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# A novel one-dimensional zinc coordination polymer containing 4-methylbenzoate and 4,4-bipyridine

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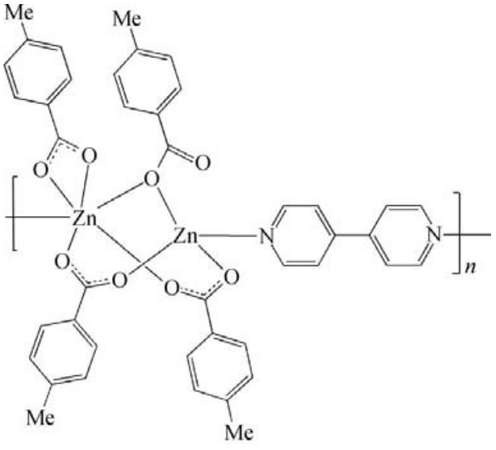
The title compound, *catena*-poly[[tris($\mu$-4-methylbenzoato)-$\kappa^2O$:$O$;$\kappa^4O$:$O'$-(4-methylbenzoato-$\kappa^2O$,$O'$)dizinc(II)]-$\mu$-4,4′-bipyridine-$\kappa^2N$:$N'$], $[Zn_2(C_8H_7O_2)_4(C_{10}H_8N_2)]_n$, is a novel coordination polymer. The asymmetric unit contains two unique $Zn^{II}$ ions, four 4-methylbenzoate ligands and one 4,4′-bipyridine (4,4′-bpy) ligand, all in general positions. The four 4-methylbenzoate ligands link the two $Zn^{II}$ centres to form a dinuclear unit, with a Zn···Zn separation of 3.188 (2) Å, which can be regarded as a supramolecular secondary building unit (SBU). These SBUs are further bridged by 4,4′-bpy ligands, forming a novel one-dimensional infinite chain. There are $\pi$–$\pi$ stacking interactions between the benzene rings of the 4-methylbenzoate ligands and the pyridyl rings of the 4,4′-bpy ligands, leading to the formation of a corrugated layer. These layers are further assembled *via* C—H···O hydrogen bonds into a three-dimensional supramolecular network structure. Coordination polymers such as the title compound are of interest for their potential applications as functional materials.

## Comment

Much research in recent years has focused on the design and synthesis of new potentially multifunctional coordination polymers with useful structure-derived properties, such as porosity, gas storage and ion exchange, or other physical properties, such as magnetism and photoluminescence (Shi *et al.*, 2004; Seo *et al.*, 2000; Kitaura *et al.*, 2002; Rowsell *et al.*, 2004; Gheorghe *et al.*, 2003). Many of the reported works are based on the use of mixed functional organic ligands containing N- and/or O-donor atoms to bind to *d*-block transition metal ions (Janiak, 1997; Kleij *et al.*, 2005; Eddaoudi *et al.*, 2000; Murugavel *et al.*, 2002). The selection of organic ligands is of great importance in the construction of specific supramolecular networks with useful physicochemical properties and intriguing structural topologies (Zhang *et al.*, 2005; Zhao *et al.*, 2003; Ren *et al.*, 2003; Gu *et al.*, 2006; Shibasaki *et al.*, 2002; Sabatini *et al.*, 1993). As is well known, 4,4′-bipyridine (4,4′-bpy) ligands may act in bidentate bridging or monodentate terminal modes, leading to the formation of a variety of one-dimensional chain, two-dimensional layer and three-dimensional network motifs (Biradha *et al.*, 2006). The 4-methylbenzoate ligand has versatile binding and coordination modes, and can also be used to construct multinuclear structures (Aliaga *et al.*, 2001; Brown *et al.*, 1993). Polynuclear *d*-block metal complexes have been found to exhibit interesting structural motifs and photoluminescence (Fu *et al.*, 2002; Harvey & Gray, 1988; Ma *et al.*, 1998; Kyle *et al.*, 1991; Henary *et al.*, 1989; Ford *et al.*, 1999). On the basis of these considerations, we chose 4-methylbenzoic acid, 4,4′-bpy and $Zn^{II}$ as our building blocks. A novel one-dimensional coordination framework, (I), resulted from the hydrothermal treatment of $ZnCl_2$ with 4-methylbenzoic acid and 4,4′-bpy in alkaline aqueous solution.



