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# Bis(4-hydroxybenzoato-$\kappa O$)bis(nicotinamide-$\kappa N$)zinc(II)

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.033
$wR$ factor = 0.095
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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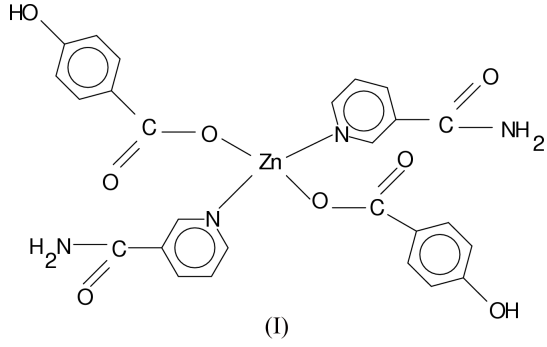
The title compound, $[Zn(C_6H_6N_2O)_2(C_7H_5O_3)_2]$, crystallizes as mononuclear molecules with distorted trigonal–bipyramidal zinc coordination. One of the 4-hydroxybenzoate ions is coordinated to zinc as a bidentate ligand, while the other is monodentate. Intermolecular hydrogen bonds between nicotinamide N and carboxyl O atoms, as well as between the nicotinamide O and hydroxybenzoate O atoms, support the molecular packing. Hydrogen bonding of the carboxylate O atoms has an effect on the delocalization in the carboxylate groups.

## Comment

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 nicotinic acid derivative *N*,*N*-diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972).




(I)

The structures of some complexes obtained from the reactions of transition metal(II) ions with different benzoic and/or nicotinic acid derivatives as ligands have been the subject of much interest in our laboratory; examples are $[Zn(C_7H_5O_3)(OH_2)_3(NA)]\cdot C_7O_3H_5$ [(II); Hökelek & Necefoğlu, 2001], $[Co(C_7H_6NO_2)_2(H_2O)_2(NA)_2]$ [(III); Hökelek & Necefoğlu, 1999*a*], $[Co(C_7H_5O_2)_2(NA)_2(H_2O)_2]$ [(IV); Hökelek & Necefoğlu, 1999*b*], $[Co(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ [(V); Hökelek & Necefoğlu, 1999*c*], $[Cu(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ [(VI); Hökelek, Budak *et al.*, 1998], $[Cu_3\{(NO_2)_2C_6H_3COO\}_6(CH_3OH)_2]_n$ [(VII); Hökelek, Mert, & Ünaleroğlu, 1998], $[Co(C_7H_4NO_4)_2(NA)_2(H_2O)_2]$ [(VIII); Hökelek & Necefoğlu, 1998], $[Cu(C_7H_4NO_4)_2(DENA)_2(H_2O)_2]$ [(IX); Hökelek *et al.*, 1997], $[Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2]$ [(X); Hökelek & Necefoğlu, 1997], $[Zn_2(C_7H_5O_3)_4(DENA)_2(H_2O)_2]$ [(XI); Hökelek & Necefoğlu, 1996],

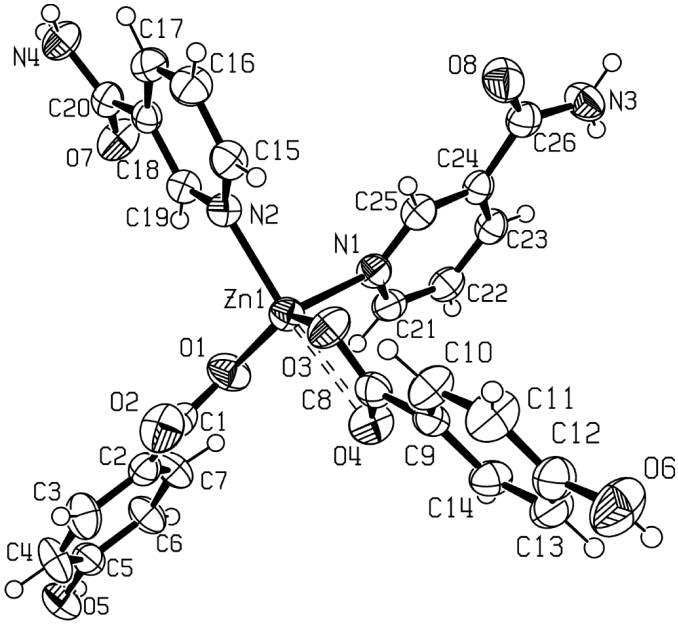



**Figure 1**
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

$[Cu(C_7H_5O_2)_2(DENA)_2]$ [(XII); Hökelek *et al.*, 1996] and $[Cu_2(C_6H_5COO)_4(DENA)_2]$ [(XIII); Hökelek *et al.*, 1995]. In (XIII), the benzoate ion acts as a bidentate ligand, but in (XI) two of the benzoate ions acts as monodentate ligands, while the other two are bidentate, bridging the two Zn atoms.

The solid-state structures of anhydrous zinc(II) carboxylates include one-dimensional (Guseinov *et al.*, 1984; Clegg *et al.*, 1986*a*), two-dimensional (Clegg *et al.*, 1986*b*, 1987) and three-dimensional (Capilla & Aranda, 1979) polymeric motifs of different types, while discrete monomeric complexes with octahedral and tetrahedral coordination geometry are found if water or other donor molecules are coordinated to Zn (van Niekerk *et al.*, 1953; Usubaliev *et al.*, 1992). In hexaaquazinc(II) bis(4-hydroxybenzoate) dihydrate, $[Zn(H_2O)_6](4\text{–}HOC_6H_4COO)_2\cdot 2H_2O$, which is isostructural with the corresponding $Mg^{II}$, $Co^{II}$, $Ni^{II}$ and $Mn^{II}$ compounds, the carboxylate ion lies outside the coordination sphere of the Zn atom (Musaev *et al.*, 1983), while $[Zn(4\text{–}HOC_6H_4COO)_2]\cdot 4C_5H_5N$ forms a clathrate, consisting of $[Zn(4\text{–}HOC_6H_4COO)_2(C_5H_5N)_2]$ units with tetrahedral coordination geometry and free pyridine molecules (Nadzhafov *et al.*, 1981).

The structure determination of the title compound, (I), a zinc complex with two NA and two 4-hydroxybenzoate ligands, was undertaken in order to determine the ligand properties of (NA) and 4-hydroxybenzoate ligands and also to compare the results obtained with those reported previously. In the monomeric title complex, $[Zn(C_7O_3H_5)_2(NA)_2]$, the Zn atom is surrounded by two NA and two 4-hydroxybenzoate ligands. One of the 4-hydroxybenzoate ions acts as a bidentate ligand, while the other and two NA are monodentate ligands. A view of the molecule with the atomic numbering scheme is shown in Fig. 1.

Although the Zn atom has four-coordination, close contact of the O4 atom [Zn1···O4 = 2.404 (2) Å] may be considered to give five-coordination; this distance is much greater than the sum of the corresponding ionic radii (2.14 Å; Day & Selbin, 1969). Similar reported Zn···O contacts are 2.50 (1) Å in $[Zn(n\text{-}HOC_6H_4COO)_2(C_5H_5N)_2]\cdot 2C_5H_5N$ (Nadzhafov *et al.*, 1981) and 2.494 (8) Å in $[Zn(p\text{-}H_2NC_6H_4COO)_2]_n\cdot 1.5nH_2O$ (Amiraslanov *et al.*, 1980). The five-coordination around $Zn^{II}$ can be described as a distorted trigonal bipyramid or a distorted square pyramid. Further information can be obtained by estimating the structural index $\tau$ (Uhlenbrock *et al.*, 1996), which represents the relative amount of trigonality [square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60^\circ$, $\alpha$ and $\beta$ being the two largest angles around the central atom]. The value of $\tau$ is 0.36 for (I) [$\alpha$ = 138.00 (7) and $\beta$ = 159.61 (6) °]. The coordination of the $Zn^{II}$ atom is therefore best described as a distorted trigonal bipyramid.

