces the mononuclear complex $[\text{Zn}(\text{H}_2\text{btc})_2(\text{L}_2)]$ [L_2 = 1-methyl-3-(pyridin-2-yl)-1*H*-pyrazole or 2,2'-bipyridine; Plater *et al.*, 2001; Chen *et al.*, 2006], which indicates that the structures of the final products are significantly influenced by the ancillary ligands.

The title compound exhibits photoluminescence in the solid state (Fig. 4). Excitation of solid samples at 341 nm at room temperature produces a luminescence peak with a maximum at 415 nm. The emission peak is essentially the same as the photoluminescence signal of the free H_3btc ligand at 408 nm ($\lambda_{\text{ex}} = 334$ nm; Chen *et al.*, 2003). This indicates that the emission band of (I) is a ligand-centred ($\pi^* \rightarrow n$) transition. Compared with the emission band for the free H_3btc ligand, a slight bathochromic shift is observed in (I), which may be related to the coordination of the Zn^{2+} ions to the Hbtc^{2-} dianions.

Experimental

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (89.2 mg, 0.3 mmol), benzene-1,3,5-tricarboxylic acid (63.1 mg, 0.3 mmol) and 2,2'-bi-1*H*-imidazole (40.2 mg, 0.3 mmol) in a 1:1:1 molar ratio in distilled water (14 ml) was introduced into a Parr Teflon-lined stainless steel vessel (25 ml). The vessel was sealed and heated to 413 K. The temperature was held for 4 d and then the mixture was allowed to cool naturally, giving colourless prism-shaped crystals. The colourless crystalline product was filtered off, washed with distilled water and dried at ambient temperature [yield 63%, based on $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$]. Analysis calculated for $\text{C}_{30}\text{H}_{20}\text{N}_8\text{O}_{12}\text{Zn}_2$: C 44.20, H 2.47, N 13.74%; found: C 44.11, H 2.36, N 13.68%. IR (KBr pellet, ν , cm^{-1}): 3435, 1725, 1611, 1567, 1437, 1420, 1374, 1164, 1120, 1084, 1070, 1001, 858, 783, 760, 674, 664, 625, 545, 530.

Crystal data

$[\text{Zn}_2(\text{C}_9\text{H}_4\text{O}_6)_2(\text{C}_6\text{H}_6\text{N}_4)_2]$	$\gamma = 93.861 (1)^\circ$
$M_r = 815.32$	$V = 749.54 (7) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.0458 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.0633 (4) \text{ \AA}$	$\mu = 1.68 \text{ mm}^{-1}$
$c = 12.2332 (7) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 106.526 (1)^\circ$	$0.33 \times 0.27 \times 0.24 \text{ mm}$
$\beta = 97.606 (1)^\circ$	

Table 1
Selected geometric parameters (\AA , $^\circ$).

Zn1—O3 ⁱ	1.9232 (14)	Zn1—N3	2.0343 (14)
Zn1—O1	1.9337 (12)	Zn1—N1	2.0696 (15)
O3 ⁱ —Zn1—O1	99.73 (6)	O3 ⁱ —Zn1—N1	107.73 (7)
O3 ⁱ —Zn1—N3	117.51 (6)	O1—Zn1—N1	117.49 (6)
O1—Zn1—N3	130.27 (6)	N3—Zn1—N1	82.69 (6)

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

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H5 \cdots O6 ⁱⁱ	0.82	1.88	2.6859 (17)	167
N2—H2A \cdots O2 ⁱⁱⁱ	0.86	1.99	2.667 (2)	135
N4—H4A \cdots O4 ^{iv}	0.86	1.82	2.6792 (19)	178

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

Data collection

Bruker APEXII CCD area-detector diffractometer	7095 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3628 independent reflections
$T_{\text{min}} = 0.606$, $T_{\text{max}} = 0.688$	3336 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	235 parameters
$wR(F^2) = 0.068$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
3628 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

O- and N-bound H atoms were located in difference maps and other H atoms were included in calculated positions. All H atoms were treated using a riding-model approximation, with O—H = 0.82 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, and with N—H = 0.86 \AA or C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 2005); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3071). Services for accessing these data are described at the back of the journal.

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