

Crystal structure of triaqua(4-cyanobenzoato- κ^2O,O')(nicotinamide- κN^1)zinc 4-cyanobenzoate

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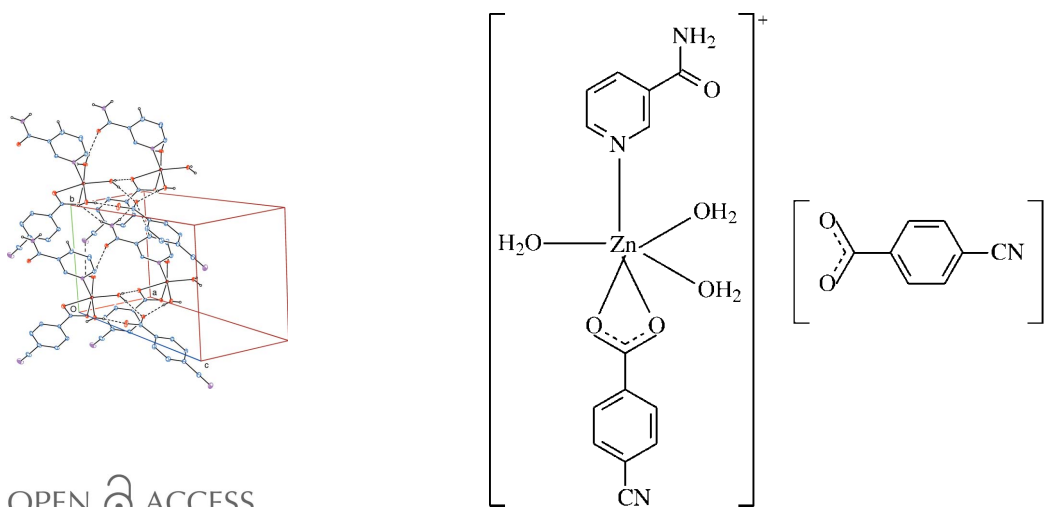
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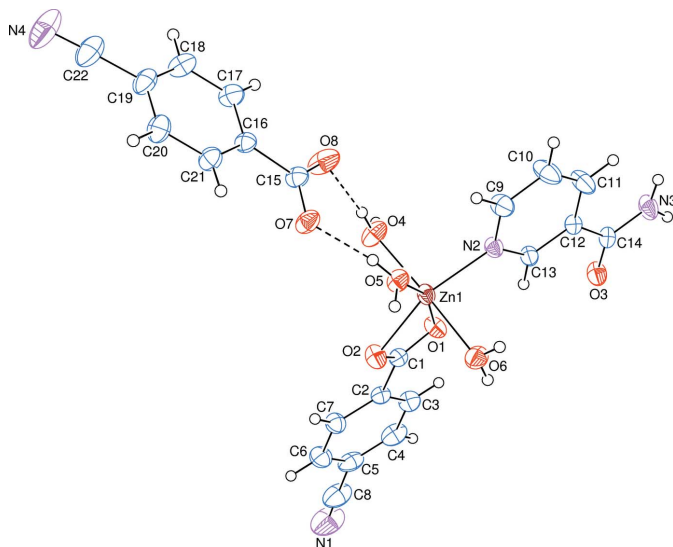
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The asymmetric unit of the title salt, $[\text{Zn}(\text{C}_8\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_6\text{N}_2\text{O})(\text{H}_2\text{O})_3]-(\text{C}_8\text{H}_4\text{NO}_2)$, contains one complex cation and one 4-cyanobenzoate (CNB) counter-anion. The Zn^{II} atom in the cation is coordinated by one 4-cyanobenzoate ligand, one nicotinamide (NA) ligand and three water molecules, the CNB anion thereby coordinating in a bidentate O,O' -mode through the carboxylate group. The latter, together with one water O atom and the N atom of the NA ligand, form a distorted square-planar arrangement, while the considerably distorted octahedral coordination sphere of the Zn^{II} atom is completed by the two O atoms of additional water molecules in the axial positions. The dihedral angles between the planar carboxylate groups and the adjacent benzene rings in the two anions are 10.25 (10) and 5.89 (14)°. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link two of the coordinating water molecules to two free CNB anions. In the crystal, further hydrogen-bonding interactions are present, namely $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds that link the molecular components, enclosing $R_2^2(12)$, $R_3^3(8)$ and $R_3^3(9)$ ring motifs and forming layers parallel to (001). $\pi-\pi$ contacts between benzene rings [centroid-to-centroid distances = 3.791 (1) and 3.882 (1) Å] may further stabilize the crystal structure.

1. Chemical context

As parts of our ongoing investigation on transition-metal complexes of nicotinamide (NA), one form of niacin (Krishnamachari, 1974), and/or the nicotinic acid derivative *N,N*-diethylnicotinamide (DENA), an important respiratory stimulant (Bigoli *et al.*, 1972), the title compound was synthesized and its crystal structure is reported herein.




Figure 1

The molecular entities of the title salt, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intermolecular O—H...O hydrogen bonds are shown as dashed lines.

