Bis(nitrato-κO)(1,4,8,11-tetraazacyclotetradecane-κ⁴/N)zinc(II) methanol monosolvate

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The two ZnII atoms in the crystal structure of the title complex, [Zn(NO3)2(C10H24N4)]/C1CH3OH, have a distorted octahedral coordination sphere, defined by 1,4,8,11-tetraazacyclotetradecane (cyclam) N atoms in the equatorial plane and nitrate O atoms in the axial sites. The conformation of the cyclam is trans-III (R, R, S, S), which is typical for metal–cyclam complexes. Nitrate anions are involved in intra- and intermolecular hydrogen bonding with the N–H groups of the ZnII–cyclam unit. Together with the methanol solvent molecule, the hydrogen-bonding network connects the ZnII–cyclam units into ribbons running parallel to the a axis.

Structure description

Cyclam is a well-known macrocyclic polyamine and water-soluble ligand that can strongly chelate transition-metal cations. As a result, various cyclam derivatives and metal complexes have been synthesized, and their crystal structures have been described. The crystal structure of the title zinc nitrate complex, on the other hand, is the first reported in this context. We anticipate that, in future, this structural property can be used in the development of new functional materials.

The asymmetric unit of the title complex, [ZnII(C10H24N4 = cyclam)](NO3)2·CH3OH, comprises two half-ZnII–cyclam complexes that are centered on Zn1 and Zn2, as well as two nitrate anions that coordinate to each ZnII atom, and a methanol solvent molecule. The two half-ZnII–cyclam complexes are completed by inversion symmetry. Each ZnII atom is coordinated in a planar fashion by the four N atoms of the cyclam ligand. N1, N2,
N1\textsuperscript{i}, and N2\textsuperscript{i} [symmetry code: (i) 2 - x, 1 - y, 1 - z] define the cyclam plane around Zn1, and nitrate atoms O1 and O1\textsuperscript{i} coordinate at the axial positions of the resulting distorted octahedron (Fig. 1). For Zn2, the equatorial plane is defined by N3, N4, N3\textsuperscript{ii}, and N4\textsuperscript{ii} [symmetry code: (ii) 1 - x, 1 - y, 1 - z], and the axially bound O atoms by O4 and O4\textsuperscript{ii} (Fig. 2). The coordination environments of the two central Zn\textsuperscript{ii} atoms are similar to that of Co(cyclam)Cl\textsubscript{2} (Oba & Mochida, 2015). The conformation of the cyclam structure is trans-III (R, R, S, S) type, which is the most energetically favorable conformation (Bosnich et al., 1965). The conformation is generally consistent with previous reports for metal–cyclam complexes such as Cu\textsuperscript{ii} (Emsley et al., 1990), Ni\textsuperscript{ii} (Prasad et al., 1987), and Pd\textsuperscript{ii} (Hunter et al., 2004). The Zn1–O1 and Zn2–O4 bond lengths are 2.3045 (18) and 2.3233 (19) Å, respectively, which is longer than in the Zn\textsuperscript{ii}–nitrate ion (ca 2.0 Å; Ichimaru et al., 2021; Kinoshita-Kikuta et al., 2021), owing to the hydrogen-bonding network detailed below. The N1–Zn1–O1 and N2–Zn2–O4 bond angles are 92.98 (8)\textdegree and 89.14 (9)\textdegree, and N3–Zn2–O4 and N4–Zn2–O4 are 91.98 (8) and 87.95 (9)\textdegree. These angles imply that both Zn\textsuperscript{ii} atoms are on the centroid of the plane created by the four cyclam N atoms. However, the two cyclam rings chelating Zn1 and Zn2 have different asymmetric structures: N1–H1 and N2–H2 have syn-configurations, while N3–H3 and N4–H4 have anti-configurations.

