

Article

Structural Characteristics of Homoleptic Zinc Complexes Incorporating Asymmetric Aminopyridinates

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Abstract

First examples of mononuclear homoleptic zinc aminopyridinates have been isolated by reacting the sterically bulky deprotonated 2-aminopyridine ligands, N-(2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridine-2-yl]-amine (**1**) and N-(2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridine-2-yl]-amine (**2**) with $[Zn\{N(SiMe_3)_2\}_2]$. Single crystal X-ray analyses of the zinc bis(aminopyridinate) complexes (**3** and **4**) reveal two different orientations of the coordinated ligands most probably due to the steric variation of the of the applied ligands. For **3** not only the two ligands show rare head to head arrangement but also one of the ligand exhibit localized and the other ligand delocalized mode of coordination. In **4** the two ligands adopt the head to tail arrangement for the two coordinated aminopyridinato ligands with anionic function localized at the amido nitrogen atom of both the ligands. NMR tube reactions between equimolar ratios of **1** or **2** and $[Zn\{N(SiMe_3)_2\}_2]$ show the possible synthesis of the mono(aminopyridinate) Zn amide complexes (**5** and **6**, respectively) in solution phase, however, the corresponding bis(aminopyridinate) Zn complexes are the selective products. Hirshfeld surface analysis and the two-dimensional fingerprint plots indicate that intermolecular $H \cdots H$ contacts and $H \cdots C/C \cdots H$ π -interactions dominate the crystal packing.

Keywords: 2-aminopyridine; homoleptic; monomeric; N-ligands; X-ray analysis; zinc



Academic Editor: Martin Lutz

Received: 9 August 2025

Revised: 12 September 2025

Accepted: 15 September 2025

Published: 19 September 2025

Citation: Noor, A.; Qayyum, S. Structural Characteristics of Homoleptic Zinc Complexes Incorporating Asymmetric Aminopyridinates. *Crystals* **2025**, *15*, 821. <https://doi.org/10.3390/cryst15090821>

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1. Introduction

2-Aminopyridinate is an interesting class of asymmetric N-ligands that was rarely explored until late 1990s [1,2]. Their extensive use in coordination chemistry has been on the rise since last couple of decades and the resulting complexes have found their potential applications particularly as catalyst precursors for nanocomposite, having metal-metal quintuple bonding and in on-purpose olefin synthesis [3–6]. Majority of these complexes are known for early transition metals and lanthanoids as compared to those of late transition metals [7–15]. The variation in their binding modes is attributed to the flexible nature of the ligands they adopt based on steric bulk and metal coordinated. For instance, the chelating binding mode has often been preferred by early transition metals to form mononuclear complexes and bridging coordination has been frequently observed for late transition metals resulting in di- or multinuclear compounds [16]. Ligands with increased steric bulk have been successfully applied to control the metal to ligand stoichiometry and prevent the oligomerization of the resulting complexes. Examples of monomeric late transition metal complexes with κ^2 -coordinated aminopyridinate ligands, is limited to manganese and group 10 metals [7,10]. We decided to extend the use of these sterically bulky

ligands to zinc as smaller ligands have been previously known to form di- or multinuclear complexes and herein report the first examples of structurally characterized mononuclear zinc aminopyridinates [8,17,18]. Structural similarities of the herein reported complexes to those of guanidinates indicate their possible catalytic applications in Tishchenko reaction, ring opening polymerization and hydroamination [19–22].

2. Materials and Methods

2.1. Materials

The syntheses and characterization have been carried out using either Schlenk technique under argon or in a N₂ filled glove box (mBraun 120-G) equipped with a high-capacity recirculator (<0.1 ppm O₂). Toluene and hexane were dried by distillation from sodium wire/benzophenone. Benzene-*d*₆ was purchased from Cambridge Isotope Laboratories and was dried, degassed and distilled before its use. Anhydrous ZnI₂ was purchased from Sigma Aldrich and used as received. Aminopyridine ligands and [Zn{N(SiM₃)₂}₂] were prepared according to reported procedures [23,24]. Elemental analyses (CHN) data were obtained on a Vario EL III instrument under inert atmosphere.

2.2. NMR Spectroscopy

NMR samples were measured at ambient temperature on a Varian 300 MHz (¹H NMR, 300 MHz; ¹³C NMR, 75 MHz) spectrometer. The chemical shifts are referenced to the residual proton impurities of C₆D₆ at 7.16 ppm for ¹H and 128 ppm for ¹³C spectra according to Figure 1.

