



# Crystal structure and Hirshfeld surface analysis of hexakis( $\mu$ -benzoato- $\kappa^2$ O:O')bis(pyridine-3-carbonitrile- $\kappa$ N<sup>1</sup>)trizinc(II)

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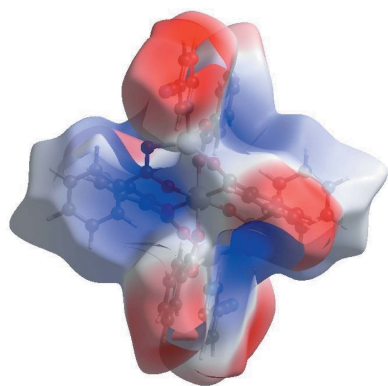
**Supporting information:** this article has supporting information at journals.iucr.org/e

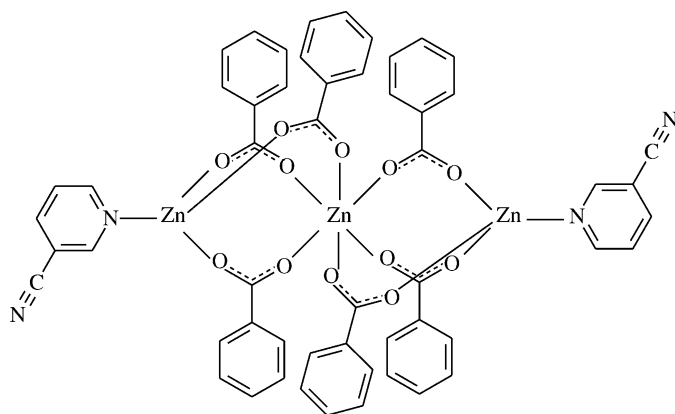
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The asymmetric unit of the title complex,  $[\text{Zn}_3(\text{C}_7\text{H}_5\text{O}_2)_6(\text{C}_6\text{H}_4\text{N}_2)_2]$ , contains one half of the complex molecule, *i.e.* one and a half  $\text{Zn}^{\text{II}}$  cations, three benzoate (Bnz) and one pyridine-3-carbonitrile (Cpy) molecule; the Bnz anions act as bidentate ligands through the carboxylate O atoms, while the Cpy ligand acts as a monodentate N(pyridine)-bonding ligand. The complete centrosymmetric trinuclear complex thus comprises a linear array of three  $\text{Zn}^{\text{II}}$  cations. The central  $\text{Zn}^{\text{II}}$  cation shows an octahedral coordination and is bridged to each of the terminal  $\text{Zn}^{\text{II}}$  cations by three Bnz anions. By additional coordination of the CPy ligand, the terminal  $\text{Zn}^{\text{II}}$  cations adopt a trigonal–pyramidal coordination environment. In the crystal, the Bnz anions link to the Cpy N atoms *via* weak C–H $\cdots$ N hydrogen bonds, forming a two-dimensional network. C–H $\cdots$  $\pi$  and  $\pi$ – $\pi$  interactions [between the benzene and pyridine rings of adjacent molecules with an intercentroid distance of 3.850 (4) Å] help to consolidate a three-dimensional architecture. The Hirshfeld surface analysis confirms the role of H-atom contacts in establishing the packing.

## 1. Chemical context

The structure–function–coordination relationships of the arylcarboxylate ion in  $\text{Zn}^{\text{II}}$  complexes of benzoic acid derivatives change depending on the nature and position of the substituent groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981). When pyridine and its derivatives are used instead of water molecules, the structure is completely different (Catterick *et al.*, 1974). The solid-state structures of anhydrous Zinc(II) carboxylates include one-dimensional, two-dimensional and three-dimensional polymeric motifs of different types, while discrete monomeric complexes with octahedral or tetrahedral coordination geometry are found if water or other donor molecules are coordinated to Zn (Usabaliev *et al.*, 1992). The structure determination of the title compound, (I), a trinuclear zinc complex with six benzoate anions and two neutral pyridine-3-carbonitrile ligands, was undertaken in order to compare the results obtained with those reported previously. In this context, we synthesized the  $\text{Zn}^{\text{II}}$ -containing title compound, hexa( $\mu$ -benzoato- $\kappa^2$ O:O')bis(pyridine-3-carbonitrile- $\kappa$ N)trizinc(II),  $[\text{Zn}_3(\text{C}_7\text{H}_5\text{O}_2)_6(\text{C}_6\text{H}_4\text{N}_2)_2]$ , and report herein its crystal and molecular structures as well as a Hirshfeld surface analysis.

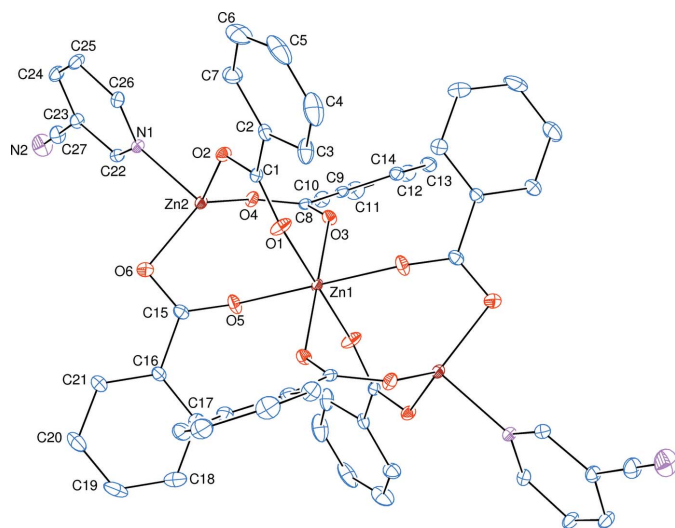




## 2. Structural commentary

The molecular structure of the title complex (I) is formed by a centrosymmetric array of three  $\text{Zn}^{\text{II}}$  cations, which are coordinated by six benzoate anions and two neutral pyridine-3-carbonitrile ligands. The middle  $\text{Zn}^{\text{II}}$  cation occupies a special position and lies on a crystallographic inversion centre. The benzoate anions act as bidentate ligands, bridging two pairs of  $\text{Zn}^{\text{II}}$  cations. The pyridine-3-carbonitrile ligands are monodentately coordinated through the pyridine N atoms (Fig. 1).

