Synthesis, structural analysis, and docking studies with SARS-CoV-2 of a trinuclear zinc complex with N-phenylanthranilic acid ligands

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The structure of a trinuclear zinc complex, hexakis(μ₂-2-anilinobenzoato)diaquatrizinc(II), [Zn₂(C₁₃H₁₀NO₂)₆(H₂O)₂] or (NPA)₆Zn₃(H₂O)₂ (NPA is 2-anilinobenzoate or N-phenylanthranilate), is reported. The complex crystallizes in the triclinic space group P1 and the central ZnII atom is located on an inversion center. The NPA ligand is found to coordinate via the carboxylate O atoms with unique C—O bond lengths that support an unequal distribution of resonance over the carboxylate fragment. The axial H₂O ligands form hydrogen bonds with neighboring molecules that stabilize the supramolecular system in rigid straight chains, with an angle of 180° along the c axis. π stacking is the primary stabilization along the a and b axes, resulting in a highly ordered supramolecular structure. Docking studies show that this unique supramolecular structure of a trinuclear zinc complex has potential for binding to the main protease (Mpro) in SARS-CoV-2 in a different location from Remdesivir, but with a similar binding strength.

1. Introduction

The design of zinc complexes as antiviral agents from simple, relatively cheap, and available ligands is of great interest in supramolecular chemistry and materials science (Batten et al., 2009). Coronaviruses such as SARS-CoV can be targeted by Zn²⁺ when combined with ionophores to increase Zn²⁺ concentrations inside the cell (te Velthuis et al., 2010). Zn²⁺ has been proposed for use as a supplement in reducing COVID-19 morbidity (Derwand & Scholz, 2020), with possible impacts on virus replication, neurological damage, and inflammation (Cereda et al., 2022). Current proposed modes of action are through inhibition of DNA and RNA replication (te Velthuis et al., 2010), so the main protease of SARS-CoV-2 (Mpro) is of particular interest for developing antiviral agents. Mpro plays a key role in the replication and transcription of SARS-CoV-2 and is the target of Remdesivir, the first therapeutic approved by the FDA for COVID-19 treatment (Beigel et al., 2020). Molecular docking studies of Remdesivir with Mpro, as compared to other potential antiviral agents, established that Remdesivir binds most strongly to Mpro based on the most favorable docking score (Naik et al., 2020). This establishes molecular docking as a possible tool for screening potential antiviral agents. The current work presents the synthesis of a novel trinuclear zinc complex and analysis of its molecular docking to Mpro.

Polynuclear complexes can be synthesized using ligands with multidentate moieties (El-Boraey & El-Salamony, 2019),
and amino acid-based ligands are often targeted because of their potential pharmacological properties (Aiyelabola et al., 2016). Although the naturally occurring α-amino acids have been studied extensively, synthetic β-amino acids have only more recently been considered for applications in coordination chemistry. This work focuses on N-phenylanthranilic acid (NPA), which is a β-amino acid. In β-amino acids, the amino group is bound to the β-carbon, which is one atom further removed from the carboxylic acid group. This contrasts with α-amino acids, in which the carbonyl C atom of the carboxylic acid group and the N atom of the amino group are bound to the same C atom, the α-carbon. Of note are the two arene arms in NPA, which can rotate freely around the amino group. This capacity for rotation minimizes steric hindrance and can therefore lead to interesting structures with versatile motifs.

NPA is reported to act as a chelating ligand for metals, with potential for coordination through both the N atom of the amino group (N) and the O atoms of the carboxyl group (–COO−) (Ros et al., 2002). NPA can also bind either through one carboxylate O atom, as in the motif Zn(Hdmpz)2(L2)2 (Hdmpz is 3,5-dimethylpyrazole and L2 is N-phenylanthranilate), or through both carboxylate O atoms, as in the dinuclear motif [Cu2(C6H5NHC6H4COO)4(CH3CH2OH)2] (Jin & Wang, 2014; Tas et al., 2010). NPA ligands were reported to coordinate to rhodium for synthesizing hydrogenation catalysts, as seen in RhPAA (PAA is N-phenylanthranilic acid) (Ros et al., 2002). Here, NPA was found to interact with the rhodium center via both the amine and carboxyl groups. Recent reports of NPA ligands coordinated to the lanthanides samarium, europium, and gadolinium in a search for novel antibacterial complexes provide several examples of NPA complexes in which the ligand is coordinated to two or three metal centers (Zapała et al., 2019). Analysis of the complexes revealed that NPA coordinates to all of these lanthanides only via the carboxylate group. Similar NPA coordination was reported in terbium complexes for luminescence studies (Fu et al., 2008).

Among the first NPA complexes with 3d transition metals reported were with CuII metal centers in tetrakis[μ-2-(phenylamino)benzoato-κ2O,O']bis[(ethanol)copper(II)] and bis[μ-2-(phenylamino)benzoato-κ2O,O']bis[(hydroxido)copper(II)] (Tas et al., 2010). Both of these complexes contain two copper centers, with NPA ligands that bridge between the two CuII centers via the carboxylate groups. Mononuclear metal complexes of NPA were reported for Cd and Zn with an additional 2,2'-bipyridine or 3,5-dimethylpyrazole ligand, and for Mn with an additional phenanthroline ligand (Jin & Wang, 2014; Tan et al., 2015).

Little attention has been focused on pharmaceutical agents and coordination compounds of NPA with Zn in a polynuclear motif, although several studies involving trinuclear zinc complexes with a variety of ligands have been reported (Liu et al., 2013; Yu et al., 2007; Neels & Stoeckli-Evans, 1999; Akine et al., 2004; Karmakar et al., 2019; Diop et al., 2014). A recurring theme in this area of research is the exploration of photoluminescence (Fu et al., 2008) and applications in DNA intercalation (Biswas et al., 2014).

In this article, the synthesis and structural characterization of a trinuclear Zn complex with NPA ligands is reported (Scheme 1). The complex was analyzed using NMR and single-crystal X-ray diffraction to confirm the NPA coordination and structural motifs. Docking studies with SARS-CoV-2 were conducted to probe the potential for the new complex to act as an antiviral agent.

![Scheme 1](https://zenodo.org/)

2. Experimental

All procedures were conducted on the bench in the presence of air and moisture, and all reagents were obtained commercially and used without further purification. Elemental analysis for C, H, and N was conducted using a Costech ECS 4010 CHNSO analyzer. 1H and 13C NMR were conducted using a Varian 400 MHz spectrometer and calibrated to residual dimethyl sulfoxide (DMSO). Associated NMR data (Brannon et al., 2021) and molecular docking data (Mbani et al., 2021) were deposited on Zenodo (https://zenodo.org/).

2.1. Synthesis and crystallization of (NPA)6Zn3(H2O)2

ZnCl2 (0.272 g, 0.002 mol) and NH4SCN (0.144 g, 0.002 mol) were dissolved in a water–ethanol solution (~10 ml, 1:5 v/v) and placed in a 100 ml Erlenmeyer flask with stirring at room temperature for about 30 min. To this solution was added an ethanolic solution (20 ml) of NPA (0.426 g, 0.002 mol). The pH of the resulting solution was adjusted to about 6 using 10% Et3N solution and stirring was continued for 24 h. A transparent crystalline complex was obtained from the solution.
by slow evaporation for several days, producing crystals suitable for X-ray analysis. Analysis calculated (%) for C$_{78}$H$_{64}$N$_6$O$_{14}$Zn$_3$: C 62.23, H 4.28, N 5.58; found: C 62.04, H 3.83, N 5.67. 1H NMR (399.777 MHz, DMSO-d$_6$, 295 K): δ 6.80 (m, 1H; $H_1$), 7.02 (t, $J$ = 8.0 Hz, 1H; $H_2$), 7.22 (d, $J$ = 8.0 Hz, 2H; $H_3$), 7.33 (m, 4H; $H_4$, $H_5$, $H_6$, $H_7$), 8.03 (d, $J$ = 8.0 Hz, 1H; $H_8$), 10.42 (br s, 1H; $H_9$). 13CN M R (100.535 MHz, DMSO-d$_6$, 295 K): δ 113.7 (C$_f$), 117.5 (C$_d$), 117.7 (C$_b$), 120.2 (C$_i$), 122.1 (C$_k$), 129.7 (C$_j$), 132.5 (C$_e$), 132.9 (C$_c$), 141.8 (C$_h$), 146.0 (C$_g$), 173.3 (C$_a$).