(I)

The asymmetric unit of (I) contains two unique $Zn^{II}$ ions, four 4-methylbenzoate ligands and one 4,4′-bpy ligand (Fig. 1). Of the two metal centres, Zn2 can be described as having a distorted octahedral coordination geometry formed by five carboxylate O atoms of four 4-methylbenzoate ligands, and one N atom of a 4,4′-bpy ligand, while Zn1 is penta-coordinated by four O atoms of three 4-methylbenzoate ligands and one N atom of the 4,4′-bpy ligand in a distorted square-pyramidal coordination geometry (Table 1). One Zn—O distance on each metal centre is distinctly longer than the others, but still within the range of a significant interaction (Addison *et al.*, 1971; Guilera *et al.*, 1999). The four 4-methylbenzoate ligands link two Zn atoms to construct a dinuclear zinc building block, with a Zn···Zn separation of 3.188 (2) Å, which can be regarded as a supramolecular secondary building unit (SBU) or knot. The construction of the knot is similar to that of the $Zn_2(acetate)_4$ unit in the infinite chains of that structure (Lee *et al.*, 2004). Unlike the symmetrical paddlewheel arrangement typically observed in $M_2(carboxylate)_4$ dimers, in (I) two of the 4-methylbenzoate ligands bridge the Zn atoms through separate O atoms, one bridges through a single O atom, and one chelates a single Zn atom only. Each 4,4′-bpy ligand bridges two neighbouring

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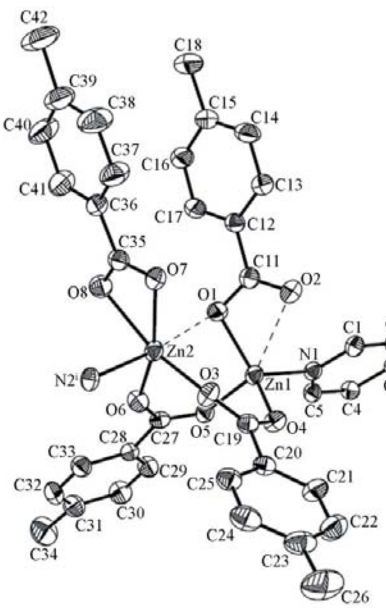

**Figure 1**
View of the asymmetric unit of (I). H atoms have been omitted for clarity. [Symmetry code: (i) $x$, $y$, $z-1$.]

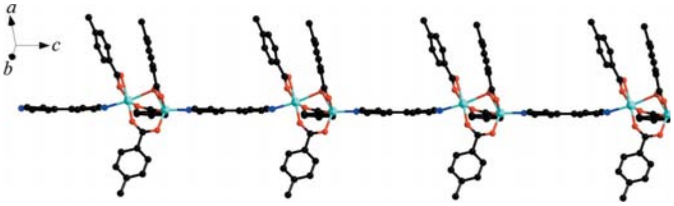

**Figure 2**
View of one infinite chain running parallel to the $c$ axis.

SBUs to form a one-dimensional infinite chain along the $c$ axis of the unit cell (Fig. 2). The distance between two knots is 14.2238 (4) Å, which is equal to the unit length of the $c$ axis. The $\pi$–$\pi$ stacking interactions and intra/intermolecular hydrogen bonds (Table 2) between carboxyl O atoms of 4-methylbenzoate ligands and 4,4′-bpy ligands assemble neighbouring chains into a corrugated layer in the $bc$ plane (Fig. 3). The centroid-to-centroid distances between the benzene rings of 4-methylbenzoate and the pyridyl rings of 4,4′-bpy of adjacent chains are 3.686 (2) and 3.697 (2) Å, respectively, thus indicating weak $\pi$–$\pi$ stacking contacts (Wu *et al.*, 2003; Pan & Xu, 2004; Li *et al.*, 2005; Deisenhofer & Michel, 1998). Moveover, hydrogen-bonding interactions (Table 2) between methyl groups and carboxylate O atoms of 4-methylbenzoate ligands lead to the formation of a three-dimensional supramolecular network structure.

