Poly[[(2-phenyl-1*H*-1,3,7,8,-tetraazacyclopenta[*l*]phenanthrene)zinc(II)]-*μ*₃-1,3-benzenedicarboxylato]

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In the title compound, $[Zn(1,3\text{-}BDC)(L)]_n$, where 1,3-BDC is the 1,3-benzenedicarboxylate dianion ($C_8H_4O_4^{2-}$) and L is 2-phenyl-1*H*-1,3,7,8,-tetraazacyclopenta[*l*]phenanthrene ($C_{19}H_{12}N_4$), each Zn^{II} atom is five-coordinated by two N atoms from one L ligand, and three O atoms from three 1,3-BDC anions, in a distorted square-based pyramidal geometry. The Zn^{II} atoms are bridged by the 1,3-BDC ligands to form a double-chain structure. N—H···O hydrogen bonds complete the structure.

Comment

Mixed-ligand coordination polymers constructed from dicarboxylate and heteroaromatic N-donor chelating ligands such as 1,10-phenanthroline (phen) and its derivatives are of special interest (Che, 2006; Che *et al.*, 2006). We report here the synthesis and crystal structure of the title compound, (I), which arose from the combination of zinc cations, 1,3-benzenedicarboxylic acid ($C_8H_6O_4$; 1,3-H₂BDC) and 2-phenyl-1*H*-1,3,7,8,-tetraazacyclopenta[*l*]phenanthrene ($C_{19}H_{12}N_4$; L). The resulting compound, $[Zn(L)(1,3\text{-}BDC)]_n$, is a one-dimensional polymer.

(I)
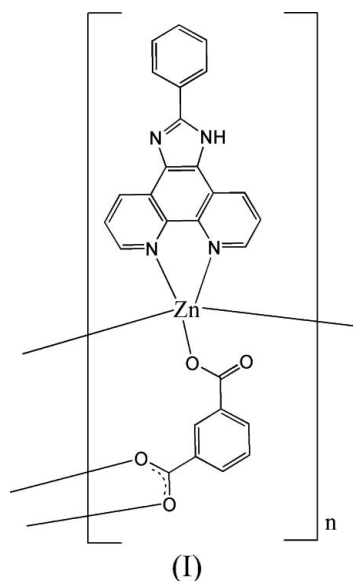
Selected bond lengths and angles are given in Table 1. The Zn^{II} atom in (I) is five-coordinated by two N atoms from a bidentate L ligand, and three O atoms from three 1,3-BDC anions in a distorted square-based pyramidal geometry, where atoms N1, N2, O3[i] and O4[ii] (see Table 1 for symmetry codes) form the basal plane and atom O1 occupies the apical position (Fig. 1). Adjacent Zn^{II} atoms are bridged by two 1,3-BDC ligands through the bidentate (C8) carboxylate groups to form
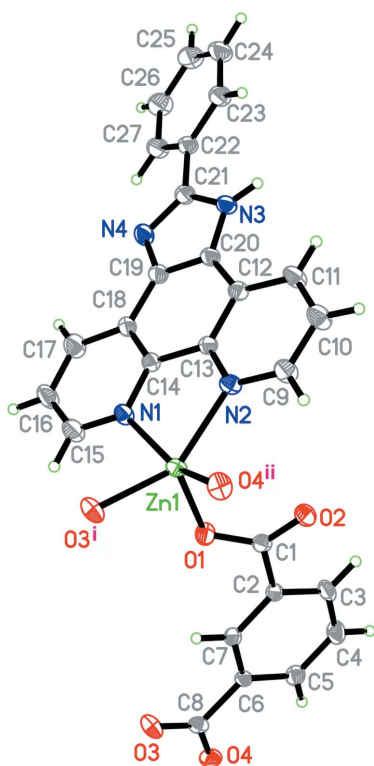
Figure 1
Part of the polymeric structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (arbitrary spheres for the H atoms). [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, -y, 1-z$.]
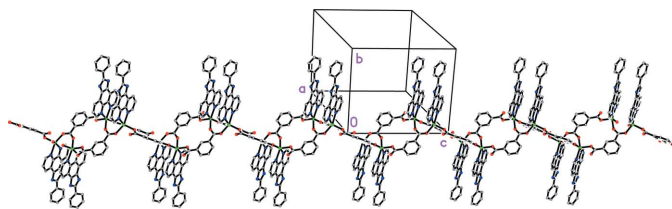

Figure 2
View of the double-chain structure in (I). H atoms have been omitted for clarity.

a dimeric building unit containing a ring of eight atoms. The carboxylate C—O bond lengths suggest that the bonding in the C1/O1/O2 group is localized and that in the C8/O3/O4 group is delocalized.

Within a dimeric unit there exist π–π interactions between the phenanthroline groups of adjacent L ligands, the shortest atom-to-atom distance being 3.562 (3) Å. The dimeric units are linked by the 1,3-BDC ligands through the monodentate (C1) carboxylate groups, generating an interesting double-chain structure propagating in [001] (Fig. 2), containing alternating eight-memberered rings (mentioned above) and 16-memberered rings of atoms. Finally, an N—H⋯O hydrogen bond involving the N atom of L and O2 (the only carboxylate O atom not bonded to Zn) completes the structure of (I) (Table 2).

Experimental

The L ligand was synthesized according to the literature (Steck & Day, 1943). A methanol solution (20 ml) of L (0.5 mmol) was added slowly to an aqueous solution (16 ml) of $ZnCl_2 \cdot 2H_2O$ (0.5 mmol) and 1,3-H_2BDC (1 mmol) with stirring at 358 K. The resulting solution was filtered, the filtrate was allowed to stand in air at room temperature for one week, and pale-yellow crystals of (I) were obtained (yield 77% based on Zn).

Crystal data

$[Zn(C_8H_4O_4)(C_{19}H_{12}N_4)]$	$Z = 8$
$M_r = 525.81$	$D_x = 1.576$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.846$ (3) Å	$\mu = 1.15$ mm^{-1}
$b = 15.932$ (3) Å	$T = 292$ (2) K
$c = 17.398$ (4) Å	Block, yellow
$\beta = 108.38$ (3)°	$0.33 \times 0.31 \times 0.29$ mm
$V = 4431.3$ (17) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	20760 measured reflections
ω scans	5026 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	3482 reflections with $I > 2\sigma(I)$
$T_{min} = 0.691$, $T_{max} = 0.719$	$R_{int} = 0.065$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 4.2485P]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
5026 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
325 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—O2	1.232 (3)	Zn1—N2	2.136 (2)
C1—O1	1.271 (3)	Zn1—O1	1.9513 (18)
C8—O3	1.247 (3)	Zn1—O3^i	2.0277 (19)
C8—O4	1.256 (3)	Zn1—O4^{iii}	2.0067 (19)
Zn1—N1	2.174 (2)		
O1—Zn1—O4^{iii}	104.22 (8)	O3^i—Zn1—N2	149.30 (9)
O1—Zn1—O3^i	95.25 (8)	O1—Zn1—N1	99.76 (9)
O4^{iii}—Zn1—O3^i	95.62 (9)	O4^{iii}—Zn1—N1	155.69 (9)
O1—Zn1—N2	112.15 (9)	O3^i—Zn1—N1	86.00 (9)
O4^{iii}—Zn1—N2	90.94 (9)	N2—Zn1—N1	76.25 (8)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3⋯O2^{iv}	0.86	1.90	2.756 (3)	170

Symmetry code: (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

All H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(carrier).

Data collection, cell refinement and data reduction: *PROCESS-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); publication material: *SHELXL97*.

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