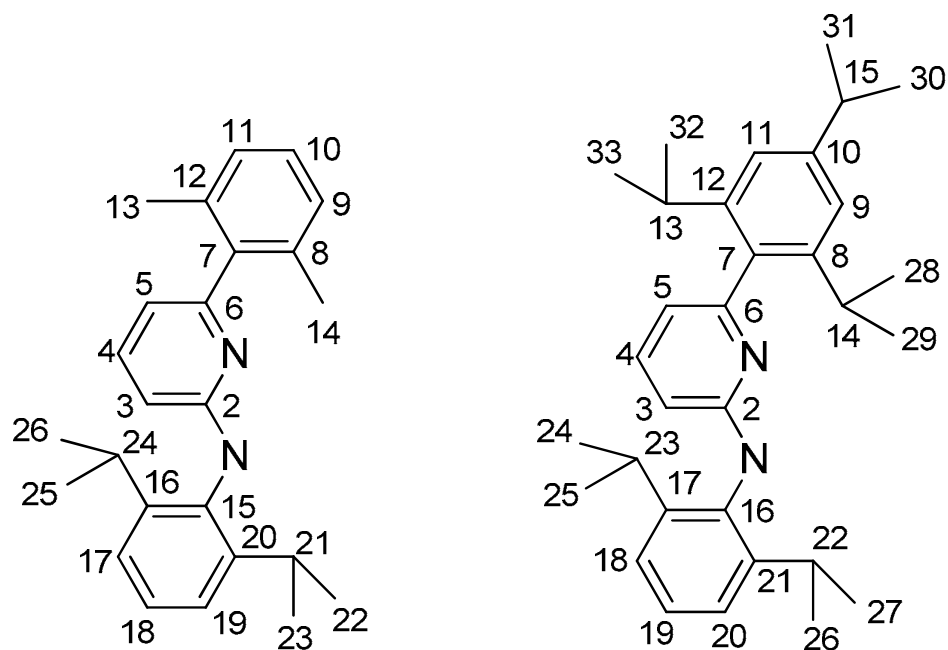


Figure 1. NMR labeling of Zn complexes.

2.3. Single Crystal X-Ray Diffraction

Single crystal suitable for X-ray analysis was selected in perfluorinated oil [25] and was irradiated with Mo-K α at 133 K on a STOE IPDSII diffractometer equipped with an Oxford Cryostream low-temperature unit. The structures were solved by direct methods and refined using SIR97 [26], SHELXL2018/3, SHELXL2019/3 [27], WinGX [28] and Olex2 [29] without applying absorption correction. Data collection and cell refinement were performed by using X-Area-STOE. All non H-atoms have been refined with anisotropic thermal parameters whereas H-atoms were added at calculated positions and refined using riding

model. Further details of the crystal structures determinations and data collection are given in Table 1 and the Cambridge Crystallographic Data Center under depository numbers of CCDC 2,479,406 and 2,479,407 for compounds **3** and **4**, respectively. These data is available free of charge at <https://www.ccdc.cam.ac.uk/structures> (accessed on 9 August 2025) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data of **3** and **4**.

	3	4
Empirical formula	C ₅₀ H ₅₈ N ₄ Zn	C ₆₄ H ₈₆ N ₄ Zn
Formula weight	780.37	976.73
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	10.244(2)	20.7130(8)
<i>b</i> [Å]	10.879(2)	23.0200(7)
<i>c</i> [Å]	20.759(4)	24.7280(8)
α [°]	82.30(3)	90
β [°]	86.28(3)	97.655(3)
γ [°]	64.44(3)	90
<i>V</i> , [Å ³]	2064.2(9)	11,685.6(7)
Crystal size, [mm ³]	0.23 × 0.13 × 0.12	0.51 × 0.36 × 0.31
ρ_{calcd} , [g cm ^{−3}]	1.256	1.110
μ , [mm ^{−1}] (Mo K α)	0.635	0.461
<i>T</i> , [K]	133(2)	133(2)
2 θ range, [°]	3.95–51.20	2.41–53.27
No. of reflections unique	8290	23,353
No. of reflections obs. [<i>I</i> > 2 σ (<i>I</i>)]	4040	12,956
No. of parameters	509	1283
<i>wR</i> ² (all data)	0.1675	0.1498
<i>R</i> value [<i>I</i> > 2 σ (<i>I</i>)]	0.0566	0.0571
Goodness of fit	0.908	0.998