In the binuclear complex (XI), the average Zn—O bond length [1.953 (2) Å] is shorter than the corresponding value in (I) [2.107 (2) Å], but Zn is four-coordinate. The average Zn—N bond length [2.075 (2) Å] in (I) is in good agreement with the values reported for tetrahedrally coordinated Zn complexes [2.006 (5) Å in $Zn_2(DENA)_2(NCS)_4$ (Bigoli *et al.*, 1973*a*), 2.054 (6) and 2.055 (6) Å in $ZnCl_2(DENA)_2$ (Khodashova *et al.*, 1978), and 2.068 (7) Å in $ZnI_2(DENA)_2$ (Sergienko *et al.*, 1978)], while it is shorter than the corresponding value in the octahedrally coordinated zinc complex $[Zn(DENA)_2(NCS)_2]\cdot 2H_2O$ [2.171 (4) Å; Bigoli *et al.*, 1973*b*]. The aromatic bonds C5—O5 [1.365 (3) Å] and C12—O6 [1.359 (3) Å] are in agreement with the corresponding values for 4-hydroxybenzoic acid monohydrate (Colapietro *et al.*, 1979).

The N1—Zn1···O4 and O3—Zn1···O4 angles are 88.86 (7) and 58.79 (6)°, respectively. The corresponding N—*M*···O and O—*M*···O (where *M* is a metal atom) angles are 90.4 (4) and 58.3 (3)° in (XI) (Hökelek *et al.*, 1996), and 89.6 (1), 89.0 (1) and 55.2 (1)° in $[Cu(Asp)_2(py)_2]$ (where Asp is acetylsalicylate and py is pyridine) (Greenaway *et al.*, 1984). The Zn1 atom lies −0.1931 (2) and 0.2208 (2) Å out of the O1/C1/O2 and O3/C8/O4 carboxyl planes, respectively.

In the carboxylate group, the C1—O1 and C8—O3 bond lengths [1.281 (3) and 1.274 (3) Å] are a little larger than the C1—O2 and C8—O4 [1.240 (3) and 1.245 (3) Å] bond lengths and may be compared with the corresponding distances in the monomeric and dimeric carboxylate pyridine complexes: 1.266 (5) and 1.248 (6) Å in (III), 1.255 (1) and 1.253 (2) Å in (IV), 1.263 (5) and 1.258 (6) Å in (V), 1.278 (3) and 1.246 (3) Å in (VI), 1.254 (2) and 1.251 (2) Å in (VIII), 1.267 (6) and 1.237 (4) Å in (IX), 1.251 (6) and 1.254 (7) Å in (X), 1.279 (4) and 1.246 (4) Å in (XI), and 1.277 (4) and 1.239 (4) Å in (XII).

One of the carboxylates is bidentate, while the other is monodentate, but the near equality of the two C—O bond lengths in each carboxylate groups (Table 1) indicates a delocalized bonding arrangement, rather than localized single

and double bonds. This may be due to the intermolecular hydrogen bonds of the carboxyl O atoms (Table 2).

The dihedral angles between the mean planes of the carboxyl groups (O1/C1/O2 and O3/C8/O4) and the phenyl rings [*A* (C2–C7) and *B* (C9–C14)] in the hydroxybenzoate anions are 12.2 (2) and 10.0 (2)°, respectively; these may be compared with the corresponding values of 24.1 (4)° in (III), 13.0 (2)° in (IV), 14.2 (3)° in (V), 23.7 (3)° in (VIII), 10.2 (7)° in (IX), 2.2 (6)° in (X), 17.9 (7) and 136.1 (2)° in (XI), and 6.7 (9)° in (XII). The configuration around the Zn1 atom is given by the torsion angles listed in Table 1.

There are intermolecular hydrogen bonds between nicotinamide N atoms and carboxyl O atoms, as well as between the nicotinamide O atoms and hydroxybenzoate O atoms of neighbouring molecules (Table 2). These intermolecular hydrogen bonds, together with dipole–dipole and van der Waals interactions, support the molecular packing.

All rings are essentially planar, with maximum deviations of 0.011 (2) Å for C7 and 0.011 (2) Å for C21. The rings are twisted with respect to each other; dihedral angles between least-squares planes are *A*/*B* = 79.36 (7), *A*/*C* = 84.50 (8), *A*/*D* = 12.62 (8), *B*/*C* = 20.39 (7), *B*/*D* = 77.28 (6) and *C*/*D* = 89.57 (7)°.

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

| | | | |
|---|---|---|---|
| Zn1—O1 | 1.9295 (16) | O8—C26 | 1.232 (3) |
| Zn1—O3 | 1.9883 (16) | C8—O4 | 1.245 (3) |
| Zn1—N1 | 2.0723 (18) | C5—O5 | 1.365 (3) |
| Zn1—N2 | 2.0784 (17) | N3—C26 | 1.329 (3) |
| Zn1—O4 | 2.4042 (18) | O7—C20 | 1.232 (3) |
| O3—C8 | 1.274 (3) | N4—C20 | 1.328 (3) |
| O2—C1 | 1.240 (3) | C12—O6 | 1.359 (3) |
| O1—C1 | 1.281 (3) | | |
| O1—Zn1—O3 | 138.00 (7) | O3—Zn1—O4 | 58.79 (6) |
| O1—Zn1—N1 | 102.07 (8) | N1—Zn1—O4 | 88.86 (7) |
| O3—Zn1—N1 | 108.05 (7) | N2—Zn1—O4 | 159.61 (6) |
| O1—Zn1—N2 | 103.94 (7) | O2—C1—O1 | 123.5 (2) |
| O3—Zn1—N2 | 100.91 (7) | O4—C8—O3 | 120.4 (2) |
| N1—Zn1—N2 | 96.70 (7) | O8—C26—N3 | 122.3 (2) |
| O1—Zn1—O4 | 93.97 (7) | O7—C20—N4 | 122.0 (2) |
| O1—Zn1—O3—C8 | 59.86 (18) | O3—Zn1—N2—C15 | 11.05 (18) |
| N1—Zn1—O3—C8 | −73.82 (15) | N1—Zn1—N2—C15 | −98.85 (17) |
| N2—Zn1—O3—C8 | −174.65 (13) | O4—Zn1—N2—C15 | 6.2 (3) |
| O1—Zn1—N2—C19 | −28.41 (17) | O3—Zn1—O1—C1 | 29.4 (2) |
| N1—Zn1—N2—C19 | 75.84 (16) | N1—Zn1—O1—C1 | 164.68 (16) |
| O4—Zn1—N2—C19 | −179.15 (16) | N2—Zn1—O1—C1 | −95.18 (16) |
| O1—Zn1—N2—C15 | 156.90 (16) | O4—Zn1—O1—C1 | 74.99 (17) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O6—H6*A*···O8$^{i}$ | 0.74 (5) | 2.03 (5) | 2.764 (3) | 175 (6) |
| O5—H5*A*···O7$^{ii}$ | 0.83 (4) | 1.91 (4) | 2.735 (3) | 175 (4) |
| N3—H3*B*···O4$^{iii}$ | 0.89 (3) | 2.04 (3) | 2.872 (3) | 155 (3) |
| N4—H4*A*···O2$^{iv}$ | 0.83 (3) | 2.26 (3) | 3.084 (3) | 171 (3) |

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

## Experimental

The title compound, (I), was prepared by the reaction of 0.02 mol of NA in $H_2O$ (50 ml), 0.01 mol of $ZnSO_4$ in $H_2O$ (100 ml), and 0.02 mol of sodium *p*-hydroxybenzoate in $H_2O$ (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for several days, giving colourless single crystals.

