



Crystal structure and Hirshfeld surface analysis of aquabis(nicotinamide- κN^1)bis(2,4,6-trimethylbenzoato- κO)zinc

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Received 21 July 2017

Accepted 9 August 2017

Edited by H. Ishida, Okayama University, Japan

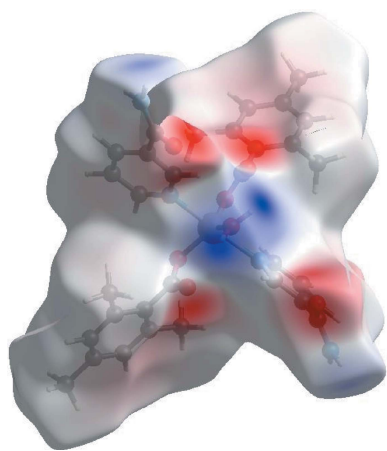
Keywords: crystal structure; zinc; transition metal complex of benzoic acid and nicotinamide derivatives.**CCDC reference:** 1567723**Supporting information:** this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title complex, $[\text{Zn}(\text{C}_{10}\text{H}_{11}\text{O}_2)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})]$, contains one half of the complex molecule, and the Zn^{II} cation and the water O atom lie on a twofold rotation axis. The Zn^{II} cation is coordinated by two carboxylate O atoms of the two symmetry-related 2,4,6-trimethylbenzoate (TMB) anions and by the water O atom at distances of 2.0311 (16) and 2.076 (2) Å to form a slightly distorted trigonal-planar arrangement, while the distorted trigonal-bipyramidal coordination sphere is completed by the two pyridine N atoms of the two symmetry-related monodentate nicotinamide (NA) ligands at distances of 2.2066 (19) Å in the axial positions. In the crystal, molecules are linked *via* intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with $R_2^2(12)$, $R_3^3(10)$ and $R_3^3(16)$ ring motifs, forming a double-column structure running along the *c*-axis direction. The Hirshfeld surface analysis of the crystal structure indicates that the most important contributions for the crystal packing are from $\text{H}\cdots\text{H}$ (58.4%), $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ (20.3%) and $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ (18.3%) interactions.

1. Chemical context

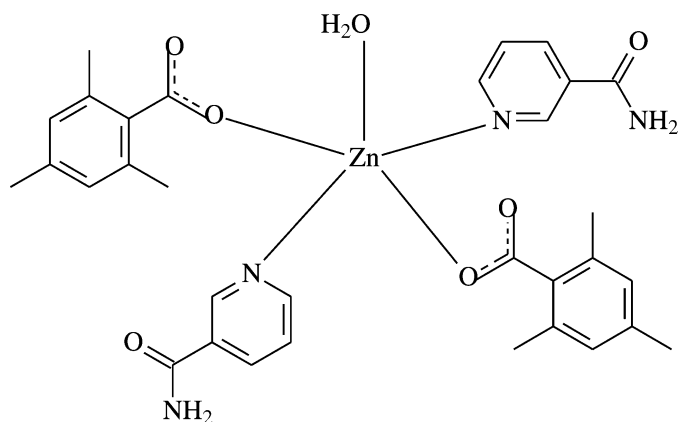
Nicotinamide (NA) is one form of niacin. A deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). The NA ring is the reactive part of nicotinamide adenine dinucleotide (NAD) and its phosphate (NADP), which are the major electron carriers in many biological oxidation-reduction reactions (You *et al.*, 1978). A nicotinic acid derivative, *N,N*-diethylnicotinamide (DENA), is an important respiratory stimulant (Bigoli *et al.*, 1972).

The transition metal complexes with ligands of biochemical interest as imidazole and some *N*-protected amino acids show interesting physical and/or chemical properties, through which they may find applications in biological systems (Antolini *et al.*, 1982). Crystal structures of metal complexes with benzoic acid derivatives have been reported extensively because of the varieties of the coordination modes [for example, Co and Cd complexes with 4-aminobenzoic acid (Chen & Chen, 2002)]. The structures of some mononuclear complexes obtained from the reactions of transition metal(II) ions with nicotinamide (NA) and some benzoic acid derivatives as ligands, *e.g.* $[\text{Zn}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2]$ [(II); Necefoğlu *et al.*, 2002], $[\text{Mn}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$ [(III); Hökelek *et al.*, 2008], $[\text{Zn}(\text{C}_8\text{H}_8\text{NO}_2)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2]\cdot\text{H}_2\text{O}$ [(IV); Hökelek *et al.*, 2009a], $[\text{Mn}(\text{C}_9\text{H}_{10}\text{NO}_2)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$ [(V);



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Hökelek *et al.*, 2009b], [Ni(C₇H₄ClO₂)₂(C₆H₆N₂O)₂(H₂O)₂] [(VI); Hökelek *et al.*, 2009c] and [Zn(C₇H₄BrO₂)₂(C₆H₆N₂O)₂(H₂O)₂] [(VII); Hökelek *et al.*, 2009d], have been determined previously. The structure determination of the title compound, [Zn(C₁₀H₁₁O₂)₂(C₆H₆ON₂)₂(H₂O)] (I), a zinc complex with two 2,4,6-trimethylbenzoate (TMB) and two nicotinamide (NA) ligands and one coordinating water molecule, was undertaken in order to compare the results obtained with those reported previously. In this context, we synthesized the title compound and report herein its crystal and molecular structures along with the Hirshfeld surface analysis.