In the title complex, (I), the four carboxylate O atoms (O1, O3, O1<sup>i</sup> and O3<sup>i</sup>) of the two symmetry-related, bidentately coordinated benzoate anions around the Zn1 atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination sphere is completed by the two carboxylate O atoms (O5 and O5<sup>i</sup>) of the two symmetry-related, bidentately coordinated benzoate anions in



**Figure 1**

The molecular structure of the title complex with the atom-numbering scheme. Unlabelled atoms are related to labelled ones by the symmetry operation  $(1 - x, 2 - y, 1 - z)$ . Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

**Table 1**  
Selected bond lengths (Å).

Zn1—O1	2.039 (4)	Zn2—O4	1.963 (4)
Zn1—O3	2.117 (3)	Zn2—O6	2.034 (4)
Zn1—O5	2.099 (4)	Zn2—N1	2.091 (4)
Zn2—O2	1.948 (4)		

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

C<sub>g</sub> is the centroid of the C19–C14 ring.

<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>
C20—H20···N2 <sup>i</sup>	0.93	2.63	3.448 (11)	147 (1)
C24—H24···C <sub>g</sub> <sup>ii</sup>	0.93	2.70	3.512 (6)	147

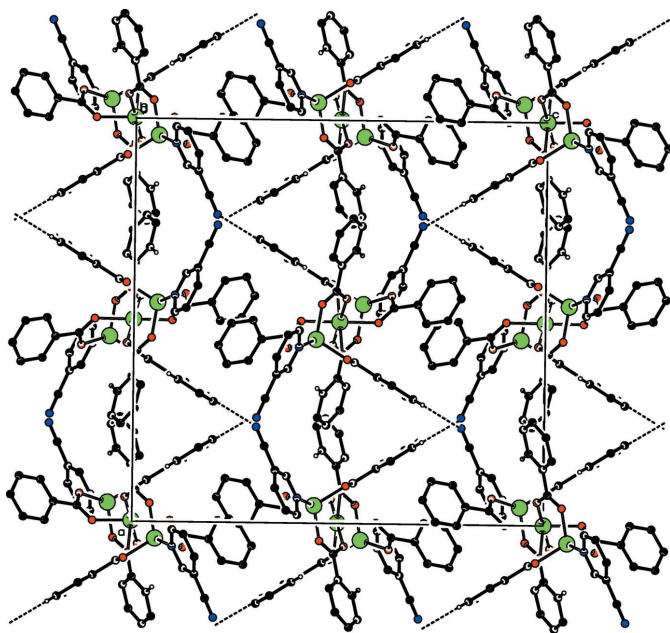
Symmetry codes: (i)  $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$ ; (ii)  $x, y - 1, z$ .

the axial positions [symmetry code: (i)  $1 - x, 2 - y, 1 - z$ ] (Fig. 1, Table 1). On the other hand, the three carboxylate O atoms (O2, O4 and O6) of the three bidentately coordinated benzoate anions around the Zn2 atom form a slightly distorted triangular planar arrangement, while the slightly distorted trigonal-pyramidal coordination sphere is completed by the pyridine N atom (N1) of the monodentately coordinated neutral pyridine-3-carbonitrile ligand in the axial position (Fig. 1, Table 1). The sum of the bond angles O2—Zn2—O4 [117.1 (2)°], O2—Zn2—O6 [111.1 (2)°] and O4—Zn2—O6 [127.4 (2)°] in the basal plane around the Zn2 atom is 355.6°. This confirms that the Zn2 atom deviates from the O2/O4/O6 basal plane; the deviation is 0.2390 (6) Å. The Zn1···Zn2 separation in the title trinuclear molecule is 3.396 (2) Å and is comparable to the corresponding *M*—*M* distance (*M* is a metal) of 3.1845 (2) Å in the structurally related transition metal(II) complex [Zn<sub>3</sub>(benz)<sub>6</sub>(nia)<sub>2</sub>] (where benz = benzoate and nia = nicotinamide) (Zeleňák *et al.*, 2004). The volume of the polyhedron of atoms (Zn1/Zn2/O1—O6/C1/C8/C15) is calculated to be 15.62 (5) Å<sup>3</sup>.

The Zn1 and Zn2 atoms lie [0.7337 (1) and −0.1793 (6) Å], [1.0911 (1) and −0.2676 (6) Å] and [1.3428 (1) and 0.0520 (7) Å] above and/or below of the planar (O1/O2/C1), (O3/O4/C8) and (O5/O6/C15) carboxylate groups, respectively. The (O1/O2/C1), (O3/O4/C8) and (O5/O6/C15) carboxylate groups are twisted away from the attached benzene (*A*, C2—C7; *B*, C9—C14; *C*, C16—C21) rings by 6.4 (3), 26.5 (3) and 5.1 (3)°, respectively, while the benzene and pyridine (*D*, N1/C22—C26) rings are oriented at dihedral angles of *A*/*B* = 76.2 (2), *A*/*C* = 82.9 (2), *A*/*D* = 6.2 (2), *B*/*C* = 89.2 (2), *B*/*D* = 70.0 (2) and *C*/*D* = 83.0 (2)°.

## 3. Supramolecular features

In the crystal, weak C—H<sub>Bnz</sub>···N<sub>Cpy</sub> (Bnz = benzoate and Cpy = pyridine-3-carbonitrile) hydrogen bonds (Table 2) link the molecules into a two-dimensional network parallel to (010) (Fig. 2). C—H···π and π—π interactions [between the benzene and pyridine rings of adjacent molecules with an inter-centroid

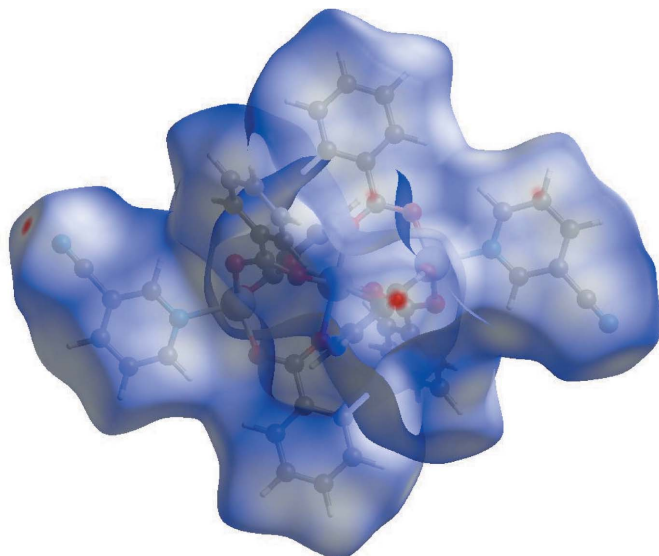


**Figure 2**  
Part of the crystal structure. Weak C–H<sub>Bnz</sub>···N<sub>Cpy</sub> (Bnz = benzoate and Cpy = pyridine-3-carbonitrile) hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted for clarity.