*Crystal data*

$[Zn(C_6H_6N_2O)_2(C_7H_5O_3)_2]$
$M_r$ = 583.85
Monoclinic, $P2_1/n$
$a$ = 10.3159 (10) Å
$b$ = 22.606 (3) Å
$c$ = 10.8926 (10) Å
$\beta$ = 95.375 (6)°
$V$ = 2529.0 (5) Å$^3$
$Z$ = 4
$D_x$ = 1.533 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 10–18°
$\mu$ = 1.03 mm$^{-1}$
$T$ = 293 (2) K
Rod, colourless
0.30 × 0.20 × 0.15 mm

*Data collection*

Enraf–Nonius TurboCAD4 diffractometer
Non-profiled $\omega$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.748, $T_{max}$ = 0.861
5409 measured reflections
5124 independent reflections
4089 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031
$\theta_{max}$ = 26.3°
$h = -12 \rightarrow 0$
$k = -28 \rightarrow 0$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.095
$S$ = 1.05
5124 reflections
440 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.716P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.49 e Å$^{-3}$

H atoms were located in a difference map and refined isotropically.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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# supporting information

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## Bis(4-hydroxybenzoato-*κO*)bis(nicotinamide-*κN*)zinc(II)

**Hacali Necefoğlu, Tuncer Hökelek, Cem Cüneyt Ersanlı and Ahmet Erdönmez**

### S1. Comment

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 nicotinic acid derivative *N*,*N*-diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972).

The structures of some complexes obtained from the reactions of transition metal(II) ions with different benzoic and/or nicotinic acid derivatives as ligands have been the subject of much interest in our laboratory; examples are $[Zn(C_7H_5O_3)(OH_2)_3(NA)]\cdot C_7O_3H_5$ [(II); Hökelek & Necefoğlu, 2001], $[Co(C_7H_6NO_2)_2(H_2O)_2(NA)_2]$ [(III); Hökelek & Necefoğlu, 1999*a*], $[Co(C_7H_5O_2)_2(NA)_2(H_2O)_2]$ [(IV); Hökelek & Necefoğlu, 1999*b*], $[Co(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ [(V); Hökelek & Necefoğlu, 1999*c*], $[Cu(C_7H_5O_3)_2(NA)_2(H_2O)_2]$ [(VI); Hökelek, Budak *et al.*, 1998], $[Cu_3\{(NO_2)_2C_6H_3COO\}_6(CH_3OH)_2]_n$ [(VII); Hökelek, Mert & Ünaleroğlu, 1998], $[Co(C_7H_4NO_4)_2(NA)_2(H_2O)_2]$ [(VIII); Hökelek & Necefoğlu, 1998], $[Cu(C_7H_4NO_4)_2(DENA)_2(H_2O)_2]$ [(IX); Hökelek *et al.*, 1997], $[Co(C_7H_5O_3)_2(DENA)_2(H_2O)_2]$ [(*X*); Hökelek & Necefoğlu, 1997], $[Zn_2(C_7H_5O_3)_4(DENA)_2(H_2O)_2]$ [(XI); Hökelek & Necefoğlu, 1996], $[Cu(C_7H_5O_2)_2(DENA)_2]$ [(XII); Hökelek *et al.*, 1996] and $[Cu_2(C_6H_5COO)_4(DENA)_2]$ [(XIII); Hökelek *et al.*, 1995]. In (XIII), the benzoate ion acts as a bidentate ligand, but in (XI) two of the benzoate ions acts as monodentate ligands, while the other two are bidentate, bridging the two Zn atoms.

The solid-state structures of anhydrous zinc(II) carboxylates include one-dimensional (Guseinov *et al.*, 1984; Clegg *et al.*, 1986*a*), two-dimensional (Clegg *et al.*, 1986*b*, 1987) and three-dimensional (Capilla & Aranda, 1979) polymeric motifs of different types, while discrete monomeric complexes with octahedral and tetrahedral coordination geometry are found if water or other donor molecules are coordinated to Zn (van Niekerk *et al.*, 1953; Usubaliev *et al.*, 1992). In hexaaquazinc(II) bis(4-hydroxybenzoate) dihydrate, $[Zn(H_2O)_6](4\text{-}HOC_6H_4COO)_2\cdot 2H_2O$, which is isostructural with the corresponding $Mg^{II}$, $Co^{II}$, $Ni^{II}$ and $Mn^{II}$ compounds, the carboxylate ion lies outside the coordination sphere of the Zn atom (Musaev *et al.*, 1983), while $[Zn(4\text{-}HOC_6H_4COO)_2]\cdot 4C_5H_5N$ forms a clathrate, consisting of $[Zn(4\text{-}HOC_6H_4COO)_2(C_5H_5N)_2]$ units with tetrahedral coordination geometry and free pyridine molecules (Nadzhafov *et al.*, 1981).

The structure determination of the title compound, (I), a zinc complex with two NA and two 4-hydroxybenzoate ligands, was undertaken in order to determine the ligand properties of (NA) and 4-hydroxybenzoate ligands and also to compare the results obtained with those reported previously. In the monomeric title complex, $[Zn(C_7O_3H_5)_2(NA)_2]$, the Zn atom is surrounded by two NA and two 4-hydroxybenzoate ligands. One of the 4-hydroxybenzoate ions acts as a bidentate ligand, while the other and two NA are monodentate ligands. A view of the molecule with the atomic numbering scheme is shown in Fig. 1.

Although the Zn atom has four-coordination, close contact of the O4 atom [Zn1···O4 = 2.404 (2) Å] may be considered to give five-coordination; this distance is much greater than the sum of the corresponding ionic radii (2.14 Å; Day & Selbin, 1969). Similar reported Zn···O contacts are 2.50 (1) Å in $[Zn(n\text{-}HOC_6H_4COO)_2(C_5H_5N)_2]\cdot 2C_5H_5N$ (Nadzhafov *et*

*al.*, 1981) and 2.494 (8) Å in $[Zn(p—H_2NC_6H_4COO)_2]_n.1.5nH_2O$ (Amiraslanov *et al.*, 1980). The five-coordination around $Zn^{II}$ can be described as a distorted trigonal bipyramid or a distorted square pyramid. Further information can be obtained by estimating the structural index $\tau$ (Uhlenbrock *et al.*, 1996), which represents the relative amount of trigonality [square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\beta-\alpha)/60°$, $\alpha$ and $\beta$ being the two largest angles around the central atom]. The value of $\tau$ is 0.36 for (I) [$\alpha$ = 138.00 (7) and $\beta$ = 159.61 (6) °]. The coordination of the $Zn^{II}$ atom is therefore best described as a distorted trigonal bipyramid.