2. Structural commentary

The asymmetric unit of the crystal structure of the mononuclear title complex contains one Zn^{II} cation (site symmetry 2), one 2,4,6-trimethylbenzoate (TMB) anion and one nicotinamide (NA) molecule together with one water molecule (point group symmetry 2), all ligands coordinating in a monodentate manner (Fig. 1). The Zn^{II} cation is penta-coor-

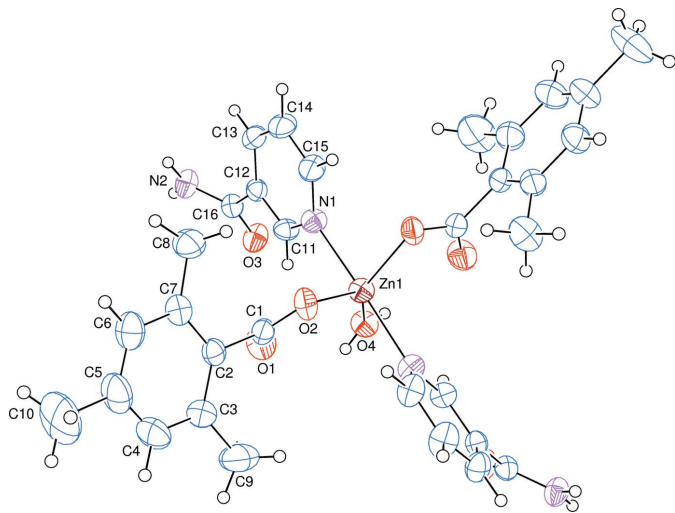


Figure 1

The molecular structure of the title complex, with the atom-numbering scheme. Unlabelled atoms are related to labelled ones by the symmetry operation $(1 - x, y, \frac{1}{2} - z)$. Displacement ellipsoids are drawn at the 40% probability level.

Table 1

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>
N2—H21···O1 ⁱ	0.91 (3)	1.88 (3)	2.766 (3)	165 (3)
N2—H22···O3 ⁱⁱⁱ	0.87 (3)	2.34 (3)	3.013 (2)	134 (2)
O4—H41···O3 ⁱⁱⁱ	0.81 (3)	1.93 (3)	2.719 (2)	165 (3)

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

minated *via* two nitrogen atoms of NA and two oxygen atoms of TMB anions and one oxygen atom of the water molecule. The two carboxylate O atoms [O2 and O2ⁱ; symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] of the two symmetry-related TMB anions and the coordinating water O atom (O4) are at distances of 2.0311 (16) and 2.076 (2) Å, respectively, around the Zn1 atom and form a slightly distorted triangular planar arrangement. The sum of the bond angles O2—Zn1—O2ⁱ [95.38 (9)°], O2—Zn1—O4 [132.31 (5)°] and O2—Zn1—O4ⁱ [132.31 (5)°] in the basal plane around Zn^{II} cation is 360°. This confirms the presence of the Zn^{II} cation with very slight deviation from the basal plane. The slightly distorted trigonal-bipyramidal coordination sphere is completed by the two pyridine N atoms (N1 and N1ⁱ) of the two symmetry-related monodentate NA ligands at distances of 2.2066 (19) Å in the axial positions. The index of trigonality τ [where $\tau = (\beta - \alpha)/60$, in which α and β are the two largest coordination angles; Addison *et al.* (1984)] was calculated as 0.65 by taking N1—Zn1—N1 as β [171.42 (8)°] and O2—Zn1—O4 as α [132.31 (5)°]. In general, $\tau = 0$ for an ideal square pyramidal and $\tau = 1$ for an ideal trigonal-pyramidal geometry. In the present case, the obtained τ value is slightly closer to a trigonal-pyramidal geometry.

The near equalities of the C1—O1 [1.240 (3) Å] and C1—O2 [1.259 (3) Å] bonds in the carboxylate groups indicate delocalized bonding arrangements rather than localized single and double bonds. The O2—C1—O1 bond angle [121.8 (2)°] seems to be slightly decreased than that present in a free acid [122.2°], in which the O2—C1—O1 bond angle may be compared with the corresponding values of 123.5 (2) and 120.4 (2)° in (II), 125.2 (5)° in (III), 119.2 (3) and 123.8 (2)° in (IV), 123.6 (3) and 119.4 (3)° in (V), 124.4 (2)° in (VI) and 124.3 (2)° in (VII), where the benzoate ions coordinate to the metal atoms only monodentately in (III), (VI) and (VII), and both monodentately and bidentately in (II), (IV) and (V). The Zn1 atom lies 0.0817 (1) Å above of the planar (O1/O2/C1) carboxylate group. In the TMB anion, the carboxylate group is twisted away from the attached benzene C2—C7 ring by 61.32 (14)°, while the benzene ring and the pyridine N1/C11—C15 ring are oriented at a dihedral angle of 81.90 (8)°.

