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# Poly[[[bis(*N*,*N*′-dimethylformamide)zinc(II)]-$\mu_3$-5-hydroxybenzene-1,3-dicarboxylato] toluene solvate]

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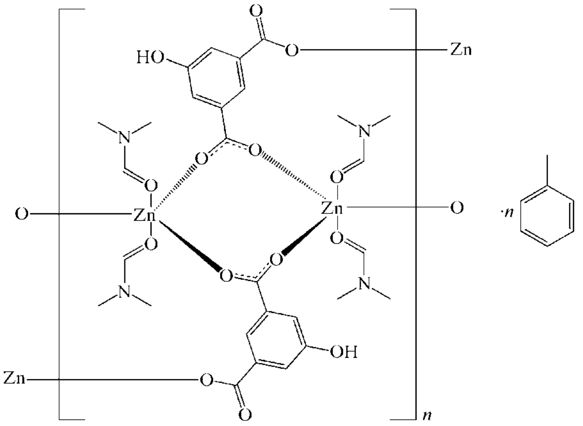
The title compound, $\{[\mathrm{Zn}(\mathrm{C_8H_4O_5})(\mathrm{C_3H_7NO})_2]\cdot0.5\mathrm{C_7H_8}\}_n$, is a one-dimensional coordination polymer in which the Zn atoms are linked by bridging 5-hydroxybenzene-1,3-dicarboxylate ligands. These polymeric chains form two-dimensional sheets *via* interchain hydrogen bonds, and these sheets, in turn, are stacked tightly with solvent toluene molecules in the interlayer space. The *N*,*N*′-dimethylformamide ligands, coordinated axially to the Zn atoms, form van der Waals contacts with ligands in neighboring sheets, and enclose the guest molecules.

## Comment

Metal–organic frameworks (MOFs) are crystalline extended structures that are self-assembled from transition metal ions and bridging organic ligands (Rowsell & Yaghi, 2004). As they have potential applications in gas storage, separation, catalysis, optoelectronics and sensors (Evans & Lin, 2001; Kitagawa *et al.*, 2004), research interest has been increasingly directed at producing new desired structural types of MOFs (Yaghi *et al.*, 2003). Among known MOFs, those with Zn as metal nodes and aromatic carboxylate groups as bridging ligands have been studied extensively (Kim *et al.*, 2001; Eddaoudi *et al.*, 2000). This is because Zn has the ability to form well defined metal clusters, such as paddle-wheel, trinuclear and basic zinc acetate units, under specific reaction conditions. Once the reaction conditions for forming the target Zn clusters, called inorganic secondary building units, are established, it is possible to predict the structural types of the resulting MOFs when they are combined with suitable organic building blocks (Eddaoudi *et al.*, 2002; Chun *et al.*, 2005). Nevertheless, new assembly rules are still to be discovered for the building blocks for the design and synthesis of MOFs that will be useful for certain applications.

One of the design strategies of MOFs is utilizing both the coordination and the hydrogen-bonding properties of the building blocks to produce extended framework structures (Wang *et al.*, 2006; Du *et al.*, 2005; Cui *et al.*, 2003; Noveron *et al.*, 2002; MacDonald *et al.*, 2000). For this purpose, we have attempted to prepare new MOFs by using zinc(II) ions and 5-hydroxybenzene-1,3-dicarboxylate, of which the hydroxy group has the potential to form hydrogen bonds between the frameworks. Although there are many examples using the ligand with Zn for framework construction, most cases contain secondary organic ligands such as bipyridyls (Cao *et al.*, 2004; Plater *et al.*, 20001).