2.2. Crystallographic details

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were placed at ideal positions excluding the H atoms on the solvent water molecules and nitrogen, which were placed manually at q-peaks.

2.3. Molecular docking

Molecular docking studies were conducted with AutoDock (Version 4.2; Trott & Olson, 2010) and CB-Dock (Liu et al., 2020; Cao & Li, 2014). The three-dimensional (3D) structure of the main protease (M$_{pro}$) of SARS-COV-2 (PDB ID: 6lu7) was reported previously with a bound N3 Michael addition inhibitor (Jin et al., 2020). The N3 inhibitor, water molecules, and cocrystallized ligands were removed from the .pdb file prior to commencing docking studies with the new structural coordinates of (NPA)$_6$Zn$_3$(H$_2$O)$_2$. Preparation of the com-

| Table 1 | Experimental details. |
|------------------|----------------------|
| **Crystal data** | [Zn$_3$(C$_{78}$H$_{64}$N$_6$O$_{14}$)$_3$(H$_2$O)$_2$] |
| Chemical formula | M$_r$ 1505.46 |
| Crystal system, space group | Triclinic, $P\overline{1}$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 11.0968 (5), 12.8319 (6), 13.3134 (6) |
| $\alpha$, $\beta$, $\gamma$ (º) | 111.703 (2), 108.028 (2), 93.125 (2) |
| $V$ (Å$^3$) | 1643.97 (13) |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.16 |
| Crystal size (mm) | 0.3 x 0.1 x 0.03 |
| **Data collection** | Bruker Kappa Venture D8 |
| Diffractometer | Multi-scan (SADABS; Bruker, 2017) |
| Absorption correction | |
| $T_{min}$, $T_{max}$ | 0.664, 0.748 |
| No. of measured, independent and observed | 86106, 10025, 8556 |
| $R_{int}$ | 0.044 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.714 |
| **Refinement** | |
| $R(F^2 > 2\sigma(F^2))$, $wR(F^2)$, $S$ | 0.030, 0.078, 1.03 |
| No. of reflections | 10025 |
| No. of parameters | 477 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta$$
\rho_{max}$, $\Delta$$
\rho_{min}$ (e Å$^{-3}$) | 0.65, −0.85 |

Computer programs: APEX3 (Bruker, 2017), SAINT (Bruker, 2017), SHELXT (Sheldrick, 2015a), SHELXL2017 (Sheldrick, 2015b), Mercury (Macrae et al., 2020), and OLEX2 (Dolomanov et al., 2009).

**Figure 1**

View of (NPA)$_6$Zn$_3$(H$_2$O)$_2$, drawn with 50% probability displacement ellipsoids. [Symmetry code: (a) $-x + 1$, $-y + 1$, $-z + 1$.]
pounds and proteins, polar H atoms, and partial charges (Kollman charges) were performed using AutoDock Tools (Version 1.5.6) that saved them as a .pdbqt file. AutoDock Vina (Version 1.1.2) was used with grid box center values at \( x = -26.283, y = 12.599, \) and \( z = 58.966 \), and offset values of 62, 126, and 92, respectively. The 3D results of the interactions between the target and compound were analyzed and illustrated with the software Discovery Studio (Version 17.2) and Chimera (Pettersen et al., 2004).

3. Results and discussion

\((\text{NPA})_6\text{Zn}_3(\text{H}_2\text{O})_2\) was synthesized from equimolar amounts of \(\text{ZnCl}_2\) and \(\text{NH}_4\text{SCN}\), followed by the addition of NPA, and adjusting the pH to 6 with triethylamine. Slow evaporation yielded transparent crystals in 54% yield that were characterized by \(^1\text{H}, ^{13}\text{C}\) COSY (correlated spectroscopy), HMBC (heteronuclear multiple bond correlation), and HSQC (heteronuclear single quantum coherence) NMR spectroscopy. The \(^1\text{H}\) NMR spectrum in DMSO-\(d_6\) revealed nine protons from the arene groups in the range 6.5–7.8 ppm, with the N—H proton found at 10.40 ppm. The observed signals are shifted from the free amino acid resonances at 6.5–7.4 ppm for the arene protons and 9.31 ppm for the N—H proton (Saito et al., 2018), supporting coordination.

Crystallographic analysis reveals that \((\text{NPA})_6\text{Zn}_3(\text{H}_2\text{O})_2\) crystallizes in the triclinic space group \(\text{P}1\) and no solvent molecules are found to be trapped in the structure (Fig. 1). The structure is centrosymmetric, with the Zn2 atom located on an inversion center. The asymmetric unit contains two Zn centers (Zn1 and Zn2), about which three NPA ligands and one H2O ligand are coordinated. The full molecule fills the unit cell, which contains three Zn atoms, six coordinated NPA ligands, and two coordinated terminal H2O ligands.

The central Zn\(^{II}\) atom, Zn2, is hexacoordinated exclusively by O atoms from the carboxylate groups of the NPA ligands. This central Zn\(^{II}\) atom has an approximately octahedral molecular geometry, with bond angles ranging from 83.78 (4)° for O2—Zn2—O4 to 96.22 (4)° for O2—Zn2—O4 [symmetry code: (i) \(-x + 1, -y + 1, -z + 1\)]. The ligand bond lengths range from 2.0219 (11) Å for Zn2—O2, to 2.0775 (10) Å for Zn2—O6, to 2.1762 (10) Å for Zn2—O4. The N atoms of the NPA ligands are not found to be involved in any coordination interaction with the Zn\(^{II}\) centers, which is consistent with predictions from hard–soft acid–base theory (HSAB). However, the H atoms on the N atoms are involved in intramolecular hydrogen bonding with the carboxylate O atoms of NPA (Fig. 2). The hydrogen-bond distances within the asymmetric unit were all around a similar length, with distances of...
2.01 (2) Å for O1···H1, 2.12 (2) Å for O4···H2, and 2.04 (2) Å for O6···H3. However, it should be noted that H atoms were fixed, or placed at calculated positions, which will affect the hydrogen-bond distances. Intramolecular hydrogen bonding between the two symmetry-generated halves of the molecule was found between H2 and O2 with a distance of 2.28 (3) Å (Fig. 3).

The exterior ZnII centers Zn1 and Zn1i are pentacoordinated, with only O atoms coordinated to these centers. The Zn—O bond lengths are generally shorter than the Zn—O bond lengths, with Zn1—O1 at 1.9298 (11) Å, Zn1—O3 at 1.9920 (10) Å, and Zn1—O5 at 1.9063 (10) Å. However, the notable outlier is that one of the O atoms coordinated to Zn1 comes from an H2O ligand, with Zn1—O7 at 2.0274 (12) Å. Because the Zn1 and Zn1i centers are pentacoordinated, there are two modes which can be used to classify their geometry: square pyramidal or trigonal bipyramidal. This distinction is made mathematically by utilizing the Addison parameter (Addison et al., 1984). In this analysis, a trigonal index (τ) is assigned according to the equation τ = (β − α)/60, where β and α are the largest angles about the metal center. If the resulting value for τ is closer to 0, the center is classified as having a square pyramidal geometry. Conversely, if τ lies closer to 1, the center is classified as having a trigonal bipyramidal geometry. This analysis for Zn1 and Zn1i yielded the value τ = 0.566, indicating that the molecular geometry of Zn1 and its symmetry-generated counterpart Zn1i are best described as trigonal bipyramidal in nature.

