Bull. Chem. Soc. Ethiop. **2023**, 37(4), 891-900.
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DOI: https://dx.doi.org/10.4314/bcse.v37i4.7

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

# SYNTHESIS AND CRYSTAL STRUCTURE OF A MIXED-LIGAND ZINC(II) COMPLEX DERIVED FROM ETHYL (2,6-DIMETHYLPHENYLCARBAMOYL) FORMATE AND 1,10-PHENANTHROLINE

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(Received June 30, 2022; Revised March 19, 2023; Accepted March 31, 2023)

**ABSTRACT**. A mixed-ligand zinc(II) complex, [Zn(Hpma)(phen)Cl] (where Hpma$^-$ = *N*-(2,6-dimethylphenyl)oxamate and phen = 1,10-phenanthroline), has been prepared by the reaction of zinc chloride, ethyl (2,6-dimethylphenylcarbamoyl)formate (Hdmp) and 1,10-phenanthroline under basic conditions in dimethylformamide. The structure of the complex was characterised by elemental analysis, IR, $^1$H-NMR, UV-Vis absorption and X-ray crystallography. The metal complex crystallises in the monoclinic system (space group *P21/c*) and is composed of the five-coordinate zinc ion in a distorted spherical square pyramidal geometry. Stabilisation of single crystals occurs through hydrogen bonds and π-π stacking interactions.

**KEY WORDS**: Zinc(II), *N*-(2,6-Dimethylphenyl)oxamate, 1,10-Phenanthroline, Crystal structure, Hydrogen bonding, π-π Stacking, Mixed-ligand

## INTRODUCTION

The second most abundant transition series, zinc, is known to play a key role in biological processes in the human body [1]. In biological systems, zinc functions at the active site of hydrolytic enzymes, such as carboxypeptidase and carbonic anhydrase or acts as a structural component of enzymes [2]. In addition to the usefulness of zinc in the elucidation of vital aspects of enzyme chemistry, zinc complexes are also significant in protein sequencing [3]. Zinc complexes containing carboxylate ligands and phenanthrolines have been extensively studied for their fascinating structures and applications, such as antimicrobial activities [1, 2, 4]. The biological significance (e.g. anticancer or antibacterial activity) and coordination flexibility of carboxylate or oxamate derivatives thus motivated the preparation of the novel zinc(II) mixed-ligand complex containing *N*-(2,6-dimethylphenyl)oxamate (Hpma$^-$) and 1,10-phenanthroline, as well as its characterisation by elemental microanalysis, FT-IR, NMR, UV-Vis spectroscopy and single-crystal X-ray diffraction. The oxamate derived ligand can have diverse chelating properties with transition or *f*-block metals, with potential to coordinate monodentately, bidentately (*O,O*- or *N,O*-donor), tridentately (*N,O,O*- or *O,O,O*-donor) or by adopting bridging modes in monoanionic or dianionic form [5-9]. The monoanionic or dianionic ligands are due to the ionisability of the carboxylic and amide protons, enabling preparation of dinuclear or polynuclear complexes [9]. The use of the bioactive 1,10-phenanthroline as a coligand in this research is attributed to its role in ensuring stability of the metal complexes [10, 11]. Therefore, the presented work aims to synthesise and characterise a zinc(II) complex with an oxamate derivative and 1,10-phenanthroline as ligands, as well as investigate the role of 1,10-phenanthroline in stabilising the complex through non-covalent interactions.

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## EXPERIMENTAL

### *Materials and measurements*

All solvents and reagents were purchased from either Merck or Sigma-Aldrich, and used without further purification.

The melting points were determined using a Stuart® Melting Point Apparatus (SMP30). The elemental analysis for carbon, hydrogen and nitrogen was performed using an Elementar Vario EL Cube Elemental Analyzer. HANNA instruments (HI) 2300 EC/TDS/NaCl Meter was used to perform conductivity measurement at room temperature. The UV-Vis spectroscopy of the free ligands and metal complexes was carried out on a PerkinElmer Lambda 35 UV/Vis spectrophotometer (path length = 1 cm). Nuclear Magnetic Resonance (NMR) spectra were obtained at room temperature using a Bruker AvanceIII 400 NMR Spectrometer. The infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer, equipped with the Platinum attenuated total reflection (ATR) attachment.