In addition to the methanol solvate molecule, two nitrate anions are involved in the formation of an inter- and intramolecular hydrogen-bonding network. The nitrate anion coordinating to Zn1 forms an intramolecular hydrogen bond (O2•••H1–N1) and an intermolecular hydrogen bond (O3•••H4–N4) (Fig. 2). N2–H2 and N3–H3 create hydrogen bonds with the other nitrate ion. As a result, the hydrogen-bond network includes all N-bound H atoms. Table 1 summarizes numerical data of the hydrogen bonding. In the crystal packing, the different moieties form ribbons parallel to the a axis through the hydrogen-bonding network (Fig. 3). The distances between Zn atoms parallel to the a axis, for example, Zn1•••Zn2, are 7.6706 (3) Å (Fig. 3). The distances between Zn atoms in neighboring ribbons, for example, Zn1•••Zn1\textsuperscript{iii} [symmetry code: (iii) x, \(\frac{1}{2} - y, -\frac{1}{2} + z\)], are 7.93804 (18) Å (Figs. 3 and 4). The nitrate ions coordinating to Zn1 and Zn2 have an N•••N distance of 3.409 (4) Å (Fig. 3).
Synthesis and crystallization

Under an argon atmosphere, zinc nitrate hexahydrate (1.5 g, 5 mmol), dissolved in dry methanol (5 ml), was added to a 20 ml dry methanolic solution of cyclam (1.0 g, 5 mmol). The reaction mixture was agitated at room temperature for 2 h before the solvent was evaporated to get a colorless solid. To obtain colorless crystals appropriate for X-ray crystallography, the crude product was dissolved in hot methanol, filtered through a cellulose filter (0.45 μm pore size) and cooled to room temperature (yield 1.7 g, 87%).

Refinement

Table 2 summarizes crystal data, data collection, and structure refinement details.

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full crystallographic data

*IUChData* (2022). 7, x220854  [https://doi.org/10.1107/S2414314622008549]

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**Bis(nitrato-κO)(1,4,8,11-tetraazacyclotetradecane-κ^4N)zinc(II)] methanol monosolvate**

**Crystal data**

\[\text{[Zn(NO}_3\text{)}_2(C_{10}H_{24}N_4)]\cdot\text{CH}_3\text{O}\]

\(M_r = 421.76\)

Monoclinic, \(P2_1/c\)

\(a = 15.3412 (5) \text{ Å}\)

\(b = 9.4306 (3) \text{ Å}\)

\(c = 12.7716 (4) \text{ Å}\)

\(β = 105.864 (4)°\)

\(V = 1777.38 (10) \text{ Å}^3\)

\(Z = 4\)

\(F(000) = 888\)

\(D_a = 1.576 \text{ Mg m}^{-3}\)

Cu \(Kα\) radiation, \(\lambda = 1.54184 \text{ Å}\)

Cell parameters from 4300 reflections

\(\theta = 3.0–68.2°\)

\(\mu = 2.36 \text{ mm}^{-1}\)

\(T = 100 \text{ K}\)

Block, clear colourless

\(0.54 \times 0.19 \times 0.09 \text{ mm}\)

**Data collection**

Rigaku XtaLAB Synergy-i diffractometer

Detector resolution: 10.0 pixels mm\(^{-1}\)

\(ω\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2022)

\(T_{\text{min}} = 0.356, T_{\text{max}} = 1.000\)

9899 measured reflections

3230 independent reflections

2568 reflections with \(I > 2σ(I)\)

\(R_{\text{int}} = 0.078\)

\(θ_{\text{max}} = 68.3°, θ_{\text{min}} = 3.0°\)

\(h = -11→1\)

\(k = -11→1\)

\(l = -15→15\)

**Refinement**

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2σ(F^2)] = 0.063\)

\(wR(F^2) = 0.188\)

\(S = 1.01\)

3230 reflections

231 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H-atom parameters constrained

\(w = 1/[σ^2(F^2) + (0.1278P)^2]\)

where \(P = (F^2_c + 2F^2_s)/3\)

\((Δ/σ)_{\text{max}} = 0.001\)

\(Δρ_{\text{max}} = 1.01\ \text{e Å}^{-3}\)

\(Δρ_{\text{min}} = -0.92\ \text{e Å}^{-3}\)