For all three NPA ligands of the asymmetric unit, both of the carboxylate O atoms are involved in coordination to Zn. This indicates that the formal negative charge of the ligand is delocalized between both O atoms instead of being localized on a single O atom. Each of the bond lengths between C and O atoms of the carboxylate groups are statistically different, indicating that the resonance is not shared equally. In all cases, the longer carboxylate C—O bond lengths are found for O atoms that are coordinated to Zn1, while shorter carboxylate C—O bond lengths are found for O atoms that are coordinated to Zn2 (Fig. 4). The longer carboxylate C—O bond lengths for C1—O1 at 1.2742 (19) Å, C14—O3 at 1.2866 (17) Å, and C27—O5 at 1.2788 (17) Å correlate with shorter Zn1—O bond lengths of Zn1—O1 at 1.9298 (11) Å, Zn1—O3 at 1.9920 (10) Å, and Zn1—O5 at 1.9063 (10) Å, respectively. By contrast, the shorter carboxylate C—O bond lengths for C1—O2 at 1.2559 (18) Å, C14—O4 at 1.2572 (17) Å, and C27—O6 at 1.2555 (17) Å correlate with...
longer Zn2—O bond lengths of Zn2—O2 at 2.0219 (11) Å, Zn2—O4 at 2.1762 (10) Å, and Zn2—O6 at 2.0775 (10) Å, respectively. The longer Zn2—O bond lengths are likely due to increased steric hindrance around the central Zn2 atom and additional intramolecular hydrogen bonding of the O atoms (O2, O4, and O6) with a neighboring NPA ligand, causing additional torsion and strain (Fig. 3).

The two water ligands are located axially along the complex. Each water ligand is involved in hydrogen bonding from an H atom to a carboxylate O of the next unit cell, with a distance of 1.80 (3) Å for H7⋯O3. As a result, each complex donates and accepts a hydrogen bond at each end, for a total of four intermolecular hydrogen bonds per molecule. Owing to symmetry-generated elements, it can be seen that all four hydrogen bonds arise from one unique bond (Fig. 5). These intermolecular hydrogen bonds are the main factor determining the arrangement of adjacent complexes. Due to the centrosymmetric nature of the complex and the axial hydrogen bonding, adjacent complexes attach end-on to form rigid straight chains, as shown in Fig. 5. The angle each chain forms is precisely 180°, such that the molecules stack perfectly when viewing a chain of complexes down the c axis (Fig. 6).

Multiple chains of the complex are stacked side-by-side (Fig. 7), with the arene groups of the NPA ligands of adjacent complexes in close proximity to one another. Perpendicular π stacking is observed between the centroid defined by atoms C8–C13 and atom C31, with a distance of 3.619 Å and an angle of 83.4° (Fig. 7). π stacking is the primary contact connecting adjacent chains of molecules along the a and b axes, while hydrogen bonding is the primary contact along the c axis.
Hirshfeld surface and fingerprint plots were calculated using the CrystalExplorer program to further quantify the intermolecular contacts present in the 3D supramolecular architecture of the complex (Spackman & Jayatilaka, 2009; Spackman & McKinnon, 2002). Significant intermolecular interactions are mapped (Fig. 8) that indicate the percentage contributions of the intermolecular contacts to the Hirshfeld surface. Significant contacts include 63.4% H···H, 25.4% H···C/C···H, 7.6% H···O/O···H, and 0.9% H···N/N···H. The largest contribution of 63.4% for H···H interactions has a high concentration at d_e = d_i = 1.02 Å, as indicated by the red regions [Fig. 8(a)]. Two sharp spikes at d_e + d_i = 1.71 Å were observed for H···O/O···H interactions and indicate strong hydrogen bonding [Fig. 8(b)]. For H···C/C···H contacts, two spikes appear at d_e + d_i = 2.25 Å, while the H···N/N···H contacts have d_e + d_i = 2.8 Å.

The newly determined structure of (NPA)_6Zn_3(H_2O)_2 was used in a molecular docking study with the main protease (Mpro) of SARS-COV-2 using AutoDock (Version 4.2) and CB-Dock to probe the potential utility of (NPA)_6Zn_3(H_2O)_2 as an antiviral agent for SARS-CoV-2. The structure of Mpro (PDB ID: 6lu7) was reported previously with a bound N3 Michael addition inhibitor (Jin et al., 2020) [Fig. 9(b)]. The N3 inhibitor, water molecules, and cocrystallized ligands were removed for docking studies with (NPA)_6Zn_3(H_2O)_2. Our docking results found the most stable confirmation with a docking score of −8.4 kcal mol⁻¹ using AutoDock and −8.2 kcal mol⁻¹ using CB-Dock. This suggests that (NPA)_6Zn_3(H_2O)_2 could be a strong inhibitor for Mpro because the docking scores are on the same order of magnitude as those reported for Remdesivir at −8.2 kcal mol⁻¹ and Baloxavir marboxil at −7.4 kcal mol⁻¹ (Naik et al., 2020). The main difference between the docking of (NPA)_6Zn_3(H_2O)_2 and Remdesivir is that a different binding location was found for (NPA)_6Zn_3(H_2O)_2 [Fig. 9(b)]. When using CB-Dock, we identified that (NPA)_6Zn_3(H_2O)_2 could also bind in the standard binding pocket with a docking score of −6.0 kcal mol⁻¹ [Fig. 9(c)]. While this is not as favorable a docking score as that of Remdesivir, it is on the same order of magnitude as scores reported for Oseltamivir at −6.1 kcal mol⁻¹ and Chloroquine at −5.7 kcal mol⁻¹ (Naik et al., 2020). Combined, these results suggest that (NPA)_6Zn_3(H_2O)_2 has potential for inhibiting Mpro of SARS-CoV-2.

Fig. 9 shows the 3D interaction between (NPA)_6Zn_3(H_2O)_2 and Mpro, which demonstrates that (NPA)_6Zn_3(H_2O)_2 targets a different area of the protein from N3. The strongest binding mode computed at −8.4 kcal mol⁻¹ of (NPA)_6Zn_3(H_2O)_2 included one hydrogen-bond contact between the (NPA)_6Zn_3(H_2O)_2 carboxylate O atom (such as O1) with amino acid residue Gln110 at a distance of 2.72 Å (Fig. 10). However, most of the stabilizing contacts result from π interactions with the benzyl groups (such as C8–C13) in (NPA)_6Zn_3(H_2O)_2. Benzyl π···anion contacts were detected with Asp153 at distances of 3.50 and 4.14 Å. Perpendicular π···π stacking was observed with Phe294 at distances of 5.33, 5.37, and 5.01 Å. Benzyl π···alkyl bond contacts were detected with Pro252 at 5.40 Å, Ile249 at 5.18 Å and 5.04 Å, and Val202 at 5.37 Å. Combined, the docking studies support that (NPA)_6Zn_3-

Figure 9
Cartoon representation of Mpro with (a) the reported N3 inhibitor, (b) (NPA)_6Zn_3(H_2O)_2 at the standard pocket site and (c) (NPA)_6Zn_3(H_2O)_2 at the new binding site.
(H₂O)₂ could bind to M<sup>pro</sup> at a different binding site than the most widely studied pocket site in M<sup>pro</sup> where N3 and Remdesivir are known to bind.