2. Structural commentary

The asymmetric unit of the crystal structure of the title salt, $[\text{Zn}(\text{C}_8\text{H}_4\text{O}_2\text{N})(\text{C}_6\text{H}_6\text{ON}_2)(\text{H}_2\text{O})_3](\text{C}_8\text{H}_4\text{O}_2\text{N})$, is composed of one complex cation and one 4-cyanobenzoate (CNB) counter-anion. The Zn^{II} atom is coordinated by one 4-cyanobenzoate (CNB) anion, one nicotinamide (NA) ligand and three water molecules, the CNB anion and NA ligand coordinating in bidentate and monodentate modes, respectively (Fig. 1).

In the cation, the four coordinating atoms (O1, O2, O5 and N2) around the Zn1 atom show a distorted square-planar arrangement, while the considerably distorted octahedral coordination environment of Zn^{II} is completed by two additional water O atoms (O4 and O6) in the axial positions (Table 1, Fig. 1).

The near equality of the C1—O1 [1.2531 (18) Å], C1—O2 [1.2591 (19) Å] and C15—O7 [1.266 (2) Å], C15—O8 [1.237 (2) Å] bonds in the carboxylate groups indicate delocalized bonding arrangements, rather than localized single and double bonds. The average Zn—O bond lengths are 2.19 (11) Å for benzoate oxygen atoms and 2.10 (9) Å for water oxygen atoms; the Zn—N bond length is 2.0545 (12) Å, close to the values in related structures. The Zn1 atom lies 0.0093 (2) Å above the planar (O1/O2/C1) carboxylate group, with a bite angle of 59.48 (4)°. Corresponding O—Zn—O angles are 60.03 (6)° in $[\text{Zn}(\text{C}_9\text{H}_{10}\text{NO}_2)(\text{C}_6\text{H}_6\text{N}_2\text{O})\cdot 2\text{H}_2\text{O}]$ (Hökelek *et al.*, 2009a), 59.02 (8)° in $[\text{Zn}(\text{C}_8\text{H}_8\text{NO}_2)(\text{C}_6\text{H}_6\text{N}_2\text{O})]\cdot\text{H}_2\text{O}$ (Hökelek *et al.*, 2009b) and 57.53 (5), 56.19 (5) and 59.04 (4)° in $[\text{Zn}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{C}_6\text{H}_6\text{N}_2\text{O})]$ (Hökelek *et al.*, 2010).

The dihedral angles between the planar carboxylate groups [(O1/O2/C1) and (O7/O8/C15)] and the adjacent benzene rings [A (C2—C7) and C (C16—C21)] are 10.25 (10) and 5.89 (14)°, respectively, while the benzene rings and benzene and pyridine [B (N2/C9—13)] rings are oriented at dihedral angles of $A/C = 77.84$ (6), $A/B = 8.97$ (5) and $B/C = 71.43$ (5)°.

Table 1
Selected bond lengths (Å).

| | | | |
|--------|-------------|--------|-------------|
| Zn1—O1 | 2.2724 (12) | Zn1—O5 | 2.0132 (11) |
| Zn1—O2 | 2.1163 (12) | Zn1—O6 | 2.1917 (14) |
| Zn1—O4 | 2.0917 (13) | Zn1—N2 | 2.0545 (12) |

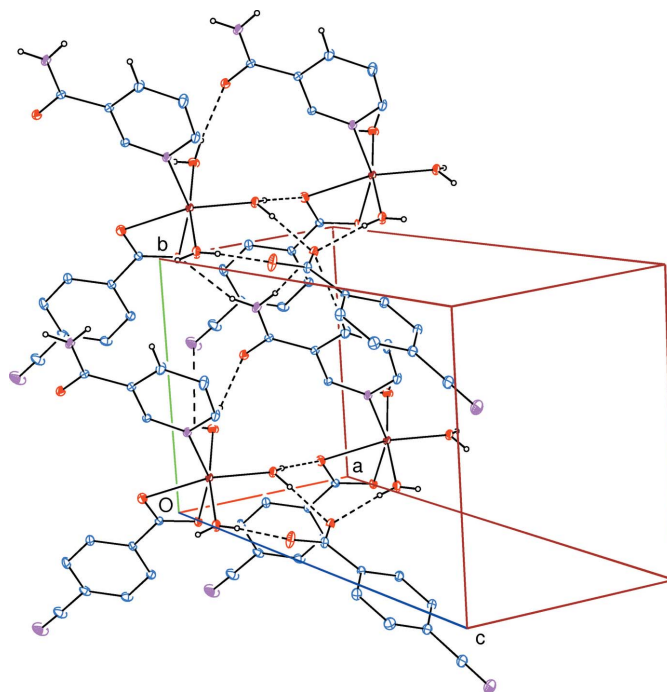
Table 2
Hydrogen-bond geometry (Å, °).