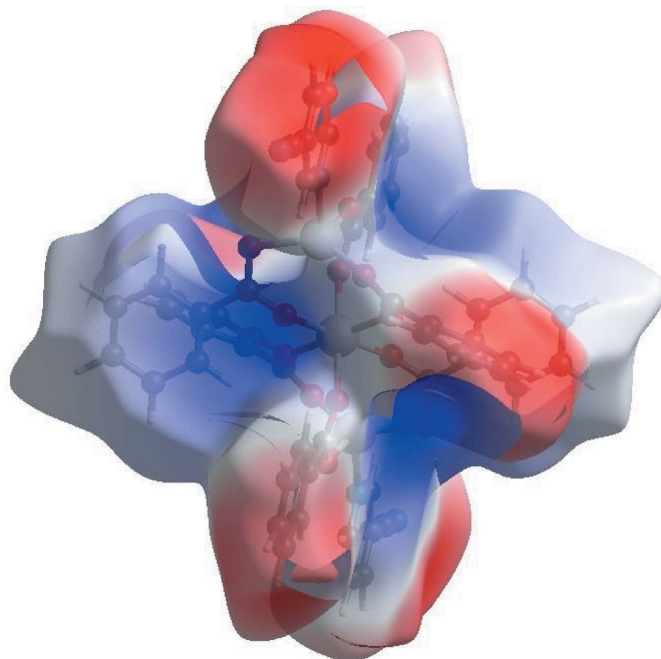
distance of 3.850 (4) Å] help to consolidate a three-dimensional architecture.

#### 4. Hirshfeld surface analysis

Visualization and exploration of intermolecular close contacts of a structure is invaluable, and this can be achieved using the Hirshfeld surface (HS) (Hirshfeld, 1977). HS analysis may be carried out to investigate the locations of atoms···atom short



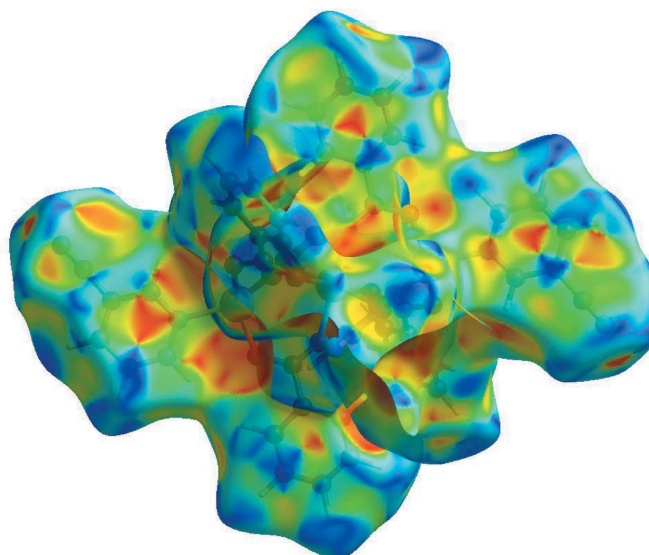
**Figure 3**  
View of the three-dimensional Hirshfeld surface of the title complex plotted over  $d_{\text{norm}}$  in the range  $-0.0957$  to  $1.6461$  a.u.



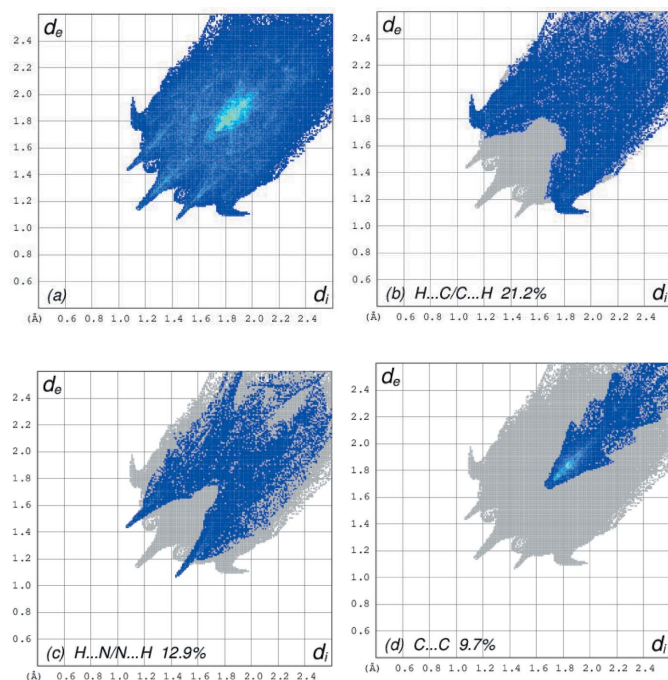
**Figure 4**  
View of the three-dimensional Hirshfeld surface of the title complex plotted over electrostatic potential energy in the range  $-1.7824$  to  $9.8050$  a.u. The hydrogen-bond donors and acceptors are viewed as blue and red regions around the atoms corresponding to positive and negative potentials, respectively.

contacts with potential to form hydrogen bonds and  $\pi$ -stacking interactions.