The overall structural motif in (I) is unprecedented, differing from those described in the review by Biradha *et al.* (2006). Besides (I), there are only two coordination polymer structures containing 4,4′-bpy and 4-methylbenzoate, in which the neighbouring lanthanide ions are linked together by two bridging–chelating carboxylate groups of 4-methylbenzoate, and the 4,4′-bpy is uncoordinated (Li *et al.*, 2004, 2006). Hydrogen bonds formed between the N atoms of uncoordinated 4,4′-bpy molecules and the O atoms of coordinated 4-methylbenzoate and included water molecules help to stabilize these structures.

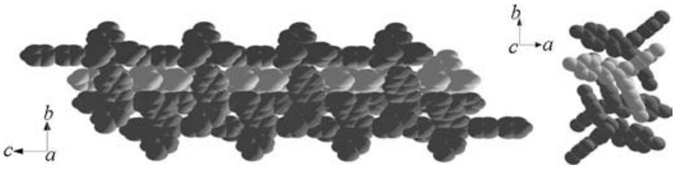

**Figure 3**
View of a corrugated layer in the $bc$ (left) and $ab$ (right) planes.

## Experimental

A mixture of zinc chloride (0.136 g, 1 mmol), 4-methylbenzoic acid (0.136 g, 1 mmol), 4,4′-bipyridine (0.156 g, 1 mmol), NaOH (0.06 g, 1.5 mmol) and $H_2O$ (12 ml) was placed in a 23 ml Teflon reactor, which was heated to 433 K for 3 d and then cooled to room temperature at a rate of 10 K h$^{-1}$. The crystals obtained were washed with water and dried in air (yield 0.37 g, 90.2%).

*Crystal data*

$[Zn_2(C_8H_7O_2)_4(C_{10}H_8N_2)]$
$M_r = 827.47$
Monoclinic, $P2_1/c$
$a = 12.3661$ (3) Å
$b = 22.0755$ (6) Å
$c = 14.2238$ (4) Å
$\beta = 95.997$ (2)°
$V = 3861.67$ (18) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.30$ mm$^{-1}$
$T = 296$ (2) K
0.30 × 0.26 × 0.20 mm

*Data collection*

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.697$, $T_{\max} = 0.781$
30933 measured reflections
6946 independent reflections
4275 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.074$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.114$
$S = 1.08$
6946 reflections
491 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.40$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.007 (3) | Zn2—O1 | 2.423 (3) |
| Zn1—O1 | 1.949 (2) | Zn2—O3 | 2.014 (2) |
| Zn1—O2 | 2.690 (2) | Zn2—O6 | 2.001 (2) |
| Zn1—O4 | 1.948 (2) | Zn2—O7 | 2.081 (2) |
| Zn1—O5 | 1.967 (2) | Zn2—O8 | 2.229 (2) |
| Zn2—N2$^{i}$ | 2.128 (3) | | |
| O4—Zn1—O1 | 122.25 (11) | O7—Zn2—N2$^{i}$ | 89.59 (11) |
| O1—Zn1—O5 | 100.88 (10) | O3—Zn2—O8 | 161.78 (10) |
| O6—Zn2—O3 | 99.05 (10) | N2$^{i}$—Zn2—O8 | 87.49 (10) |
| O6—Zn2—O7 | 159.70 (10) | O6—Zn2—O1 | 89.40 (9) |
| O6—Zn2—N2$^{i}$ | 93.87 (11) | N2$^{i}$—Zn2—O1 | 173.62 (9) |

Symmetry code: (i) $x$, $y$, $z-1$.

Carbon-bound H atoms were placed at calculated positions and treated as riding on their parent C atoms, with C—H = 0.93–0.96 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C10—H10···O8$^{ii}$ | 0.93 | 2.40 | 3.328 (5) | 172 |
| C4—H4···O8$^{ii}$ | 0.93 | 2.56 | 3.462 (4) | 165 |
| C1—H1···O2 | 0.93 | 2.41 | 3.111 (5) | 133 |

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

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); 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: SQ3142). Services for accessing these data are described at the back of the journal.

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