

Poly[[triazquazinc(II)]- μ_3 -4-nitro-
phthalato- κ^3 O¹:O²:O^{2'}]

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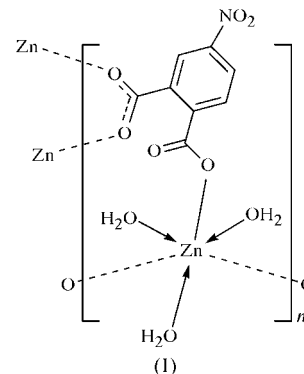
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In the title complex, $[\text{Zn}(\text{C}_8\text{H}_3\text{NO}_6)(\text{H}_2\text{O})_3]_n$, the two carboxylate groups of the 4-nitrophthalate dianion ligands have monodentate and 1,3-bridging modes, and Zn atoms are interconnected by three O atoms from the two carboxylate groups into a zigzag one-dimensional chain along the *b*-axis direction. The Zn atom shows distorted octahedral coordination as it is bonded to three O atoms from carboxylate groups of three 4-nitrophthalate ligands and to three O atoms of three non-equivalent coordinated water molecules. The one-dimensional chains are aggregated into two-dimensional layers through inter-chain hydrogen bonding. The whole three-dimensional structure is further maintained and stabilized by inter-layer hydrogen bonds.

Comment

Aromatic dicarboxylate ligands, such as phthalic acid (H_2phth), have been used in the construction of polymeric metal complexes because they can act in bis-monodentate, bis-bidentate or a combination of coordination modes to form short bridges *via* one carboxylate end or long bridges *via* the benzene ring, leading a great variety of structures. For example, as a bis-monodentate ligand, the phthalate dianion is known to bond to metals, leading to a one-dimensional chain complex, *e.g.* in $\{[\text{Cu}(\text{phth})(1,10\text{-phenanthroline})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (Ye, Sun *et al.*, 2005), $[\text{Mn}(\text{phth})(\text{pyrazine})(\text{H}_2\text{O})_2]_n$ (Ma *et al.*, 2004) and $[\text{Zn}(\text{phth})(1\text{-methylimidazole})_2]_n$ (Baca *et al.*, 2004). On the other hand, in bis-bidentate and combined modes of coordination, the phthalate dianion can be found chelating through the two carboxylate O atoms, as in $[\text{Co}(\text{phth})(2,2'\text{-biimidazole})_2]_n$ (Ye, Ding *et al.*, 2005), $\{[\text{Ni}(\text{phth})(4,4'\text{-bipyridine})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}_n$ (Yang *et al.*, 2003), $[(\text{bpy})_2\text{Zn}(\text{phth})\text{H}(\text{phth})\text{Zn}(\text{bpy})_2](\text{Hphth}) \cdot \text{H}_2\text{phth} \cdot 2\text{H}_2\text{O}$ (bpy is 2,2'-bipyridine) (Baca *et al.*, 2003) and $\{[\text{Cu}_2(\text{phth})_2(\text{imidazole})_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (Fu *et al.*, 2006). However, in spite of this wealth of possibilities, only a few complexes of metal–nitrophthalate systems have been reported to date. We have used

the 4-nitrophthalate dianion as a ligand and obtained the title novel six-coordinate 4-nitrophthalate–zinc complex, (I). We describe here the structure of this one-dimensional metal–nitrophthalate coordination polymer, in which O–H...O inter-chain bonding leads to a three-dimensional supra-molecular network.



The asymmetric unit in (I) comprises one Zn atom, one complete 4-nitrophthalate dianion and three non-equivalent water molecules, and is shown in Fig. 1 in a symmetry-expanded view, which displays the full coordination of the Zn atom. Selected geometric parameters are given in Table 1.