(I)

We report here the crystal structure of the title compound, (I), which contains Zn–organic chains that interact with neighboring chains *via* hydrogen bonds between the peripheral hydroxy groups and uncoordinated O atoms of the

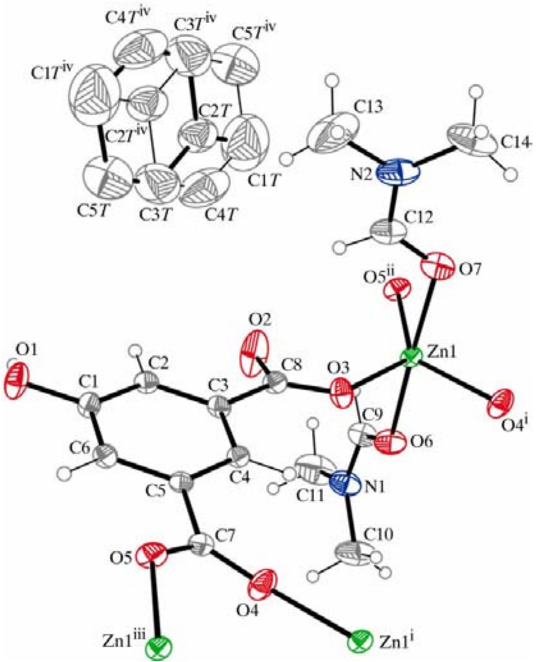


**Figure 1**
A fragment of the polymeric structure and the toluene solvent molecule, shown with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Toluene is disordered over two sites with equal probabilities. $C1T$ and $C1T^{\mathrm{iv}}$ are assigned as methyl C atoms in the fused toluene models. H atoms of the disordered toluene molecule have been omitted for clarity. [Symmetry codes: (i) $-x + 1$ , $-y + 1$, $-z + 1$; (ii) $x$, $y + 1$, $z$; (iii) $x$, $y - 1$, $z$; (iv) $-x + 2$, $-y + 1$, $-z + 2$.]

carboxylate groups. The Zn atoms have trigonal–bipyramidal coordination geometry, with two axial dimethylformamide O atoms (O6 and O7) and three equatorial carboxylate O atoms (O3, O4 and O5), as shown in Fig. 1. The distances and angles related to Zn (listed in Table 1) match well with those of similar coordination complexes (Evans *et al.*, 2000; Grewe *et al.*, 1982).

Toluene, the included solvent molecule, sits on an inversion center and is disordered over two sites. Of the two carboxylate groups of the organic linker, one links two Zn atoms in a bis-monodentate fashion *via* atoms O4 and O5, and the other is coordinated to the next Zn atom through one of the carboxylate O atoms, O3. The resulting one-dimensional ladder-like chain running along the *b* axis and parallel to the *bc* plane is depicted in Fig. 2. The remaining uncoordinated O atom of the carboxylate group, O2, is engaged in a hydrogen bond with the hydroxy group of a neighboring metal-organic chain (Table 2). These hydrogen bonds between peripheral hydroxy groups and neighboring carboxylate groups link the one-dimensional chains to form a layer.

The chains are stacked along the *a* axis, with the protruding dimethylformamide ligands arranged in a herringbone fashion and forming van der Waals contacts, as shown in Fig. 3(*a*). This packing of the chains leaves no voids. However, between these stacks there is room for guest molecules, the toluene molecules being surrounded by six dimethylformamide molecules, as shown in Fig. 3(*b*). Therefore, the title compound has chains formed by coordination bonds between carboxylate groups and Zn atoms; these chains in turn form tight stacks along the *a* axis and hydrogen bonds to neighboring stacks, between which are pores for the guest molecules.