2.4. Syntheses

Synthesis of 3: Toluene (25 mL) was added to **1** (358 mg, 1 mmol) and [Zn{N(SiMe₃)₂}]₂ (193 mg, 0.5 mmol) at room temperature and stirred for four hours at room temperature. Toluene was removed in vacuum and the material was dissolved in hexane (20 mL) that afforded yellow crystals of the product at −25 °C. Yield: 0.368g (94%). C₅₀H₅₈N₄Zn (780.4): Calcd. C 76.95 H 7.49 N 7.18; found C 76.81 H 7.72 N 6.91. ¹H NMR: δ = 0.99 (d, 12H, *J* = 7.0 Hz, H^{22,23,25,26}), 1.12 (d, 12H, *J* = 7.0 Hz, H^{22,23,25,26}), 2.06 (s, 12H, H^{13,14}), 3.32 (sep, 4H, *J* = 7.0 Hz, H^{21,24}), 5.51 (d, 2H, *J* = 7.0 Hz, H³), 5.73 (d, 2H, *J* = 7.0 Hz, H⁵), 6.72 (tr, 2H, *J* = 7.0 Hz, H⁴), 6.96–7.08 (m, 12H, H^{9,10,11,17,18,19}) ppm. ¹³C NMR: δ = 20.5 (C^{13,14}), 23.3 (C^{22,23,25,26}), 24.3 (C^{22,23,25,26}), 28.8 (C^{21,24}), 104.5 (C³), 109.2 (C⁵), 123.8 (C^{9,11}), 125.1 (C⁴), 127.8 (C^{17,19}), 128.1 (C¹⁸), 128.5 (C¹⁵), 135.8 (C^{8,12}), 139.6 (C¹⁰), 140.3 (C⁷), 144.9 (C^{16,20}), 156.4 (C⁶), 169.5 (C²) ppm.

Synthesis of 4: Hexane (25 mL) was added to **2** (228 mg, 0.5 mmol) and [Zn{N(SiMe₃)₂}]₂ (97 mg, 0.25 mmol) at room temperature and was stirred for two hours at 60 °C. The reaction mixture was brought to room temperature and was then cooled to −25 °C to afford yellow crystals of the product. Yield: 0.20 g (82%). C₆₄H₈₆N₄Zn (976.77): Calcd. C 78.70 H 8.87 N 5.74; found C 78.50 H 9.14 N 5.68. ¹H NMR: δ = 0.89 (br d, 24H, H^{28,29,32,33}), 1.12 (d, 12H, *J* = 6.9 Hz, H^{30,31}), 1.21 (d, 12H, *J* = 6.9 Hz, H^{24,25/26,27}), 1.29 (d, 12H, *J* = 6.9 Hz, H^{24,25/26,27}), 2.81 (sept, 6H, *J* = 6.9 Hz, H^{13,14,15}), 3.47 (br sept, 4H, H^{22,23}), 5.52 (d, 2H, *J* = 6.9 Hz, H³), 5.96 (d, 2H, *J* = 6.9 Hz, H⁵), 6.68 (t, 2H, *J* = 6.9 Hz, H⁴), 7.02 (s, 4H, H^{9,11}), 7.13 (s, 6H, H^{18,19,20}). ¹³C

NMR: δ = 23.8 (C^{28,29,32,33}), 24.3 (C^{24,25,26,27}), 24.4 (C^{24,25,26,27}), 24.5 (C^{28,29,32,33}), 24.6 (C^{30,31}), 28.6 (C^{22,23}), 30.7 (C^{13,14}), 34.9 (C¹⁵), 104.4 (C³), 110.3 (C⁵), 112.5 (C¹⁹), 120.9 (C^{9,11}), 124.1 (C^{18,20}), 125.7 (C⁷), 136.3 (C⁴), 139.1 (C¹⁰), 145.6 (C^{17,21}), 146.5 (C^{8,12}), 148.6 (C¹⁶), 158.1 (C⁶), 168.5 (C²) ppm.

Synthesis of **5**: Benzene-*d*₆ (0.4 mL) was added to **1** (36 mg, 0.1 mmol) and [Zn{N(SiMe₃)₂}]₂ (39 mg, 0.1 mmol) at room temperature in an NMR tube and the reaction mixture was shaken for 10 min to form clear solution before NMR measurements. ¹H NMR: δ = 0.1 (s, 18H^{SiMe3}), 1.20 (d, 6H, *J* = 6.7 Hz, H^{22,23,25,26}), 1.26 (d, 6H, *J* = 6.7 Hz, H^{22,23,25,26}), 2.17 (s, 6H, H^{13,14}), 3.49 (sep, 2H, *J* = 6.7 Hz, H^{21,24}), 5.56 (d, 1H, *J* = 8.4 Hz, H³), 5.89 (d, 1H, *J* = 6.9 Hz, H⁵), 6.83 (tr, 1H, *J* = 7.6 Hz, H⁴), 6.95–7.20 (m, 6H, H^{9,10,11,17,18,19}) ppm. ¹³C NMR: δ = 5.10 (C^{SiMe3}), 20.5 (C^{13,14}), 23.3 (C^{22,23,25,26}), 24.4 (C^{22,23,25,26}), 28.8 (C^{21,24}), 104.5 (C³), 109.2 (C⁵), 123.9 (C^{9,11}), 125.1 (C⁴), 127.8 (C^{17,19}), 128.1 (C¹⁸), 128.5 (C¹⁵), 135.8 (C^{8,12}), 139.6 (C¹⁰), 140.3 (C⁷), 145.0 (C^{16,20}), 156.4 (C⁶), 169.5 (C²) ppm.