3. Supramolecular features

In the crystal, the NH₂ group links to the non-coordinating carboxylate and NA oxygen atoms *via* intermolecular N—H···O hydrogen bonds, and the water molecule links to the NA oxygen atoms *via* intermolecular O—H···O hydrogen bonds (Table 1). These hydrogen bonds, enclosing $R_2^2(12)$,

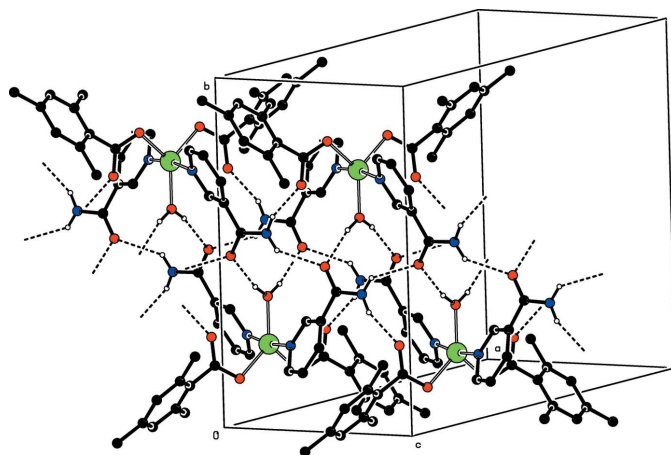


Figure 2
Part of the crystal structure. $O-H_{\text{coordW}} \cdots O_{\text{NA}}$, $N-H_{\text{NA}} \cdots O_c$ and $N-H_{\text{NA}} \cdots O_{\text{NA}}$ (coordW = coordinating water, c = carboxylate and NA = nicotinamide) hydrogen bonds, enclosing $R_3^2(12)$, $R_3^3(10)$ and $R_3^3(16)$ ring motifs, are shown as dashed lines. Non-bonding H atoms have been omitted for clarity.

$R_3^3(10)$ and $R_3^3(16)$ ring motifs, link the molecules into a network consisting of a double-column structure running along the c -axis direction (Fig. 2). No significant π - π , $C-H \cdots \pi$ or $C-H \cdots O$ interactions are observed.

4. Hirshfeld surface analysis

A Hirshfeld surface (HS) analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) was carried out by using *Crystal Explorer 17.5* (Turner *et al.*, 2017) in order to visualize the intermolecular interactions in the crystal of the title complex. In the HS plotted over d_{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

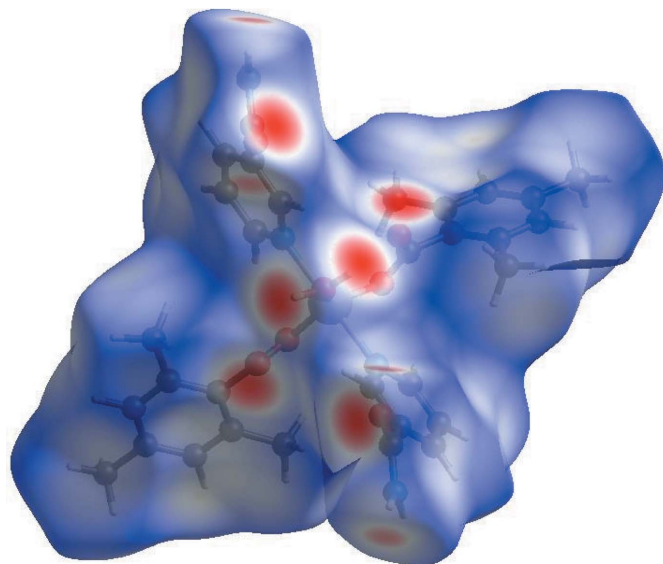


Figure 3
View of the three-dimensional Hirshfeld surface of the title complex plotted over d_{norm} in the range -0.6568 to 1.4993 a.u.