A Bruker Kappa Apex II diffractometer was used in single-crystal X-ray diffraction analyses at 200 K, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). APEX2 was used for data collection and *SAINT* software for data reduction and cell refinement [12]. The structures were solved by direct methods using SHELXT-2018/2 and refined by least-squares procedures using SHELXL-2018/3 with ShelXle as a graphical interface [13-15]. Data were corrected for absorption effects using the numerical method implemented in SADABS [12]. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms placed in calculated positions were included in the refinement in the riding model approximation [$U_{\mathrm{iso}}$(H) set to $1.2U_{\mathrm{eq}}$(C)]. The methyl group hydrogen atoms were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite) [$U_{\mathrm{iso}}$(H) set to $1.5U_{\mathrm{eq}}$(C)] [14]. The nitrogen-bound hydrogen atoms were located on a difference Fourier map and refined freely. Molecular graphics were obtained using *ORTEPIII* and *Mercury 3.6* softwares [16, 17]. Zinc complex geometry analysis was enabled by the *SHAPE 2.1* software [18]. The polyhedral representation was generated using *VESTA* software [19].

### *Synthesis of the proligand ethyl (2,6-dimethylphenylcarbamoyl)formate (Hdmp)*

The proligand Hdmp was synthesised according to the literature procedure [20].

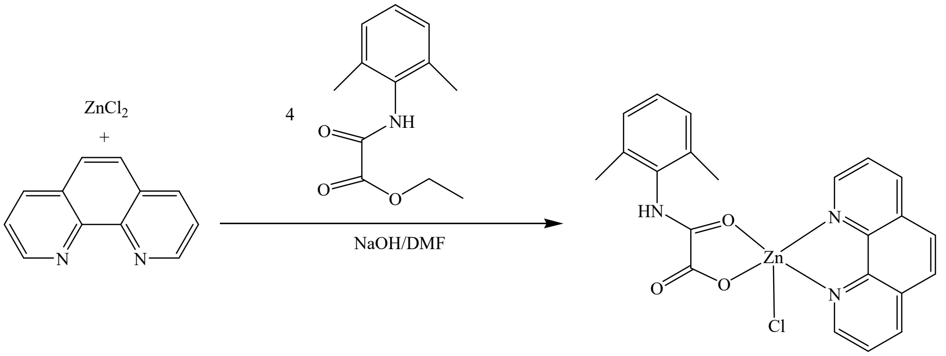
### *Synthesis of [Zn(Hpma)(phen)Cl]*

A solution of phen (0.224 g, 1.24 mmol) and $ZnCl_2$ (0.169 g, 1.25 mmol) in 6 ml DMF was stirred for 2 hours at room temperature. Hdmp (1.10 g, 4.97 mmol) was then added in the presence of 4.97 $cm^3$ of 1 M NaOH, and stirring was continued for 1 hour. The clear colourless solution formed was filtered off to remove undissolved material and left to crystallise at room temperature. White single crystals suitable for X-ray crystallography were obtained after 3 days. Yield: 58.5%, m.p. = 283.2 $^{o}$C. Anal. calcd. for $C_{22}H_{18}ClN_3O_3Zn$ (FW 473.23): C, 55.84; H, 3.83; N, 8.88. Found: C, 55.35; H, 3.42; N, 8.78. Conductivity (25 $^{o}$C, $10^{-3}$ M, DMF): 13.52 $ohm^{-1}cm^2mol^{-1}$. UV-Vis (DMF, $\lambda_{max}$ nm): 324, 342. IR data (KBr, $cm^{-1}$): *v*(N-H) 3252(w), *v*(C=O) 1666, 1638(s), *v*(C=C) 1525(s), *v*(C-H) 855, 722(s), *v*(Zn-O) 514(m), *v*(Zn-N) 469(w).

## RESULTS AND DISCUSSION

### *Synthesis, elemental microanalysis and molar conductance*

The use of 1 M NaOH as a base led to hydrolysis of the proligand Hdmp to yield monoanionic *N*-(2,6-dimethylphenyl)oxamate ($Hpma^-$) which then coordinated to the Zn(II) ion in a bidentate fashion (Scheme 1). The molecular formula of the Zn(II) complex agrees with the elemental analysis of carbon, hydrogen and nitrogen. The deviation of found percentages for elemental carbon and hydrogen from calculated values by 0.49 and 0.41%, respectively, can be a result of a small amount of organic solvent molecules. The molar conductivity value of the DMF solution of the metal complex at room temperature is 13.52 ohm$^{-1}$cm$^{2}$mol$^{-1}$. This shows the non-ionic nature of this coordination compound and hence its non-electrolytic nature [4].