In the HS with  $d_{\text{norm}}$  (Fig. 3), the white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distant contact) than the van der Waals radii, respectively. The bright-red spot appearing near Cpy-N2 indicates its role as the respective donor and/or



**Figure 5**  
Hirshfeld surface of the title complex plotted over shape-index.


**Figure 6**

The selected two-dimensional fingerprint plots for the title complex, showing (a) all interactions, and delineated into (b)  $H \cdots C/C \cdots H$ , (c)  $H \cdots N/N \cdots H$  and (d)  $C \cdots C$  interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

acceptor in the dominant  $C-H \cdots N$  hydrogen bond; it also appears as blue and/or red regions, respectively, corresponding to positive or negative potentials on the HS mapped over electrostatic potential (Fig. 4). The shape-index of the HS is a tool to visualize the  $\pi$ - $\pi$  stacking by the presence of adjacent red and/or blue triangles; if there are no adjacent red and/or blue triangles, then there are no  $\pi$ - $\pi$  interactions. Fig. 5 clearly suggests that there are  $\pi$ - $\pi$  interactions in (I).

The overall two-dimensional fingerprint plot, Fig. 6a, and those delineated into  $H \cdots C/C \cdots H$ ,  $H \cdots N/N \cdots H$  and  $C \cdots C$

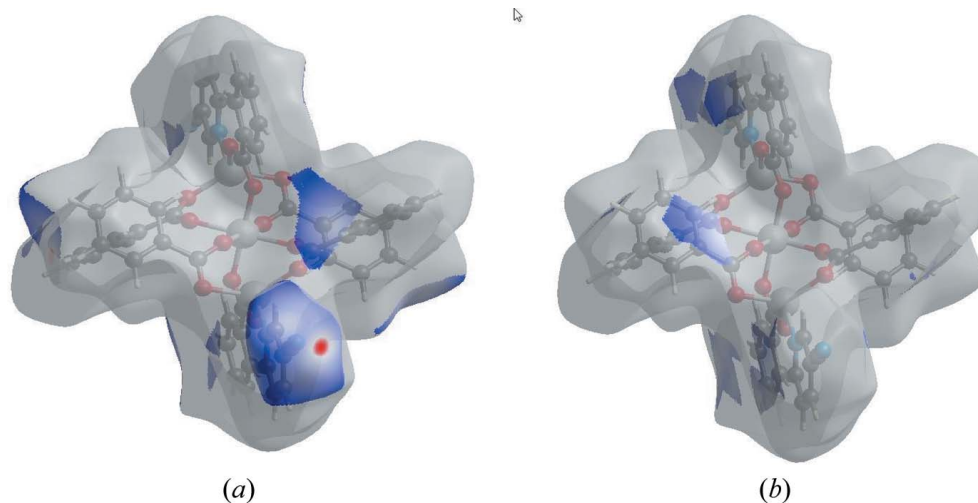
**Table 3**

Experimental details.

Crystal data	
Chemical formula	$[Zn_3(C_6H_5O_2)_6(C_6H_4N_2)_2]$
$M_r$	1130.99
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	296
$a, b, c$ (Å)	21.7698 (4), 10.7768 (2), 22.2272 (4)
$V$ (Å <sup>3</sup> )	5214.70 (17)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.43
Crystal size (mm)	0.25 × 0.15 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2012)
$T_{min}$ , $T_{max}$	0.769, 0.805
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	57535, 5205, 4090
$R_{int}$	0.044
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.061, 0.136, 1.25
No. of reflections	5205
No. of parameters	332
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.51, -0.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

contacts are illustrated in Fig. 6 *b-d*, respectively, together with their relative contributions to the Hirshfeld surface. The widely scattered points of high density are due to the  $C-H \cdots \pi$  interactions in the crystal, resulting in the fingerprint plot delineated into  $H \cdots C/C \cdots H$  contacts with 21.2% contribution to the HS, Fig. 6*b*. In the fingerprint plot delineated into  $H \cdots N / N \cdots H$  contacts, the 12.9% contribution to the HS arises from the  $C-H \cdots N$  hydrogen bonding and is viewed as a pair of spikes with the tip at  $d_e + d_i \sim 2.6$  Å in Fig. 6*c*. Finally, the  $C \cdots C$  contacts assigned to short interatomic  $C \cdots C$  contacts and  $\pi$ - $\pi$  stacking interactions with


**Figure 7**

The Hirshfeld surface representations with the function  $d_{norm}$  plotted onto the surface for (a)  $H \cdots N / N \cdots H$  and (b)  $C \cdots C$  interactions.

9.7% contribution to the HS appear as an arrow-shaped distribution of points in Fig. 6*d*, with the vertex at  $d_e = d_i \sim 1.65 \text{ \AA}$ .

The Hirshfeld surface representations with the function  $d_{\text{norm}}$  plotted onto the surface are shown for the H...N/N...H and C...C interactions in Fig. 7*a* and *b*, respectively.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The crystal packing is dominated by van der Waals interactions and hydrogen bonding.

## 5. Synthesis and crystallization

The title compound was prepared by the reaction of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (1.44 g, 5 mmol) in  $\text{H}_2\text{O}$  (25 ml) and pyridine-3-carbonitrile (1.04 g, 10 mmol) in water (25 ml) with sodium benzoate (1.44 g, 10 mmol) in water (100 ml) at room temperature. The mixture was filtered and set aside to crystallize at ambient temperature for several days, giving colourless single crystals (yield: 1.55 g, 82%).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geom-

etrically with C—H = 0.93 Å and constrained to ride on their parent atoms [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

## Acknowledgements

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of hexakis( $\mu$ -benzoato- $\kappa^2$ O:O')bis(pyridine-3-carbonitrile- $\kappa$ N<sup>1</sup>)trizinc(II)

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### Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

### Hexakis( $\mu$ -benzoato- $\kappa^2$ O:O')bis(pyridine-3-carbonitrile- $\kappa$ N<sup>1</sup>)trizinc(II)

#### Crystal data

[Zn<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>)<sub>6</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)<sub>2</sub>]

$M_r = 1130.99$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 21.7698$  (4) Å

$b = 10.7768$  (2) Å

$c = 22.2272$  (4) Å

$V = 5214.70$  (17) Å<sup>3</sup>

$Z = 4$

$F(000) = 2304$

$D_x = 1.441$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9334 reflections

$\theta = 3.2$ – $26.4^\circ$

$\mu = 1.43$  mm<sup>-1</sup>

$T = 296$  K

Prism, colourless

$0.25 \times 0.15 \times 0.14$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\phi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