In the binuclear complex (XI), the average Zn—O bond length [1.953 (2) Å] is shorter than the corresponding value in (I) [2.107 (2) Å], but Zn is four-coordinate. The average Zn—N bond length [2.075 (2) Å] in (I) is in good agreement with the values reported for tetrahedrally coordinated Zn complexes [2.006 (5) Å in $Zn_2(DENA)_2(NCS)_4$ (Bigoli *et al.*, 1973*a*), 2.054 (6) and 2.055 (6) Å in $ZnCl_2(DENA)_2$ (Khodashova *et al.*, 1978), and 2.068 (7) Å in $ZnI_2(DENA)_2$ (Sergienko *et al.*, 1978)], while it is shorter than the corresponding value in the octahedrally coordinated zinc complex $[Zn(DENA)_2(NCS)_2]\cdot 2H_2O$ [2.171 (4) Å; Bigoli *et al.*, 1973*b*]. The aromatic bonds C5—O5 [1.365 (3) Å] and C12—O6 [1.359 (3) Å] are in agreement with the corresponding values for 4-hydroxybenzoic acid monohydrate (Colapietro *et al.*, 1979).

The N1—Zn1···O4 and O3—Zn1···O4 angles are 88.86 (7) and 58.79 (6)°, respectively. The corresponding N—M···O and O—M···O (where *M* is metal atom) angles are 90.4 (4) and 58.3 (3)° in (XI) (Hökelek *et al.*, 1996), and 89.6 (1), 89.0 (1) and 55.2 (1)° in $[Cu(Asp)_2(py)_2]$ (where Asp is acetylsalicylate and py is pyridine) (Greenaway *et al.*, 1984). The Zn1 atom lies −0.1931 (2) and 0.2208 (2) Å out of the O1/C1/O2 and O3/C8/O4 carboxyl planes, respectively.

In the carboxylate group, the C1—O1 and C8—O3 bond lengths [1.281 (3) and 1.274 (3) Å] are a little larger than the C1—O2 and C8—O4 [1.240 (3) and 1.245 (3) Å] bond lengths and may be compared with the corresponding distances in the monomeric and dimeric carboxylate pyridine complexes: 1.266 (5) and 1.248 (6) Å in (III), 1.255 (1) and 1.253 (2) Å in (IV), 1.263 (5) and 1.258 (6) Å in (V), 1.278 (3) and 1.246 (3) Å in (VI), 1.254 (2) and 1.251 (2) Å in (VIII), 1.267 (6) and 1.237 (4) Å in (IX), 1.251 (6) and 1.254 (7) Å in (*X*), 1.279 (4) and 1.246 (4) Å in (XI), and 1.277 (4) and 1.239 (4) Å in (XII).

One of the carboxylates is bidentate, while the other is monodentate, but the near equality of the two C—O bond lengths in each carboxylate groups (Table 1) indicates a delocalized bonding arrangement, rather than localized single and double bonds. This may be due to the intermolecular hydrogen bonds of the carboxyl O atoms (Table 2).

The dihedral angles between the mean planes of the carboxyl groups (O1/C1/O2 and O3/C8/O4) and the phenyl rings [A (C2—C7) and B (C9—C14)] in the hydroxybenzoate anions are 12.2 (2) and 10.0 (2)°, respectively; these may be compared with the corresponding values of 24.1 (4)° in (III), 13.0 (2)° in (IV), 14.2 (3)° in (V), 23.7 (3)° in (VIII), 10.2 (7)° in (IX), 2.2 (6)° in (*X*), 17.9 (7) and 136.1 (2)° in (XI), and 6.7 (9)° in (XII). The configuration around the Zn1 atom is given by the torsion angles listed in Table 1.

There are intermolecular hydrogen bonds between nicotinamide N atoms and carboxyl O atoms, as well as between the nicotinamide O atoms and hydroxybenzoate O atoms of neighbouring molecules (Table 2). These intermolecular hydrogen bonds, together with dipole-dipole and van der Waals interactions, support the molecular packing.

All rings are essentially planar, with maximum deviations of 0.011 (2) Å for C7 and 0.011 (2) Å for C21. The rings are twisted with respect to each other; dihedral angles between least-squares planes are A/B = 79.36 (7), A/C = 84.50 (8), A/D = 12.62 (8), B/C = 20.39 (7), B/D = 77.28 (6) and C/D = 89.57 (7)°.

## S2. Experimental

The title compound, (I), was prepared by the reaction of 0.02 mol of NA, in $H_2O$ (50 ml), 0.01 mol of $ZnSO_4$ in $H_2O$ (100 ml), and 0.02 mol of sodium *p*-hydroxybenzoate in $H_2O$ (100 ml). The mixture was filtered and set aside to crystallize at

ambient temperature for several days, giving colourless single crystals.

### S3. Refinement

H atoms were located in a difference map and refined isotropically.

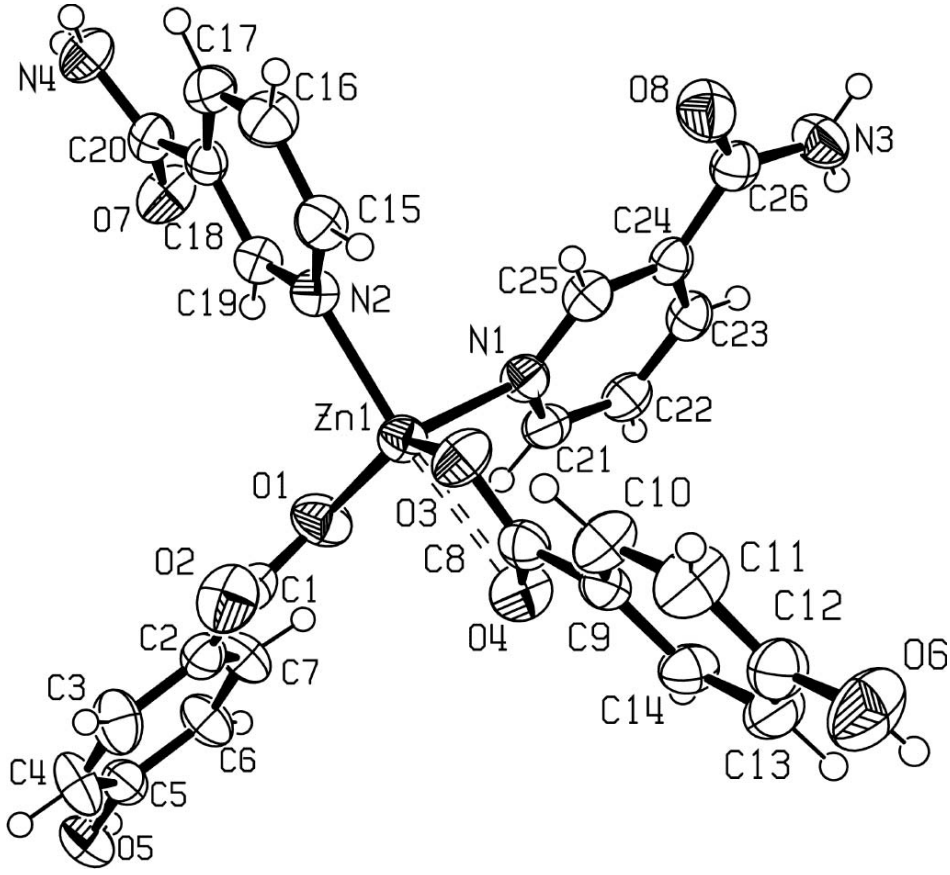


**Figure 1**

An *ORTEP-3* (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

**(I)**

*Crystal data*

$[Zn(C_6H_6N_2O)_2(C_7H_5O_3)_2]$
$M_r$ = 583.85
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a$ = 10.3159 (10) Å
$b$ = 22.606 (3) Å
$c$ = 10.8926 (10) Å
$\beta$ = 95.375 (6)°
$V$ = 2529.0 (5) Å$^3$
$Z$ = 4
$F(000)$ = 1200
$D_x$ = 1.533 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10–18°
$\mu$ = 1.03 mm$^{-1}$
$T$ = 293 K
Rod-shaped, colourless
0.30 × 0.20 × 0.15 mm