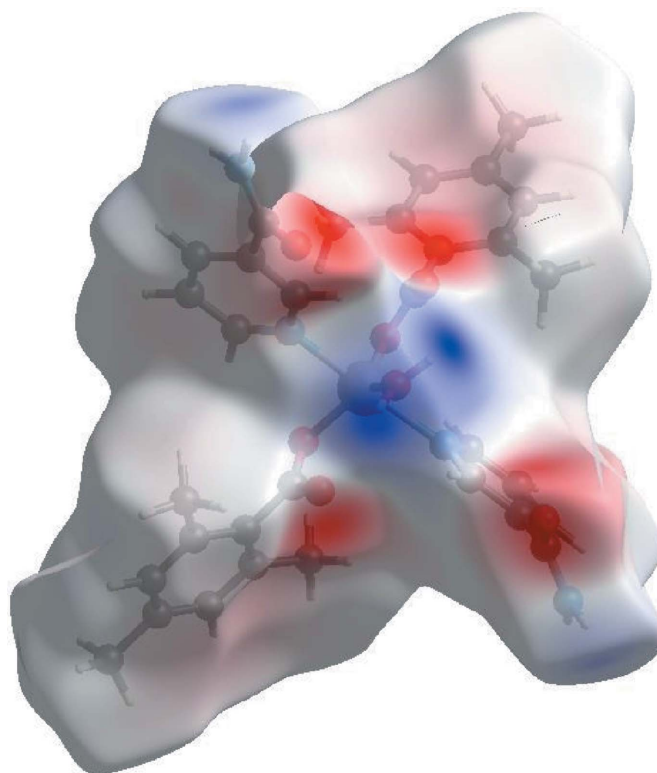
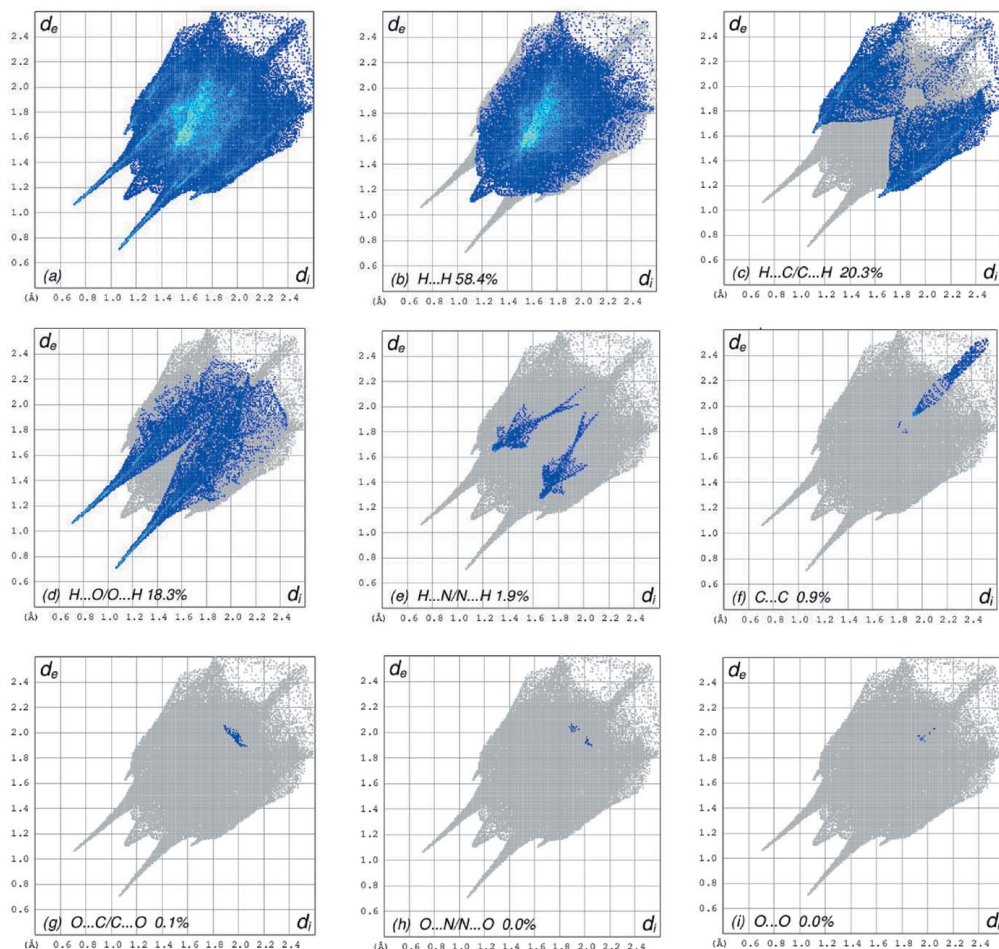


Figure 4
View of the three-dimensional Hirshfeld surface of the title complex plotted over electrostatic potential energy in the range -0.1036 to 0.2354 a.u. using the STO-3G basis set at the Hartree-Fock level of theory. $N-H \cdots O$ and $O-H \cdots O$ hydrogen-bond donors and acceptors are viewed as blue and red regions around the atoms corresponding to positive and negative potentials, respectively.

Waals radii, respectively (Venkatesan *et al.*, 2016). The bright-red spots appearing near atoms O1, O3, H21, H22 and H41 indicate their role as the respective donors and acceptors in the dominant $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds. These O and H atoms also appear as blue and red regions, respectively, corresponding to positive and negative potentials on the HS mapped over electrostatic potential (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005) as shown in Fig. 4. The blue regions indicate the positive electrostatic potential (hydrogen bond donors), while the red regions indicate the negative electrostatic potential (hydrogen bond acceptors). The overall two-dimensional fingerprint plot and those delineated into $H \cdots H$, $H \cdots C/C \cdots H$, $H \cdots O/O \cdots H$, $H \cdots N/N \cdots H$, $C \cdots C$, $O \cdots C/C \cdots O$, $O \cdots N/N \cdots O$ and $O \cdots O$ contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 5 *a-i*, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is $H \cdots H$ contributing 58.4% to the overall crystal packing, which is reflected in Fig. 5*b* as widely scattered points of high density due to the large hydrogen content of the molecule. In the absence of $C-H \cdots \pi$ interactions in the crystal, the pair of characteristic wings resulting in the fingerprint plot delineated into $H \cdots C/C \cdots H$ contacts with 20.3% contribution to the HS, Fig. 5*c*, and the pair of thin edges at $d_e + d_i \sim 2.9$ Å result from short interatomic $H \cdots C/C \cdots H$ contacts. In the fingerprint plot delineated into $H \cdots O/O \cdots H$


Figure 5

The full two-dimensional fingerprint plots for the title complex, showing (a) all interactions, and delineated into (b) $H \cdots H$, (c) $H \cdots C/C \cdots H$, (d) $H \cdots O/O \cdots H$, (e) $H \cdots N/N \cdots H$, (f) $C \cdots C$, (g) $O \cdots C/C \cdots O$, (h) $O \cdots N/N \cdots O$ and (i) $O \cdots O$ 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.