4. Conclusion
The trinuclear zinc complex (NPA)<sub>6</sub>Zn₃(H₂O)₂ was synthesized and characterized crystallographically. The crystal structure is symmetric about the central Zn<sup>II</sup> atom (Zn2), which has approximate octahedral geometry, flanked by outer Zn<sup>II</sup> atoms (Zn2 and Zn2') with highly contorted trigonal bipyramidal molecular geometries. The macromolecular stabilization is facilitated by intramolecular hydrogen bonding within the NPA ligand, hydrogen bonding between H₂O and carboxylate O atoms of adjacent molecules, and perpendicular π stacking between adjacent molecules. Hydrogen bonding is only observed along the crystallographic a axis, while π stacking is only observed along the b and c axes. Most notably, the supramolecular stabilization results in a perfect alignment of (NPA)<sub>6</sub>Zn₃(H₂O)₂ molecules along the a axis, such that only one molecule is seen when looking down this axis. Molecular docking studies of (NPA)<sub>6</sub>Zn₃(H₂O)₂ with the M<sup>pro</sup> portion of SARS-COV-2 suggest that (NPA)<sub>6</sub>Zn₃(H₂O)₂ could bind to M<sup>pro</sup> with a similar docking score as Remdesivir, but at a different binding site than the typically targeted pocket site where Remdesivir binds. (NPA)<sub>6</sub>Zn₃(H₂O)₂ also binds to the same pocket as Remdesivir, with a slightly less favorable docking score, but on the same order of magnitude as other M<sup>pro</sup> inhibitors. This suggests that trinuclear Zn complexes should be further explored for antiviral activity for SARS-CoV-2.

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Synthesis, structural analysis, and docking studies with SARS-CoV-2 of a trinuclear zinc complex with N-phenylantranilic acid ligands

Armel L. Mbani O., Evan F. Bonnand, Awawou G. Paboudam, Jacob P. Brannon, Kevyn D. Gardner-Ricossa, S. Chantal E. Stieber and Moise O. Agwara

Computing details
Data collection: APEX3 (Bruker, 2017); cell refinement: SAINT (Bruker, 2017); data reduction: SAINT (Bruker, 2017); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2017 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Hexakis(μ₂-2-anilinobenzoato)diaquatrizinc(II)

Crystal data

\[\text{[Zn}_3\text{(C}_13\text{H}_10\text{NO}_2)_6\text{(H}_2\text{O})_2]\]

\(M_r = 1505.46\)

Triclinic, \(P\bar{1}\)

\(a = 11.0968\ (5) \, \text{Å}\)

\(b = 12.8319\ (6) \, \text{Å}\)

\(c = 13.3134\ (6) \, \text{Å}\)

\(α = 111.703\ (2)°\)

\(β = 108.028\ (2)°\)

\(γ = 93.125\ (2)°\)

\(V = 1643.97\ (13) \, \text{Å}^3\)

\(Z = 1\)

\(F(000) = 776\)

\(D_x = 1.521\ \text{Mg} \, \text{m}^{-3}\)

Mo Ka radiation, \(λ = 0.71073\ \text{Å}\)

Cell parameters from 9800 reflections

\(\theta = 2.5–38.9°\)

\(µ = 1.16\ \text{mm}^{-1}\)

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

Prism, clear colourless

\(0.3 \times 0.1 \times 0.03\ \text{mm}\)

Data collection

Bruker Kappa Venture D8 diffractometer

Radiation source: microfocus sealed X-ray tube, Incoatec μs

Mirror optics monochromator

Detector resolution: 7.9 pixels mm⁻¹

\(ω\) and \(φ\) scans

Absorption correction: multi-scan (SADABS; Bruker, 2017)

\(T_{\text{min}} = 0.664, T_{\text{max}} = 0.748\)

86106 measured reflections

10025 independent reflections

8556 reflections with \(I > 2σ(I)\)

\(R_{\text{int}} = 0.044\)

\(θ_{\text{max}} = 30.5°, θ_{\text{min}} = 2.9°\)

\(h = -15→15\)

\(k = -18→18\)

\(l = -19→19\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2σ(F^2)] = 0.030\)

\(wR(F^2) = 0.078\)

\(S = 1.03\)

477 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

Acta Cryst. (2022). C78, 231-239 [https://doi.org/10.1107/S205322962200239X]
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 1.352P]$  
where $P = (F_o^2 + 2F_c^2)/3$  
$(\Delta/\sigma)_{\text{max}} = 0.001$

**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.** (NPA)$_6$Zn$_3$(H$_2$O)$_2$ was mounted on a Bruker Kappa Venture D8 instrument on a Kapton sample holder that was then placed in a liquid nitrogen stream to cool the sample down to 100 K. The sample was run with a molybdenum micro source (Mo Ka, $\lambda = 0.71073$ Å) using a Photon II detector. The unit cell of was determined prior to full data collection, and data were integrated using the Bruker SAINT program using SADABS for absorption correction. Structural refinement was conducted using APEX3 and OLEX2 software that interfaced with the SHELXL PC Suite (Dolomanov et al., 2009; Sheldrick, 2015). All non-H atoms were refined using anisotropic thermal parameters.