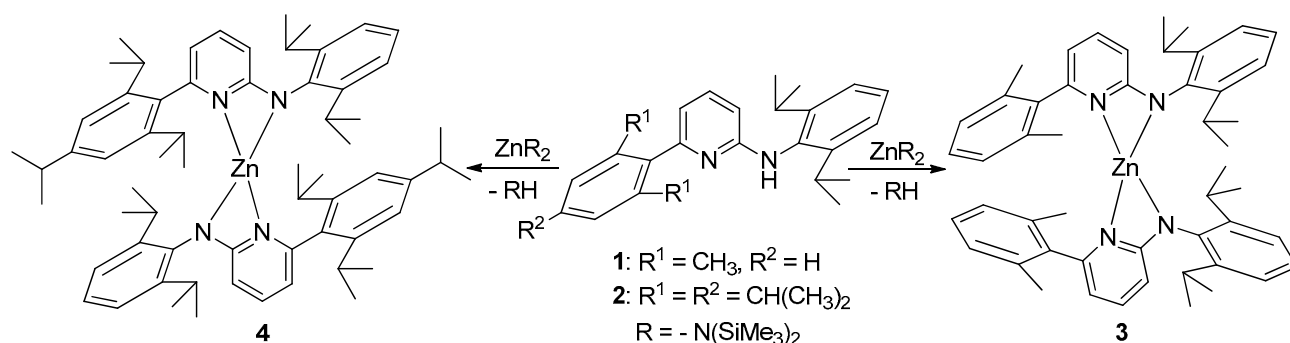
Synthesis of **6**: Benzene-*d*₆ (0.4 mL) was added to **2** (23 mg, 0.05 mmol) and [Zn{N(SiMe₃)₂}]₂ (19.5 mg, 0.05 mmol) at room temperature in an NMR tube and the reaction mixture was shaken for 10 min to form clear solution before NMR measurements. ¹H NMR: δ = 0.1 (s, 18H^{SiMe3}), 1.12 (d, 6H, *J* = 7.0 Hz, H^{30,31}), 1.19 (d, 6H, *J* = 7.0 Hz, H^{28,29/32,33}), 1.21 (dd, 12H, H^{28,29/32,33/24,25/26,27}), 1.37 (d, 6H, *J* = 7.0 Hz, H^{24,25/26,27}), 2.82 (sept, 1H, *J* = 7.0 Hz, H¹⁹), 2.98 (sept, 2H, *J* = 7.0 Hz, H^{13,14}), 3.50 (sept, 2H, *J* = 7.0 Hz, H^{22,23}), 5.60 (d, 1H, *J* = 7.0 Hz, H³), 6.18 (d, 1H, *J* = 7.0 Hz, H⁵), 6.83 (t, 1H, *J* = 6.9 Hz, H⁴), 7.13 (s, 2H, H^{9,11}), 7.20 (s, 3H, H^{18,19,20}). ¹³C NMR: δ = 5.1 (C^{SiMe3}), 24.0 (C^{28,29,32,33}), 24.3 (C^{24,25,26,27}), 24.4 (C^{24,25,26,27}), 24.6 (C^{28,29,32,33}), 25.6 (C^{30,31}), 28.8 (C^{22,23}), 30.8 (C^{13,14}), 34.9 (C¹⁵), 103.8 (C³), 111.9 (C⁵), 121.3 (C^{9,11}), 124.2 (C^{18,20}), 121.3 (C¹⁹), 126.0 (C⁷), 134.7 (C⁴), 140.0 (C¹⁰), 145.3 (C^{17,21}), 146.6 (C^{8,12}), 149.7 (C¹⁶), 156.8 (C⁶), 169.3 (C²) ppm.

2.5. Hirshfeld Surface Analysis

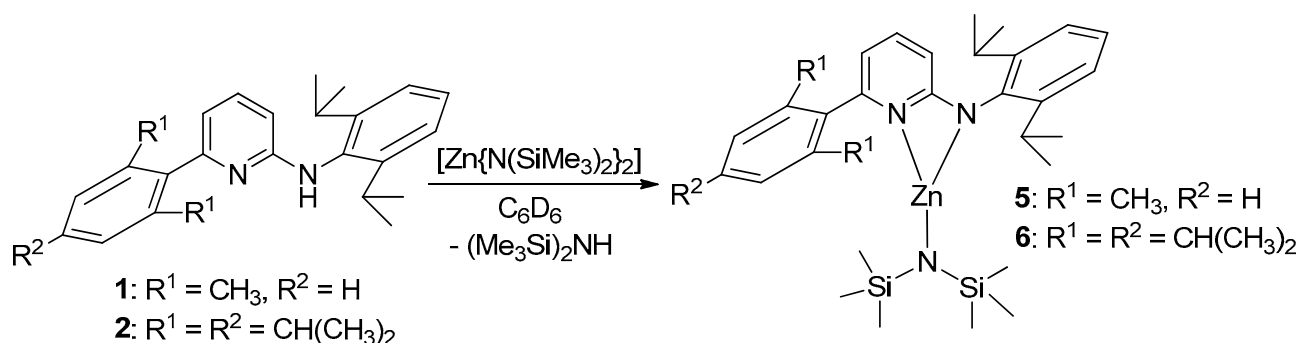
Hirshfeld surface analyses and corresponding fingerprint plots were generated using the CIF files of **3** and **4** by applying Crystal Explorer 17.5 software [30].

