metal-organic compounds

catena-Poly[[[triaquazinc(II)]-*μ*-2-nitroterephthalato-κO^1:$\kappa^2 O^4,O^{4'}$] monohydrate]

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The title complex, $\{[Zn(C_8H_3NO_6)(H_2O)_3]\cdot H_2O\}_n$, has a one-dimensional chain structure. The two carboxylate groups of the dianionic 2-nitroterephthalate ligand adopt mono- and bidentate chelating modes. The Zn atom shows distorted octahedral coordination, bonded to three O atoms from two carboxylate groups and 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 stabilized by inter-layer hydrogen bonds.

Comment

Metal–organic networks or coordination polymers have attracted much attention recently in the area of topology design and for their potential applications in adsorption, catalysis, luminescence, magnetism, *etc.* (Blatov *et al.*, 2004; James, 2003; Janiak, 2003). The use of dicarboxylate ligands as small building blocks to generate metal–organic frameworks of different dimensionalities may lead to interesting network architectures (Rodríguez-Martín *et al.*, 2002; Guo & Zhao, 2006). In particular, aromatic dicarboxylate ligands such as terephthalate (benzene-1,4-dicarboxylate, bdc) have been used in the architecture of polymeric metal complexes because

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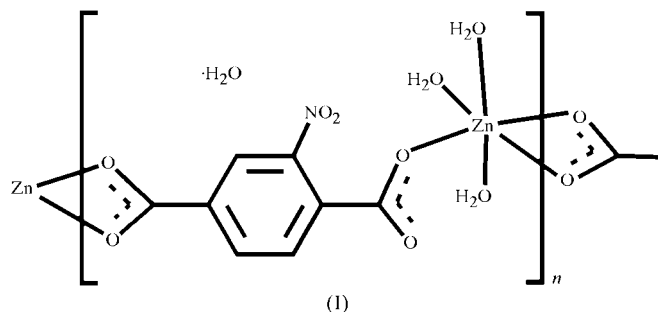
they can adopt bis-monodentate, bis-bidentate and combined modes of coordination to form short bridges *via* one carboxylate end, or long bridges *via* the aromatic ring, and this can lead to a great variety of structures. For example, as a bis-monodentate ligand, the terephthalate dianion is known to bond to metals to give one-dimensional chain complexes, *e.g.* in $[Cu(bdc)(N\text{-}MeIm)_2]_n$ (where *N*-MeIm is *N*-methylimidazole) (Liu *et al.*, 2005), $[Zn(bdc)(H_2O)_2]_n$ (Ding *et al.*, 2003) and $\{[Co(bdc)(4\text{-}picoline)_2(H_2O)_2](4\text{-}picoline)\}_n$ (Groeneman *et al.*, 1999). On the other hand, in its bis-bidentate and combined modes of coordination, the terephthalate dianion can be found to chelate through the two carboxylate O atoms, as in $[Cr(OH)(bdc)]_{4n}[HO_2C{-}C_6H_4{-}CO_2H]_{3n}$ (Millange *et al.*, 2002), $[Cu(L)(bdc)]_n$ [*L* is *N*-(2-aminoethyl)-3-amino-1-propanol] (Mukherjee *et al.*, 2004) and $[Ni(bdc)(2,2'\text{-}bipy)(H_2O)_2]_n$ (2,2'-bipy is 2,2'-bipyridine) (Go *et al.*, 2004). However, in spite of this wealth of possibilities, only a few complexes of metal–nitroterephthalate systems have been reported to date. We have used the 2-nitroterephthalate dianion as a ligand, and have obtained the title novel six-coordinate 2-nitroterephthalate–zinc complex, (I). We describe here the structure of this one-dimensional metal–nitroterephthalate coordination polymer, with strong O—H⋯O inter-chain bonding leading to a three-dimensional supramolecular network.
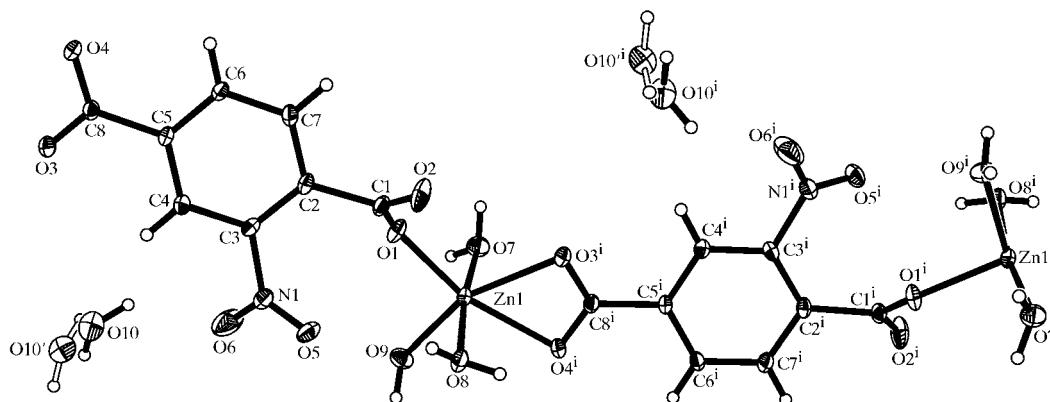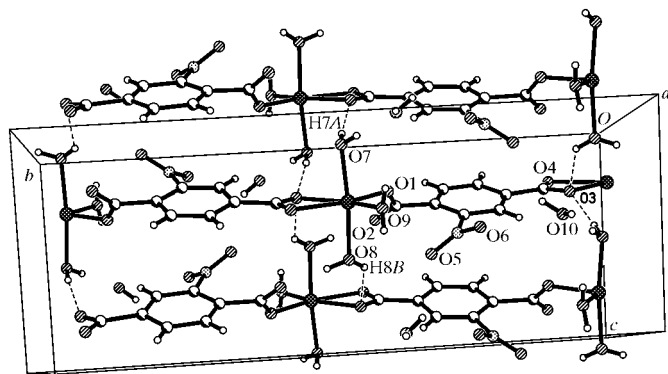