| $D\text{—H}\cdots A$ | $D\text{—H}$ | $H\cdots A$ | $D\cdots A$ | $D\text{—H}\cdots A$ |
|----------------------------|--------------|-------------|-------------|----------------------|
| N3—H31...O2 ⁱ | 0.82 (2) | 2.13 (3) | 2.914 (2) | 162 (2) |
| N3—H32...O7 ⁱ | 0.92 (3) | 2.35 (2) | 3.261 (2) | 171 (2) |
| O4—H41...O7 ⁱⁱ | 0.75 (2) | 2.04 (2) | 2.7890 (17) | 173 (3) |
| O4—H42...O8 | 0.76 (3) | 1.89 (3) | 2.6547 (18) | 175 (3) |
| O5—H51...O7 | 0.80 (2) | 1.83 (2) | 2.6264 (17) | 171 (3) |
| O5—H52...O1 ⁱⁱⁱ | 0.74 (2) | 2.05 (2) | 2.7610 (17) | 164 (2) |
| O6—H61...O3 ⁱⁱⁱ | 0.75 (3) | 2.05 (3) | 2.7993 (19) | 170 (3) |
| O6—H62...N1 ^{iv} | 0.76 (3) | 2.17 (3) | 2.918 (3) | 170 (3) |
| C11—H11...O7 ⁱ | 0.93 | 2.49 | 3.415 (2) | 177 |

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

3. Supramolecular features

In the crystal, N—H...O_c (c = carboxylate), O—H_w...O_c (w = water), O—H_w...O_n (n = nicotinamide), O—H_w...N_n as well as C—H...O_c hydrogen bonds (Table 2) link the molecular components, enclosing $R_2^2(12)$, $R_3^3(8)$ and $R_3^3(9)$ ring motifs (Bernstein *et al.*, 1995), forming layers parallel to (001) (Fig. 2). Additional π — π contacts between the benzene rings, $Cg1\cdots Cg1^i$ and $Cg1\cdots Cg3^{ii}$ [symmetry codes: (i) $1 - x, -y,$


Figure 2

A partial packing diagram of the title complex. Intermolecular N—H...O, O—H...O, O—H...N and C—H...O hydrogen bonds are shown as dashed lines, enclosing $R_2^2(12)$, $R_3^3(8)$ and $R_3^3(9)$ ring motifs. Non-bonding H atoms have been omitted for clarity.

Table 3
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | [Zn(C ₈ H ₄ NO ₂)(C ₆ H ₆ N ₂ O)- (H ₂ O) ₃](C ₈ H ₄ NO ₂) |
| <i>M_r</i> | 533.81 |
| Crystal system, space group | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 296 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 6.0858 (2), 8.7031 (3), 22.2357 (6) |
| α , β , γ (°) | 81.882 (2), 87.806 (3), 88.007 (3) |
| <i>V</i> (Å ³) | 1164.55 (6) |
| <i>Z</i> | 2 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 1.11 |
| Crystal size (mm) | 0.45 × 0.36 × 0.25 |
| Data collection | |
| Diffractometer | Bruker SMART BREEZE CCD |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker, 2012) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.625, 0.758 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 27167, 5839, 5450 |
| <i>R_{int}</i> | 0.034 |
| (<i>sin</i> θ / λ) _{max} (Å ⁻¹) | 0.670 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.030, 0.080, 1.05 |
| No. of reflections | 5839 |
| No. of parameters | 348 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 0.35, -0.33 |

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

−*z*; (ii) 1 − *x*, −*y*, 1 − *z*, where *Cg*1 and *Cg*3 are the centroids of rings *A* and *C*, respectively], may further stabilize the structure, with centroid-to-centroid distances of 3.791 (1) Å and 3.882 (1) Å, respectively.

4. Synthesis and crystallization

The title compound was prepared by the reaction of ZnSO₄·7H₂O (1.44 g, 5 mmol) in H₂O (30 ml) and nicotina-

mid (1.22 g, 50 mmol) in H₂O (50 ml) with sodium 4-cyano-benzoate (1.69 g, 10 mmol) in H₂O (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for several days, giving colourless single crystals.

5. Refinement

The experimental details including the crystal data, data collection and refinement are summarized in Table 3. Atoms H31 and H32 (as part of the NH₂ group) and H41, H42, H51, H52, H61 and H62 (as part of the water molecules) were located in a difference Fourier map and were refined freely. The aromatic C-bound H atoms were positioned geometrically with C–H = 0.93 Å, and constrained to ride on their parent atoms, with *U*_{iso}(H) = 1.2*U*_{eq}(C).

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supporting information

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Crystal structure of triaqua(4-cyanobenzoato- κ^2O,O')(nicotinamide- κN^1)zinc 4-cyanobenzoate

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Computing details

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

Triaqua(4-cyanobenzoato- κ^2O,O')(nicotinamide- κN^1)zinc 4-cyanobenzoate

Crystal data

$[\text{Zn}(\text{C}_8\text{H}_4\text{NO}_2)(\text{C}_6\text{H}_6\text{N}_2\text{O})(\text{H}_2\text{O})_3](\text{C}_8\text{H}_4\text{NO}_2)$

$M_r = 533.81$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 6.0858$ (2) Å

$b = 8.7031$ (3) Å

$c = 22.2357$ (6) Å

$\alpha = 81.882$ (2)°

$\beta = 87.806$ (3)°

$\gamma = 88.007$ (3)°

$V = 1164.55$ (6) Å³

$Z = 2$

$F(000) = 548$

$D_x = 1.522$ Mg m⁻³

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

Cell parameters from 9885 reflections

$\theta = 2.4$ – 28.4 °

$\mu = 1.11$ mm⁻¹

$T = 296$ K

Prism, translucent light colourless

$0.45 \times 0.36 \times 0.25$ 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)