3. Results

Reacting two equivalents of the aminopyridine ligands, N-(2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridine-2-yl]-amine (**1**) or N-(2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridine-2-yl]-amine (**2**) [23] with zinc bis(trimethylsilyl)amide yielded the corresponding zinc bis(aminopyridinate) complexes (**3** and **4**, respectively) in quantitative yields (Scheme 1). Reaction between equimolar ratios of **1** or **2** and [Zn{N(SiMe₃)₂}]₂ allowed the NMR based evidence of the mono(aminopyridinate) zinc amide complex (**5** and **6**, respectively) in solution phase (Scheme 2).



Scheme 1. Synthetic route of homoleptic bis(aminopyridinate) zinc complexes.



Scheme 2. Synthesis of mono(aminopyridinate) zinc complexes.

^1H NMR of **3** and **5** shows the typical two doublets, one singlet and one septet in the aliphatic region for the aminopyridinate ligand. For **3** the two doublets for the eight methyl groups of the four isopropyl substituents could be observed at $\delta = 0.99$ and 1.12 ppm, a singlet for the four methyl substituents at $\delta = 2.06$ ppm and one septet at $\delta = 3.32$ ppm for the four CH protons of the isopropyl groups (Figure S1). In **5** these signals are slightly shifted towards low field (Figure S3). Complex **4** shows three well resolved and one broad doublet for the CH_3 and two septets with one being broad for the CH protons of the isopropyl groups in the aliphatic region (Figure S2). This fluxional behavior is known for such bulky metal aminopyridinates and therefore no investigations were made of this dynamic behavior by variable temperature NMR studies [23,31]. On the other hand **6**, that carries one such bulky aminopyridinate ligand shows well resolved signals (Figure S4). ^1H NMR of both mono(aminopyridinate) zinc complexes show a singlet at $\delta = 0.1$ ppm for the SiMe_3 groups indicating the magnetic equivalency of all the protons of the methyl groups. NMR studies show that the formation of **5** and **6** is not very selective and preferably leads to bis(aminopyridinate) complexes. The composition of **3** and **4** has been further confirmed by elemental analysis.

Yellow color single crystals of **3** (blocks) and **4** (cubes) suitable for X-ray measurements were obtained from concentrated hexane solutions showing the first examples of structurally characterized mononuclear zinc aminopyridinates. In both complexes, Zn atoms are four coordinated in which the aminopyridinate ligands are κ^2 -coordinated in strained chelating mode (Figures 2 and 3, respectively). In both compounds the ZnNCN four membered heterocycles are planar and twisted with respect to each other having C–Zn–C angles of 175.70 (**3**) and, 167.30 and 165.66° (**4**), respectively. Noteworthy, are the different orientations of the coordinated ligands. Complex **3** shows rare *cisoid* arrangement of the two coordinated ligands. The only known examples with such *cisoid* arrangement have been recently reported [32]. The two ligands also exhibit different modes of coordination for the two ligands. For one of the ligand, the two Zn–N bonds [Zn1–N1 $2.029(4)$ and Zn1–N2 $2.043(4)$ Å] show delocalization but the other ligand exhibits localized binding mode with short Zn– N_{amido} bond [Zn1–N3 $1.964(4)$ Å] and long Zn– $\text{N}_{\text{pyridine}}$ [Zn1–N4 $2.121(4)$ Å] bond [33]. Complex **4** that contains the sterically more bulky ligand shows the common *transoid* arrangement of the ligands with localized binding mode of coordination known for a number of divalent homoleptic aminopyridinate complexes [10]. The unit cell contains two independent molecules with similar orientation of the coordinated ligands. Worth mentioning is the obvious difference in Zn– $\text{N}_{\text{pyridine}}$ bond distances [Zn1–N $2.303(3)$ and Zn2–N $2.228(3)$ Å] that particularly effects the N_{amido} –Zn– N_{amido} bond angles [N1–Zn1–N3 $153.69(12)$ and N5–Zn2–N7 $145.72(12)^\circ$]. However, the Zn– N_{amido} bond distances for the two molecules are comparable [Zn1–N1 $1.901(3)$ and Zn1–N3 $1.904(3)$ Å and Zn2–N5 $1.923(3)$, Zn2–N7 $1.925(3)$ Å]. Likewise, other bond distances of the aromatic rings and aliphatic groups show minor variations. An overlap of the two molecules suggests that they are very

similar with minor variations in the orientation of the alkyl substituents having an RMSD value (without inversion) of 0.826 Å (Figure 4).