**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.** All hydrogen atoms were placed using a geometrical computation.
### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x         | y         | z         | Ueq * | Ueq |
|---|-----------|-----------|-----------|-------|-----|
| Zn1 | 1.000000  | 0.500000  | 0.500000  | 0.0174(3) |     |
| Zn2 | 0.500000  | 0.500000  | 0.500000  | 0.0210(3) |     |
| O1  | 0.90165(12)| 0.6144(2) | 0.57953(17)| 0.0228(5) |     |
| O4  | 0.41074(12)| 0.4107(2) | 0.60524(17)| 0.0240(5) |     |
| O3  | 0.77063(11)| 0.6485(2) | 0.60726(18)| 0.0285(6) |     |
| O2  | 0.83570(14)| 0.4444(3) | 0.6451(2)  | 0.0327(6) |     |
| N4  | 0.60866(19)| 0.5006(2) | 0.6400(3)  | 0.0180(7) |     |
| H4  | 0.664921   | 0.519254  | 0.617093  | 0.022*(7)|     |
| O7  | 0.81007(13)| 0.9063(2) | 0.4951(2)  | 0.0361(6) |     |
| H7  | 0.812347   | 0.819336  | 0.516078  | 0.043*(7)|     |
| O6  | 0.28873(13)| 0.3907(2) | 0.6578(2)  | 0.0392(7)|     |
| O5  | 0.31960(14)| 0.5903(2) | 0.5959(2)  | 0.0373(7)|     |
| N2  | 0.89281(18)| 0.4685(3) | 0.3604(2)  | 0.0212(6)|     |
| H2  | 0.835219   | 0.491792  | 0.379058  | 0.025*(6)|     |
| N1  | 0.98381(15)| 0.3061(3) | 0.5702(2)  | 0.0214(6)|     |
| H1  | 0.933487   | 0.318926  | 0.605250  | 0.026*(6)|     |
| N5  | 0.83550(14)| 0.5680(3) | 0.6110(2)  | 0.0174(6)|     |
| N6  | 0.33879(16)| 0.4640(3) | 0.6198(2)  | 0.0203(6)|     |
| N3  | 0.47857(15)| 0.7086(2) | 0.5418(2)  | 0.0206(6)|     |
| H3  | 0.428178   | 0.705969  | 0.577575  | 0.025*(7)|     |
| C9  | 0.62304(18)| 0.3673(3) | 0.7042(2)  | 0.0228(7)|     |
| H9A | 0.570572   | 0.350872  | 0.733703  | 0.027*(6)|     |
| H9B | 0.677734   | 0.377161  | 0.766423  | 0.027*(6)|     |
| C5  | 0.90590(18)| 0.5758(3) | 0.2809(2)  | 0.0273(7)|     |
| H5A | 0.849116   | 0.587691  | 0.221956  | 0.033*(6)|     |
| H5B | 0.954085   | 0.544320  | 0.248060  | 0.033*(6)|     |
| C8  | 0.59354(18)| 0.6245(3) | 0.7040(2)  | 0.0241(7)|     |
| H8A | 0.650488   | 0.649443  | 0.759304  | 0.029*(7)|     |
| H8B | 0.547153   | 0.601449  | 0.742138  | 0.029*(7)|     |
| C6  | 0.45112(18)| 0.8098(3) | 0.4500(2)  | 0.0243(7)|     |
| H6A | 0.501178   | 0.820272  | 0.415422  | 0.029*(7)|     |
| H6B | 0.439699   | 0.903787  | 0.478126  | 0.029*(7)|     |
| C7  | 0.56169(17)| 0.7496(3) | 0.6268(2)  | 0.0242(7)|     |
| H7A | 0.548869   | 0.832283  | 0.668051  | 0.029*(7)|     |
| H7B | 0.609813   | 0.776730  | 0.592444  | 0.029*(7)|     |
| C1  | 1.06750(19)| 0.2846(3) | 0.6595(3)  | 0.0286(7)|     |
| H1A | 1.116932   | 0.251144  | 0.629517  | 0.034*(7)|     |
| H1B | 1.057015   | 0.211822  | 0.710621  | 0.034*(7)|     |
| C10 | 0.63455(18)| 0.2400(3) | 0.6356(2)  | 0.0243(7)|     |
| H10A| 0.658080   | 0.159721  | 0.685250  | 0.029*(7)|     |
| H10B| 0.681107   | 0.263706  | 0.597912  | 0.029*(7)|     |
| C2  | 0.95855(19)| 0.1838(3) | 0.4955(3)  | 0.0294(8)|     |
| H2A | 0.947341   | 0.100243  | 0.536938  | 0.035*(8)|     |
| H2B | 1.009659   | 0.160697  | 0.465025  | 0.035*(8)|     |
| C4  | 0.88514(18)| 0.3207(3) | 0.3175(3)  | 0.0298(8)|     |
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| H4A | 0.940106 | 0.297254 | 0.294672 | 0.036* |
| H4B | 0.832302 | 0.314258 | 0.252673 | 0.036* |
| C3  | 0.87418 (19) | 0.2135 (3) | 0.4024 (3) | 0.0316 (8) |
| H3A | 0.853153 | 0.122895 | 0.364889 | 0.038* |
| H3B | 0.825874 | 0.247888 | 0.433994 | 0.038* |
| C11 | 0.7259 (2) | 0.9615 (4) | 0.5002 (3) | 0.0329 (7) |
| H11A| 0.676872 | 0.901659 | 0.457126 | 0.049* |
| H11B| 0.718800 | 1.058159 | 0.470901 | 0.049* |
| H11C| 0.723491 | 0.963070 | 0.576083 | 0.049* |