*Data collection*

Enraf Nonius TurboCAD4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
non–profiled $\omega$ scans
Absorption correction: $\psi$ scan (North et al., 1968)
$T_{min}$ = 0.748, $T_{max}$ = 0.861
5409 measured reflections
5124 independent reflections
4089 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031
$\theta_{max}$ = 26.3°, $\theta_{min}$ = 2.1°
$h$ = −12→0
$k$ = −28→0
$l$ = −13→13
3 standard reflections every 120 min
intensity decay: 1%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.095
$S$ = 1.05
5124 reflections
440 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.716P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.49 e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Zn1 | 0.75623 (2) | 0.883728 (11) | 0.86158 (2) | 0.03518 (10) |
| O1 | 0.76143 (17) | 0.84265 (8) | 1.01724 (15) | 0.0508 (4) |
| O2 | 0.88676 (19) | 0.91508 (7) | 1.09916 (17) | 0.0558 (5) |
| O3 | 0.87220 (15) | 0.93536 (7) | 0.77245 (16) | 0.0459 (4) |
| O4 | 0.96989 (17) | 0.85151 (7) | 0.82001 (16) | 0.0490 (4) |
| O5 | 0.91427 (18) | 0.72931 (9) | 1.54104 (15) | 0.0508 (4) |
| O6 | 1.3646 (2) | 0.96147 (12) | 0.4693 (2) | 0.0731 (7) |
| O7 | 0.27913 (17) | 0.87490 (7) | 1.03315 (18) | 0.0515 (4) |
| O8 | 0.5124 (2) | 0.86786 (8) | 0.39748 (16) | 0.0564 (5) |
| N1 | 0.67746 (17) | 0.82025 (8) | 0.73917 (17) | 0.0373 (4) |
| N2 | 0.59081 (16) | 0.93635 (8) | 0.85935 (15) | 0.0335 (4) |
| N3 | 0.5000 (2) | 0.77479 (12) | 0.3258 (2) | 0.0517 (5) |
| N4 | 0.1655 (2) | 0.95877 (10) | 1.0012 (2) | 0.0449 (5) |
| C1 | 0.8329 (2) | 0.86633 (10) | 1.1065 (2) | 0.0397 (5) |
| C2 | 0.8500 (2) | 0.83090 (10) | 1.22303 (19) | 0.0361 (5) |