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

|   | x       | y       | z       | $U_{iso}$/$U_{eq}$ |
|---|---------|---------|---------|-------------------|
| Zn1 | 0.21623 (2) | 0.57673 (2) | 0.53262 (2) | 0.01224 (4) |
| Zn2 | 0.5000000 | 0.5000000 | 0.5000000 | 0.01101 (5) |
| O3  | 0.18796 (10) | 0.46312 (9)  | 0.59622 (9)  | 0.01493 (19) |
| O5  | 0.33767 (10) | 0.71566 (9)  | 0.63184 (9)  | 0.0163 (2)   |
| O6  | 0.50591 (10) | 0.67473 (9)  | 0.57499 (9)  | 0.0156 (2)   |
| O4  | 0.38584 (10) | 0.46623 (9)  | 0.59513 (10) | 0.0169 (2)   |
| O7  | 0.05686 (11) | 0.64469 (11) | 0.54001 (12) | 0.0257 (3)   |
| O2  | 0.34886 (11) | 0.47459 (10) | 0.35584 (9)  | 0.0199 (2)   |
| O1  | 0.15384 (11) | 0.48147 (10) | 0.36899 (9)  | 0.0207 (2)   |
| N2  | 0.52659 (12) | 0.32556 (11) | 0.66916 (12) | 0.0165 (2)   |
| N3  | 0.70966 (13) | 0.84458 (12) | 0.65803 (12) | 0.0209 (3)   |
| N1  | −0.05046 (13) | 0.40036 (14) | 0.17526 (12) | 0.0248 (3)   |
| C29 | 0.47282 (14) | 0.91895 (12) | 0.80522 (13) | 0.0152 (3)   |
| H29 | 0.392254  | 0.886185  | 0.802241  | 0.018*       |
| C28 | 0.52736 (13) | 0.85540 (11) | 0.72560 (12) | 0.0128 (2)   |
| C16 | 0.41632 (13) | 0.28630 (12) | 0.68010 (12) | 0.0137 (2)   |
| C33 | 0.64919 (14) | 0.90238 (12) | 0.73231 (12) | 0.0154 (3)   |
| C2  | 0.16772 (14) | 0.37100 (13) | 0.18719 (12) | 0.0165 (3)   |
| C26 | 0.75406 (14) | 0.31903 (13) | 0.72482 (13) | 0.0169 (3)   |
| H26 | 0.771698  | 0.394102  | 0.783266  | 0.020*       |
| C3  | 0.03344 (14) | 0.35001 (13) | 0.12401 (12) | 0.0169 (3)   |
| C21 | 0.62687 (14) | 0.26427 (13) | 0.65586 (13) | 0.0153 (3)   |
| C30 | 0.53243 (15) | 1.02765 (12) | 0.88784 (13) | 0.0175 (3)   |
| H30 | 0.494528  | 1.068533  | 0.941905  | 0.021*       |
| C32 | 0.70667 (15) | 1.01528 (13) | 0.81453 (14) | 0.0203 (3)   |
| H32 | 0.786401  | 1.049860  | 0.817622  | 0.024*       |
| C7  | 0.24937 (16) | 0.31571 (15) | 0.13244 (14) | 0.0225 (3)   |
| H7  | 0.339316  | 0.331356  | 0.175194  | 0.027*       |
| C17 | 0.41055 (15) | 0.19384 (13) | 0.71268 (14) | 0.0183 (3)   |
| H17 | 0.481000  | 0.154891  | 0.720440  | 0.022*       |
| Atom | x     | y     | z     | Ueq  |
|------|-------|-------|-------|------|
| C22  | 0.60164 (15) | 0.15393 (14) | 0.57133 (14) | 0.0201 (3) |
| H22  | 0.515144    | 0.116452    | 0.523614    | 0.024*    |
| C19  | 0.19940 (15) | 0.21460 (15) | 0.72331 (15) | 0.0228 (3) |
| H19  | 0.127418    | 0.191002    | 0.739352    | 0.027*    |
| C18  | 0.30479 (16) | 0.15924 (15) | 0.73335 (15) | 0.0218 (3) |
| H18  | 0.303180    | 0.096516    | 0.754887    | 0.026*    |
| C20  | 0.20171 (14) | 0.30396 (14) | 0.68974 (13) | 0.0182 (3) |
| H20  | 0.130606    | 0.342222    | 0.683176    | 0.022*    |
| C15  | 0.30715 (13) | 0.33982 (12) | 0.66494 (12) | 0.0138 (2) |
| C25  | 0.85502 (15) | 0.26398 (14) | 0.70820 (15) | 0.0215 (3) |
| H25  | 0.941724    | 0.302140    | 0.754172    | 0.026*    |
| C34  | 0.84477 (15) | 0.86983 (13) | 0.68544 (15) | 0.0193 (3) |
| C14  | 0.29532 (13) | 0.42742 (12) | 0.61725 (12) | 0.0129 (2) |
| C31  | 0.64947 (15) | 1.07621 (13) | 0.89027 (14) | 0.0201 (3) |
| H31  | 0.690087    | 1.151989    | 0.944656    | 0.024*    |
| C4   | −0.01196 (15) | 0.27355 (14) | 0.00644 (13) | 0.0195 (3) |
| H4   | −0.101030   | 0.259682    | −0.038487   | 0.023*    |
| C27  | 0.45353 (13) | 0.74034 (12) | 0.63763 (12) | 0.0129 (2) |
| C24  | 0.82974 (16) | 0.15365 (15) | 0.62484 (16) | 0.0247 (3) |
| H24  | 0.898868    | 0.115683    | 0.614252    | 0.030*    |
| C1   | 0.22793 (14) | 0.44702 (12) | 0.31205 (12) | 0.0161 (3) |
| C23  | 0.70285 (17) | 0.09865 (15) | 0.55673 (16) | 0.0248 (3) |
| H23  | 0.685355    | 0.022754    | 0.499856    | 0.030*    |
| C5   | 0.07081 (16) | 0.21858 (15) | −0.04435 (13) | 0.0224 (3) |
| H5   | 0.037349    | 0.165888    | −0.123144   | 0.027*    |
| C35  | 0.93108 (17) | 0.88179 (14) | 0.79226 (17) | 0.0273 (4) |
| H35  | 0.899654    | 0.873909    | 0.848340    | 0.033*    |
| C9   | −0.27061 (16) | 0.33864 (14) | 0.15414 (14) | 0.0224 (3) |
| H9   | −0.238626   | 0.311924    | 0.213239    | 0.027*    |
| C8   | −0.18516 (15) | 0.38650 (14) | 0.11840 (13) | 0.0207 (3) |
| C6   | 0.20304 (17) | 0.23893 (16) | 0.01791 (15) | 0.0268 (3) |
| H6   | 0.259623    | 0.200922    | −0.017628   | 0.032*    |
| C10  | −0.40284 (17) | 0.32986 (15) | 0.10340 (16) | 0.0274 (4) |
| H10  | −0.460956   | 0.299287    | 0.129504    | 0.033*    |
| C39  | 0.89097 (18) | 0.88128 (14) | 0.60371 (17) | 0.0258 (3) |
| H39  | 0.832464    | 0.873032    | 0.530741    | 0.031*    |
| C13  | −0.23263 (17) | 0.42410 (16) | 0.03090 (15) | 0.0265 (3) |
| H13  | −0.174607   | 0.457781    | 0.006907    | 0.032*    |
| C11  | −0.44982 (17) | 0.36558 (17) | 0.01499 (16) | 0.0312 (4) |
| H11  | −0.540240   | 0.358033    | −0.020802   | 0.037*    |
| C12  | −0.36467 (18) | 0.41245 (18) | −0.02135 (16) | 0.0309 (4) |
| H12  | −0.396992   | 0.436662    | −0.082321   | 0.037*    |
| C36  | 1.06257 (19) | 0.90516 (17) | 0.8164 (2)  | 0.0407 (5) |
| H36  | 1.121435    | 0.913366    | 0.889251    | 0.049*    |
| C38  | 1.0236 (2)  | 0.90494 (16) | 0.6292 (2)  | 0.0392 (5) |
| H38  | 1.055534    | 0.913039    | 0.573478    | 0.047*    |
| C37  | 1.10874 (19) | 0.91665 (17) | 0.7347 (3)  | 0.0463 (6) |
| H37  | 1.199117    | 0.932597    | 0.751558    | 0.056*    |
Atomic displacement parameters (Å²)