Atomic displacement parameters (Å²)

|     | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|-----|-----|-----|-----|-----|-----|-----|
| Zn1 | 0.0152 (4) | 0.0120 (4) | 0.0215 (4) | −0.00113 (18) | −0.0010 (3) | 0.0007 (2) |
| Zn2 | 0.0191 (4) | 0.0141 (5) | 0.0245 (4) | 0.00029 (19) | −0.0030 (3) | −0.0013 (2) |
| O1  | 0.0144 (9) | 0.0192 (11) | 0.0366 (12) | −0.0024 (8) | 0.0099 (8) | −0.0047 (9) |
| O4  | 0.0131 (9) | 0.0232 (12) | 0.0364 (11) | 0.0042 (8) | 0.0080 (8) | 0.0045 (10) |
| O3  | 0.0145 (9) | 0.0193 (12) | 0.0517 (14) | 0.0038 (8) | 0.0093 (9) | −0.0010 (10) |
| O2  | 0.0258 (11) | 0.0225 (13) | 0.0545 (16) | 0.0051 (10) | 0.0188 (11) | 0.0139 (12) |
| O5  | 0.0137 (12) | 0.0149 (15) | 0.0229 (15) | −0.0021 (8) | 0.0010 (11) | −0.0007 (9) |
| O7  | 0.0321 (11) | 0.0227 (13) | 0.0584 (16) | 0.0018 (9) | 0.0207 (11) | 0.0021 (12) |
| O6  | 0.0214 (10) | 0.0341 (14) | 0.0685 (17) | 0.0064 (10) | 0.0229 (11) | 0.0227 (13) |
| O5  | 0.0291 (11) | 0.0165 (13) | 0.0733 (19) | 0.0070 (10) | 0.0258 (12) | 0.0078 (12) |
| N2  | 0.0146 (12) | 0.0234 (13) | 0.0230 (15) | 0.0013 (11) | 0.0006 (10) | −0.0039 (12) |
| N1  | 0.0165 (11) | 0.0156 (13) | 0.0339 (14) | 0.0035 (9) | 0.0102 (10) | 0.0027 (11) |
| N5  | 0.0095 (10) | 0.0179 (14) | 0.0224 (12) | −0.0002 (10) | 0.0002 (9) | −0.0036 (11) |
| N6  | 0.0106 (11) | 0.0263 (15) | 0.0211 (13) | 0.0018 (12) | −0.0007 (9) | 0.0019 (12) |
| N3  | 0.0162 (11) | 0.0163 (13) | 0.0283 (13) | −0.0028 (9) | 0.0045 (9) | −0.0011 (10) |
| C9  | 0.0156 (12) | 0.0218 (17) | 0.0293 (15) | 0.0014 (12) | 0.0036 (11) | 0.0049 (13) |
| C5  | 0.0182 (13) | 0.039 (2) | 0.0228 (15) | 0.0049 (13) | 0.0017 (11) | 0.0058 (14) |
| C8  | 0.0189 (13) | 0.0247 (18) | 0.0267 (15) | −0.0022 (12) | 0.0030 (11) | −0.0063 (14) |
| C6  | 0.0166 (13) | 0.0168 (15) | 0.0376 (17) | −0.0011 (11) | 0.0042 (11) | 0.0004 (14) |
| C7  | 0.0183 (13) | 0.0202 (16) | 0.0319 (16) | −0.0049 (12) | 0.0030 (11) | −0.0059 (14) |
| C1  | 0.0208 (14) | 0.0287 (19) | 0.0354 (18) | 0.0094 (13) | 0.0059 (12) | 0.0119 (15) |
| C10 | 0.0172 (12) | 0.0186 (16) | 0.0331 (16) | 0.0021 (12) | 0.0001 (11) | 0.0036 (14) |
| C2  | 0.0238 (15) | 0.0110 (15) | 0.055 (2) | −0.0010 (12) | 0.0142 (14) | −0.0033 (14) |
| C4  | 0.0153 (13) | 0.036 (2) | 0.0357 (18) | −0.0025 (14) | 0.0035 (12) | −0.0174 (16) |
| C3  | 0.0178 (13) | 0.0199 (17) | 0.057 (2) | −0.0060 (12) | 0.0104 (13) | −0.0149 (15) |
| C11 | 0.0259 (13) | 0.0356 (19) | 0.0372 (19) | 0.0017 (17) | 0.0084 (12) | 0.0016 (16) |