| | | | | |
|---|---|---|---|---|
| C3 | 0.9082 (3) | 0.85423 (11) | 1.3320 (2) | 0.0519 (6) |
| C4 | 0.9281 (3) | 0.82086 (12) | 1.4371 (2) | 0.0546 (7) |
| C5 | 0.8922 (2) | 0.76198 (10) | 1.4358 (2) | 0.0394 (5) |
| C6 | 0.8348 (2) | 0.73762 (11) | 1.3280 (2) | 0.0452 (5) |
| C7 | 0.8124 (2) | 0.77220 (11) | 1.2237 (2) | 0.0436 (5) |
| C8 | 0.9676 (2) | 0.90006 (10) | 0.7659 (2) | 0.0372 (5) |
| C9 | 1.07416 (19) | 0.91741 (9) | 0.69028 (19) | 0.0341 (4) |
| C10 | 1.0820 (2) | 0.97336 (11) | 0.6404 (2) | 0.0466 (6) |
| C11 | 1.1794 (3) | 0.98740 (13) | 0.5666 (3) | 0.0572 (7) |
| C12 | 1.2707 (2) | 0.94520 (12) | 0.5421 (2) | 0.0476 (6) |
| C13 | 1.2636 (2) | 0.88913 (12) | 0.5909 (2) | 0.0482 (6) |
| C14 | 1.1659 (2) | 0.87582 (11) | 0.6644 (2) | 0.0419 (5) |
| C15 | 0.5763 (2) | 0.98543 (10) | 0.7896 (2) | 0.0399 (5) |
| C16 | 0.4627 (2) | 1.01752 (11) | 0.7803 (2) | 0.0458 (6) |
| C17 | 0.3605 (2) | 0.99941 (10) | 0.8439 (2) | 0.0404 (5) |
| C18 | 0.37350 (19) | 0.94894 (9) | 0.91583 (18) | 0.0315 (4) |
| C19 | 0.4912 (2) | 0.91906 (9) | 0.92089 (19) | 0.0339 (4) |
| C20 | 0.2681 (2) | 0.92475 (9) | 0.9878 (2) | 0.0357 (5) |
| C21 | 0.6834 (2) | 0.76251 (10) | 0.7703 (2) | 0.0389 (5) |
| C22 | 0.6438 (2) | 0.71868 (10) | 0.6889 (2) | 0.0413 (5) |
| C23 | 0.5934 (2) | 0.73319 (10) | 0.5712 (2) | 0.0384 (5) |
| C24 | 0.58346 (19) | 0.79243 (9) | 0.53787 (19) | 0.0341 (4) |
| C25 | 0.6282 (2) | 0.83412 (10) | 0.6248 (2) | 0.0374 (5) |
| C26 | 0.5294 (2) | 0.81442 (10) | 0.4142 (2) | 0.0395 (5) |
| H3A | 0.467 (3) | 0.7854 (14) | 0.255 (3) | 0.066 (9)* |
| H3B | 0.512 (3) | 0.7365 (14) | 0.340 (3) | 0.061 (9)* |
| H4A | 0.160 (3) | 0.9934 (15) | 0.975 (3) | 0.064 (9)* |
| H4B | 0.106 (3) | 0.9433 (12) | 1.037 (2) | 0.051 (8)* |
| H5A | 0.873 (4) | 0.6979 (17) | 1.534 (3) | 0.094 (13)* |
| H6A | 1.407 (5) | 0.937 (2) | 0.454 (5) | 0.13 (2)* |
| H31 | 0.932 (3) | 0.8927 (14) | 1.332 (3) | 0.070 (10)* |
| H41 | 0.962 (3) | 0.8356 (12) | 1.510 (3) | 0.055 (7)* |
| H61 | 0.814 (3) | 0.6949 (14) | 1.323 (3) | 0.066 (8)* |
| H71 | 0.778 (3) | 0.7547 (13) | 1.150 (2) | 0.059 (8)* |
| H101 | 1.024 (3) | 1.0018 (13) | 0.661 (3) | 0.063 (8)* |
| H111 | 1.183 (3) | 1.0263 (15) | 0.533 (3) | 0.075 (9)* |
| H131 | 1.324 (3) | 0.8588 (13) | 0.572 (3) | 0.060 (8)* |
| H141 | 1.154 (2) | 0.8388 (12) | 0.700 (2) | 0.052 (7)* |
| H151 | 0.648 (2) | 1.0001 (10) | 0.749 (2) | 0.037 (6)* |
| H161 | 0.459 (3) | 1.0502 (13) | 0.732 (3) | 0.061 (8)* |
| H171 | 0.281 (2) | 1.0187 (12) | 0.838 (2) | 0.046 (7)* |
| H191 | 0.503 (2) | 0.8867 (11) | 0.972 (2) | 0.044 (7)* |
| H211 | 0.715 (2) | 0.7538 (11) | 0.852 (2) | 0.042 (6)* |
| H221 | 0.649 (2) | 0.6810 (12) | 0.715 (2) | 0.046 (7)* |
| H231 | 0.568 (2) | 0.7063 (10) | 0.520 (2) | 0.032 (6)* |
| H251 | 0.625 (2) | 0.8752 (10) | 0.603 (2) | 0.030 (6)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.03253 (14) | 0.03641 (15) | 0.03653 (15) | −0.00278 (10) | 0.00285 (10) | 0.00115 (10) |
| O1 | 0.0511 (10) | 0.0595 (11) | 0.0409 (9) | −0.0047 (8) | −0.0003 (7) | 0.0140 (8) |
| O2 | 0.0715 (12) | 0.0347 (9) | 0.0632 (11) | 0.0019 (8) | 0.0164 (9) | 0.0081 (8) |
| O3 | 0.0371 (8) | 0.0428 (9) | 0.0601 (10) | 0.0010 (7) | 0.0157 (7) | 0.0033 (8) |
| O4 | 0.0479 (9) | 0.0448 (9) | 0.0551 (10) | −0.0018 (7) | 0.0100 (8) | 0.0127 (8) |
| O5 | 0.0558 (11) | 0.0586 (11) | 0.0360 (9) | −0.0091 (9) | −0.0057 (7) | 0.0053 (8) |
| O6 | 0.0657 (13) | 0.0806 (16) | 0.0790 (15) | 0.0114 (12) | 0.0382 (11) | 0.0275 (12) |
| O7 | 0.0523 (10) | 0.0359 (9) | 0.0695 (11) | 0.0007 (7) | 0.0224 (9) | 0.0111 (8) |
| O8 | 0.0768 (13) | 0.0454 (10) | 0.0475 (10) | 0.0066 (9) | 0.0079 (9) | 0.0084 (8) |
| N1 | 0.0346 (9) | 0.0355 (9) | 0.0416 (10) | −0.0017 (7) | 0.0023 (8) | −0.0032 (8) |
| N2 | 0.0326 (9) | 0.0336 (9) | 0.0345 (9) | −0.0014 (7) | 0.0038 (7) | 0.0021 (7) |
| N3 | 0.0571 (13) | 0.0534 (14) | 0.0424 (12) | −0.0031 (11) | −0.0079 (10) | −0.0042 (10) |
| N4 | 0.0380 (11) | 0.0397 (12) | 0.0590 (13) | 0.0012 (9) | 0.0160 (9) | 0.0024 (10) |
| C1 | 0.0381 (12) | 0.0390 (12) | 0.0433 (12) | 0.0089 (9) | 0.0113 (10) | 0.0033 (10) |
| C2 | 0.0329 (11) | 0.0378 (11) | 0.0382 (11) | 0.0010 (9) | 0.0062 (8) | −0.0011 (9) |
| C3 | 0.0699 (17) | 0.0354 (13) | 0.0505 (14) | −0.0094 (12) | 0.0062 (12) | −0.0092 (11) |
| C4 | 0.0749 (18) | 0.0527 (15) | 0.0344 (12) | −0.0132 (13) | −0.0041 (12) | −0.0126 (11) |
| C5 | 0.0361 (11) | 0.0479 (13) | 0.0340 (11) | −0.0034 (10) | 0.0018 (9) | −0.0017 (9) |
| C6 | 0.0541 (14) | 0.0408 (13) | 0.0390 (12) | −0.0152 (11) | −0.0052 (10) | 0.0010 (10) |
| C7 | 0.0476 (13) | 0.0456 (13) | 0.0360 (12) | −0.0129 (11) | −0.0052 (10) | −0.0001 (10) |
| C8 | 0.0347 (11) | 0.0387 (11) | 0.0373 (11) | −0.0050 (9) | −0.0008 (9) | −0.0039 (9) |
| C9 | 0.0312 (11) | 0.0372 (11) | 0.0331 (10) | −0.0001 (8) | −0.0018 (8) | −0.0005 (8) |
| C10 | 0.0421 (13) | 0.0377 (12) | 0.0617 (15) | 0.0043 (10) | 0.0140 (11) | 0.0030 (11) |
| C11 | 0.0568 (16) | 0.0448 (14) | 0.0728 (18) | 0.0010 (12) | 0.0204 (14) | 0.0160 (13) |
| C12 | 0.0412 (13) | 0.0597 (15) | 0.0434 (13) | 0.0003 (11) | 0.0110 (10) | 0.0077 (11) |
| C13 | 0.403 (13) | 0.0538 (15) | 0.0513 (14) | 0.0106 (11) | 0.0092 (11) | 0.0062 (11) |
| C14 | 0.0368 (12) | 0.0425 (13) | 0.0459 (13) | 0.0048 (10) | 0.0018 (10) | 0.0087 (10) |
| C15 | 0.0418 (12) | 0.0420 (12) | 0.0366 (11) | −0.0039 (10) | 0.0082 (9) | 0.0051 (9) |
| C16 | 0.0538 (14) | 0.0405 (13) | 0.0439 (13) | 0.0043 (11) | 0.0085 (11) | 0.0137 (10) |
| C17 | 0.0399 (13) | 0.0389 (12) | 0.0422 (12) | 0.0062 (10) | 0.0031 (10) | 0.0020 (10) |
| C18 | 0.0325 (10) | 0.0302 (10) | 0.0314 (10) | −0.0032 (8) | 0.0019 (8) | −0.0050 (8) |
| C19 | 0.0353 (11) | 0.0313 (11) | 0.0352 (11) | −0.0024 (8) | 0.0034 (8) | 0.0026 (9) |
| C20 | 0.0346 (11) | 0.0326 (11) | 0.0403 (11) | −0.0039 (9) | 0.0059 (9) | −0.0046 (9) |
| C21 | 0.0344 (11) | 0.0405 (12) | 0.0421 (12) | 0.0046 (9) | 0.0040 (9) | 0.0022 (10) |
| C22 | 0.0407 (12) | 0.0327 (11) | 0.0514 (13) | 0.0042 (9) | 0.0088 (10) | 0.0023 (10) |
| C23 | 0.0371 (11) | 0.0342 (12) | 0.0444 (12) | −0.0027 (9) | 0.0064 (9) | −0.0068 (10) |
| C24 | 0.0302 (10) | 0.0361 (11) | 0.0371 (11) | −0.0011 (8) | 0.0084 (8) | −0.0024 (9) |
| C25 | 0.0379 (12) | 0.0315 (11) | 0.0432 (12) | −0.0015 (9) | 0.0057 (9) | −0.0002 (9) |
| C26 | 0.0331 (11) | 0.0439 (13) | 0.0422 (12) | −0.0015 (9) | 0.0080 (9) | 0.0016 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Zn1—O1 | 1.9295 (16) | C18—C20 | 1.501 (3) |
| Zn1—O3 | 1.9883 (16) | C5—O5 | 1.365 (3) |
| Zn1—N1 | 2.0723 (18) | C5—C6 | 1.379 (3) |