$T_{\min} = 0.625$, $T_{\max} = 0.758$

27167 measured reflections

5839 independent reflections

5450 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 1.9$ °

$h = -7 \rightarrow 8$

$k = -11 \rightarrow 11$

$l = -29 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.080$

$S = 1.05$

5839 reflections

348 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

$$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.4376P]$$

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

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

$$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|----------------------------------|
| Zn1 | 0.90164 (3) | 0.228852 (18) | 0.220630 (8) | 0.02931 (6) |
| O1 | 0.58663 (19) | 0.18054 (14) | 0.17586 (6) | 0.0398 (3) |
| O2 | 0.89148 (19) | 0.04418 (14) | 0.16835 (6) | 0.0386 (3) |
| O3 | 0.1991 (2) | 0.64093 (14) | 0.17635 (6) | 0.0425 (3) |
| O4 | 0.8145 (2) | 0.08998 (17) | 0.30208 (6) | 0.0456 (3) |
| H41 | 0.698 (4) | 0.078 (3) | 0.3136 (11) | 0.051 (7)* |
| H42 | 0.887 (4) | 0.079 (3) | 0.3298 (12) | 0.060 (7)* |
| O5 | 1.21393 (19) | 0.21434 (14) | 0.24815 (6) | 0.0346 (2) |
| H51 | 1.258 (4) | 0.162 (3) | 0.2779 (11) | 0.057 (7)* |
| H52 | 1.298 (4) | 0.209 (2) | 0.2238 (9) | 0.035 (5)* |
| O6 | 1.0470 (3) | 0.36922 (16) | 0.14029 (6) | 0.0442 (3) |
| H61 | 1.087 (4) | 0.447 (3) | 0.1457 (11) | 0.052 (7)* |
| H62 | 0.983 (4) | 0.379 (3) | 0.1113 (12) | 0.060 (8)* |
| O7 | 1.38028 (19) | 0.02307 (15) | 0.33815 (5) | 0.0413 (3) |
| O8 | 1.0769 (2) | 0.0341 (2) | 0.39584 (6) | 0.0620 (4) |
| N1 | 0.1949 (5) | -0.3612 (3) | -0.03004 (10) | 0.0940 (9) |
| N2 | 0.7668 (2) | 0.42834 (14) | 0.24805 (6) | 0.0315 (3) |
| N3 | 0.2052 (3) | 0.83017 (18) | 0.23482 (8) | 0.0454 (4) |
| H31 | 0.101 (4) | 0.872 (3) | 0.2162 (11) | 0.058 (7)* |
| H32 | 0.269 (4) | 0.879 (3) | 0.2633 (11) | 0.057 (6)* |
| N4 | 1.7600 (4) | -0.5182 (3) | 0.61042 (11) | 0.0876 (8) |
| C1 | 0.6926 (2) | 0.07134 (17) | 0.15590 (7) | 0.0292 (3) |
| C2 | 0.5848 (2) | -0.02630 (17) | 0.11607 (6) | 0.0294 (3) |
| C3 | 0.3787 (3) | 0.0185 (2) | 0.09399 (8) | 0.0381 (3) |
| H3 | 0.3076 | 0.1079 | 0.1044 | 0.046* |
| C4 | 0.2796 (3) | -0.0701 (2) | 0.05652 (8) | 0.0469 (4) |
| H4 | 0.1420 | -0.0405 | 0.0413 | 0.056* |
| C5 | 0.3867 (3) | -0.2038 (2) | 0.04169 (8) | 0.0470 (4) |
| C6 | 0.5917 (4) | -0.2502 (2) | 0.06388 (9) | 0.0473 (4) |
| H6 | 0.6618 | -0.3402 | 0.0538 | 0.057* |