$T_{\min} = 0.769$ ,  $T_{\max} = 0.805$

57535 measured reflections

5205 independent reflections

4090 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 26.3^\circ$ ,  $\theta_{\min} = 2.8^\circ$

$h = -27 \rightarrow 27$

$k = -12 \rightarrow 9$

$l = -27 \rightarrow 27$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.136$

$S = 1.25$

5205 reflections

332 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 23.0318P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.51$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.53$  e Å<sup>-3</sup>

Extinction correction: *SHELXL97* (Sheldrick, 2008),  $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0033 (2)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{iso}^*/U_{eq}$
Zn1	0.5000	1.0000	0.5000	0.0328 (2)
Zn2	0.54302 (3)	0.72121 (5)	0.44260 (3)	0.03771 (19)
O1	0.4419 (2)	0.8554 (4)	0.51623 (18)	0.0620 (12)
O2	0.45578 (16)	0.6924 (3)	0.45634 (16)	0.0465 (9)
O3	0.49893 (17)	0.9704 (4)	0.40584 (14)	0.0465 (9)
O4	0.56537 (18)	0.8269 (3)	0.37406 (16)	0.0488 (9)
O5	0.57926 (19)	0.8901 (4)	0.50701 (17)	0.0606 (12)
O6	0.5925 (2)	0.6912 (4)	0.51883 (19)	0.0621 (11)
N1	0.5624 (2)	0.5518 (4)	0.40092 (19)	0.0405 (10)
N2	0.7379 (3)	0.3920 (7)	0.2993 (3)	0.097 (2)
C1	0.4237 (2)	0.7599 (5)	0.4913 (2)	0.0385 (11)
C2	0.3595 (2)	0.7168 (5)	0.5033 (2)	0.0452 (12)
C3	0.3211 (3)	0.7890 (7)	0.5383 (3)	0.074 (2)
H3	0.3343	0.8653	0.5529	0.089*
C4	0.2615 (4)	0.7454 (11)	0.5515 (5)	0.112 (4)
H4	0.2352	0.7932	0.5749	0.135*
C5	0.2423 (4)	0.6337 (12)	0.5300 (5)	0.115 (4)
H5	0.2029	0.6057	0.5386	0.137*
C6	0.2798 (4)	0.5641 (9)	0.4966 (4)	0.100 (3)
H6	0.2663	0.4875	0.4826	0.120*
C7	0.3387 (3)	0.6039 (7)	0.4822 (3)	0.0672 (18)
H7	0.3640	0.5545	0.4585	0.081*
C8	0.5356 (2)	0.9277 (5)	0.3681 (2)	0.0383 (11)
C9	0.5447 (3)	0.9980 (5)	0.3106 (2)	0.0414 (12)
C10	0.5983 (3)	0.9883 (6)	0.2789 (3)	0.0588 (16)
H10	0.6289	0.9348	0.2923	0.071*
C11	0.6075 (4)	1.0582 (7)	0.2266 (3)	0.078 (2)
H11	0.6445	1.0533	0.2058	0.094*
C12	0.5609 (4)	1.1346 (7)	0.2062 (3)	0.077 (2)
H12	0.5664	1.1804	0.1712	0.092*
C13	0.5067 (4)	1.1432 (6)	0.2372 (3)	0.0680 (19)
H13	0.4755	1.1946	0.2231	0.082*
C14	0.4982 (3)	1.0756 (5)	0.2896 (2)	0.0516 (14)

H14	0.4615	1.0820	0.3107	0.062*
C15	0.5997 (2)	0.8003 (6)	0.5365 (2)	0.0447 (13)
C16	0.6358 (2)	0.8249 (5)	0.5925 (2)	0.0442 (12)
C17	0.6485 (3)	0.9441 (6)	0.6100 (3)	0.0621 (16)
H17	0.6345	1.0107	0.5871	0.075*
C18	0.6823 (4)	0.9651 (8)	0.6621 (4)	0.089 (2)
H18	0.6914	1.0458	0.6739	0.106*
C19	0.7022 (4)	0.8669 (10)	0.6959 (4)	0.098 (3)
H19	0.7250	0.8815	0.7306	0.118*
C20	0.6892 (4)	0.7477 (10)	0.6794 (4)	0.102 (3)
H20	0.7028	0.6814	0.7026	0.122*
C21	0.6555 (3)	0.7270 (7)	0.6276 (3)	0.0717 (19)
H21	0.6459	0.6461	0.6163	0.086*
C22	0.6160 (2)	0.5327 (5)	0.3742 (2)	0.0457 (13)
H22	0.6449	0.5962	0.3741	0.055*
C23	0.6306 (3)	0.4213 (5)	0.3463 (2)	0.0478 (13)
C24	0.5872 (3)	0.3277 (6)	0.3463 (3)	0.0590 (16)
H24	0.5956	0.2521	0.3278	0.071*
C25	0.5316 (3)	0.3474 (5)	0.3739 (3)	0.0573 (16)
H25	0.5018	0.2857	0.3742	0.069*
C26	0.5208 (3)	0.4603 (5)	0.4012 (2)	0.0465 (13)
H26	0.4834	0.4732	0.4204	0.056*
C27	0.6905 (3)	0.4056 (7)	0.3197 (3)	0.0641 (17)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.0425 (4)	0.0234 (4)	0.0325 (4)	0.0037 (3)	-0.0005 (3)	-0.0020 (3)
Zn2	0.0439 (3)	0.0301 (3)	0.0391 (3)	0.0032 (2)	-0.0002 (3)	-0.0042 (2)
O1	0.082 (3)	0.044 (2)	0.060 (2)	-0.025 (2)	0.026 (2)	-0.0145 (19)
O2	0.0406 (19)	0.044 (2)	0.055 (2)	0.0035 (16)	0.0040 (17)	-0.0146 (17)
O3	0.050 (2)	0.060 (2)	0.0294 (17)	0.0131 (19)	0.0000 (16)	-0.0042 (16)
O4	0.067 (2)	0.035 (2)	0.044 (2)	0.0047 (18)	0.0064 (18)	-0.0003 (16)
O5	0.059 (3)	0.079 (3)	0.044 (2)	0.034 (2)	-0.0014 (19)	0.007 (2)
O6	0.074 (3)	0.057 (3)	0.056 (2)	-0.001 (2)	-0.015 (2)	-0.008 (2)
N1	0.046 (2)	0.033 (2)	0.043 (2)	0.0014 (19)	-0.0009 (19)	-0.0049 (18)
N2	0.077 (4)	0.122 (6)	0.091 (5)	0.026 (4)	0.035 (4)	-0.009 (4)
C1	0.043 (3)	0.032 (3)	0.041 (3)	-0.001 (2)	-0.002 (2)	0.005 (2)
C2	0.035 (3)	0.047 (3)	0.054 (3)	0.006 (2)	-0.002 (2)	0.012 (3)
C3	0.057 (4)	0.068 (5)	0.098 (5)	0.021 (3)	0.023 (4)	0.023 (4)
C4	0.059 (5)	0.129 (8)	0.149 (9)	0.039 (6)	0.038 (6)	0.048 (8)
C5	0.031 (4)	0.171 (11)	0.141 (9)	-0.007 (5)	-0.008 (5)	0.075 (9)
C6	0.060 (5)	0.121 (8)	0.120 (7)	-0.050 (5)	-0.019 (5)	0.037 (6)
C7	0.062 (4)	0.068 (4)	0.071 (4)	-0.018 (3)	-0.010 (3)	0.009 (4)
C8	0.048 (3)	0.034 (3)	0.033 (2)	-0.003 (2)	-0.007 (2)	-0.005 (2)
C9	0.057 (3)	0.037 (3)	0.030 (2)	-0.007 (3)	-0.002 (2)	-0.007 (2)
C10	0.070 (4)	0.059 (4)	0.048 (3)	-0.002 (3)	0.013 (3)	0.001 (3)
C11	0.097 (6)	0.084 (5)	0.055 (4)	-0.012 (5)	0.021 (4)	0.004 (4)