Figure 1
The structure of (I), showing the atom-numbering scheme and the coordination polyhedra for the Zn atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbirtrary radii. A disordered water molecule is shown. [Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.]

The asymmetric unit in the structure of (I) comprises one Zn atom, one complete 2-nitroterephthalate dianion and four non-equivalent water molecules, and 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 of (I) is surrounded by an O_6 donor set with octahedral geometry. The four equatorial sites are occupied by three O atoms from a monodentate carboxylate group (O1) and a bidentate carboxylate group [O3^i and O4^i; symmetry code: (i) $-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$], and by one coordinated water molecule, O9. Atoms O7 and O8 from two other water molecules occupy two of the opposing apices of the octahedron. The Zn—O(water) distances range from 2.051 (2) to 2.090 (2) Å and the Zn—O(2-nitroterephthalate) distances are in the range 1.987 (2)–2.253 (2) Å. Of these Zn—O distances, Zn—O3^i and Zn—O4^i are the longest. The cis-O—Zn—O angles range from 85.32 (8) to 105.49 (9)°, except for O3^i—Zn1—O4^i, which is 58.80 (8)°. The trans-O—Zn—O angles span the range 156.60 (9)–172.19 (8)°. Thus, the coordination octahedron around the Zn atom is significantly distorted.

In the present structure, the versatility of the dianionic 2-nitroterephthalate ligand can be clearly seen. Mono- and bidentate chelating and bridging bonding modes are present. Atom O1 of the O1/C1/O2 carboxylate group has a monodentate mode, while atoms O3 and O4 of the O3/C8/O4 carboxylate group adopt a bidentate 1,2-chelating mode to the Zn atom. These adopt a bridging mode via the aromatic ring to connect two Zn atoms. The O—C—O angle for the monodentate carboxylate group (O1/C1/O2) is 127.5 (3)°, notably larger than the value of 120.8 (3)° for the chelating carboxylate group. The two C—O bond distances (O1—C1 and O2—C1) of the monodentate carboxylate group are 1.267 (4) and 1.232 (4) Å, respectively, while the two C—O bond distances (O3—C8 and O4—C8) of the chelating carboxylate group are 1.262 (4) and 1.259 (4) Å, respectively. This indicates that the mesomeric effect for the chelating carboxylate group is greater than that of the monodentate carboxylate group.