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| Zn1—N2 | 2.0784 (17) | C5—C4 | 1.381 (4) |
| Zn1—O4 | 2.4042 (18) | N3—C26 | 1.329 (3) |
| Zn1—C8 | 2.530 (2) | N3—H3B | 0.89 (3) |
| O3—C8 | 1.274 (3) | N3—H3A | 0.85 (3) |
| O2—C1 | 1.240 (3) | C9—C10 | 1.382 (3) |
| N2—C19 | 1.337 (3) | C6—C7 | 1.381 (3) |
| N2—C15 | 1.345 (3) | C6—H61 | 0.99 (3) |
| O1—C1 | 1.281 (3) | C21—C22 | 1.367 (3) |
| C1—C2 | 1.498 (3) | C21—H211 | 0.94 (2) |
| N1—C25 | 1.338 (3) | C7—H71 | 0.93 (3) |
| N1—C21 | 1.349 (3) | C22—H221 | 0.90 (3) |
| C24—C25 | 1.384 (3) | C17—C16 | 1.376 (3) |
| C24—C23 | 1.389 (3) | C17—H171 | 0.92 (3) |
| C24—C26 | 1.494 (3) | O7—C20 | 1.232 (3) |
| C25—H251 | 0.96 (2) | O5—H5A | 0.83 (4) |
| C19—C18 | 1.386 (3) | N4—C20 | 1.328 (3) |
| C19—H191 | 0.92 (3) | N4—H4A | 0.83 (3) |
| C2—C3 | 1.383 (3) | N4—H4B | 0.83 (3) |
| C2—C7 | 1.383 (3) | C10—C11 | 1.381 (4) |
| C15—C16 | 1.374 (3) | C10—H101 | 0.92 (3) |
| C15—H151 | 0.96 (2) | C12—O6 | 1.359 (3) |
| O8—C26 | 1.232 (3) | C12—C13 | 1.379 (4) |
| C8—O4 | 1.245 (3) | C12—C11 | 1.384 (4) |
| C8—C9 | 1.487 (3) | C13—H131 | 0.97 (3) |
| C14—C13 | 1.377 (4) | C11—H111 | 0.95 (3) |
| C14—C9 | 1.382 (3) | C16—H161 | 0.91 (3) |
| C14—H141 | 0.94 (3) | C4—C3 | 1.371 (4) |
| C23—C22 | 1.377 (3) | C4—H41 | 0.90 (3) |
| C23—H231 | 0.85 (2) | C3—H31 | 0.90 (3) |
| C18—C17 | 1.384 (3) | O6—H6A | 0.74 (5) |

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|---|---|---|---|
| O1—Zn1—O3 | 138.00 (7) | O5—C5—C4 | 119.3 (2) |
| O1—Zn1—N1 | 102.07 (8) | C6—C5—C4 | 119.1 (2) |
| O3—Zn1—N1 | 108.05 (7) | C26—N3—H3B | 120.9 (19) |
| O1—Zn1—N2 | 103.94 (7) | C26—N3—H3A | 121 (2) |
| O3—Zn1—N2 | 100.91 (7) | H3B—N3—H3A | 118 (3) |
| N1—Zn1—N2 | 96.70 (7) | C14—C9—C10 | 118.4 (2) |
| O1—Zn1—O4 | 93.97 (7) | C14—C9—C8 | 119.3 (2) |
| O3—Zn1—O4 | 58.79 (6) | C10—C9—C8 | 122.2 (2) |
| N1—Zn1—O4 | 88.86 (7) | C5—C6—C7 | 120.0 (2) |
| N2—Zn1—O4 | 159.61 (6) | C5—C6—H61 | 120.5 (17) |
| O1—Zn1—C8 | 118.55 (7) | C7—C6—H61 | 119.5 (17) |
| O3—Zn1—C8 | 29.79 (7) | O8—C26—N3 | 122.3 (2) |
| N1—Zn1—C8 | 97.89 (7) | O8—C26—C24 | 119.7 (2) |
| N2—Zn1—C8 | 130.54 (7) | N3—C26—C24 | 118.0 (2) |
| O4—Zn1—C8 | 29.08 (6) | N1—C21—C22 | 122.3 (2) |
| C8—O3—Zn1 | 99.37 (14) | N1—C21—H211 | 116.4 (15) |
| C19—N2—C15 | 118.32 (19) | C22—C21—H211 | 121.2 (15) |

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| C19—N2—Zn1 | 119.71 (14) | C6—C7—C2 | 121.5 (2) |
| C15—N2—Zn1 | 121.76 (14) | C6—C7—H71 | 119.0 (18) |
| C1—O1—Zn1 | 115.62 (15) | C2—C7—H71 | 119.2 (18) |
| O2—C1—O1 | 123.5 (2) | C21—C22—C23 | 119.7 (2) |
| O2—C1—C2 | 120.8 (2) | C21—C22—H221 | 118.2 (16) |
| O1—C1—C2 | 115.7 (2) | C23—C22—H221 | 122.1 (16) |
| C25—N1—C21 | 117.75 (19) | C16—C17—C18 | 119.5 (2) |
| C25—N1—Zn1 | 121.91 (15) | C16—C17—H171 | 122.6 (16) |
| C21—N1—Zn1 | 120.16 (15) | C18—C17—H171 | 117.9 (16) |
| C25—C24—C23 | 117.8 (2) | C5—O5—H5A | 110 (3) |
| C25—C24—C26 | 117.56 (19) | C8—O4—Zn1 | 81.08 (13) |
| C23—C24—C26 | 124.7 (2) | C20—N4—H4A | 122 (2) |
| N1—C25—C24 | 123.4 (2) | C20—N4—H4B | 116.0 (19) |
| N1—C25—H251 | 117.2 (13) | H4A—N4—H4B | 122 (3) |
| C24—C25—H251 | 119.4 (13) | O7—C20—N4 | 122.0 (2) |
| N2—C19—C18 | 123.32 (19) | O7—C20—C18 | 119.93 (19) |
| N2—C19—H191 | 118.3 (17) | N4—C20—C18 | 118.1 (2) |
| C18—C19—H191 | 118.3 (17) | C11—C10—C9 | 120.8 (2) |
| C3—C2—C7 | 117.4 (2) | C11—C10—H101 | 120.4 (18) |
| C3—C2—C1 | 122.1 (2) | C9—C10—H101 | 118.7 (18) |
| C7—C2—C1 | 120.5 (2) | O6—C12—C13 | 122.7 (2) |
| N2—C15—C16 | 121.7 (2) | O6—C12—C11 | 117.5 (2) |
| N2—C15—H151 | 119.8 (14) | C13—C12—C11 | 119.8 (2) |
| C16—C15—H151 | 118.4 (14) | C14—C13—C12 | 119.5 (2) |
| O4—C8—O3 | 120.4 (2) | C14—C13—H131 | 119.8 (17) |
| O4—C8—C9 | 120.8 (2) | C12—C13—H131 | 120.6 (17) |
| O3—C8—C9 | 118.7 (2) | C10—C11—C12 | 119.9 (2) |
| O4—C8—Zn1 | 69.84 (12) | C10—C11—H111 | 119.3 (19) |
| O3—C8—Zn1 | 50.84 (11) | C12—C11—H111 | 120.7 (19) |
| C9—C8—Zn1 | 167.70 (16) | C15—C16—C17 | 119.6 (2) |
| C13—C14—C9 | 121.5 (2) | C15—C16—H161 | 117.2 (18) |
| C13—C14—H141 | 124.8 (16) | C17—C16—H161 | 123.2 (18) |
| C9—C14—H141 | 113.7 (16) | C3—C4—C5 | 120.2 (2) |
| C22—C23—C24 | 119.0 (2) | C3—C4—H41 | 123.3 (18) |
| C22—C23—H231 | 120.4 (15) | C5—C4—H41 | 116.5 (17) |
| C24—C23—H231 | 120.6 (15) | C4—C3—C2 | 121.7 (2) |
| C17—C18—C19 | 117.56 (19) | C4—C3—H31 | 120 (2) |
| C17—C18—C20 | 124.01 (19) | C2—C3—H31 | 118 (2) |
| C19—C18—C20 | 118.44 (19) | C12—O6—H6A | 113 (4) |
| O5—C5—C6 | 121.6 (2) | | |