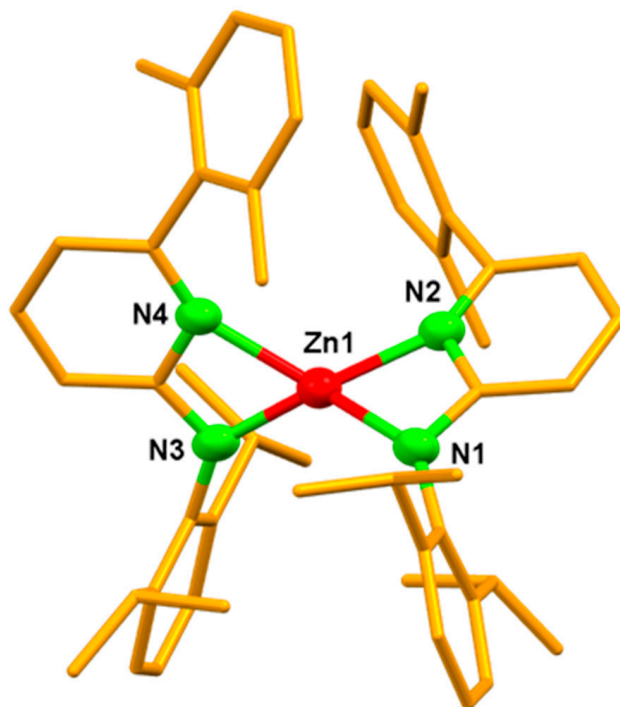


Figure 2. Molecular structure of complex **3** with ellipsoids set at 50% probability. H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–N3 1.964(4), Zn1–N1 2.029(4), Zn1–N2 2.043(4), Zn1–N4 2.121(4); N3–Zn1–N1 128.46(14), N3–Zn1–N2 147.06(15), N1–Zn1–N2 66.09(13), N3–Zn1–N4 65.80(14), N1–Zn1–N4 140.94(15), N2–Zn1–N4 124.80(13).

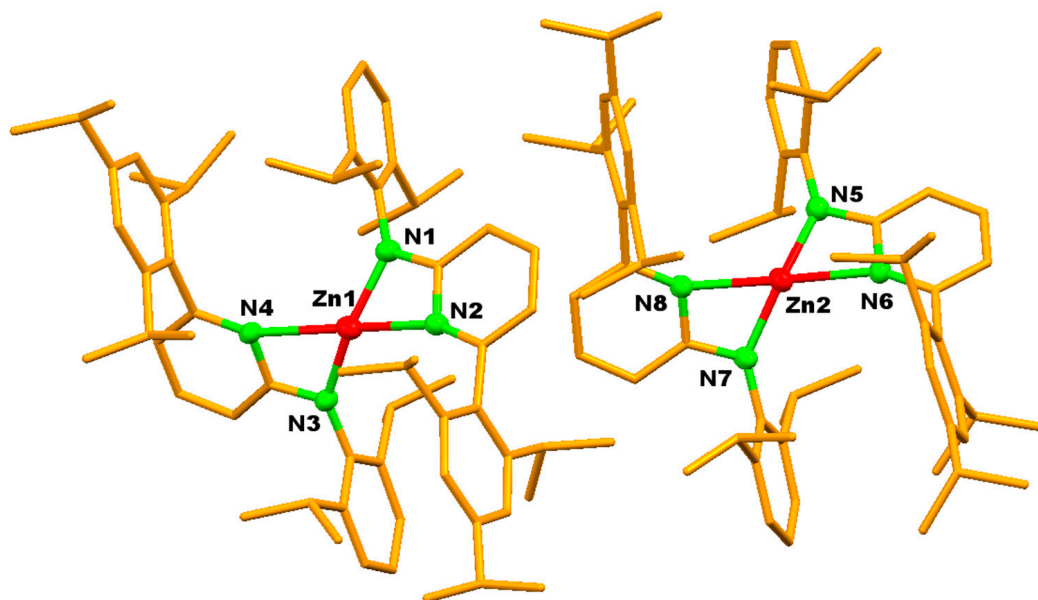


Figure 3. Molecular structure of complex **4** with ellipsoids set at 50% probability. H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–N1 1.901(3), Zn1–N3 1.904(3), Zn1–N2 2.307(3), Zn1–N4 2.300(3), Zn2–N5 1.923(3), Zn2–N7 1.925(3), Zn2–N6 2.225(3), Zn2–N8 2.232(3); N1–Zn1–N3 153.69(12), N1–Zn1–N4 119.53(10), N3–Zn1–N4 63.63(10), N1–Zn1–N2 63.53(10), N3–Zn1–N2 120.90(10), N4–Zn1–N2 165.27(10), N5–Zn2–N7 145.72(12), N5–Zn2–N6 64.70(11), N7–Zn2–N6 120.40(11), N5–Zn2–N8 122.61(11), N7–Zn2–N8 64.77(10), N6–Zn2–N8 161.26(10).