C12	0.124 (7)	0.067 (5)	0.039 (3)	-0.016 (5)	-0.001 (4)	0.010 (3)
C13	0.095 (5)	0.063 (4)	0.046 (4)	-0.004 (4)	-0.019 (4)	0.006 (3)
C14	0.065 (4)	0.049 (3)	0.041 (3)	-0.002 (3)	-0.008 (3)	-0.002 (2)
C15	0.033 (3)	0.061 (4)	0.039 (3)	0.006 (2)	0.001 (2)	-0.004 (3)
C16	0.042 (3)	0.052 (3)	0.038 (3)	0.005 (2)	-0.005 (2)	0.001 (2)
C17	0.059 (4)	0.060 (4)	0.067 (4)	0.000 (3)	-0.008 (3)	-0.005 (3)
C18	0.097 (6)	0.090 (6)	0.079 (5)	-0.019 (5)	-0.018 (5)	-0.025 (5)
C19	0.088 (6)	0.140 (9)	0.066 (5)	-0.005 (6)	-0.040 (4)	-0.016 (5)
C20	0.117 (7)	0.112 (7)	0.076 (5)	0.026 (6)	-0.048 (5)	0.006 (5)
C21	0.086 (5)	0.067 (4)	0.062 (4)	0.009 (4)	-0.030 (4)	0.003 (3)
C22	0.047 (3)	0.044 (3)	0.046 (3)	-0.003 (2)	-0.004 (2)	-0.005 (2)
C23	0.052 (3)	0.051 (3)	0.041 (3)	0.012 (3)	0.007 (2)	-0.008 (2)
C24	0.074 (4)	0.041 (3)	0.062 (4)	0.007 (3)	0.001 (3)	-0.015 (3)
C25	0.062 (4)	0.036 (3)	0.074 (4)	-0.004 (3)	0.003 (3)	-0.013 (3)
C26	0.050 (3)	0.040 (3)	0.049 (3)	0.006 (2)	0.006 (2)	0.001 (2)
C27	0.068 (4)	0.071 (4)	0.054 (4)	0.018 (3)	0.014 (3)	-0.006 (3)

*Geometric parameters (Å, °)*

Zn1—O1	2.039 (4)	C8—C9	1.500 (7)
Zn1—O1 <sup>i</sup>	2.039 (4)	C9—C10	1.367 (8)
Zn1—O3	2.117 (3)	C9—C14	1.393 (8)
Zn1—O3 <sup>i</sup>	2.117 (3)	C10—C11	1.400 (9)
Zn1—O5	2.099 (4)	C10—H10	0.9300
Zn1—O5 <sup>i</sup>	2.099 (4)	C11—C12	1.382 (10)
Zn2—O2	1.948 (4)	C11—H11	0.9300
Zn2—O4	1.963 (4)	C12—C13	1.370 (10)
Zn2—O5	2.446 (5)	C12—H12	0.9300
Zn2—O6	2.034 (4)	C13—C14	1.385 (8)
Zn2—N1	2.091 (4)	C13—H13	0.9300
Zn2—C15	2.571 (5)	C14—H14	0.9300
O1—C1	1.235 (6)	C15—C16	1.494 (7)
O2—C1	1.274 (6)	C16—C17	1.370 (8)
O3—C8	1.245 (6)	C16—C21	1.381 (8)
O4—C8	1.272 (6)	C17—C18	1.391 (9)
O5—C15	1.251 (7)	C17—H17	0.9300
O6—C15	1.250 (7)	C18—C19	1.369 (12)
N1—C22	1.326 (7)	C18—H18	0.9300
N1—C26	1.339 (7)	C19—C20	1.366 (12)
N2—C27	1.138 (8)	C19—H19	0.9300
C1—C2	1.496 (7)	C20—C21	1.384 (9)
C2—C7	1.381 (8)	C20—H20	0.9300
C2—C3	1.383 (8)	C21—H21	0.9300
C3—C4	1.411 (11)	C22—C23	1.387 (7)
C3—H3	0.9300	C22—H22	0.9300
C4—C5	1.361 (14)	C23—C24	1.382 (8)
C4—H4	0.9300	C23—C27	1.441 (8)
C5—C6	1.335 (14)	C24—C25	1.373 (8)