|   | U¹¹  | U¹²  | U¹³  | U¹²  | U¹³  | U¹³  |
|---|------|------|------|------|------|------|
| Zn1 | 0.00879 (7) | 0.01233 (8) | 0.01258 (8) | −0.00010 (5) | 0.00274 (6) | 0.00297 (6) |
| Zn2 | 0.00780 (10) | 0.01103 (10) | 0.01193 (10) | 0.00122 (7) | 0.00275 (8) | 0.00293 (8) |
| O3  | 0.0111 (4) | 0.0154 (5) | 0.0185 (5) | 0.0039 (4) | 0.0047 (4) | 0.0077 (4) |
| O5  | 0.0103 (4) | 0.0150 (5) | 0.0184 (5) | −0.0016 (4) | 0.0047 (4) | 0.0020 (4) |
| O6  | 0.0153 (5) | 0.0124 (4) | 0.0168 (5) | −0.0005 (4) | 0.0075 (4) | 0.0025 (4) |
| O4  | 0.0158 (5) | 0.0182 (5) | 0.0230 (5) | 0.0051 (4) | 0.0110 (4) | 0.0115 (4) |
| O7  | 0.0115 (5) | 0.0166 (5) | 0.0392 (7) | 0.0030 (4) | 0.0039 (5) | 0.0049 (5) |
| O2  | 0.0152 (5) | 0.0220 (5) | 0.0175 (5) | −0.0016 (4) | −0.0004 (4) | 0.0084 (4) |
| O1  | 0.0172 (5) | 0.0243 (6) | 0.0132 (5) | −0.0028 (4) | 0.0022 (4) | 0.0032 (4) |
| N2  | 0.0115 (5) | 0.0190 (6) | 0.0252 (6) | 0.0053 (5) | 0.0086 (5) | 0.0135 (5) |
| N3  | 0.0144 (6) | 0.0165 (6) | 0.0230 (6) | −0.0039 (5) | 0.0095 (5) | −0.0027 (5) |
| N1  | 0.0155 (6) | 0.0360 (8) | 0.0114 (6) | 0.0019 (6) | 0.0021 (5) | 0.0001 (6) |
| C29 | 0.0127 (6) | 0.0144 (6) | 0.0173 (6) | 0.0016 (5) | 0.0061 (5) | 0.0047 (5) |
| C28 | 0.0108 (6) | 0.0115 (6) | 0.0136 (6) | 0.0007 (5) | 0.0027 (5) | 0.0039 (5) |
| C16 | 0.0107 (6) | 0.0174 (6) | 0.0140 (6) | 0.0024 (5) | 0.0044 (5) | 0.0076 (5) |
| C33 | 0.0118 (6) | 0.0147 (6) | 0.0162 (6) | −0.0003 (5) | 0.0048 (5) | 0.0029 (5) |
| C2  | 0.0149 (6) | 0.0177 (6) | 0.0136 (6) | −0.0009 (5) | 0.0028 (5) | 0.0054 (5) |
| C26 | 0.0138 (6) | 0.0192 (7) | 0.0198 (7) | 0.0035 (5) | 0.0055 (5) | 0.0107 (6) |
| C3  | 0.0145 (6) | 0.0192 (7) | 0.0137 (6) | −0.0004 (5) | 0.0036 (5) | 0.0049 (5) |
| C21 | 0.0120 (6) | 0.0200 (7) | 0.0202 (7) | 0.0062 (5) | 0.0078 (5) | 0.0126 (6) |
| C30 | 0.0179 (7) | 0.0146 (6) | 0.0170 (6) | 0.0030 (5) | 0.0069 (5) | 0.0025 (5) |
| C32 | 0.0150 (7) | 0.0159 (7) | 0.0227 (7) | −0.0037 (5) | 0.0065 (6) | 0.0012 (6) |
| C7  | 0.0152 (7) | 0.0283 (8) | 0.0194 (7) | 0.0011 (6) | 0.0036 (6) | 0.0074 (6) |
| C17 | 0.0150 (6) | 0.0216 (7) | 0.0225 (7) | 0.0048 (5) | 0.0064 (5) | 0.0137 (6) |
| C22 | 0.0141 (6) | 0.0226 (7) | 0.0221 (7) | 0.0035 (6) | 0.0045 (6) | 0.0092 (6) |
| C19 | 0.0158 (7) | 0.0331 (9) | 0.0286 (8) | 0.0032 (6) | 0.0106 (6) | 0.0203 (7) |
| C18 | 0.0192 (7) | 0.0263 (8) | 0.0273 (8) | 0.0036 (6) | 0.0082 (6) | 0.0190 (7) |
| C20 | 0.0135 (6) | 0.0250 (7) | 0.0213 (7) | 0.0047 (5) | 0.0083 (5) | 0.0132 (6) |
| C15 | 0.0117 (6) | 0.0161 (6) | 0.0151 (6) | 0.0023 (5) | 0.0055 (5) | 0.0074 (5) |
| C25 | 0.0120 (6) | 0.0263 (8) | 0.0285 (8) | 0.0047 (6) | 0.0057 (6) | 0.0148 (7) |
| C34 | 0.0147 (7) | 0.0127 (6) | 0.0292 (8) | 0.0004 (5) | 0.0109 (6) | 0.0048 (6) |
| C14 | 0.0115 (6) | 0.0139 (6) | 0.0118 (6) | 0.0025 (5) | 0.0044 (5) | 0.0035 (5) |
| C31 | 0.0190 (7) | 0.0144 (6) | 0.0192 (7) | −0.0009 (5) | 0.0047 (6) | 0.0008 (5) |
| C4  | 0.0152 (7) | 0.0232 (7) | 0.0136 (6) | −0.0021 (6) | 0.0028 (5) | 0.0033 (6) |
| C27 | 0.0112 (6) | 0.0130 (6) | 0.0128 (6) | 0.0006 (5) | 0.0029 (5) | 0.0048 (5) |
| C24 | 0.0183 (7) | 0.0272 (8) | 0.0349 (9) | 0.0108 (6) | 0.0135 (7) | 0.0151 (7) |
| C1  | 0.0168 (7) | 0.0149 (6) | 0.0145 (6) | −0.0004 (5) | 0.0021 (5) | 0.0069 (5) |
| C23 | 0.0225 (8) | 0.0220 (7) | 0.0297 (8) | 0.0072 (6) | 0.0112 (7) | 0.0084 (7) |
| C5  | 0.0206 (7) | 0.0264 (8) | 0.0135 (6) | −0.0002 (6) | 0.0048 (6) | 0.0025 (6) |
C35  0.0219 (8)  0.0187 (7)  0.0367 (9)  0.0010 (6)  0.0053 (7)  0.0110 (7)  
C9   0.0220 (7)  0.0215 (7)  0.0176 (7)  0.0034 (6)  0.0087 (6)  0.0003 (6)  
C8   0.0146 (7)  0.0243 (7)  0.0136 (6)  0.0016 (6)  0.0038 (5)  −0.0011 (6)  
C6   0.0212 (8)  0.0337 (9)  0.0211 (8)  0.0064 (7)  0.0088 (6)  0.0052 (7)  
C10  0.0193 (8)  0.0256 (8)  0.0283 (8)  0.0018 (6)  0.0116 (7)  −0.0009 (7)  
C39  0.0270 (8)  0.0187 (7)  0.0393 (10) 0.0077 (6)  0.0219 (8)  0.0112 (7)  
C13  0.0227 (8)  0.0318 (9)  0.0191 (7)  0.0023 (7)  0.0061 (6)  0.0056 (7)  
C11  0.0163 (7)  0.0332 (9)  0.0279 (9)  0.0066 (7)  0.0037 (6)  −0.0018 (7)  
C12  0.0258 (9)  0.0375 (10) 0.0207 (8)  0.0102 (7)  0.0028 (7)  0.0065 (7)  
C36  0.0194 (8)  0.0237 (9)  0.0672 (15) 0.0031 (7) −0.0011 (9)  0.0195 (9)  
C38  0.0336 (10) 0.0251 (9)  0.0799 (16) 0.0133 (8)  0.0415 (11)  0.0253 (10) 
C37  0.0161 (8)  0.0241 (9)  0.105 (2)  0.0072 (7)  0.0233 (11)  0.0304 (11) 

**Geometric parameters (Å, °)**

| Bond                  | Distance (Å) | Angle (°)  |
|-----------------------|--------------|------------|
| Zn1—O3                | 1.9920 (10)  | C7—H7      | 0.9500 |
| Zn1—O5                | 1.9063 (10)  | C7—C6      | 1.381 (2) |
| Zn1—O7                | 2.0274 (12)  | C17—H17    | 0.9500 |
| Zn1—O1                | 1.9298 (11)  | C17—C18    | 1.372 (2) |
| Zn2—O6i               | 2.0775 (10)  | C22—H22    | 0.9500 |
| Zn2—O6                | 2.0775 (10)  | C22—C23    | 1.386 (2) |
| Zn2—O4i               | 2.1762 (10)  | C19—H19    | 0.9500 |
| Zn2—O4                | 2.1762 (10)  | C19—C18    | 1.398 (2) |
| Zn2—O2                | 2.0219 (11)  | C19—C20    | 1.378 (2) |
| Zn2—O2i               | 2.0219 (11)  | C18—H18    | 0.9500 |
| O3—C14                | 1.2866 (17)  | C20—H20    | 0.9500 |
| O5—C27                | 1.2788 (17)  | C20—C15    | 1.4080 (19) |
| O6—C27                | 1.2555 (17)  | C15—C14    | 1.4752 (19) |
| O4—C14                | 1.2572 (17)  | C25—H25    | 0.9500 |
| O7—H7A                | 0.90 (3)     | C25—C24    | 1.384 (2) |
| O7—H7B                | 0.84 (3)     | C34—C35    | 1.394 (3) |
| O2—C1                 | 1.2559 (18)  | C34—C39    | 1.387 (2) |
| O1—C1                 | 1.2742 (19)  | C31—H31    | 0.9500 |
| N2—C16                | 1.3674 (18)  | C4—H4      | 0.9500 |
| N2—C21                | 1.4151 (18)  | C4—C5      | 1.379 (2) |
| N2—H2                 | 0.81 (2)     | C24—H24    | 0.9500 |
| N3—C3                 | 1.3787 (19)  | C24—C23    | 1.390 (2) |
| N3—C34                | 1.4166 (19)  | C23—H23    | 0.9500 |
| N3—H3                 | 0.80 (2)     | C5—H5      | 0.9500 |
| N1—C3                 | 1.372 (2)    | C5—C6      | 1.398 (2) |
| N1—C8                 | 1.418 (2)    | C35—H35    | 0.9500 |
| N1—H1                 | 0.83 (2)     | C35—C36    | 1.383 (3) |
| C29—H29               | 0.9500       | C9—H9      | 0.9500 |
| C29—C28               | 1.4024 (19)  | C9—C8      | 1.391 (2) |
| C29—C30               | 1.381 (2)    | C9—C10     | 1.391 (2) |
| C28—C33               | 1.4126 (19)  | C8—C13     | 1.389 (2) |
| C28—C27               | 1.4893 (19)  | C6—H6      | 0.9500 |
| C16—C17               | 1.410 (2)    | C10—H10    | 0.9500 |
| Bond                     | Length (Å)   | Bond                     | Length (Å)   |
|-------------------------|--------------|-------------------------|--------------|
| C16—C15                 | 1.4220 (19)  | C10—C11                 | 1.383 (3)    |
| C33—C32                 | 1.414 (2)    | C39—H39                 | 0.9500       |
| C2—C3                   | 1.419 (2)    | C39—C38                 | 1.393 (3)    |
| C2—C7                   | 1.397 (2)    | C13—H13                 | 0.9500       |
| C2—C1                   | 1.484 (2)    | C13—C12                 | 1.386 (2)    |
| C26—H26                 | 0.9500       | C11—H11                 | 0.9500       |
| C26—Z21                 | 1.393 (2)    | C11—C12                 | 1.387 (3)    |
| C26—C25                 | 1.388 (2)    | C12—H12                 | 0.9500       |
| C3—C4                   | 1.410 (2)    | C36—H36                 | 0.9500       |
| C3—C4                   | 1.410 (2)    | C36—C37                 | 1.387 (4)    |
| C39—C38                 | 1.393 (2)    | C38—H38                 | 0.9500       |
| C39—C38                 | 1.393 (2)    | C38—C37                 | 1.377 (4)    |
| C32—H32                 | 0.9500       | C37—H37                 | 0.9500       |
| C32—C31                 | 1.378 (2)    |                          |              |