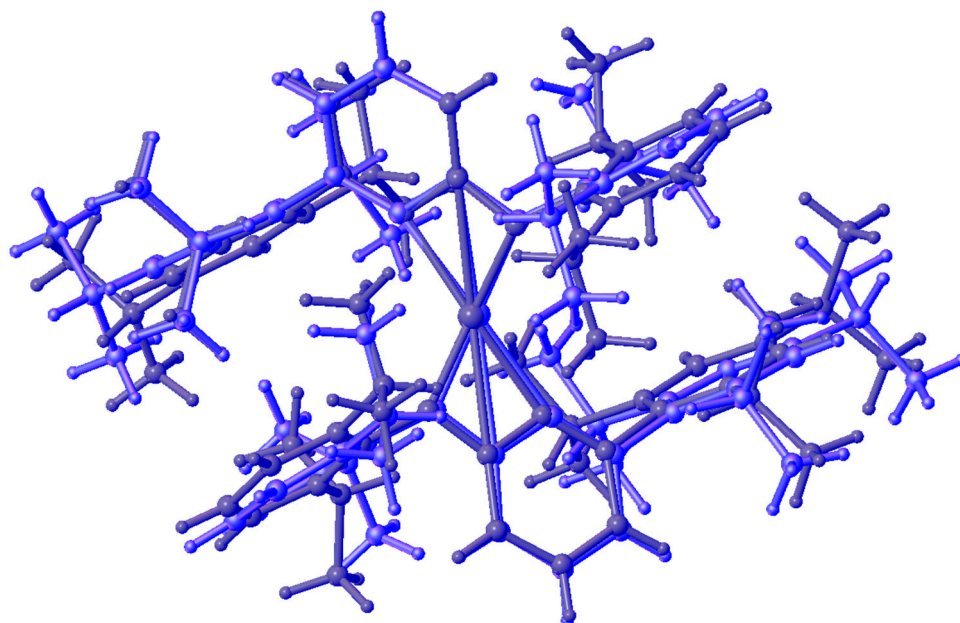


Figure 4. An overlay diagram of the two independent molecules in the asymmetric unit of **4**.

The coordination around the four coordinated Zn atoms can be best described as distorted tetrahedral in **3** ($\tau_4 = 0.51$; $\tau_4 = 360^\circ - (\alpha + \beta)/141^\circ$, where α and β are the two largest θ angles) with angles around Zn atom are in the range 65.80(14)–140.94(15)° [34]. This “flattened” tetrahedral geometry in **3** is in contrast to the distorted square planar geometries known for other homoleptic bis(aminopyridinate) complexes and is rather more comparable to those known for closely related zinc bis(guanidinate) [10,19–21,34]. For **4**, the tau values suggest distorted square planar arrangement around Zn atom ($\tau_4 = 0.29$ and 0.38). This difference in geometries can also be clearly seen from the overlapping figure of **3** with one molecule of **4** (Figure 5).

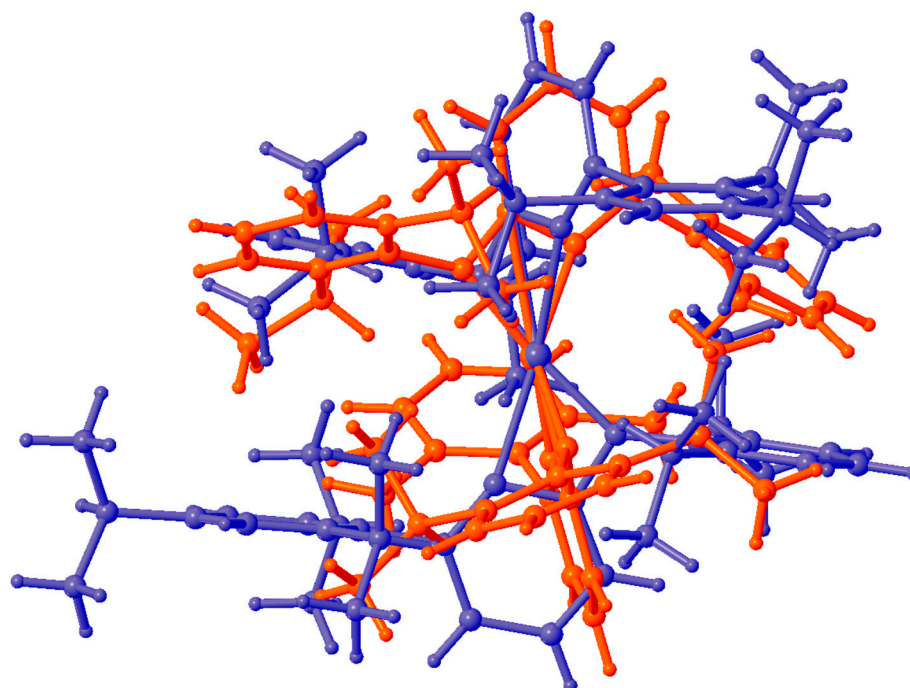


Figure 5. Overlapping view of **3** (orange) with one of the two molecules of **4** (Blue).