C5—H5	0.9300	C24—H24	0.9300
C6—C7	1.388 (9)	C25—C26	1.379 (7)
C6—H6	0.9300	C25—H25	0.9300
C7—H7	0.9300	C26—H26	0.9300
O1 <sup>i</sup> —Zn1—O1	180.000 (1)	O3—C8—O4	124.9 (5)
O1 <sup>i</sup> —Zn1—O5	86.25 (19)	O3—C8—C9	118.2 (5)
O1—Zn1—O5	93.75 (19)	O4—C8—C9	116.9 (5)
O1 <sup>i</sup> —Zn1—O5 <sup>i</sup>	93.75 (19)	C10—C9—C14	119.6 (5)
O1—Zn1—O5 <sup>i</sup>	86.25 (19)	C10—C9—C8	120.9 (5)
O5—Zn1—O5 <sup>i</sup>	180.000 (1)	C14—C9—C8	119.5 (5)
O1 <sup>i</sup> —Zn1—O3	86.97 (16)	C9—C10—C11	120.5 (7)
O1—Zn1—O3	93.03 (16)	C9—C10—H10	119.7
O5—Zn1—O3	89.85 (14)	C11—C10—H10	119.7
O5 <sup>i</sup> —Zn1—O3	90.15 (14)	C12—C11—C10	119.2 (7)
O1 <sup>i</sup> —Zn1—O3 <sup>i</sup>	93.03 (16)	C12—C11—H11	120.4
O1—Zn1—O3 <sup>i</sup>	86.97 (16)	C10—C11—H11	120.4
O5—Zn1—O3 <sup>i</sup>	90.15 (14)	C13—C12—C11	120.5 (6)
O5 <sup>i</sup> —Zn1—O3 <sup>i</sup>	89.85 (14)	C13—C12—H12	119.8
O3—Zn1—O3 <sup>i</sup>	180.000 (1)	C11—C12—H12	119.8
O2—Zn2—O4	117.11 (16)	C12—C13—C14	120.1 (7)
O2—Zn2—O6	111.11 (17)	C12—C13—H13	119.9
O4—Zn2—O6	127.42 (18)	C14—C13—H13	119.9
O2—Zn2—N1	97.29 (16)	C13—C14—C9	120.0 (6)
O4—Zn2—N1	96.46 (16)	C13—C14—H14	120.0
O6—Zn2—N1	97.08 (17)	C9—C14—H14	120.0
O2—Zn2—O5	109.96 (14)	O6—C15—O5	121.2 (5)
O4—Zn2—O5	86.72 (15)	O6—C15—C16	119.7 (5)
O6—Zn2—O5	57.31 (15)	O5—C15—C16	119.1 (5)
N1—Zn2—O5	147.56 (15)	O6—C15—Zn2	51.1 (3)
O2—Zn2—C15	113.20 (16)	O5—C15—Zn2	70.1 (3)
O4—Zn2—C15	108.58 (17)	C16—C15—Zn2	170.7 (4)
O6—Zn2—C15	28.58 (17)	C17—C16—C21	119.6 (6)
N1—Zn2—C15	123.54 (17)	C17—C16—C15	120.6 (5)
O5—Zn2—C15	28.74 (15)	C21—C16—C15	119.8 (5)
C1—O1—Zn1	139.2 (4)	C16—C17—C18	119.7 (7)
C1—O2—Zn2	122.6 (3)	C16—C17—H17	120.1
C8—O3—Zn1	135.6 (3)	C18—C17—H17	120.1
C8—O4—Zn2	116.7 (3)	C19—C18—C17	120.0 (8)
C15—O5—Zn1	140.2 (4)	C19—C18—H18	120.0
C15—O5—Zn2	81.2 (3)	C17—C18—H18	120.0
Zn1—O5—Zn2	96.39 (16)	C20—C19—C18	120.9 (7)
C15—O6—Zn2	100.3 (4)	C20—C19—H19	119.6
C22—N1—C26	118.9 (5)	C18—C19—H19	119.6
C22—N1—Zn2	120.8 (4)	C19—C20—C21	119.1 (8)
C26—N1—Zn2	120.3 (4)	C19—C20—H20	120.4
O1—C1—O2	125.0 (5)	C21—C20—H20	120.4
O1—C1—C2	118.7 (5)	C16—C21—C20	120.8 (7)