Scheme 1. Synthetic route of the zinc complex from ethyl (2,6-dimethylphenylcarbamoyl)formate (Hdmp) and 1,10-phenanthroline.

### *IR spectra*

The IR spectra of Hdmp, phen and the synthesised complex are displayed in Figure 1. The strong *v*(N-H) of Hdmp is found in the high-frequency region at 3252 cm$^{-1}$ – this band is found at almost the same position in the complex, thus indicating the non-involvement of the oxamate nitrogen atom in direct bonding to the metal [20]. In the proligand Hdmp, the C=O stretching vibrations occur at 1763 and 1688 cm$^{-1}$, while these bands are shifted to lower wavenumbers in the metal complex (1666–1638 cm$^{-1}$), thus attesting participation of the oxamate *O*-atoms in direct complexation to zinc [4, 20]. The shifts observed in the spectra of the complex are due to the weakening of the C=O bonds upon coordination [4, 21, 22]. The *v*(C=C) in Hdmp at 1525 cm$^{-1}$ remained unshifted in the title compound, while the C=C vibration of free phen appear at 1505 cm$^{-1}$ [1, 11]. The free ligand 1,10-phenanthroline monohydrate exhibits a broad vibration band with a maximum at 3371 cm$^{-1}$, indicating the presence of a water molecule [4, 21, 23]. This band completely disappears in the spectrum of the Zn(II) complex. The bands observed at 514 and 469 cm$^{-1}$ have been assigned to *v*(Zn-O) and *v*(Zn-N), respectively [1, 4].

### *NMR spectra*

The $^{1}$H NMR spectra of the free ligands and the zinc(II) complex in DMSO-$d_6$ are shown in Figure 2. The $^{1}$H NMR spectrum of the complex indicates the disappearance of the ethyl group of Hdmp (δ = 1.33 and 4.31 ppm), thus supporting formation of the Hpma$^{-}$ moiety from Hdmp [20]. The spectrum of the metal complex also displays Hpma$^{-}$ methyl proton signal at 1.94 ppm, an indication that the methyl groups undergo a significant upfield shift in the chemical environment relative to Hdmp (δ = 2.14 ppm) upon hydrolysis [24]. Downfield to the methyl proton peak of the complex, is a resonance assigned to the aromatic proton signals of the oxamate ligand (7.01 ppm), which are more shielded than the proligand aromatic protons (7.11 ppm). The resonances due to phen protons at 9.11, 8.48, 7.99 and 7.76 ppm appear as only three signals (8.90, 8.28 and

8.09 ppm) after coordination to the metal ion [21]. The N-H group peak of the proligand gives a signal at 10.29 ppm, a downfield shift from that of the complex (10.76 ppm), suggesting hydrolysis of Hdmp to $Hpma^{-}$, as well as participation of the oxamate moiety in complexation [20].

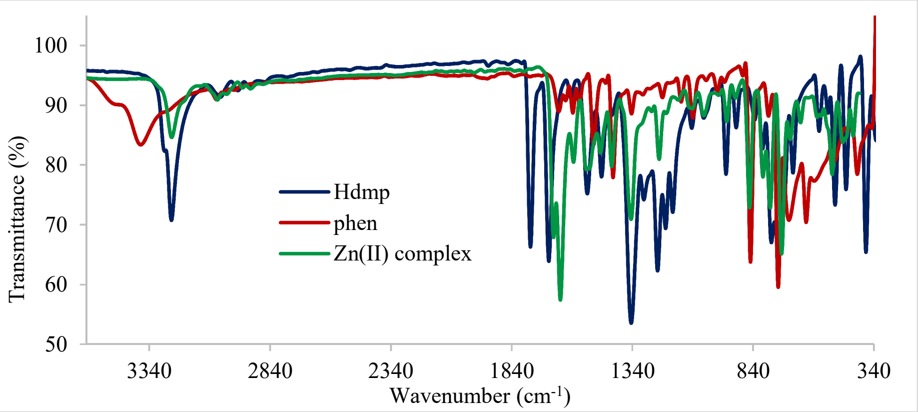


Figure 1. Overlay IR spectra of Hdmp, phen and the coordination compound.