| | | | | |
|-----|------------|---------------|--------------|------------|
| C7 | 0.6911 (3) | -0.16065 (19) | 0.10140 (8) | 0.0371 (3) |
| H7 | 0.8286 | -0.1905 | 0.1167 | 0.045* |
| C8 | 0.2809 (5) | -0.2932 (3) | 0.00172 (10) | 0.0665 (7) |
| C9 | 0.8671 (3) | 0.4895 (2) | 0.29107 (8) | 0.0417 (4) |
| H9 | 0.9926 | 0.4393 | 0.3078 | 0.050* |
| C10 | 0.7913 (3) | 0.6238 (3) | 0.31145 (10) | 0.0558 (5) |
| H10 | 0.8666 | 0.6654 | 0.3407 | 0.067* |
| C11 | 0.6017 (3) | 0.6963 (2) | 0.28798 (9) | 0.0491 (5) |
| H11 | 0.5467 | 0.7867 | 0.3017 | 0.059* |
| C12 | 0.4942 (2) | 0.63340 (16) | 0.24389 (7) | 0.0299 (3) |
| C13 | 0.5853 (3) | 0.50013 (16) | 0.22481 (7) | 0.0303 (3) |
| H13 | 0.5169 | 0.4585 | 0.1943 | 0.036* |
| C14 | 0.2868 (3) | 0.70160 (16) | 0.21562 (7) | 0.0317 (3) |
| C15 | 1.2702 (3) | -0.0089 (2) | 0.38754 (7) | 0.0346 (3) |
| C16 | 1.3816 (3) | -0.11192 (18) | 0.43897 (7) | 0.0318 (3) |
| C17 | 1.2673 (3) | -0.1557 (2) | 0.49338 (8) | 0.0423 (4) |
| H17 | 1.1254 | -0.1161 | 0.4993 | 0.051* |
| C18 | 1.3630 (3) | -0.2582 (2) | 0.53905 (8) | 0.0503 (5) |
| H18 | 1.2857 | -0.2876 | 0.5755 | 0.060* |
| C19 | 1.5746 (3) | -0.3167 (2) | 0.53011 (8) | 0.0446 (4) |
| C20 | 1.6928 (3) | -0.2701 (2) | 0.47640 (9) | 0.0445 (4) |
| H20 | 1.8358 | -0.3079 | 0.4708 | 0.053* |
| C21 | 1.5961 (3) | -0.1669 (2) | 0.43142 (8) | 0.0379 (3) |
| H21 | 1.6757 | -0.1340 | 0.3957 | 0.046* |
| C22 | 1.6768 (4) | -0.4285 (3) | 0.57586 (10) | 0.0600 (6) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|-------------|--------------|--------------|--------------|--------------|
| Zn1 | 0.02640 (10) | 0.02670 (9) | 0.03590 (11) | 0.00369 (6) | -0.00771 (7) | -0.00734 (7) |
| O1 | 0.0353 (6) | 0.0404 (6) | 0.0465 (7) | 0.0023 (5) | -0.0002 (5) | -0.0171 (5) |
| O2 | 0.0304 (6) | 0.0382 (6) | 0.0498 (7) | 0.0022 (5) | -0.0125 (5) | -0.0126 (5) |
| O3 | 0.0435 (7) | 0.0344 (6) | 0.0514 (7) | 0.0022 (5) | -0.0162 (6) | -0.0087 (5) |
| O4 | 0.0294 (7) | 0.0607 (8) | 0.0418 (7) | -0.0051 (6) | -0.0061 (6) | 0.0118 (6) |
| O5 | 0.0247 (5) | 0.0420 (6) | 0.0354 (6) | 0.0037 (5) | -0.0037 (5) | 0.0001 (5) |
| O6 | 0.0579 (8) | 0.0391 (7) | 0.0365 (7) | -0.0094 (6) | -0.0098 (6) | -0.0044 (5) |
| O7 | 0.0318 (6) | 0.0549 (7) | 0.0333 (6) | 0.0080 (5) | -0.0017 (5) | 0.0055 (5) |
| O8 | 0.0332 (7) | 0.1071 (13) | 0.0398 (7) | 0.0214 (7) | -0.0021 (5) | 0.0051 (7) |
| N1 | 0.135 (2) | 0.0930 (17) | 0.0616 (13) | -0.0520 (16) | -0.0348 (14) | -0.0149 (12) |
| N2 | 0.0299 (6) | 0.0296 (6) | 0.0357 (7) | 0.0044 (5) | -0.0043 (5) | -0.0070 (5) |
| N3 | 0.0446 (9) | 0.0346 (7) | 0.0583 (10) | 0.0146 (6) | -0.0166 (8) | -0.0113 (7) |
| N4 | 0.0892 (16) | 0.0843 (15) | 0.0815 (15) | -0.0089 (13) | -0.0451 (13) | 0.0280 (12) |
| C1 | 0.0297 (7) | 0.0299 (7) | 0.0277 (7) | -0.0022 (5) | -0.0016 (5) | -0.0031 (5) |
| C2 | 0.0284 (7) | 0.0334 (7) | 0.0267 (7) | -0.0051 (6) | -0.0011 (5) | -0.0043 (5) |
| C3 | 0.0307 (8) | 0.0458 (9) | 0.0380 (8) | -0.0017 (7) | -0.0046 (6) | -0.0049 (7) |