| Bond                     | Length (Å)   | Bond                     | Length (Å)   |
|-------------------------|--------------|-------------------------|--------------|
| O3—Zn1—O7               | 97.20 (5)    | C18—C19—H19             | 120.6        |
| O5—Zn1—O3               | 118.92 (5)   | C20—C19—H19             | 120.6        |
| O5—Zn1—O7               | 95.94 (5)    | C20—C19—C18             | 118.87 (14)  |
| O5—Zn1—O1               | 135.15 (5)   | C17—C18—C19             | 121.21 (14)  |
| O1—Zn1—O3               | 101.15 (5)   | C17—C18—H18             | 119.4        |
| O1—Zn1—O7               | 98.30 (5)    | C19—C18—H18             | 119.4        |
| O6—Zn2—O6               | 180.0        | C19—C20—H20             | 119.3        |
| O6—Zn2—O4               | 87.99 (4)    | C19—C20—C15             | 121.44 (14)  |
| O6—Zn2—O4               | 92.00 (4)    | C15—C20—H20             | 119.3        |
| O6—Zn2—O4               | 88.00 (4)    | C15—C20—C15             | 122.83 (12)  |
| O6—Zn2—O4               | 92.00 (4)    | C20—C15—C16             | 119.33 (13)  |
| O4—Zn2—O4               | 180.00 (4)   | C20—C15—C14             | 117.73 (13)  |
| O2—Zn2—O6               | 93.86 (4)    | C26—C25—H25             | 119.9        |
| O2—Zn2—O6               | 86.14 (4)    | C24—C25—C26             | 120.20 (15)  |
| O2—Zn2—O6               | 86.14 (4)    | C24—C25—H25             | 119.9        |
| O2—Zn2—O6               | 93.85 (4)    | C35—C34—N3              | 120.97 (15)  |
| O2—Zn2—O4               | 96.22 (4)    | C39—C34—N3              | 119.10 (16)  |
| O2—Zn2—O4               | 83.78 (4)    | C39—C34—C35             | 119.92 (16)  |
| O2—Zn2—O4               | 96.22 (4)    | O3—C14—C15              | 118.44 (12)  |
| O2—Zn2—O4               | 83.78 (4)    | O4—C14—O3               | 119.60 (13)  |
| O2—Zn2—O2               | 180.0        | O4—C14—C15              | 121.96 (12)  |
| O14—O3—Zn1              | 104.17 (9)   | C30—C31—H31             | 119.7        |
| C27—O5—Zn1              | 127.60 (9)   | C32—C31—C30             | 120.62 (14)  |
| C27—O6—Zn2              | 137.10 (9)   | C32—C31—H31             | 119.7        |
| C14—O4—Zn2              | 161.37 (10)  | C3—C4—H4                | 119.5        |
| Zn1—O7—H7A              | 129.0 (18)   | C5—C4—C3                | 121.07 (14)  |
| Zn1—O7—H7B              | 123.9 (19)   | C5—C4—H4                | 119.5        |
| H7A—O7—H7B              | 106 (3)      | O5—C27—C28              | 115.79 (12)  |
| C1—O2—Zn2               | 142.24 (10)  | O6—C27—O5               | 124.31 (13)  |
| C1—O1—Zn1               | 123.40 (10)  | O6—C27—C28              | 119.89 (12)  |
| C16—N2—C21              | 125.40 (13)  | C25—C24—H24             | 120.1        |
| C16—N2—H2               | 118.8 (16)   | C25—C24—C23             | 119.74 (15)  |
| C21—N2—H2               | 115.4 (16)   | C23—C24—H24             | 120.1        |
| Bond                  | Angle (°) (ESD) | Bond                  | Angle (°) (ESD) |
|----------------------|----------------|----------------------|----------------|
| C33—N3—C34          | 122.70 (13)    | O2—C1—O1            | 123.47 (14)    |
| C33—N3—H3           | 114.7 (15)     | O2—C1—C2            | 118.44 (14)    |
| C34—N3—H3           | 118.4 (15)     | O1—C1—C2            | 118.09 (13)    |
| C3—N1—C8            | 125.41 (13)    | C22—C23—C24         | 120.36 (16)    |
| C3—N1—H1            | 118.4 (16)     | C22—C23—H23         | 119.8          |
| C8—N1—H1            | 115.7 (16)     | C24—C23—H23         | 119.8          |
| C28—C29—H29         | 118.9          | C4—C5—H5            | 119.4          |
| C30—C29—H29         | 118.9          | C4—C5—C6            | 121.24 (15)    |
| C30—C29—C28         | 122.13 (13)    | C6—C5—H5            | 119.4          |
| C29—C28—C33         | 119.06 (13)    | C34—C35—H35         | 120.1          |
| C29—C28—C27         | 118.00 (12)    | C36—C35—C34         | 119.87 (19)    |
| C33—C28—C27         | 122.94 (12)    | C36—C35—H35         | 120.1          |
| N2—C16—C17          | 120.21 (13)    |                      |                |
| N2—C16—C15          | 121.75 (13)    | C10—C9—H9           | 120.0          |
| N3—C16—C15          | 117.98 (13)    | C10—C9—C8           | 120.04 (17)    |
| N3—C33—C28          | 122.43 (13)    | C9—C8—N1            | 119.28 (15)    |
| N3—C33—C32          | 119.45 (13)    | C13—C8—N1           | 120.97 (15)    |
| C28—C33—C32         | 118.03 (13)    | C13—C8—C9           | 119.70 (15)    |
| C3—C2—C1            | 123.36 (14)    | C7—C6—C5            | 118.31 (15)    |
| C7—C2—C3            | 119.75 (14)    | C7—C6—H6            | 120.8          |
| C7—C2—C1            | 116.86 (13)    | C5—C6—H6            | 120.8          |
| C21—C26—H26         | 120.0          | C9—C10—H10          | 120.0          |
| C25—C26—H26         | 120.0          | C11—C10—C9          | 120.07 (17)    |
| N1—C3—C2            | 121.58 (13)    | C11—C10—H10         | 120.0          |
| N1—C3—C4            | 120.70 (14)    | C34—C39—H39         | 120.2          |
| C4—C3—C2            | 117.71 (14)    | C34—C39—C38         | 119.63 (19)    |
| C26—C21—N2           | 119.87 (14)   | C38—C39—H39         | 120.2          |
| C22—C21—N2           | 118.72 (14)   | C8—C13—H13          | 120.0          |
| C22—C21—C26          | 121.48 (13)   | C12—C13—C8          | 119.98 (17)    |
| C29—C30—H30         | 121.58 (13)   | C12—C13—H13         | 120.0          |
| C29—C30—C31          | 118.65 (14)   | C10—C11—H11         | 120.1          |
| C31—C30—H30         | 120.7         | C12—C11—C12         | 119.88 (16)    |
| C33—C32—H32          | 119.3         | C12—C11—H11         | 120.1          |
| C31—C32—C33          | 121.37 (14)   | C13—C12—C11         | 120.29 (18)    |
| C31—C32—H32          | 119.3         | C13—C12—H12         | 119.9          |
| C2—C7—H7            | 119.1         | C11—C12—H12         | 119.9          |
| C6—C7—C2            | 121.88 (15)   | C35—C36—H36         | 119.9          |
| C6—C7—H7            | 119.1         | C37—C36—H36         | 119.9          |
| C16—C17—H17          | 119.5         | C39—C38—H38         | 119.8          |
| C18—C17—C16          | 121.07 (14)   | C37—C38—C39         | 120.4 (2)      |
| C18—C17—H17          | 119.5         | C37—C38—H38         | 119.8          |
| C21—C22—H22          | 120.0         | C36—C37—H37         | 120.0          |
| C23—C22—C21          | 119.94 (15)   | C38—C37—C36         | 120.01 (18)    |
| C23—C22—H22          | 120.0         | C38—C37—H37         | 120.0          |
| Zn1—O3—C14—O4        | -0.51 (15)    | C3—C4—C5—C6         | -1.7 (3)       |
| Zn1—O3—C14—C15      | -179.36 (10)  | C21—N2—C16—C17      | 18.7 (2)       |