Geometric parameters (Å, °)

|     |  |  | N3—C7 | 1.483 (3) |
|-----|---|---|-------|---------|
| Zn1 | O1 | 2.3045 (18) |       |         |
| Zn1 | O1i| 2.3045 (18) | C9—H9A| 0.9900  |
| Zn1 | N2 | 2.090 (3)   | C9—H9B| 0.9900  |
| Zn2 | N2i| 2.090 (3)   | C9—C10| 1.524 (4) |
| Zn1 | Ni | 2.081 (2)   | C5—H5A| 0.9900  |
| Zn1 | Ni | 2.081 (2)   | C5—H5B| 0.9900  |
| Bond          | Distance (Å) | Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|--------------|--------------|
| Zn2—O4ii     | 2.3233 (19)  | C5—C1i       | 1.520 (4)    | O4—N6        | 1.272 (3)    |
| Zn2—O4       | 2.3232 (19)  | C8—H8A       | 0.9900       | O3—N5        | 1.242 (3)    |
| Zn2—N4ii     | 2.085 (3)    | C8—H8B       | 0.9900       | O2—N5        | 1.244 (4)    |
| Zn2—N4       | 2.085 (3)    | C8—C7        | 1.530 (4)    | N4—H4        | 1.0000       |
| Zn2—N3       | 2.087 (2)    | C6—H6A       | 0.9900       | N4—C9        | 1.484 (4)    |
| Zn2—N3ii     | 2.087 (2)    | C6—H6B       | 0.9900       | N4—C8        | 1.480 (4)    |
| O1—N5        | 1.267 (3)    | C6—C10ii     | 1.535 (4)    | O7—H7        | 0.8603       |
| O4—N6        | 1.272 (3)    | C7—H7A       | 0.9900       | O7—C11       | 1.410 (4)    |
| O3—N5        | 1.242 (3)    | C7—H7B       | 0.9900       | O6—N6        | 1.228 (3)    |
| O2—N5        | 1.244 (4)    | C1—H1A       | 0.9900       | O5—N6        | 1.245 (4)    |
| N4—H4        | 1.0000       | C1—H1B       | 0.9900       | N2—H2        | 1.0000       |
| N4—C9        | 1.484 (4)    | C8—H8A       | 0.9900       | N2—C5        | 1.485 (4)    |
| N4—C8        | 1.480 (4)    | C8—H8B       | 0.9900       | N2—C4        | 1.490 (4)    |
| O7—H7        | 0.8603       | C2—H2A       | 0.9900       | N1—H1        | 1.0000       |
| O7—C11       | 1.410 (4)    | C2—H2B       | 0.9900       | N1—C1        | 1.480 (4)    |
| O6—N6        | 1.228 (3)    | C2—C3        | 1.525 (4)    | N1—C2        | 1.480 (4)    |
| O5—N6        | 1.245 (4)    | C4—H4A       | 0.9900       | O1—Zn1—O1    | 180.0        |
| N2—H2        | 1.0000       | C4—H4B       | 0.9900       | N2—Zn1—O1    | 90.86 (9)    |
| N2—C5        | 1.485 (4)    | C4—C3        | 1.525 (5)    | N2—Zn1—O1i   | 90.86 (9)    |
| N2—C4        | 1.490 (4)    | C3—H3A       | 0.9900       | N2—Zn1—O1ii  | 89.14 (9)    |
| N1—H1        | 1.0000       | C3—H3B       | 0.9900       | N1i—Zn1—O1   | 180.00 (15)  |
| N1—C1        | 1.480 (4)    | C11—H11A     | 0.9800       | N1i—Zn1—O1i  | 92.98 (8)    |
| N1—C2        | 1.480 (4)    | C11—H11B     | 0.9800       | N1i—Zn1—O1ii | 87.02 (8)    |
| N3—H3        | 1.0000       | C11—H11C     | 0.9800       | N1—Zn1—O1    | 87.02 (8)    |
| N3—C6        | 1.481 (4)    | O4—Zn2—O4ii  | 1.520 (4)    | N1—Zn1—O1i   | 92.98 (8)    |
| O4—Zn2—O4ii  | 180.0        | N3—C6—H6A    | 109.3        | N1—Zn1—O1ii  | 87.02 (8)    |
| N4i—Zn2—O4i  | 87.95 (9)    | N3—C6—H6B    | 109.3        | N1—Zn1—N2    | 85.19 (10)   |
| N4i—Zn2—O4ii | 92.05 (9)    | N3—C6—C10ii  | 111.7 (2)    | N1—Zn1—N2i   | 94.81 (10)   |
| N4i—Zn2—O4   | 92.05 (9)    | N3—C6—C10ii  | 111.7 (2)    | O4—Zn2—O4ii  | 180.0        |
| N4i—Zn2—N4   | 180.0        | C7—C8—H8A    | 109.9        | N4—Zn2—O4ii  | 180.0        |