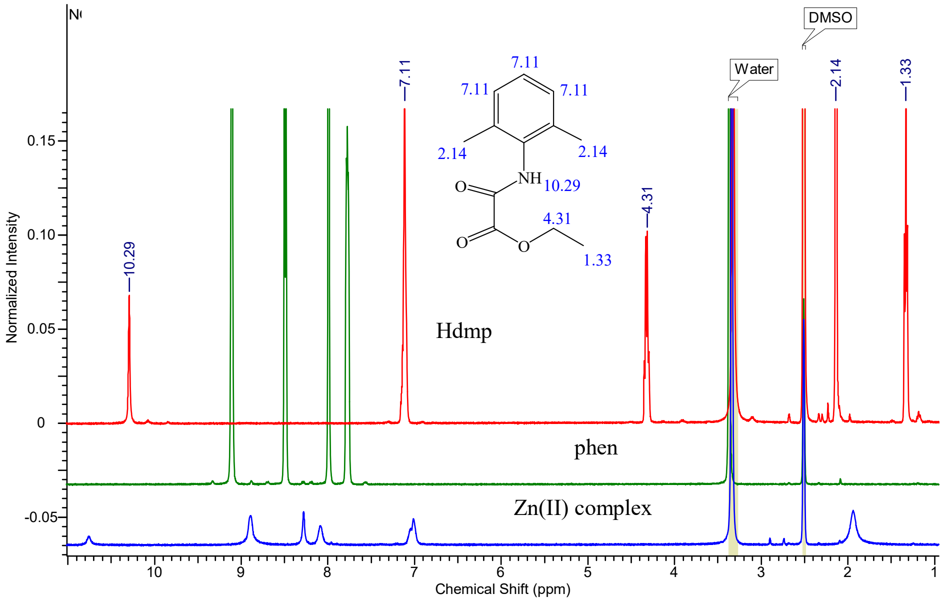


Figure 2. $^{1}H$ NMR spectra of Hdmp, phen and the Zn(II) complex.

*UV-Vis spectra*

The UV-Vis spectra of the free ligand and the metal complex, recorded in DMF (Figure 3), display intense absorption bands in the UV region (320–327 nm), that correspond to the ligand-centred $\pi \rightarrow \pi^*$ transitions [4,25]. A broad absorption band centred at approximately 342 nm, belonging to the metal complex may be assigned to the $n \rightarrow \pi^*$ transition of the NH-CO groups of $Hpma^-$ or the C=N groups of phen [4,26].

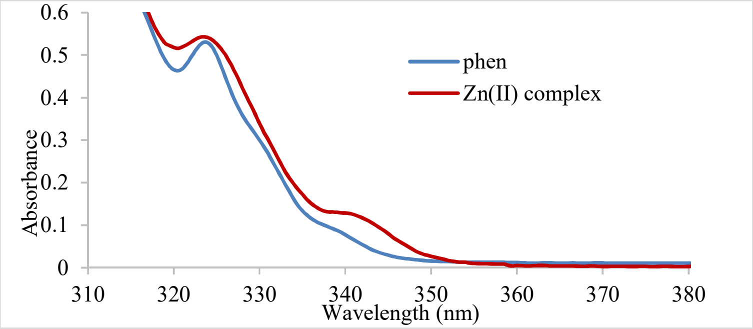


Figure 3.UV-Vis spectra of the free phen and the Zn(II) complex.

*Crystal structure*

The monomeric five-coordinate zinc complex crystallises in the monoclinic system (space group *P21/c*) (Table 1) and exhibits a distorted spherical square pyramidal geometry with a deviation parameter (CShM value) from ideal geometry of 0.67048 (Table 2, Figure 4a) [18, 27, 28]. The Zn ion is penta-coordinated by two nitrogen atoms from one phen ligand, two oxygen atoms from a bidentate oxamate moiety and one chloride ion (Figure 4b). Selected bond lengths and angles are listed in Table 3, with Zn-N and Zn-O bond distances in the ranges 2.1096(13)–2.1103(13) and 2.0410(12)–2.1106(11) Å, respectively, whereas the Zn-Cl bond length is 2.2565(5) Å. The longest bond length in Zn-Cl compared to Zn-O and Zn-N indicates that the Zn-Cl bond is the weakest [29]. The ligand bite angles of the 5-membered chelate rings are almost equal as shown by coordinating bond angles of N-Zn-N = 79.20(5)° and O-Zn-O = 79.63(4)°. Bond parameters are normal and the values fall within the range of the related coordination compounds [2, 30].