| C4 | 0.0367 (9) | 0.0646 (12) | 0.0392 (9) | -0.0136 (8) | -0.0115 (7) | -0.0005 (8) |
| C5 | 0.0598 (12) | 0.0532 (10) | 0.0296 (8) | -0.0268 (9) | -0.0066 (8) | -0.0038 (7) |
| C6 | 0.0640 (12) | 0.0378 (9) | 0.0433 (9) | -0.0094 (8) | -0.0034 (8) | -0.0138 (7) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C7 | 0.0378 (9) | 0.0358 (8) | 0.0389 (8) | -0.0015 (6) | -0.0039 (7) | -0.0086 (6) |
| C8 | 0.0899 (17) | 0.0679 (14) | 0.0446 (11) | -0.0359 (13) | -0.0173 (11) | -0.0057 (10) |
| C9 | 0.0352 (9) | 0.0491 (9) | 0.0435 (9) | 0.0117 (7) | -0.0118 (7) | -0.0156 (7) |
| C10 | 0.0502 (11) | 0.0651 (12) | 0.0609 (12) | 0.0198 (9) | -0.0255 (9) | -0.0379 (10) |
| C11 | 0.0477 (10) | 0.0479 (10) | 0.0580 (11) | 0.0169 (8) | -0.0167 (9) | -0.0292 (9) |
| C12 | 0.0306 (7) | 0.0262 (6) | 0.0324 (7) | 0.0019 (5) | -0.0020 (6) | -0.0028 (5) |
| C13 | 0.0314 (7) | 0.0262 (6) | 0.0338 (7) | 0.0008 (5) | -0.0052 (6) | -0.0056 (5) |
| C14 | 0.0323 (8) | 0.0248 (6) | 0.0369 (8) | 0.0010 (5) | -0.0034 (6) | -0.0007 (5) |
| C15 | 0.0281 (7) | 0.0446 (8) | 0.0308 (7) | 0.0026 (6) | -0.0058 (6) | -0.0048 (6) |
| C16 | 0.0306 (7) | 0.0363 (7) | 0.0292 (7) | -0.0011 (6) | -0.0064 (6) | -0.0055 (6) |
| C17 | 0.0365 (9) | 0.0542 (10) | 0.0354 (8) | 0.0005 (7) | -0.0010 (7) | -0.0041 (7) |
| C18 | 0.0545 (11) | 0.0608 (12) | 0.0331 (9) | -0.0055 (9) | -0.0020 (8) | 0.0031 (8) |
| C19 | 0.0488 (10) | 0.0434 (9) | 0.0407 (9) | -0.0062 (8) | -0.0185 (8) | 0.0028 (7) |
| C20 | 0.0351 (9) | 0.0472 (9) | 0.0496 (10) | 0.0035 (7) | -0.0121 (7) | 0.0003 (8) |
| C21 | 0.0334 (8) | 0.0428 (8) | 0.0362 (8) | 0.0003 (7) | -0.0040 (6) | -0.0007 (7) |
| C22 | 0.0617 (13) | 0.0613 (13) | 0.0544 (12) | -0.0092 (10) | -0.0247 (10) | 0.0090 (10) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|---------|-----------|
| Zn1—O1 | 2.2724 (12) | C5—C4 | 1.388 (3) |
| Zn1—O2 | 2.1163 (12) | C5—C6 | 1.385 (3) |
| Zn1—O4 | 2.0917 (13) | C5—C8 | 1.444 (3) |
| Zn1—O5 | 2.0132 (11) | C6—H6 | 0.9300 |
| Zn1—O6 | 2.1917 (14) | C7—C6 | 1.387 (2) |
| Zn1—N2 | 2.0545 (12) | C7—H7 | 0.9300 |
| Zn1—C1 | 2.5276 (15) | C9—C10 | 1.372 (2) |
| O1—C1 | 1.2531 (18) | C9—H9 | 0.9300 |
| O2—C1 | 1.2591 (19) | C10—H10 | 0.9300 |
| O3—C14 | 1.230 (2) | C11—C10 | 1.380 (3) |
| O4—H41 | 0.75 (3) | C11—H11 | 0.9300 |
| O4—H42 | 0.77 (3) | C12—C11 | 1.384 (2) |
| O5—H51 | 0.80 (3) | C12—C13 | 1.382 (2) |
| O5—H52 | 0.74 (2) | C12—C14 | 1.498 (2) |
| O6—H61 | 0.75 (3) | C13—H13 | 0.9300 |
| O6—H62 | 0.76 (3) | C14—N3 | 1.327 (2) |
| O7—C15 | 1.266 (2) | C15—O8 | 1.237 (2) |
| N1—C8 | 1.136 (3) | C15—C16 | 1.516 (2) |
| N2—C9 | 1.335 (2) | C16—C17 | 1.384 (2) |
| N2—C13 | 1.3351 (19) | C16—C21 | 1.387 (2) |
| N3—H31 | 0.82 (3) | C17—C18 | 1.385 (3) |
| N3—H32 | 0.91 (3) | C17—H17 | 0.9300 |
| N4—C22 | 1.136 (3) | C18—H18 | 0.9300 |
| C1—C2 | 1.494 (2) | C19—C18 | 1.386 (3) |
| C2—C3 | 1.388 (2) | C19—C22 | 1.447 (3) |
| C2—C7 | 1.390 (2) | C20—C19 | 1.388 (3) |
| C3—C4 | 1.380 (2) | C20—H20 | 0.9300 |
| C3—H3 | 0.9300 | C21—C20 | 1.381 (2) |
| C4—H4 | 0.9300 | C21—H21 | 0.9300 |