$O \cdots H$ contacts (Fig. 5d), the 18.3% contribution to the HS arises from the intermolecular $O-H \cdots O$ hydrogen bonding and is viewed as pair of spikes with the tip at $d_e + d_i \sim 1.9$ Å. The short $H \cdots O/O \cdots H$ contacts are masked by strong $O-H \cdots O$ hydrogen bonding in this plot. The $H \cdots N/N \cdots H$ contacts in the structure with 1.9% contribution to the HS has a symmetrical distribution of points with the tips at $d_e + d_i \sim 2.8$ Å arising from the short interatomic $H \cdots N/N \cdots H$ contact (Fig. 5e). The HSs mapped over shape-index, curviness and those with the function d_{norm} plotted onto the surface are shown for the $H \cdots H$, $H \cdots C/C \cdots H$, $H \cdots O/O \cdots H$ and $H \cdots N/N \cdots H$ interactions are shown in Figs. s1–s3 in the Supporting Information.

5. Synthesis and crystallization

The title compound was prepared by the reaction of $ZnSO_4 \cdot 7H_2O$ (0.72 g, 2.5 mmol) in H_2O (50 ml) and nicotinamide (0.61 g, 5 mmol) in H_2O (25 ml) with sodium 2,4,6-trimethylbenzoate (0.93 g, 5 mmol) in H_2O (150 ml) at room temperature. The mixture was set aside to crystallize at ambient temperature for ten weeks, giving colourless single

crystals (yield: 1.39 g, 85%). FT-IR: 3396, 3111, 2953, 2919, 2740, 2321, 1947, 1693, 1665, 1621, 1601, 1584, 1445, 1397, 1199, 1113, 1047, 860, 839, 797, 731, 647, 614, 545, 559 cm^{-1} .

6. Refinement

The experimental details including the crystal data, data collection and refinement are summarized in Table 2. The H atom of the water molecule was located in a difference-Fourier map and refined freely. H atoms of the NH_2 group were also located in a difference Fourier map and the positions were refined with $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(N)$. The C-bound H atoms were positioned geometrically with $C-H = 0.93$ and 0.96 Å for aromatic and methyl H-atoms, respectively, and refined as riding with $U_{\text{iso}}(H) = k \times U_{\text{eq}}(C)$, where $k = 1.5$ for methyl H-atoms and $k = 1.2$ for aromatic H-atoms.

Acknowledgements

The authors acknowledge the Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Zn(C ₁₀ H ₁₁ O ₂) ₂ (C ₆ H ₆ N ₂ O) ₂ ·(H ₂ O)]
<i>M_r</i>	654.02
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.4004 (5), 15.1685 (4), 9.2353 (3)
<i>V</i> (Å ³)	3278.06 (15)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.80
Crystal size (mm)	0.42 × 0.36 × 0.21
Data collection	
Diffractometer	Bruker SMART BREEZE CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.730, 0.850
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	44050, 4104, 3310
<i>R_{int}</i>	0.036
(sin θ/λ) _{max} (Å ⁻¹)	0.669
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.045, 0.127, 1.08
No. of reflections	4104
No. of parameters	213
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.29, -0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2015).

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

- Antolini, L., Battaglia, L. P., Corradi, A. B., Marcotrigiano, G., Menabue, L., Pellacani, G. C. & Saladini, M. (1982). *Inorg. Chem.* **21**, 1391–1395.
- Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1972). *Acta Cryst.* **B28**, 962–966.
- Bruker (2012). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
- Chen, H. J. & Chen, X. M. (2002). *Inorg. Chim. Acta*, **329**, 13–21.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Hirshfeld, H. L. (1977). *Theor. Chim. Acta*, **44**, 129–138.
- Hökelek, T., Çaylak, N. & Necefoğlu, H. (2008). *Acta Cryst.* **E64**, m505–m506.
- Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009a). *Acta Cryst.* **E65**, m1365–m1366.
- Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009b). *Acta Cryst.* **E65**, m1037–m1038.
- Hökelek, T., Dal, H., Tercan, B., Özbek, F. E. & Necefoğlu, H. (2009c). *Acta Cryst.* **E65**, m466–m467.
- Hökelek, T., Dal, H., Tercan, B., Özbek, F. E. & Necefoğlu, H. (2009d). *Acta Cryst.* **E65**, m607–m608.
- Jayatilaka, D., Grimwood, D. J., Lee, A., Lemay, A., Russel, A. J., Taylor, C., Wolff, S. K., Cassam-Chenai, P. & Whitton, A. (2005). *TONTO - A System for Computational Chemistry*. Available at: <http://hirshfeldsurface.net/>
- Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Necefoğlu, H., Hökelek, T., Ersanlı, C. C. & Erdönmez, A. (2002). *Acta Cryst.* **E58**, m758–m761.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). *CrystEngComm*, **10**, 377–388.
- Spek, A. L. (2015). *Acta Cryst.* **C71**, 9–18.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.
- Venkatesan, P., Thamocharan, S., Ilangovan, A., Liang, H. & Sundius, T. (2016). *Spectrochim. Acta Part A*, **153**, 625–636.
- You, K.-S., Arnold, L. J. Jr, Allison, W. S. & Kaplan, N. O. (1978). *Trends Biochem. Sci.* **3**, 265–268.

supporting information

Acta Cryst. (2017). E73, 1348-1352 [https://doi.org/10.1107/S2056989017011690]

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE*; 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, 2015).