Table 3 shows that the bond angles Cl1-Zn1-O31 [109.88(4)°] and Cl1-Zn1-O32 [105.28(4)°] of the oxamate chelate, as well as Cl1- Zn1-N1 [107.20(4)°] and Cl1- Zn1-N10 [101.18(4)°] of the phenanthroline moiety vary. This variation can be ascribed to slightly twisted geometry as indicated by O32-C30-C31-O31 (oxamate) and N10-C11-C14-N1 (phenanthroline) torsion angles equal to -2.2(2) and 1.3(2)°, respectively.

The crystal structure of the zinc complex is stabilised through intermolecular N-H···O hydrogen bonds (Table 3, Figure 4c) and π-π interactions [2]. These N-H···O links are apparent between the amide N-H groups of one molecule and the uncoordinated *O*-atoms of the oxamate group from an adjacent molecule. Additionally, the crystal packing of the complex is supplemented by weak $C\text{-}H_{Hpma-}\cdots O$, $C\text{-}H_{phen}\cdots O$ and $C\text{-}H_{phen}\cdots Cl$ contacts.

Parallel-displaced aromatic π···π interactions also provide structural stability, with the most significant stacking interactions being formed by the six- and ten-membered rings of phen (Table 4, Figure 4d) [31, 32]. The minimum ring centroid distance (Cg3-Cg7) between the 6- and 10-member phen rings is equal to 3.5679(9) Å, and the Cg7 of phen is offset by 1.217 Å from the ideal stacking position.

Table 1. Crystal and structure refinement data.

| | |
|---|---|
| Formula | $C_{22}H_{18}ClN_3O_3Zn$ |
| $M_r$ (g.mol$^{-1}$) | 473.23 |
| Crystal system | Monoclinic |
| Space group | *P21/c* (No. 14) |
| *a, b, c* [Å] | 10.1655(2), 15.5046(3), 13.9922(3) |
| α, β, γ (°) | 90, 109.077(1), 90 |
| $V$ (Å$^3$) | 2084.22(7) |
| $Z$ | 4 |
| ρ (g.cm$^{-3}$) | 1.508 |
| μ (mm$^{-1}$) | 1.335 |
| $F$(000) | 968 |
| Crystal size (mm) | 0.14 × 0.25 × 0.28 |
| Temperature (K) | 200 |
| Mo $K\alpha$ radiation, λ (Å) | 0.71073 |
| θ (min-max) (°) | 2.0, 28.3 |
| Data set | $-13 \leq h \leq 13$; $-20 \leq k \leq 20$; $-17 \leq l \leq 18$ |
| Tot., Unique data, $R_{int}$ | 39560, 5191, 0.028 |
| Observed [I>2σ(I)] reflections | 4347 |
| $N_{\text{reflections}}$, $N_{\text{parameters}}$ | 5191, 273 |
| $R[F^2>2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.0263, 0.0650, 1.03 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ (e.Å$^{-3}$) | -0.29, 0.36 |

Table 2. Continuous Shape Measures calculation of the title compound using *SHAPE 2.1*.

| Geometry | Symmetry | CShM value |
|---|---|---|
| Pentagon (PP-5) | $D_{5h}$ | 30.59313 |
| Vacant octahedron (vOC-5) | $C_{4v}$ | 3.20550 |
| Trigonal bipyramid (TBPY-5) | $D_{3h}$ | 4.09481 |
| Spherical square pyramid (SPY-5) | $C_{4v}$ | 0.67048 |
| Johnson trigonal bipyramid J12 (JTBPY-5) | $D_{3h}$ | 7.33953 |

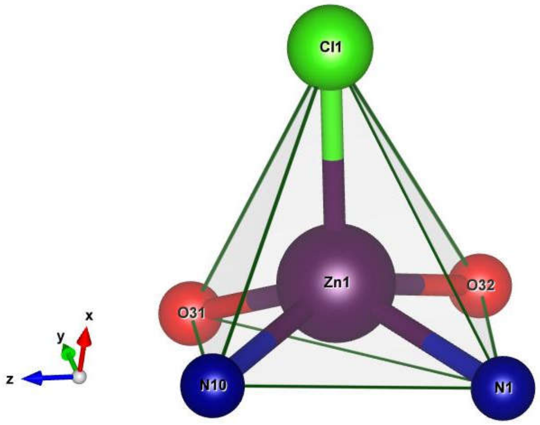


Figure 4a. Polyhedral view of the Zn(II) coordination compound.