| | | | |
|------------|-------------|-------------|-------------|
| O2—Zn1—O1 | 59.48 (4) | C5—C4—H4 | 120.2 |
| O4—Zn1—O1 | 92.90 (5) | C4—C5—C8 | 118.5 (2) |
| O5—Zn1—O1 | 162.17 (5) | C6—C5—C4 | 121.15 (16) |
| O6—Zn1—O1 | 95.68 (5) | C6—C5—C8 | 120.4 (2) |
| N2—Zn1—O1 | 91.98 (5) | C5—C6—C7 | 119.12 (18) |
| O5—Zn1—O2 | 102.69 (5) | C5—C6—H6 | 120.4 |
| O4—Zn1—O2 | 93.77 (6) | C7—C6—H6 | 120.4 |
| N2—Zn1—O2 | 150.78 (5) | C2—C7—H7 | 120.1 |
| O5—Zn1—O4 | 87.85 (6) | C6—C7—C2 | 119.86 (17) |
| N2—Zn1—O4 | 93.81 (6) | C6—C7—H7 | 120.1 |
| O2—Zn1—O6 | 87.82 (5) | N1—C8—C5 | 178.7 (3) |
| O4—Zn1—O6 | 170.83 (6) | N2—C9—C10 | 122.20 (16) |
| O5—Zn1—O6 | 82.99 (6) | N2—C9—H9 | 118.9 |
| N2—Zn1—O6 | 89.13 (5) | C10—C9—H9 | 118.9 |
| O5—Zn1—N2 | 105.76 (5) | C9—C10—C11 | 119.10 (17) |
| O1—Zn1—C1 | 29.66 (4) | C9—C10—H10 | 120.5 |
| O2—Zn1—C1 | 29.82 (5) | C11—C10—H10 | 120.5 |
| O4—Zn1—C1 | 93.91 (5) | C10—C11—C12 | 119.40 (16) |
| O5—Zn1—C1 | 132.51 (5) | C10—C11—H11 | 120.3 |
| O6—Zn1—C1 | 91.96 (5) | C12—C11—H11 | 120.3 |
| N2—Zn1—C1 | 121.41 (5) | C11—C12—C14 | 123.93 (14) |
| C1—O1—Zn1 | 86.53 (9) | C13—C12—C11 | 117.67 (14) |
| C1—O2—Zn1 | 93.49 (9) | C13—C12—C14 | 118.40 (14) |
| Zn1—O4—H41 | 123.9 (18) | N2—C13—C12 | 123.08 (14) |
| Zn1—O4—H42 | 122.6 (19) | N2—C13—H13 | 118.5 |
| H42—O4—H41 | 107 (3) | C12—C13—H13 | 118.5 |
| Zn1—O5—H51 | 126.1 (17) | O3—C14—N3 | 122.30 (15) |
| Zn1—O5—H52 | 114.8 (16) | O3—C14—C12 | 121.07 (14) |
| H52—O5—H51 | 107 (2) | N3—C14—C12 | 116.63 (15) |
| Zn1—O6—H61 | 115.0 (18) | O7—C15—C16 | 117.31 (14) |
| Zn1—O6—H62 | 118 (2) | O8—C15—O7 | 124.46 (15) |
| H61—O6—H62 | 110 (3) | O8—C15—C16 | 118.19 (15) |
| C9—N2—Zn1 | 118.11 (11) | C17—C16—C15 | 120.11 (14) |
| C13—N2—Zn1 | 123.38 (10) | C17—C16—C21 | 119.38 (15) |
| C9—N2—C13 | 118.51 (13) | C21—C16—C15 | 120.49 (14) |
| C14—N3—H31 | 115.4 (17) | C16—C17—C18 | 120.40 (17) |
| C14—N3—H32 | 123.8 (15) | C16—C17—H17 | 119.8 |
| H31—N3—H32 | 120 (2) | C18—C17—H17 | 119.8 |
| O1—C1—Zn1 | 63.82 (8) | C17—C18—C19 | 119.64 (17) |
| O2—C1—Zn1 | 56.69 (8) | C17—C18—H18 | 120.2 |
| C2—C1—Zn1 | 175.80 (11) | C19—C18—H18 | 120.2 |
| O1—C1—O2 | 120.51 (14) | C18—C19—C20 | 120.37 (16) |
| O1—C1—C2 | 120.21 (14) | C18—C19—C22 | 121.19 (19) |
| O2—C1—C2 | 119.28 (13) | C20—C19—C22 | 118.43 (19) |
| C3—C2—C1 | 119.43 (14) | C19—C20—H20 | 120.3 |
| C3—C2—C7 | 120.58 (15) | C21—C20—C19 | 119.37 (17) |
| C7—C2—C1 | 119.99 (14) | C21—C20—H20 | 120.3 |