Aquabis(nicotinamide- κN^1)bis(2,4,6-trimethylbenzoato- κO)zinc

Crystal data

$[\text{Zn}(\text{C}_{10}\text{H}_{11}\text{O}_2)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{H}_2\text{O})]$

$M_r = 654.02$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 23.4004$ (5) Å

$b = 15.1685$ (4) Å

$c = 9.2353$ (3) Å

$V = 3278.06$ (15) Å³

$Z = 4$

$F(000) = 1368$

$D_x = 1.325$ Mg m⁻³

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

Cell parameters from 9891 reflections

$\theta = 2.7\text{--}28.4^\circ$

$\mu = 0.80$ mm⁻¹

$T = 296$ K

Block, colourless

$0.42 \times 0.36 \times 0.21$ mm

Data collection

Bruker SMART BREEZE CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2012)

$T_{\min} = 0.730$, $T_{\max} = 0.850$

44050 measured reflections

4104 independent reflections

3310 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 28.4^\circ$, $\theta_{\min} = 1.6^\circ$

$h = -29 \rightarrow 31$

$k = -20 \rightarrow 18$

$l = -12 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.127$

$S = 1.08$

4104 reflections

213 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 atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 1.7904P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$$

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.5000	0.74469 (2)	0.2500	0.04143 (13)
O1	0.41787 (9)	0.77620 (12)	0.4394 (2)	0.0656 (5)
O2	0.44479 (7)	0.65455 (11)	0.33298 (16)	0.0544 (4)
O3	0.57370 (8)	0.99041 (10)	0.66283 (17)	0.0589 (4)
O4	0.5000	0.88159 (15)	0.2500	0.0502 (5)
H41	0.5262 (12)	0.9122 (18)	0.222 (3)	0.057 (8)*
N1	0.55509 (9)	0.75557 (11)	0.4431 (2)	0.0449 (4)
N2	0.58656 (10)	0.91889 (14)	0.8743 (2)	0.0522 (5)
H21	0.5893 (13)	0.867 (2)	0.924 (3)	0.078*
H22	0.5842 (13)	0.969 (2)	0.920 (3)	0.078*
C1	0.41195 (9)	0.69614 (15)	0.4166 (2)	0.0436 (5)
C2	0.36403 (9)	0.64607 (14)	0.4853 (2)	0.0433 (5)
C3	0.30732 (11)	0.6708 (2)	0.4566 (3)	0.0657 (7)
C4	0.26398 (12)	0.6235 (3)	0.5224 (4)	0.0879 (10)
H4	0.2263	0.6396	0.5041	0.106*
C5	0.27421 (13)	0.5537 (3)	0.6139 (4)	0.0834 (10)
C6	0.33025 (13)	0.53126 (19)	0.6414 (3)	0.0664 (7)
H6	0.3379	0.4846	0.7038	0.080*
C7	0.37565 (10)	0.57607 (14)	0.5789 (2)	0.0481 (5)
C8	0.43568 (12)	0.5514 (2)	0.6170 (3)	0.0692 (7)
H8A	0.4354	0.5117	0.6980	0.104*
H8B	0.4568	0.6035	0.6420	0.104*
H8C	0.4534	0.5231	0.5356	0.104*
C9	0.29388 (16)	0.7462 (3)	0.3543 (5)	0.1093 (15)
H9A	0.2533	0.7555	0.3514	0.164*
H9B	0.3074	0.7319	0.2589	0.164*
H9C	0.3124	0.7988	0.3877	0.164*
C10	0.22443 (18)	0.5042 (4)	0.6832 (6)	0.144 (2)
H10A	0.1901	0.5384	0.6732	0.217*
H10B	0.2323	0.4949	0.7840	0.217*
H10C	0.2196	0.4484	0.6358	0.217*
C11	0.55380 (9)	0.82679 (13)	0.5282 (2)	0.0431 (5)