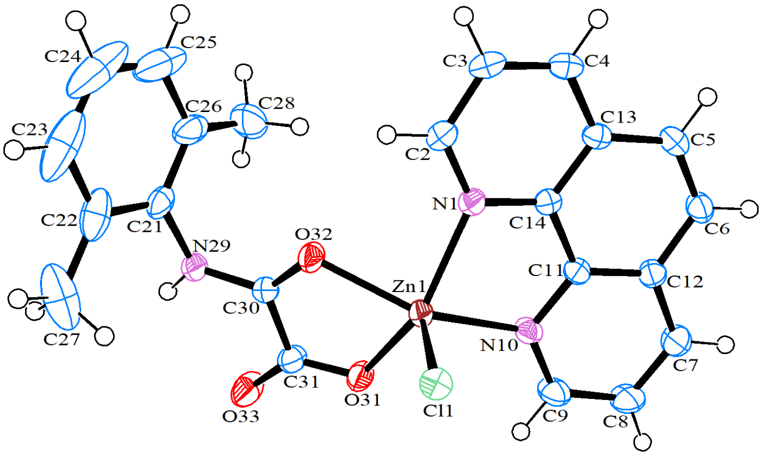


Figure 4b. Molecular structure of the Zn(II) complex showing 50% probability displacement ellipsoids.

Table 3. Selected bond parameters for the title compound.

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| Zn1-Cl1 | 2.2565(5) | O31-Zn1-O32 | 79.63(4) |
| Zn1-O31 | 2.0410(12) | N1-Zn1-N10 | 79.20(5) |
| Zn1-O32 | 2.1106(11) | O31-C31-C30 | 113.84(14) |
| Zn1-N1 | 2.1096(13) | Cl1-Zn1-O31 | 109.88(4) |
| Zn1-N10 | 2.1103(13) | Cl1-Zn1-O32 | 105.28(4) |
| | | Cl1-Zn1-N1 | 107.20(4) |
| | | Cl1-Zn1-N10 | 101.18(4) |

| Hydrogen-bonding geometry (Å, °) for the Zn(II) compound | | | | |
|---|---|---|---|---|
| *D*-H···*A* | *D*-H | H···*A* | *D*···*A* | *D*-H···*A* |
| N29-H29···O33 | 0.8800 | 2.3900 | 2.7318(18) | 100.00 |
| N29-H29···O33$^{\mathrm{i}}$ | 0.8800 | 2.0700 | 2.895(2) | 155.00 |
| C2-H2···O32 | 0.9500 | 2.5800 | 3.0903(19) | 114.00 |
| C3-H3···O33 | 0.9500 | 2.4200 | 3.321(2) | 159.00 |
| C8-H8···Cl1 | 0.9500 | 2.7100 | 3.5659(18) | 151.00 |
| C27-H27C···O33$^{\mathrm{i}}$ | 0.9800 | 2.5900 | 3.381(3) | 138.00 |

*D* = donor, *A* = acceptor; Symmetry codes: i) 1-*x*, 2-*y*, 1-*z*.

Table 4. Selected π-π stacking interactions for the mixed-ligand Zn(II) complex.

| Cg(I)···Cg(J) | Cg-Cg (Å) | Dihedral Angle (°) | Beta angle (°) | Gamma angle (°) | Perpendicular distance of Cg(I) on ring J (Å) | Slippage (Å) |
|---|---|---|---|---|---|---|
| Cg3···Cg3$^{\mathrm{i}}$ | 3.9535(9) | 0.00(8) | 31.8 | 31.8 | 3.3612(7) | 2.081 |
| Cg3···Cg5$^{\mathrm{i}}$ | 3.5709(10) | 1.42(8) | 20.3 | 18.9 | 3.3794(7) | 1.237 |
| Cg3···Cg7$^{\mathrm{i}}$ | 3.5679(9) | 0.68(7) | 19.9 | 19.6 | 3.3618(7) | 1.217 |
| Cg3···Cg9$^{\mathrm{i}}$ | 3.8086(8) | 0.82(6) | 28.8 | 28.3 | 3.3546(7) | 1.836 |
| Cg5···Cg7$^{\mathrm{i}}$ | 3.9616(9) | 0.74(7) | 31.2 | 31.9 | 3.3640(7) | 2.052 |
| Cg7···Cg7$^{\mathrm{i}}$ | 3.5725(8) | 0.00(5) | 19.8 | 19.8 | 3.3615(5) | 1.209 |