O2—C1—C2	116.3 (5)	C16—C21—H21	119.6
C7—C2—C3	119.2 (6)	C20—C21—H21	119.6
C7—C2—C1	121.3 (5)	N1—C22—C23	122.4 (5)
C3—C2—C1	119.4 (6)	N1—C22—H22	118.8
C2—C3—C4	119.1 (8)	C23—C22—H22	118.8
C2—C3—H3	120.5	C24—C23—C22	118.4 (5)
C4—C3—H3	120.5	C24—C23—C27	122.1 (5)
C5—C4—C3	120.2 (9)	C22—C23—C27	119.5 (6)
C5—C4—H4	119.9	C25—C24—C23	119.3 (5)
C3—C4—H4	119.9	C25—C24—H24	120.4
C6—C5—C4	120.4 (8)	C23—C24—H24	120.4
C6—C5—H5	119.8	C24—C25—C26	118.9 (6)
C4—C5—H5	119.8	C24—C25—H25	120.6
C5—C6—C7	121.3 (9)	C26—C25—H25	120.6
C5—C6—H6	119.4	N1—C26—C25	122.2 (5)
C7—C6—H6	119.4	N1—C26—H26	118.9
C2—C7—C6	119.8 (8)	C25—C26—H26	118.9
C2—C7—H7	120.1	N2—C27—C23	179.1 (8)
C6—C7—H7	120.1		
O5—Zn1—O1—C1	-70.0 (6)	C2—C3—C4—C5	0.1 (13)
O5 <sup>i</sup> —Zn1—O1—C1	110.0 (6)	C3—C4—C5—C6	0.4 (15)
O3—Zn1—O1—C1	20.0 (6)	C4—C5—C6—C7	-0.8 (15)
O3 <sup>i</sup> —Zn1—O1—C1	-160.0 (6)	C3—C2—C7—C6	-0.3 (10)
O4—Zn2—O2—C1	-92.5 (4)	C1—C2—C7—C6	176.9 (6)
O6—Zn2—O2—C1	65.8 (4)	C5—C6—C7—C2	0.7 (12)
N1—Zn2—O2—C1	166.4 (4)	Zn1—O3—C8—O4	47.4 (8)
O5—Zn2—O2—C1	4.2 (4)	Zn1—O3—C8—C9	-133.9 (4)
C15—Zn2—O2—C1	35.0 (4)	Zn2—O4—C8—O3	8.8 (7)
O1 <sup>i</sup> —Zn1—O3—C8	73.7 (5)	Zn2—O4—C8—C9	-169.9 (3)
O1—Zn1—O3—C8	-106.3 (5)	O3—C8—C9—C10	153.9 (5)
O5—Zn1—O3—C8	-12.5 (5)	O4—C8—C9—C10	-27.4 (7)
O5 <sup>i</sup> —Zn1—O3—C8	167.5 (5)	O3—C8—C9—C14	-25.2 (7)
O2—Zn2—O4—C8	46.3 (4)	O4—C8—C9—C14	153.6 (5)
O6—Zn2—O4—C8	-108.0 (4)	C14—C9—C10—C11	1.8 (9)
N1—Zn2—O4—C8	147.9 (4)	C8—C9—C10—C11	-177.3 (6)
O5—Zn2—O4—C8	-64.5 (4)	C9—C10—C11—C12	-1.9 (10)
C15—Zn2—O4—C8	-83.4 (4)	C10—C11—C12—C13	0.9 (11)
O1 <sup>i</sup> —Zn1—O5—C15	143.5 (6)	C11—C12—C13—C14	0.2 (11)
O1—Zn1—O5—C15	-36.5 (6)	C12—C13—C14—C9	-0.4 (9)
O3—Zn1—O5—C15	-129.6 (6)	C10—C9—C14—C13	-0.6 (8)
O3 <sup>i</sup> —Zn1—O5—C15	50.4 (6)	C8—C9—C14—C13	178.5 (5)
O1 <sup>i</sup> —Zn1—O5—Zn2	-132.68 (16)	Zn2—O6—C15—O5	-1.5 (6)
O1—Zn1—O5—Zn2	47.32 (16)	Zn2—O6—C15—C16	-178.8 (4)
O3—Zn1—O5—Zn2	-45.71 (15)	Zn1—O5—C15—O6	90.6 (7)
O3 <sup>i</sup> —Zn1—O5—Zn2	134.29 (15)	Zn2—O5—C15—O6	1.2 (5)
O2—Zn2—O5—C15	102.1 (3)	Zn1—O5—C15—C16	-92.0 (7)
O4—Zn2—O5—C15	-140.2 (3)	Zn2—O5—C15—C16	178.6 (5)

O6—Zn2—O5—C15	-0.8 (3)	Zn1—O5—C15—Zn2	89.4 (6)
N1—Zn2—O5—C15	-43.3 (5)	O2—Zn2—C15—O6	91.9 (4)
O2—Zn2—O5—Zn1	-37.85 (19)	O4—Zn2—C15—O6	-136.3 (4)
O4—Zn2—O5—Zn1	79.85 (17)	N1—Zn2—C15—O6	-24.9 (4)
O6—Zn2—O5—Zn1	-140.7 (2)	O5—Zn2—C15—O6	-178.7 (6)
N1—Zn2—O5—Zn1	176.7 (2)	O2—Zn2—C15—O5	-89.5 (3)
C15—Zn2—O5—Zn1	-139.9 (4)	O4—Zn2—C15—O5	42.4 (3)
O2—Zn2—O6—C15	-100.0 (4)	O6—Zn2—C15—O5	178.7 (6)
O4—Zn2—O6—C15	55.6 (4)	N1—Zn2—C15—O5	153.8 (3)
N1—Zn2—O6—C15	159.3 (4)	O6—C15—C16—C17	174.7 (6)
O5—Zn2—O6—C15	0.8 (3)	O5—C15—C16—C17	-2.7 (8)
O2—Zn2—N1—C22	169.8 (4)	O6—C15—C16—C21	-6.6 (8)
O4—Zn2—N1—C22	51.3 (4)	O5—C15—C16—C21	176.0 (6)
O6—Zn2—N1—C22	-77.8 (4)	C21—C16—C17—C18	1.6 (10)
O5—Zn2—N1—C22	-42.7 (5)	C15—C16—C17—C18	-179.7 (6)
C15—Zn2—N1—C22	-66.1 (4)	C16—C17—C18—C19	-0.6 (12)
O2—Zn2—N1—C26	-10.7 (4)	C17—C18—C19—C20	-0.3 (14)
O4—Zn2—N1—C26	-129.2 (4)	C18—C19—C20—C21	0.2 (15)
O6—Zn2—N1—C26	101.8 (4)	C17—C16—C21—C20	-1.7 (11)
O5—Zn2—N1—C26	136.8 (4)	C15—C16—C21—C20	179.6 (7)
C15—Zn2—N1—C26	113.5 (4)	C19—C20—C21—C16	0.8 (13)
Zn1—O1—C1—O2	33.4 (9)	C26—N1—C22—C23	0.2 (8)
Zn1—O1—C1—C2	-147.8 (5)	Zn2—N1—C22—C23	179.7 (4)
Zn2—O2—C1—O1	6.3 (7)	N1—C22—C23—C24	0.4 (9)
Zn2—O2—C1—C2	-172.5 (3)	N1—C22—C23—C27	-178.1 (5)
O1—C1—C2—C7	-172.7 (5)	C22—C23—C24—C25	-0.3 (9)
O2—C1—C2—C7	6.2 (7)	C27—C23—C24—C25	178.1 (6)
O1—C1—C2—C3	4.5 (8)	C23—C24—C25—C26	-0.3 (10)
O2—C1—C2—C3	-176.6 (5)	C22—N1—C26—C25	-0.9 (8)
C7—C2—C3—C4	-0.1 (10)	Zn2—N1—C26—C25	179.6 (4)
C1—C2—C3—C4	-177.4 (6)	C24—C25—C26—N1	0.9 (9)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg is the centroid of the C19–C14 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C20—H20 $\cdots$ N2 <sup>ii</sup>	0.93	2.63	3.448 (11)	147 (1)
C24—H24 $\cdots$ Cg <sup>iii</sup>	0.93	2.70	3.512 (6)	147

Symmetry codes: (ii)  $-x+3/2, -y+1, z+1/2$ ; (iii)  $x, y-1, z$ .