H11	0.5294	0.8726	0.5026	0.052*
C12	0.58642 (9)	0.83658 (13)	0.6518 (2)	0.0396 (4)
C13	0.62260 (11)	0.76826 (16)	0.6900 (3)	0.0521 (5)
H13	0.6449	0.7718	0.7732	0.063*
C14	0.62482 (12)	0.69502 (16)	0.6023 (3)	0.0605 (7)
H14	0.6492	0.6485	0.6248	0.073*
C15	0.59098 (11)	0.69098 (15)	0.4816 (2)	0.0524 (6)
H15	0.5930	0.6410	0.4235	0.063*
C16	0.58181 (9)	0.92186 (14)	0.7316 (2)	0.0427 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0472 (2)	0.02853 (19)	0.0485 (2)	0.000	0.00026 (14)	0.000
O1	0.0772 (12)	0.0463 (10)	0.0733 (12)	-0.0103 (9)	0.0122 (10)	-0.0028 (9)
O2	0.0569 (9)	0.0608 (10)	0.0456 (8)	-0.0090 (8)	0.0146 (7)	-0.0075 (7)
O3	0.0898 (12)	0.0369 (8)	0.0499 (9)	0.0059 (8)	0.0028 (8)	0.0006 (7)
O4	0.0559 (14)	0.0318 (11)	0.0630 (14)	0.000	0.0037 (11)	0.000
N1	0.0525 (11)	0.0331 (9)	0.0490 (10)	0.0057 (7)	-0.0026 (8)	-0.0027 (8)
N2	0.0718 (13)	0.0428 (11)	0.0422 (10)	-0.0075 (9)	0.0027 (9)	-0.0030 (8)
C1	0.0462 (11)	0.0490 (12)	0.0355 (9)	-0.0037 (9)	0.0004 (8)	0.0012 (8)
C2	0.0450 (11)	0.0459 (11)	0.0389 (10)	-0.0030 (9)	0.0039 (8)	-0.0067 (8)
C3	0.0488 (13)	0.087 (2)	0.0613 (15)	0.0026 (13)	-0.0020 (11)	0.0045 (14)
C4	0.0415 (14)	0.135 (3)	0.088 (2)	-0.0110 (17)	0.0016 (13)	0.002 (2)
C5	0.0654 (18)	0.105 (3)	0.080 (2)	-0.0333 (17)	0.0173 (15)	-0.0014 (19)
C6	0.0767 (18)	0.0598 (16)	0.0626 (15)	-0.0218 (13)	0.0108 (13)	0.0010 (12)
C7	0.0555 (13)	0.0386 (11)	0.0501 (11)	-0.0058 (9)	0.0068 (10)	-0.0057 (9)
C8	0.0644 (16)	0.0619 (16)	0.0814 (18)	0.0082 (13)	0.0039 (14)	0.0188 (14)
C9	0.070 (2)	0.142 (4)	0.116 (3)	0.021 (2)	-0.014 (2)	0.046 (3)
C10	0.091 (3)	0.186 (5)	0.157 (4)	-0.069 (3)	0.034 (3)	0.024 (4)
C11	0.0447 (11)	0.0342 (10)	0.0506 (11)	0.0086 (8)	-0.0034 (9)	-0.0035 (8)
C12	0.0422 (10)	0.0376 (10)	0.0391 (9)	0.0020 (8)	0.0046 (8)	0.0031 (8)
C13	0.0596 (14)	0.0548 (13)	0.0420 (11)	0.0116 (11)	-0.0022 (10)	0.0076 (10)
C14	0.0782 (17)	0.0474 (13)	0.0559 (13)	0.0274 (12)	-0.0024 (12)	0.0056 (10)
C15	0.0722 (15)	0.0354 (11)	0.0497 (12)	0.0134 (10)	0.0015 (11)	-0.0015 (9)
C16	0.0467 (11)	0.0384 (11)	0.0431 (10)	-0.0022 (8)	0.0034 (8)	-0.0006 (8)

Geometric parameters (Å, °)

Zn1—O2 ⁱ	2.0311 (16)	C6—C5	1.379 (5)
Zn1—O2	2.0311 (16)	C6—H6	0.9300
Zn1—O4	2.076 (2)	C7—C6	1.387 (3)
Zn1—N1	2.2066 (19)	C7—C8	1.496 (4)
Zn1—N1 ⁱ	2.2066 (19)	C8—H8A	0.9600
O1—C1	1.240 (3)	C8—H8B	0.9600
O2—C1	1.259 (3)	C8—H8C	0.9600
O3—C16	1.233 (3)	C9—H9A	0.9600
O4—H41	0.81 (3)	C9—H9B	0.9600