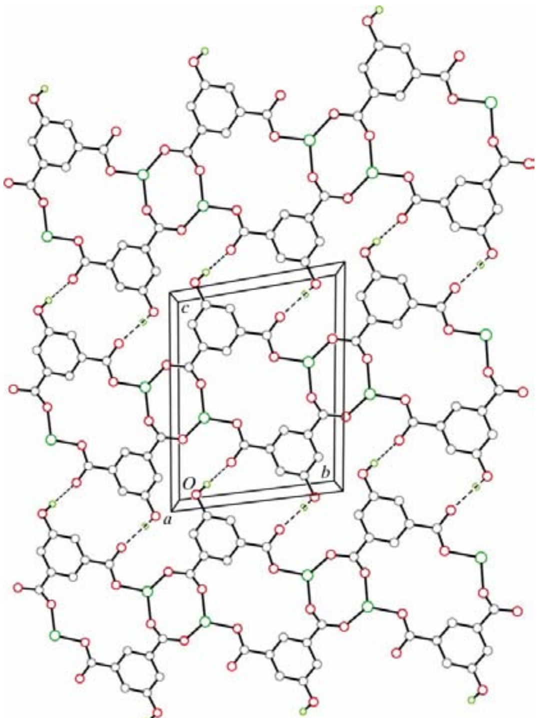
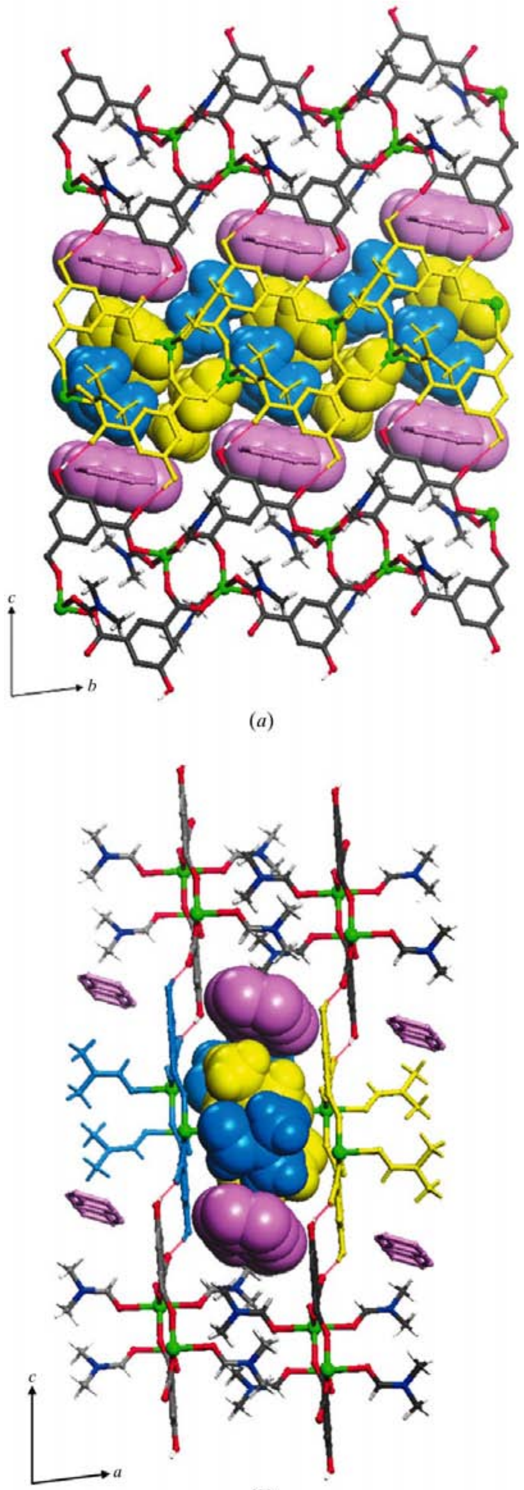


**Figure 2**
A ball-and-stick representation of the chains formed *via* hydrogen bonding (dotted lines). Atoms O1 act as donors and O2 as acceptors. Hydroxy H atoms attached to atoms O1 are represented as small balls. Dimethylformamide and toluene molecules have been omitted for simplicity. H atoms of benzene rings have also been omitted.