| N4i—Zn2—N3   | 94.42 (9)    | C7—C8—H8B    | 109.9        | N4—Zn2—O4ii  | 180.0        |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| N4—Zn2—N3           | 94.42 (9) | N3—C7—C8             | 109.2 (2) |
| N4—Zn2—N3           | 85.58 (9) | N3—C7—H7A            | 109.8     |
| N4>Zn2—N3           | 85.58 (9) | N3—C7—H7B            | 109.8     |
| N3—Zn2—O4           | 88.02 (8) | C8—C7—H7A            | 109.8     |
| N3—Zn2—O4           | 91.98 (8) | C8—C7—H7B            | 109.8     |
| N3—Zn2—O4           | 91.98 (8) | H7A—C7—H7B           | 108.3     |
| N3—Zn2—N3           | 88.02 (8) | N1—C1—C5             | 108.9 (2) |
| N3—Zn2—N3           | 180.0     | N1—C1—H1A            | 109.9     |
| N5—O1—Zn1           | 130.97 (17) | N1—C1—H1B           | 109.9     |
| N6—O4—Zn2           | 127.85 (18) | C5—C1—H1A           | 109.9     |
| Zn2—N4—H4           | 107.5     | C5—C1—H1B            | 109.9     |
| C9—N4—Zn2           | 115.77 (18) | H1A—C1—H1B         | 108.3     |
| C9—N4—H4            | 107.5     | C9—C10—C6            | 116.0 (2) |
| C8—N4—Zn2           | 105.45 (18) | C9—C10—H10A        | 108.3     |
| C8—N4—H4            | 107.5     | C9—C10—H10B          | 108.3     |
| C8—N4—C9            | 112.7 (3) | C6—C10—H10A          | 108.3     |
| C11—O7—H7           | 107.3     | C6—C10—H10B          | 108.3     |
| Zn1—N2—H2           | 107.8     | H10A—C10—H10B        | 107.4     |
| C5—N2—Zn1           | 105.34 (18) | N1—C2—H2A           | 109.2     |
| C5—N2—H2            | 107.8     | N1—C2—H2B            | 109.2     |
| C5—N2—C4            | 113.4 (3) | N1—C2—C3             | 112.1 (2) |
| C4—N2—Zn1           | 114.27 (19) | H2A—C2—H2B        | 107.9     |
| C4—N2—H2            | 107.8     | C3—C2—H2A            | 109.2     |
| Zn1—N1—H1           | 106.5     | C3—C2—H2B            | 109.2     |
| C1—N1—Zn1           | 105.80 (17) | N2—C4—H4A           | 109.3     |
| C1—N1—H1            | 106.5     | N2—C4—H4B            | 109.3     |
| C2—N1—Zn1           | 116.65 (18) | N2—C4—C3            | 111.8 (3) |
| C2—N1—H1            | 106.5     | H4A—C4—H4B           | 107.9     |
| C2—N1—C1            | 114.1 (2) | C3—C4—H4A            | 109.3     |
| O3—N5—O1            | 118.6 (2) | C3—C4—H4B            | 109.3     |
| O3—N5—O2            | 120.8 (2) | C2—C3—H3A            | 108.2     |
| O2—N5—O1            | 120.6 (2) | C2—C3—H3B            | 108.2     |
| O6—N6—O4            | 119.8 (3) | C4—C3—C2             | 116.2 (2) |
| O6—N6—O5            | 120.3 (2) | C4—C3—H3A            | 108.2     |
| O5—N6—O4            | 119.9 (2) | C4—C3—H3B            | 108.2     |
| Zn2—N3—H3           | 106.8     | H3A—C3—H3B           | 107.4     |
| C6—N3—Zn2           | 115.81 (18) | O7—C11—H11A       | 109.5     |
| C6—N3—H3            | 106.8     | O7—C11—H11B          | 109.5     |
| C6—N3—C7            | 114.4 (2) | O7—C11—H11C          | 109.5     |
| C7—N3—Zn2           | 105.63 (17) | H11A—C11—H11B      | 109.5     |
| C7—N3—H3            | 106.8     | H11A—C11—H11C        | 109.5     |
| N4—C9—H9A           | 109.2     | H11B—C11—H11C        | 109.5     |
| N4—C9—H9B           | 109.2     |                       |           |