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| O1—Zn1—O3—C8 | 59.86 (18) | N1—Zn1—C8—C9 | 78.4 (7) |
| N1—Zn1—O3—C8 | −73.82 (15) | N2—Zn1—C8—C9 | −27.5 (8) |
| N2—Zn1—O3—C8 | −174.65 (13) | O4—Zn1—C8—C9 | 151.5 (8) |
| O4—Zn1—O3—C8 | 3.36 (12) | C25—C24—C23—C22 | 1.6 (3) |
| O1—Zn1—N2—C19 | −28.41 (17) | C26—C24—C23—C22 | −179.2 (2) |
| O3—Zn1—N2—C19 | −174.26 (15) | N2—C19—C18—C17 | −0.6 (3) |
| N1—Zn1—N2—C19 | 75.84 (16) | N2—C19—C18—C20 | 179.18 (18) |

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| O4—Zn1—N2—C19 | −179.15 (16) | C13—C14—C9—C10 | 0.1 (4) |
| C8—Zn1—N2—C19 | −177.76 (14) | C13—C14—C9—C8 | 177.5 (2) |
| O1—Zn1—N2—C15 | 156.90 (16) | O4—C8—C9—C14 | 9.9 (3) |
| O3—Zn1—N2—C15 | 11.05 (18) | O3—C8—C9—C14 | −168.6 (2) |
| N1—Zn1—N2—C15 | −98.85 (17) | Zn1—C8—C9—C14 | −138.6 (7) |
| O4—Zn1—N2—C15 | 6.2 (3) | O4—C8—C9—C10 | −172.7 (2) |
| C8—Zn1—N2—C15 | 7.6 (2) | O3—C8—C9—C10 | 8.8 (3) |
| O3—Zn1—O1—C1 | 29.4 (2) | Zn1—C8—C9—C10 | 38.7 (8) |
| N1—Zn1—O1—C1 | 164.68 (16) | O5—C5—C6—C7 | 179.2 (2) |
| N2—Zn1—O1—C1 | −95.18 (16) | C4—C5—C6—C7 | −0.9 (4) |
| O4—Zn1—O1—C1 | 74.99 (17) | C25—C24—C26—O8 | −8.2 (3) |
| C8—Zn1—O1—C1 | 58.65 (18) | C23—C24—C26—O8 | 172.6 (2) |
| Zn1—O1—C1—O2 | 6.4 (3) | C25—C24—C26—N3 | 172.4 (2) |
| Zn1—O1—C1—C2 | −172.88 (14) | C23—C24—C26—N3 | −6.7 (3) |
| O1—Zn1—N1—C25 | 163.89 (16) | C25—N1—C21—C22 | 1.4 (3) |
| O3—Zn1—N1—C25 | −45.78 (18) | Zn1—N1—C21—C22 | −173.84 (17) |
| N2—Zn1—N1—C25 | 58.03 (17) | C5—C6—C7—C2 | 2.1 (4) |
| O4—Zn1—N1—C25 | −102.30 (17) | C3—C2—C7—C6 | −1.6 (4) |
| C8—Zn1—N1—C25 | −74.58 (17) | C1—C2—C7—C6 | 175.8 (2) |
| O1—Zn1—N1—C21 | −21.09 (18) | N1—C21—C22—C23 | −1.3 (3) |
| O3—Zn1—N1—C21 | 129.25 (16) | C24—C23—C22—C21 | −0.3 (3) |
| N2—Zn1—N1—C21 | −126.94 (16) | C19—C18—C17—C16 | 0.5 (3) |
| O4—Zn1—N1—C21 | 72.73 (16) | C20—C18—C17—C16 | −179.3 (2) |
| C8—Zn1—N1—C21 | 100.45 (17) | O3—C8—O4—Zn1 | 5.3 (2) |
| C21—N1—C25—C24 | 0.1 (3) | C9—C8—O4—Zn1 | −173.20 (19) |
| Zn1—N1—C25—C24 | 175.21 (16) | O1—Zn1—O4—C8 | −149.43 (14) |
| C23—C24—C25—N1 | −1.6 (3) | O3—Zn1—O4—C8 | −3.44 (13) |
| C26—C24—C25—N1 | 179.22 (19) | N1—Zn1—O4—C8 | 108.55 (14) |
| C15—N2—C19—C18 | 0.4 (3) | N2—Zn1—O4—C8 | 2.2 (3) |
| Zn1—N2—C19—C18 | −174.45 (15) | C17—C18—C20—O7 | 168.2 (2) |
| O2—C1—C2—C3 | 10.4 (3) | C19—C18—C20—O7 | −11.5 (3) |
| O1—C1—C2—C3 | −170.3 (2) | C17—C18—C20—N4 | −12.4 (3) |
| O2—C1—C2—C7 | −166.9 (2) | C19—C18—C20—N4 | 167.8 (2) |
| O1—C1—C2—C7 | 12.4 (3) | C14—C9—C10—C11 | −0.1 (4) |
| C19—N2—C15—C16 | −0.2 (3) | C8—C9—C10—C11 | −177.5 (2) |
| Zn1—N2—C15—C16 | 174.61 (18) | C9—C14—C13—C12 | 0.2 (4) |
| Zn1—O3—C8—O4 | −6.5 (2) | O6—C12—C13—C14 | 179.8 (3) |
| Zn1—O3—C8—C9 | 172.11 (16) | C11—C12—C13—C14 | −0.5 (4) |
| O1—Zn1—C8—O4 | 35.29 (15) | C9—C10—C11—C12 | −0.2 (4) |
| O3—Zn1—C8—O4 | 174.1 (2) | O6—C12—C11—C10 | −179.8 (3) |
| N1—Zn1—C8—O4 | −73.12 (14) | C13—C12—C11—C10 | 0.5 (4) |
| N2—Zn1—C8—O4 | −179.00 (12) | N2—C15—C16—C17 | 0.1 (4) |
| O1—Zn1—C8—O3 | −138.79 (14) | C18—C17—C16—C15 | −0.3 (4) |
| N1—Zn1—C8—O3 | 112.81 (14) | O5—C5—C4—C3 | 179.2 (2) |
| N2—Zn1—C8—O3 | 6.93 (17) | C6—C5—C4—C3 | −0.8 (4) |
| O4—Zn1—C8—O3 | −174.1 (2) | C5—C4—C3—C2 | 1.3 (4) |
| O1—Zn1—C8—C9 | −173.2 (7) | C7—C2—C3—C4 | −0.1 (4) |
| O3—Zn1—C8—C9 | −34.4 (7) | C1—C2—C3—C4 | −177.4 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O6—H6*A*···O8$^{i}$ | 0.74 (5) | 2.03 (5) | 2.764 (3) | 175 (6) |
| O5—H5*A*···O7$^{ii}$ | 0.83 (4) | 1.91 (4) | 2.735 (3) | 175 (4) |
| N3—H3*B*···O4$^{iii}$ | 0.89 (3) | 2.04 (3) | 2.872 (3) | 155 (3) |
| N4—H4*A*···O2$^{iv}$ | 0.83 (3) | 2.26 (3) | 3.084 (3) | 171 (3) |

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