(*a*)

(*b*)

**Figure 3**
The packing structure of (I) showing toluene guest molecules, viewed (*a*) from the top and (*b*) from the side. In order to show the molecular contacts, some of the toluene and dimethylformamide molecules are shown as CPK models using a full van der Waals scale. (Among the six chains shown in the figures, two chains are highlighted in yellow and blue in the online version of the journal. In addition, toluene molecules are drawn in pink online.)

## Experimental

5-Hydroxybenzene-1,3-dicarboxylic acid (99%, Aldrich, 18 mg, 0.10 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.13 mmol) were dissolved in a mixture of dimethylformamide (0.5 ml) and toluene (2 ml) in a 4 ml vial. The vial was placed in a larger vial containing a mixture of toluene (1 ml) and triethylamine (0.05 ml). The larger vial was capped tightly and left to stand at room temperature for 5 d, yielding crystals suitable for X-ray crystallographic study.

### *Crystal data*

$[Zn(C_8H_4O_5)(C_3H_7NO)_2] \cdot 0.5C_7H_8$
$M_r = 437.74$
Triclinic, $P\bar{1}$
$a = 8.9582$ (6) Å
$b = 9.8360$ (6) Å
$c = 11.9183$ (7) Å
$\alpha = 79.294$ (1)°
$\beta = 81.822$ (1)°
$\gamma = 69.526$ (1)°

$V = 963.28$ (10) Å$^3$
$Z = 2$
$D_x = 1.509$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 1.32$ mm$^{-1}$
$T = 173$ (2) K
Plate, colorless
0.25 × 0.10 × 0.07 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.734$, $T_{max} = 0.914$

4875 measured reflections
3337 independent reflections
2921 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.075$
$S = 0.99$
3337 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.5366P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{min} = -0.37$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—O4$^i$ | 1.9662 (17) | Zn1—O6 | 2.1286 (18) |
| Zn1—O3 | 1.9795 (16) | Zn1—O7 | 2.1661 (18) |
| Zn1—O5$^{ii}$ | 1.9820 (15) | | |
| O4$^i$—Zn1—O3 | 100.50 (7) | O5$^{ii}$—Zn1—O6 | 93.44 (7) |
| O4$^i$—Zn1—O5$^{ii}$ | 129.78 (7) | O4$^i$—Zn1—O7 | 87.92 (8) |
| O3—Zn1—O5$^{ii}$ | 129.36 (7) | O3—Zn1—O7 | 89.45 (7) |
| O4$^i$—Zn1—O6 | 90.45 (7) | O5$^{ii}$—Zn1—O7 | 87.08 (7) |
| O3—Zn1—O6 | 91.53 (7) | O6—Zn1—O7 | 178.23 (7) |

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

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H1$\cdots$O2$^v$ | 0.83 (2) | 1.87 (2) | 2.685 (3) | 171 (3) |

Symmetry code: (v) $-x+1, -y+1, -z+2$.

The toluene molecule is disordered around an inversion center at $(1,\frac{1}{2},1)$ and hence one-half is unique in the asymmetric unit. The site-occupation factors of C1*T*, C2*T*, C3*T*, C4*T* and C5*T* were allocated the fixed values 1.0, 0.5, 1.0, 0.5 and 0.5, respectively. The eight H atoms of the disordered toluene molecule were incorporated into the structural model with reasonable geometry and fixed site-occupation factors of 0.5. Their positions were fixed during the refinement process. Most H atoms attached to other C atoms could be found in difference Fourier maps, and were then placed in calculated positions and refined by applying a riding model [for aromatic H atoms, C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$; for H atoms of $CH_3$ groups in the dimethylformamide ligands, C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$]. The hydroxy H atom was located in a difference Fourier map, and its position and displacement parameter were refined with distance restraints of O—H = 0.85 (2) Å. Friedel equivalents were merged before the final refinement.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL* and *MS Modeling* (Accelrys, 2005).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3025). Services for accessing these data are described at the back of the journal.

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