The Zn atom is octahedrally coordinated by six O-atom donors (Fig. 1). The four equatorial coordination sites are occupied by two coordinated water molecules (O7 and O8)

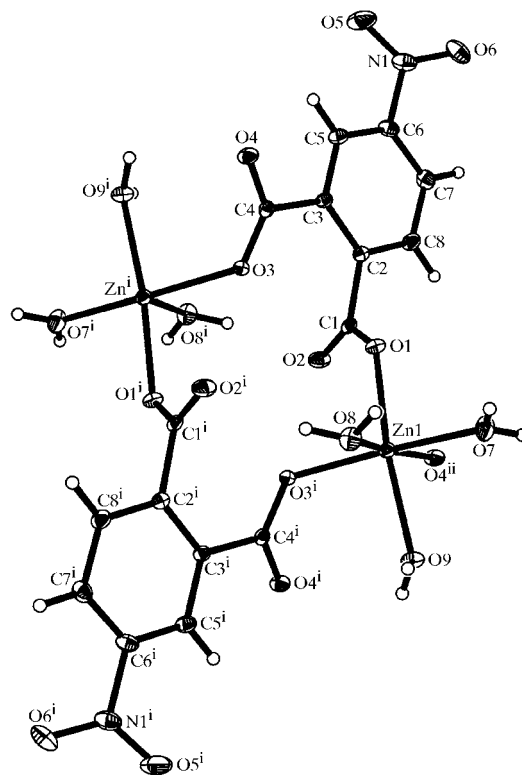


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination polyhedra for the Zn atoms; displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, y - 1, z$.]

and two O atoms (O4ⁱⁱ and O3ⁱ) from two 4-nitrophthalate ligands. Atom O1 and the third coordinated water molecule (O9) occupy the apical sites of the octahedron. The Zn—O(water) distances range from 2.0976 (18) to 2.2104 (16) Å and the Zn—O(nitrophthalate) distances cover the range 2.0335 (16)–2.0822 (15) Å. The Zn—O(water) bonds are slightly longer than those in [Zn(2-nitroterephthalate)·(H₂O)₃]·H₂O (Guo & Guo, 2007), where they range from 2.051 (2) to 2.090 (2) Å. The *cis*-O—Zn—O angles in (I) range

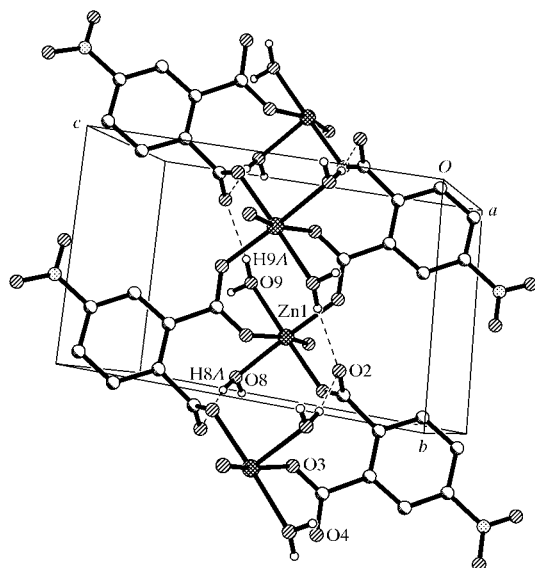


Figure 2
A view of the packing of (I) down the *a* axis, showing the one-dimensional chain along the *b*-axis direction for Zn atoms and the hydrogen-bonding interactions within the chain as dashed lines.