In the crystallographic c direction, perpendicular to the direction of chain propagation, neighbouring chains are linked together via O8—H8B···O3^{ii} (part of a bifurcated hydrogen bond) and O7—H7A···O3^{iii} hydrogen-bond interactions (symmetry codes and geometric details are given in Table 2). This results in the Zn atoms stacking in a zigzag fashion along the c direction and the aryl rings of the 2-nitroterephthalate ligands stacking along the c direction, ca 3.93 Å apart. In this way, a two-dimensional layer is formed parallel to the bc plane (Fig. 2). Supramolecular connectivity within this layer is further enhanced by hydrogen bonds involving the uncoordinated water molecules (Table 2).

The three coordinated water molecules, a disordered water molecule and the nitro group (O5/N1/O6) also engage in hydrogen bonds (Table 2), which influence the conformation

(a)

(b)
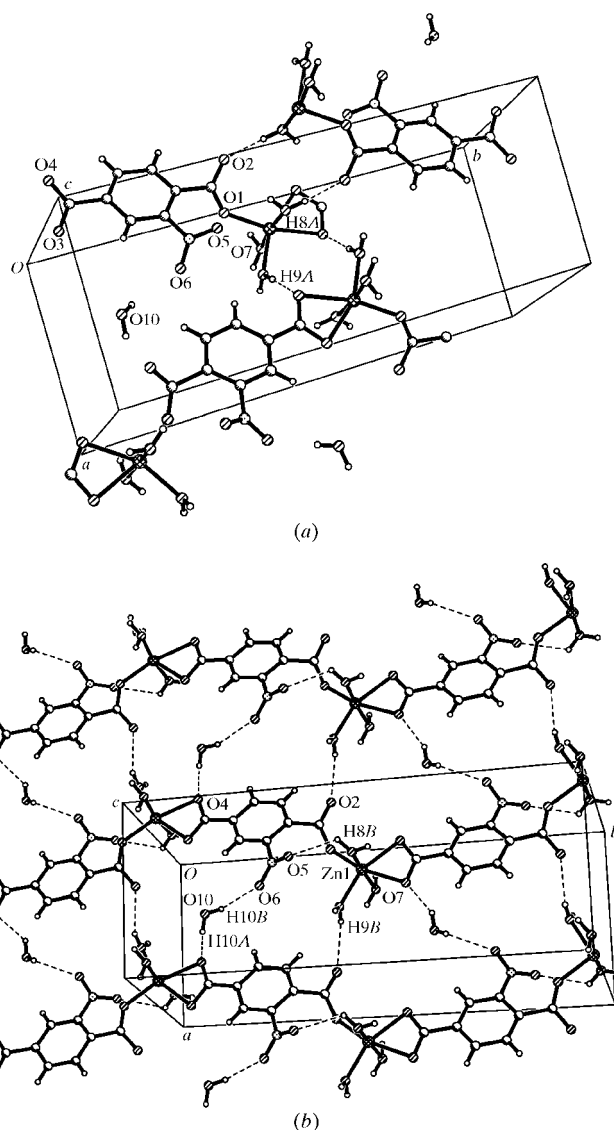
Figure 3
Packing diagrams for (I), viewed down the c axis, showing the hydrogen-bonding interactions (dashed lines) in the direction of the ab plane for (a) the O8—H8A···O2 and O9—H9A···O4 hydrogen bonds, and (b) the hydrogen bonds involving O9—H9B···O2, O8—H8B···O5, O10—H10B···O6, O10—H10A···O4, etc. The minor disorder component has been omitted.

Figure 2
The packing of (I), showing the hydrogen-bond interactions (dashed lines) in the direction of the bc plane, viewed down the a axis. The minor disorder component has been omitted.

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of the polymer. The strong hydrogen bond O8—H8A···O2^v plays an important role (Brown, 1976) in the aggregation of the one-dimensional polymer through the formation of a 12-membered hydrogen-bonded $R_2^2(12)$ ring (Bernstein *et al.*, 1995) between chains (Fig. 3*a*). Furthermore, the hydrogen bond O9—H9A···O4^{vi} links each chain to its neighbour *via* an $R_2^2(8)$ grouping (Fig. 3*a*). The resulting supramolecular aggregation yields a zigzag stack of Zn atoms along the *a* direction. Also in the *a* direction, perpendicular to the direction of chain propagation, O9—H9B···O2^{iv} hydrogen bonds link neighbouring chains together and complete a two-dimensional layer parallel to the crystallographic *ab* plane (Fig. 3*b*). Other hydrogen bonds, such as O8—H8B···O5, O10—H10B···O6, O10—H10A···O4^{iv} and O10$'$—H11A···O4^{iv}, involving free water molecules, further enhance the aggregation in this layer.