*Acta Cryst.* (2022). C78, 231-239
| Bond/Angle | Zn1—O5—C27—O6 | 1.2 (2) | C21—N2—C16—C15 | −164.39 (14) |
|-----------|----------------|---------|-----------------|------------|
|           | Zn1—O5—C27—C28 | −178.84 (9) | C21—C26—C25—C24 | −1.4 (2) |
|           | Zn1—O1—C1—O2  | −2.4 (2) | C21—C22—C23—C24 | −1.1 (3) |
|           | Zn1—O1—C1—C2  | 178.08 (10) | C30—C29—C28—C33 | 2.1 (2) |
|           | Zn2—O6—C27—O5  | −34.5 (2) | C30—C29—C28—C27 | −178.18 (14) |
|           | Zn2—O6—C27—C28 | 145.52 (11) | C7—C2—C3—N1 | 178.35 (16) |
|           | Zn2—O4—C14—O3  | −71.0 (3) | C7—C2—C3—C4 | −0.5 (2) |
|           | Zn2—O4—C14—C15 | 107.8 (3) | C7—C2—C1—O2 | 13.3 (2) |
|           | Zn2—O2—C1—O1  | 40.1 (3) | C7—C2—C1—O1 | −167.15 (14) |
|           | Zn2—O2—C1—C2  | −140.43 (14) | C17—C16—C15—C20 | 4.0 (2) |
|           | N2—C16—C17—C18 | 174.60 (15) | C17—C16—C15—C14 | −172.21 (13) |
|           | N2—C16—C15—C20 | −172.99 (14) | C19—C20—C15—C16 | −3.0 (2) |
|           | N2—C16—C15—C14 | 10.8 (2) | C19—C20—C15—C14 | 173.35 (15) |
|           | N2—C21—C22—C23 | 176.60 (14) | C18—C19—C20—C15 | 0.4 (3) |
|           | N3—C33—C32—C31 | 179.89 (16) | C20—C19—C18—C17 | 1.3 (3) |
|           | N3—C34—C35—C36 | 179.26 (16) | C20—C15—C14—O3 | −2.8 (2) |
|           | N3—C34—C39—C38 | −179.35 (15) | C20—C15—C14—O4 | 178.34 (14) |
|           | N1—C3—C4—C5 | −177.00 (16) | C15—C16—C17—C18 | −2.4 (2) |
|           | N1—C8—C13—C12 | −178.26 (16) | C25—C26—C21—N2 | −175.45 (14) |
|           | C29—C28—C33—N3 | 179.21 (14) | C25—C26—C21—C22 | 0.7 (2) |
|           | C29—C28—C33—C32 | −4.3 (2) | C25—C24—C23—C22 | 0.4 (3) |
|           | C29—C28—C27—O5 | 9.52 (19) | C34—N3—C33—C28 | −157.76 (15) |
|           | C29—C28—C27—O6 | −170.54 (13) | C34—N3—C33—C32 | 25.8 (2) |
|           | C29—C30—C31—C32 | −2.4 (2) | C34—C35—C36—C37 | 0.0 (3) |
|           | C28—C29—C30—C31 | 1.3 (2) | C34—C39—C38—C37 | 0.2 (3) |
|           | C28—C33—C32—C31 | 3.3 (2) | C4—C5—C6—C7 | 0.2 (3) |
|           | C16—N2—C21—C26 | −132.15 (16) | C27—C28—C33—N3 | −0.5 (2) |
|           | C16—N2—C21—C22 | 51.8 (2) | C27—C28—C33—C32 | 175.99 (14) |
|           | C16—C17—C18—C19 | −0.2 (3) | C1—C2—C3—N1 | 0.5 (2) |
|           | C16—C15—C14—O3 | 173.38 (13) | C1—C2—C3—C4 | −178.34 (14) |
|           | C16—C15—C14—O4 | −5.4 (2) | C1—C2—C7—C6 | 176.93 (16) |
|           | C33—N3—C34—C35 | 47.6 (2) | C35—C34—C39—C38 | −0.1 (2) |
|           | C33—N3—C34—C39 | −133.18 (17) | C35—C36—C37—C38 | 0.1 (3) |
|           | C33—C28—C27—O5 | −170.79 (13) | C9—C8—C13—C12 | −0.8 (3) |
|           | C33—C28—C27—O6 | 9.2 (2) | C9—C10—C11—C12 | −1.4 (3) |
|           | C33—C32—C31—C30 | 0.0 (3) | C8—N1—C3—C2 | 178.42 (16) |
|           | C2—C3—C4—C5 | 1.9 (2) | C8—N1—C3—C4 | −2.8 (3) |
|           | C2—C7—C6—C5 | 1.2 (3) | C8—C9—C10—C11 | 1.9 (2) |
|           | C26—C21—C22—C23 | 0.5 (2) | C8—C13—C12—C11 | 1.4 (3) |
|           | C26—C25—C24—C23 | 0.8 (3) | C10—C9—C8—N1 | 176.66 (15) |
|           | C3—N1—C8—C9 | 118.66 (18) | C10—C9—C8—C13 | −0.8 (2) |
|           | C3—N1—C8—C13 | −63.9 (2) | C10—C11—C12—C13 | −0.3 (3) |
|           | C3—C2—C7—C6 | −1.0 (3) | C39—C34—C35—C36 | 0.1 (2) |
|           | C3—C2—C1—O2 | −168.80 (14) | C39—C38—C37—C36 | −0.2 (3) |

Symmetry code: (i) −x+1, −y+1, −z+1.