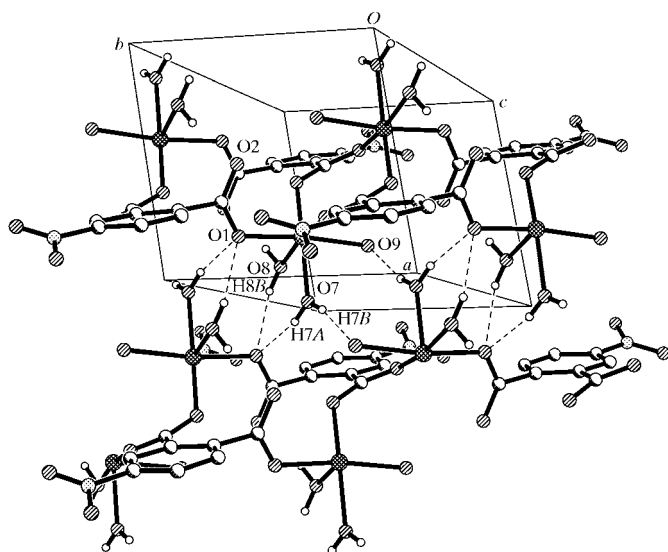


Figure 3
The packing of (I), viewed down the *c* axis, showing the O7—H7A···O1^v, O7—H7B···O9^{vi} and O8—H8B···O1^v hydrogen-bond interactions parallel to the *ab* plane as dashed lines. Symmetry codes are as given in Table 2.

from 81.93 (7) to 106.52 (7)°, and the *trans*-O—Zn—O angles cover the range 164.03 (7)–172.87 (6)°. Thus, the structure of the title complex shows the Zn atom center to be in a distorted octahedral environment with a facial disposition of water molecules.

In the present structure, monodentate, bidentate 1,3-bridging and 1,6-bridging modes *via* the benzene ring are present (Fig. 2). Atom O1 has a monodentate mode, and atoms O3 and O4 have both a monodentate mode and a bidentate 1,3-bridging mode of connection with two Zn atoms. The Zn atoms are interconnected by three O atoms from the two carboxylate groups of the 4-nitrophthalate dianion into a zigzag one-dimensional chain along the *b*-axis direction. In the chain, atoms O1 and O3 adopt a 1,6-bridging bonding mode *via* the benzene ring to connect with two Zn atoms. In this way, two 4-nitrophthalate dianions interconnect with Zn atoms into two different rings, *viz.* 14-membered and eight-membered, with the 4-nitrophthalate anions arranged alternately along the infinite one-dimensional chains (Fig. 2). This results in Zn···Zn separations within the chains of 5.686 (1) and 4.176 (6) Å. The mean planes of the O1/C1/O2 carboxylate group and the benzene ring make a dihedral angle of 80.0 (3)°, and the corresponding value for the O3/C4/O4 carboxylate group is 19.1 (3)°; the C—O bond lengths (O1—C1 and O2—C1) of the monodentate carboxylate group are 1.276 (3) and 1.240 (3) Å, respectively, and the C—O bond lengths (O3—C4 and O4—C4) of the 1,3-bridging carboxylate group are 1.259 (3) and 1.252 (3) Å, respectively. This indicates that the mesomeric effect for the 1,3-bridging carboxylate group is somewhat greater than that of the monodentate carboxylate group.

The three water molecules and the nitro group (O5/N1/O6) are engaged in distinct hydrogen-bond interactions (Table 2). In the *bc* plane, neighboring chains are linked *via* weak O9—H9B···O5ⁱⁱⁱ hydrogen-bond interactions. In this way, a complete two-dimensional layer is formed parallel to the *bc* plane. The noncoordinated O2 atom is involved in two hydrogen bonds, *viz.* O8—H8A···O2ⁱ and O9—H9A···O2^{iv}; these play an important role in the propagation of the one-dimensional chain structure, because they participate in the formation of two 12-membered hydrogen-bonded rings [*R*₂²(12) graph sets; Bernstein *et al.*, 1995] (Fig. 2). This also results in the aryl rings of the 4-nitrophthalate ligands stacking in an offset fashion along the *a*-axis direction. In the crystallographic *ab* plane, O7—H7A···O1^v, O7—H7B···O9^{vi} and O8—H8B···O1^v hydrogen bonds link neighboring chains together *via* three different *R*₂²(8) rings and complete a two-dimensional layer parallel to the *ab* plane (Fig. 3). Thus, the three-dimensional connectivity of the structure is achieved.