Experimental

The addition of anhydrous sodium carbonate (0.43 g, 4 mmol) to a stirred solution of zinc nitrate hexahydrate (1.2 g, 4 mmol) in water (30 ml) produced a white precipitate, which was filtered off and washed with distilled water. The precipitate was subsequently added to a stirred solution of 2-nitroterephthalic acid (0.53 g, 2.5 mmol) in boiling water (20.0 ml) over a period of 5 min. After filtration, slow evaporation over a period of two weeks at room temperature yielded colourless needle-like crystals of (I).

Crystal data

[Zn(C8H3NO6)(H2O)3]·H2O	V = 1216.6 (4) Å^3
M_r = 346.55	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 7.8862 (12) Å	μ = 2.07 mm^{-1}
b = 20.501 (5) Å	T = 294 (2) K
c = 7.7119 (13) Å	0.20 × 0.12 × 0.08 mm
β = 102.633 (16)°	

Data collection

Bruker SMART CCD area-detector diffractometer	6933 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2489 independent reflections
	2153 reflections with $I > 2\sigma(I)$
T_{min} = 0.743, T_{max} = 0.845	R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	36 restraints
$wR(F^2)$ = 0.081	H-atom parameters constrained
S = 1.12	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
2489 reflections	$\Delta\rho_{min}$ = −0.59 e Å^{-3}
191 parameters	

All water H atoms were found in difference Fourier maps and were fixed during refinement at O—H distances of 0.85 Å, with U_{iso}(H) = 1.2U_{eq}(O). The noncoordinated water molecule is disordered over at least two sites; the refined occupancy factors for atoms O10 and O10$'$ were 0.740 (2) and 0.260 (2). The H atoms of the CH groups were treated as riding, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve and refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

Zn1—O3^i	2.211 (2)	Zn1—O7	2.090 (2)
Zn1—O4^i	2.253 (2)	O1—C1	1.267 (4)
Zn1—O1	1.987 (2)	O2—C1	1.232 (4)
Zn1—O9	2.051 (2)	O3—C8	1.262 (4)
Zn1—O8	2.089 (2)	O4—C8	1.259 (4)
O1—Zn1—O9	97.77 (9)	O9—Zn1—O4^i	97.85 (8)
O1—Zn1—O8	95.59 (8)	O8—Zn1—O4^i	87.20 (7)
O9—Zn1—O8	89.37 (9)	O7—Zn1—O4^i	85.32 (8)
O1—Zn1—O7	92.22 (9)	O3^i—Zn1—O4^i	58.80 (8)
O9—Zn1—O7	89.44 (9)	O8—Zn1—O7	172.19 (8)
O1—Zn1—O3^i	105.49 (9)	O9—Zn1—O3^i	156.60 (9)
O8—Zn1—O3^i	90.80 (8)	O1—Zn1—O4^i	164.16 (9)
O7—Zn1—O3^i	87.24 (8)	O2—C1—O1	127.5 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8B···O3^{ii}	0.85	2.31	2.966 (3)	135
O7—H7A···O3^{iii}	0.85	1.95	2.783 (3)	164
O7—H7B···O10^{iii}	0.85	1.86	2.699 (5)	169
O9—H9B···O10^{iii}	0.85	2.22	2.977 (14)	149
O7—H7B···O10$'^{iii}$	0.85	1.75	2.584 (11)	167
O10—H10B···O6	0.85	2.38	2.957 (9)	126
O8—H8B···O5	0.85	2.47	2.974 (3)	119
O9—H9B···O2^{iv}	0.85	2.44	2.987 (3)	123
O10—H10A···O4^{iv}	0.85	2.38	2.858 (5)	116
O10$'$—H11A···O4^{iv}	0.85	2.28	2.855 (11)	125
O8—H8A···O2^v	0.85	1.82	2.672 (3)	177
O9—H9A···O4^{vi}	0.85	1.93	2.778 (3)	170
O10$'$—H11B···O7^{vii}	0.85	2.50	2.94 (3)	113

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3096). Services for accessing these data are described at the back of the journal.

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