Cg-Cg = distance between ring centroids; Slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I; Symmetry codes: i) 2-*x*, 1-*y*, 1-*z*. Cg3: N1→C2→C3→C4→C13→C14, Cg5: C5→C6→C12→C11→C14→C13, Cg7: N1→C2→C3→C4→C13→C5→C6→C12→C11→C14, Cg9: N1→C2→C3→C4→C13→C5→C6→C12→C7→C8→C9→N10→C11→C14.

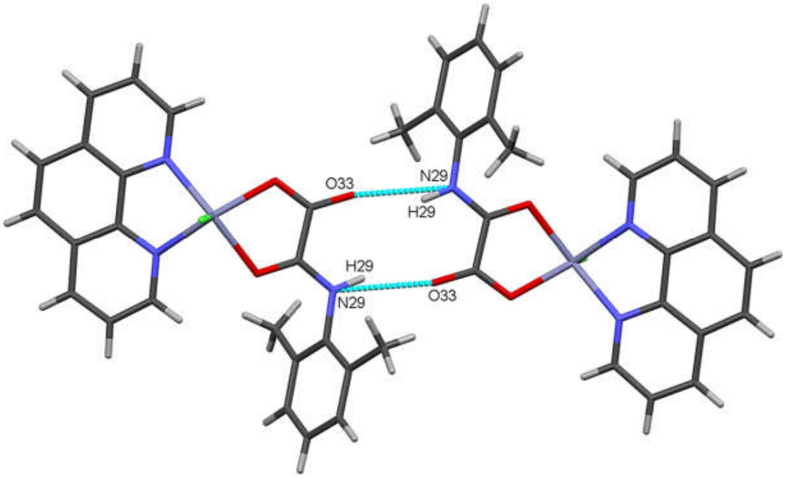


Figure 4c. Perspective view of the intermolecular hydrogen bonding interactions in the mixed-ligand zinc complex (hydrogen bonds are drawn as dashed cyan lines).

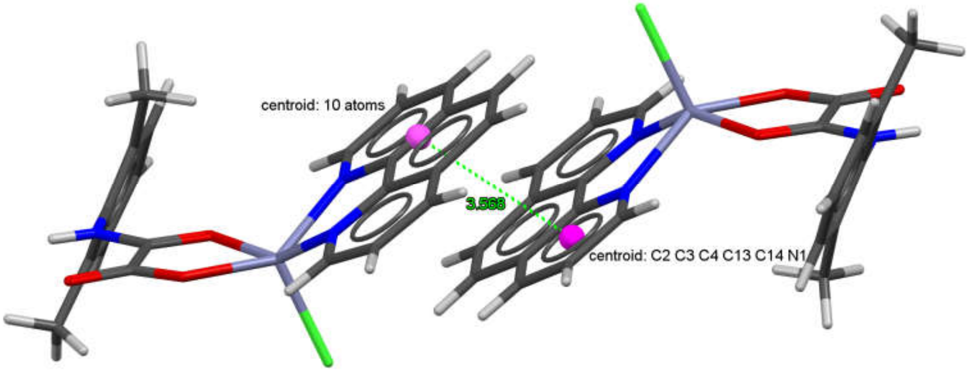


Figure 4d. An illustration of parallel displaced π-π interactions in the zinc(II) complex (π-π stacking shown with a dashed green line).

## CONCLUSIONS

The mixed-ligand complex of zinc(II) metal cation was synthesised with Hpma$^-$ and 1,10-phenanthroline ligands, with the ratio of Zn(II):Hpma$^-$:phen determined as 1:1:1. The synthesised complex has been characterised by micro elemental analysis, IR, NMR and UV-Vis spectroscopy analyses, as well as single crystal X-ray crystallography. The oxamate ligand and phen are both coordinated in bidentate modes, giving a five-coordinate complex [Zn(Hpma)(phen)Cl], displaying spherical square pyramidal geometry.

## ACKNOWLEDGEMENTS

We thank the National Research Foundation (unique grant number: 106004) and the Nelson Mandela University PGRS for financial assistance.

## SUPPLEMENTARY DATA

CCDC 1977267 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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