\[ \text{Zn1—O1—N5—O3} \quad -149.2 (2) \quad \text{N4—C9—C10—C6} \quad -71.3 (3) \]
\[ \text{Zn1—O1—N5—O2} \quad 30.9 (4) \quad \text{N4—C8—C7—N3} \quad 57.2 (3) \]
\[ \text{Zn1—N2—C5—C1} \quad -42.5 (2) \quad \text{N2—C4—C3—C2} \quad -73.0 (3) \]
\[ \text{Zn1—N2—C4—C3} \quad 57.8 (3) \quad \text{N1—C2—C3—C4} \quad 70.0 (3) \]
Zn1—N1—C1—C5i 41.5 (2) C9—N4—C8—C7 −169.3 (2)
Zn1—N1—C2—C3 −53.7 (3) C5—N2—C4—C3 178.6 (2)
Zn2—O4—N6—O6 164.3 (2) C8—N4—C9—C10 177.6 (2)
Zn2—O4—N6—O5 −16.1 (4) C6—N3—C7—C8 −168.6 (2)
Zn2—N4—C9—C10 56.1 (3) C7—N3—C6—C10ii 179.3 (2)
Zn2—N4—C8—C7 −42.1 (2) C1—N1—C2—C3 −177.7 (2)
Zn2—N3—C6—C10ii 56.1 (3) C2—N1—C1—C5 i 171.1 (2)
Zn2—N3—C7—C8 −40.1 (2) C4—N2—C5—C1 i −168.2 (2)

Symmetry codes: (i) −x+2, −y+1, −z+1; (ii) −x+1, −y+1, −z+1.

| Hydrogen-bond geometry (Å, °) |
|-----------------------------|
| D—H···A         | D—H | H···A | D···A | D—H···A |
| N1—H1···O2    | 1.00 | 2.08  | 2.995 (3) | 151     |
| N2—H2···O5ii  | 1.00 | 2.60  | 3.497 (4) | 149     |
| N2—H2···O6i   | 1.00 | 2.14  | 3.036 (4) | 148     |
| N3—H3···O5    | 1.00 | 2.06  | 2.931 (3) | 145     |
| N4—H4···O3    | 1.00 | 2.06  | 2.977 (3) | 152     |
| O7—H7···O1    | 0.86 | 2.38  | 3.144 (3) | 148     |
| O7—H7···O3    | 0.86 | 2.18  | 2.966 (3) | 151     |

Symmetry code: (ii) −x+1, −y+1, −z+1.