N1—C11	1.336 (3)	C9—H9C	0.9600
N1—C15	1.338 (3)	C10—H10A	0.9600
N2—C16	1.324 (3)	C10—H10B	0.9600
N2—H21	0.91 (3)	C10—H10C	0.9600
N2—H22	0.87 (3)	C11—H11	0.9300
C2—C1	1.496 (3)	C12—C11	1.382 (3)
C2—C3	1.404 (3)	C12—C13	1.384 (3)
C2—C7	1.396 (3)	C12—C16	1.493 (3)
C3—C4	1.383 (4)	C13—C14	1.376 (3)
C3—C9	1.516 (4)	C13—H13	0.9300
C4—H4	0.9300	C14—H14	0.9300
C5—C4	1.375 (5)	C15—C14	1.369 (3)
C5—C10	1.526 (4)	C15—H15	0.9300
O2 ⁱ —Zn1—O2	95.38 (9)	C6—C7—C8	119.9 (2)
O2—Zn1—O4	132.31 (5)	C7—C8—H8A	109.5
O2 ⁱ —Zn1—O4	132.31 (5)	C7—C8—H8B	109.5
O2—Zn1—N1	96.72 (7)	C7—C8—H8C	109.5
O2 ⁱ —Zn1—N1	89.07 (7)	H8A—C8—H8B	109.5
O2—Zn1—N1 ⁱ	89.07 (7)	H8A—C8—H8C	109.5
O2 ⁱ —Zn1—N1 ⁱ	96.72 (7)	H8B—C8—H8C	109.5
O4—Zn1—N1	85.71 (4)	C3—C9—H9A	109.5
O4—Zn1—N1 ⁱ	85.71 (4)	C3—C9—H9B	109.5
N1—Zn1—N1 ⁱ	171.42 (8)	C3—C9—H9C	109.5
C1—O2—Zn1	106.41 (14)	H9A—C9—H9B	109.5
Zn1—O4—H41	125 (2)	H9A—C9—H9C	109.5
C11—N1—Zn1	121.50 (14)	H9B—C9—H9C	109.5
C11—N1—C15	116.7 (2)	C5—C10—H10A	109.5
C15—N1—Zn1	121.76 (15)	C5—C10—H10B	109.5
C16—N2—H21	122.6 (19)	C5—C10—H10C	109.5
C16—N2—H22	117 (2)	H10A—C10—H10B	109.5
H21—N2—H22	121 (3)	H10A—C10—H10C	109.5
O1—C1—O2	121.8 (2)	H10B—C10—H10C	109.5
O1—C1—C2	120.6 (2)	N1—C11—C12	124.08 (19)
O2—C1—C2	117.6 (2)	N1—C11—H11	118.0
C3—C2—C1	119.5 (2)	C12—C11—H11	118.0
C7—C2—C1	120.20 (19)	C11—C12—C13	117.9 (2)
C7—C2—C3	120.3 (2)	C11—C12—C16	117.47 (18)
C2—C3—C9	121.0 (3)	C13—C12—C16	124.6 (2)
C4—C3—C2	118.1 (3)	C12—C13—H13	120.7
C4—C3—C9	120.9 (3)	C14—C13—C12	118.5 (2)
C3—C4—H4	118.6	C14—C13—H13	120.7
C5—C4—C3	122.8 (3)	C13—C14—H14	120.2
C5—C4—H4	118.6	C15—C14—C13	119.6 (2)
C4—C5—C6	118.0 (3)	C15—C14—H14	120.2
C4—C5—C10	120.2 (4)	N1—C15—C14	123.1 (2)
C6—C5—C10	121.8 (4)	N1—C15—H15	118.4
C5—C6—C7	122.0 (3)	C14—C15—H15	118.4

C5—C6—H6	119.0	O3—C16—N2	123.7 (2)
C7—C6—H6	119.0	O3—C16—C12	119.17 (18)
C2—C7—C8	121.3 (2)	N2—C16—C12	117.14 (19)
C6—C7—C2	118.8 (2)		
O2 ⁱ —Zn1—O2—C1	166.98 (17)	C7—C2—C3—C9	-179.5 (3)
O4—Zn1—O2—C1	-13.02 (17)	C1—C2—C7—C6	179.7 (2)
N1—Zn1—O2—C1	77.29 (14)	C1—C2—C7—C8	2.2 (3)
N1 ⁱ —Zn1—O2—C1	-96.36 (14)	C3—C2—C7—C6	0.6 (3)
O2—Zn1—N1—C11	-106.95 (18)	C3—C2—C7—C8	-176.9 (2)
O2 ⁱ —Zn1—N1—C11	157.75 (18)	C2—C3—C4—C5	-0.2 (5)
O2—Zn1—N1—C15	72.40 (19)	C9—C3—C4—C5	178.8 (4)
O2 ⁱ —Zn1—N1—C15	-22.91 (19)	C6—C5—C4—C3	0.7 (6)
O4—Zn1—N1—C11	25.19 (17)	C10—C5—C4—C3	180.0 (4)
O4—Zn1—N1—C15	-155.46 (19)	C7—C6—C5—C4	-0.7 (5)
Zn1—O2—C1—O1	-2.4 (3)	C7—C6—C5—C10	-179.9 (3)
Zn1—O2—C1—C2	175.91 (15)	C2—C7—C6—C5	0.1 (4)
Zn1—N1—C11—C12	178.69 (16)	C8—C7—C6—C5	177.5 (3)
C15—N1—C11—C12	-0.7 (3)	C13—C12—C11—N1	-0.1 (3)
Zn1—N1—C15—C14	-178.6 (2)	C16—C12—C11—N1	177.5 (2)
C11—N1—C15—C14	0.8 (4)	C11—C12—C13—C14	0.9 (3)
C3—C2—C1—O1	60.0 (3)	C16—C12—C13—C14	-176.5 (2)
C3—C2—C1—O2	-118.4 (2)	C11—C12—C16—O3	-33.6 (3)
C7—C2—C1—O1	-119.1 (2)	C11—C12—C16—N2	146.1 (2)
C7—C2—C1—O2	62.5 (3)	C13—C12—C16—O3	143.8 (2)
C1—C2—C3—C4	-179.6 (3)	C13—C12—C16—N2	-36.4 (3)
C1—C2—C3—C9	1.4 (4)	C12—C13—C14—C15	-0.9 (4)
C7—C2—C3—C4	-0.5 (4)	N1—C15—C14—C13	0.0 (4)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H21 \cdots O1 ⁱⁱ	0.91 (3)	1.88 (3)	2.766 (3)	165 (3)
N2—H22 \cdots O3 ⁱⁱⁱ	0.87 (3)	2.34 (3)	3.013 (2)	134 (2)
O4—H41 \cdots O3 ^{iv}	0.81 (3)	1.93 (3)	2.719 (2)	165 (3)

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