| | | | |
|----------------|--------------|-----------------|--------------|
| C2—C3—H3 | 120.2 | C16—C21—H21 | 119.6 |
| C4—C3—C2 | 119.68 (17) | C20—C21—C16 | 120.76 (16) |
| C4—C3—H3 | 120.2 | C20—C21—H21 | 119.6 |
| C3—C4—C5 | 119.60 (17) | N4—C22—C19 | 178.0 (3) |
| C3—C4—H4 | 120.2 | | |
| O2—Zn1—O1—C1 | -0.14 (9) | C9—N2—C13—C12 | -1.1 (2) |
| O4—Zn1—O1—C1 | -92.81 (10) | O1—C1—C2—C3 | 9.5 (2) |
| O5—Zn1—O1—C1 | -0.8 (2) | O1—C1—C2—C7 | -170.49 (14) |
| O6—Zn1—O1—C1 | 83.95 (10) | O2—C1—C2—C3 | -169.34 (14) |
| N2—Zn1—O1—C1 | 173.27 (9) | O2—C1—C2—C7 | 10.6 (2) |
| O1—Zn1—O2—C1 | 0.14 (8) | C1—C2—C3—C4 | 179.15 (15) |
| O4—Zn1—O2—C1 | 91.28 (10) | C7—C2—C3—C4 | -0.8 (2) |
| O5—Zn1—O2—C1 | 179.92 (9) | C1—C2—C7—C6 | -179.31 (15) |
| O6—Zn1—O2—C1 | -97.77 (10) | C3—C2—C7—C6 | 0.7 (2) |
| N2—Zn1—O2—C1 | -13.46 (16) | C2—C3—C4—C5 | 0.5 (3) |
| O1—Zn1—N2—C9 | 163.71 (13) | C6—C5—C4—C3 | 0.1 (3) |
| O1—Zn1—N2—C13 | -16.72 (13) | C8—C5—C4—C3 | -179.13 (17) |
| O2—Zn1—N2—C9 | 175.39 (12) | C4—C5—C6—C7 | -0.2 (3) |
| O2—Zn1—N2—C13 | -5.04 (19) | C8—C5—C6—C7 | 178.95 (17) |
| O4—Zn1—N2—C9 | 70.67 (14) | C2—C7—C6—C5 | -0.1 (3) |
| O4—Zn1—N2—C13 | -109.76 (13) | N2—C9—C10—C11 | 1.8 (4) |
| O5—Zn1—N2—C9 | -18.17 (14) | C12—C11—C10—C9 | -0.9 (4) |
| O5—Zn1—N2—C13 | 161.40 (12) | C13—C12—C11—C10 | -0.8 (3) |
| O6—Zn1—N2—C9 | -100.64 (14) | C14—C12—C11—C10 | 179.55 (19) |
| O6—Zn1—N2—C13 | 78.93 (13) | C11—C12—C13—N2 | 1.9 (2) |
| C1—Zn1—N2—C9 | 167.60 (12) | C14—C12—C13—N2 | -178.46 (14) |
| C1—Zn1—N2—C13 | -12.83 (15) | C11—C12—C14—O3 | 179.62 (17) |
| O1—Zn1—C1—O2 | -179.76 (15) | C11—C12—C14—N3 | 0.1 (3) |
| O2—Zn1—C1—O1 | 179.76 (15) | C13—C12—C14—O3 | 0.0 (2) |
| O4—Zn1—C1—O1 | 88.99 (10) | C13—C12—C14—N3 | -179.54 (15) |
| O4—Zn1—C1—O2 | -90.77 (10) | O7—C15—C16—C17 | -177.65 (16) |
| O5—Zn1—C1—O1 | 179.65 (9) | O7—C15—C16—C21 | 0.4 (2) |
| O5—Zn1—C1—O2 | -0.11 (12) | O8—C15—C16—C17 | 0.1 (3) |
| O6—Zn1—C1—O1 | -98.06 (10) | O8—C15—C16—C21 | 178.16 (18) |
| O6—Zn1—C1—O2 | 82.18 (10) | C15—C16—C17—C18 | 175.64 (17) |
| N2—Zn1—C1—O1 | -7.89 (11) | C21—C16—C17—C18 | -2.4 (3) |
| N2—Zn1—C1—O2 | 172.35 (9) | C15—C16—C21—C20 | -175.12 (16) |
| Zn1—O1—C1—O2 | 0.23 (14) | C17—C16—C21—C20 | 3.0 (3) |
| Zn1—O1—C1—C2 | -178.65 (12) | C16—C17—C18—C19 | 0.1 (3) |
| Zn1—O2—C1—O1 | -0.25 (15) | C20—C19—C18—C17 | 1.7 (3) |
| Zn1—O2—C1—C2 | 178.64 (11) | C22—C19—C18—C17 | -177.64 (19) |
| Zn1—N2—C9—C10 | 178.82 (17) | C21—C20—C19—C18 | -1.2 (3) |
| C13—N2—C9—C10 | -0.8 (3) | C21—C20—C19—C22 | 178.15 (18) |
| Zn1—N2—C13—C12 | 179.33 (11) | C16—C21—C20—C19 | -1.1 (3) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N3—H31 \cdots O2 ⁱ | 0.82 (2) | 2.13 (3) | 2.914 (2) | 162 (2) |
| N3—H32 \cdots O7 ⁱ | 0.92 (3) | 2.35 (2) | 3.261 (2) | 171 (2) |
| O4—H41 \cdots O7 ⁱⁱ | 0.75 (2) | 2.04 (2) | 2.7890 (17) | 173 (3) |
| O4—H42 \cdots O8 | 0.76 (3) | 1.89 (3) | 2.6547 (18) | 175 (3) |
| O5—H51 \cdots O7 | 0.80 (2) | 1.83 (2) | 2.6264 (17) | 171 (3) |
| O5—H52 \cdots O1 ⁱⁱⁱ | 0.74 (2) | 2.05 (2) | 2.7610 (17) | 164 (2) |
| O6—H61 \cdots O3 ⁱⁱⁱ | 0.75 (3) | 2.05 (3) | 2.7993 (19) | 170 (3) |
| O6—H62 \cdots N1 ^{iv} | 0.76 (3) | 2.17 (3) | 2.918 (3) | 170 (3) |
| C11—H11 \cdots O7 ⁱ | 0.93 | 2.49 | 3.415 (2) | 177 |

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