Experimental

Zinc oxide (0.25 g, 3 mmol) was added to a stirred solution of 4-nitrophthalic acid (0.53 g, 2.5 mmol) in boiling water (20.0 ml) over a period of 20 min. After filtration, slow evaporation of the solvent over a period of two weeks at room temperature provided colorless block-shaped crystals of (I).

Crystal data

[Zn(C₈H₃NO₆)(H₂O)₃]
M_r = 328.53
 Triclinic, *P* $\bar{1}$
a = 7.0758 (12) Å
b = 7.2954 (12) Å
c = 10.8601 (18) Å
 α = 97.317 (2)°
 β = 91.591 (3)°
 γ = 100.621 (3)°
V = 545.76 (16) Å³
Z = 2
 Mo *K* α radiation
 μ = 2.30 mm⁻¹
T = 294 (2) K
 0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.721, *T_{max}* = 0.802
 2827 measured reflections
 1910 independent reflections
 1751 reflections with *I* > 2σ(*I*)
R_{int} = 0.014

Refinement

R[*F*² > 2σ(*F*²)] = 0.023
wR(*F*²) = 0.061
S = 1.10
 1910 reflections
 172 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}}$ = 0.36 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.30 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------------------------------|-------------|--------------------------|-------------|
| Zn1—O3 ⁱ | 2.0561 (16) | Zn1—O9 | 2.2104 (16) |
| Zn1—O4 ⁱⁱ | 2.0335 (16) | O1—C1 | 1.276 (3) |
| Zn1—O1 | 2.0822 (15) | O2—C1 | 1.240 (3) |
| Zn1—O7 | 2.0976 (18) | O3—C4 | 1.259 (3) |
| Zn1—O8 | 2.1595 (16) | O4—C4 | 1.252 (3) |
| O4 ⁱⁱ —Zn1—O3 ⁱ | 106.52 (7) | O7—Zn1—O8 | 81.93 (7) |
| O4 ⁱⁱ —Zn1—O1 | 88.65 (6) | O4 ⁱⁱ —Zn1—O9 | 91.12 (6) |
| O3 ⁱ —Zn1—O1 | 97.36 (6) | O3 ⁱ —Zn1—O9 | 89.54 (6) |
| O4 ⁱⁱ —Zn1—O7 | 88.42 (7) | O1—Zn1—O9 | 172.87 (6) |
| O3 ⁱ —Zn1—O7 | 164.03 (7) | O7—Zn1—O9 | 84.46 (7) |
| O1—Zn1—O7 | 88.41 (7) | O8—Zn1—O9 | 87.34 (7) |
| O4 ⁱⁱ —Zn1—O8 | 170.33 (7) | O2—C1—O1 | 126.5 (2) |
| O3 ⁱ —Zn1—O8 | 83.02 (7) | O4—C4—O3 | 126.6 (2) |
| O1—Zn1—O8 | 91.70 (7) | | |

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

All water H atoms were found in difference Fourier maps. However, during refinement, they were fixed at O—H distances of 0.85–0.86 Å, with *U*_{iso}(H) = 1.2*U*_{eq}(O). The H atoms of CH groups were treated as riding [C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O9—H9B...O5 ⁱⁱⁱ | 0.85 | 2.38 | 3.027 (3) | 134 |
| O8—H8A...O2 ⁱ | 0.86 | 2.06 | 2.904 (3) | 170 |
| O9—H9A...O2 ^{iv} | 0.86 | 1.98 | 2.794 (2) | 158 |
| O7—H7A...O1 ^v | 0.85 | 1.97 | 2.804 (2) | 166 |
| O7—H7B...O9 ^{vi} | 0.85 | 1.99 | 2.817 (2) | 164 |
| O8—H8B...O1 ^v | 0.86 | 2.24 | 3.043 (2) | 156 |

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

structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: AV3117). Services for accessing these data are described at the back of the journal.

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