The data suggest that the crystal packings of both the complexes are stabilized by intermolecular C-H $\cdots$ H and C-H $\cdots$ C π -interactions and in both cases the bulkier aromatic substituents of the two ligands are involved in such kind of interactions. For instance, in **3** the H-atoms of the aromatic ring present on the amido-N atom show C-H $\cdots$ H interactions ($d(\text{H40}\cdots\text{H50B})$ 2.306 Å) with the isopropyl group and C-H $\cdots$ C π -interactions ($d(\text{C2}\cdots\text{H39})$ 2.817 Å) with the pyridine ring of the neighboring molecule (Figure 6).

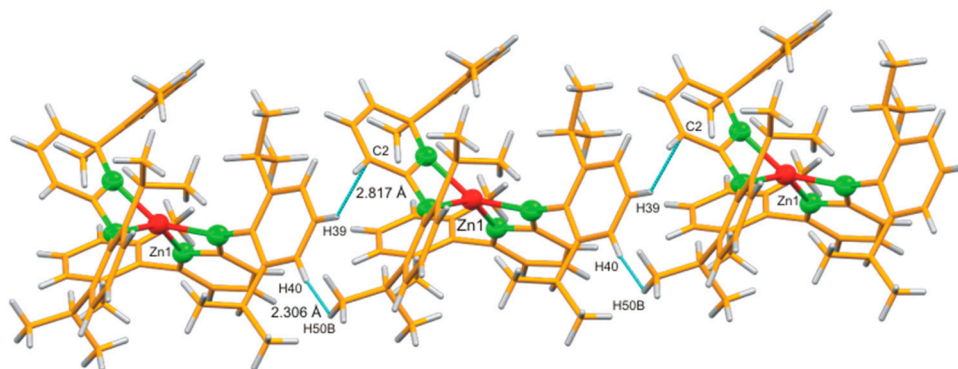


Figure 6. View of the intermolecular interactions in **3** shown as blue dotted lines. Color scheme: Zn = red; N = green; C = orange; and H = white.

On the other hand in **4**, the 2,4,6-triisopropylphenyl substituent present at the 6th position of the pyridine ring is involved in such kind of intermolecular interactions (Figure 7). The C-H $\cdots$ C π -interactions are evident between the C27 and C28 of phenyl and H119 of pyridine ring ($d(\text{C}\cdots\text{H})$ 2.830 and 2.854 Å, respectively) of the two molecules present in the unit cell. The closest C-H $\cdots$ H interactions are visible between the aliphatic and pyridine as well as between the aliphatic H-atoms ($d(\text{H}\cdots\text{H})$ 2.221 Å and 2.386 Å, respectively) of the neighboring as well as the two independent molecules present in the asymmetric unit.

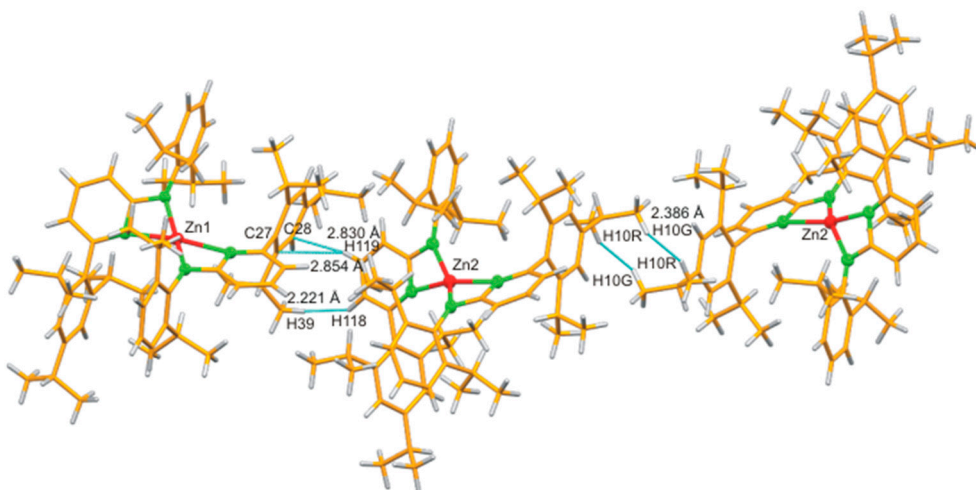


Figure 7. View of the intermolecular interactions in **4** shown as blue dotted lines. Color scheme: Zn = red; N = green; C = orange; and H = white.

The non-covalent intermolecular interactions in the crystal packings of **3** and **4** were further calculated using the CrystalExplorer 17.5 software that automatically modified the C-H bond lengths to 1.083 Å. The calculated Hirshfeld Surfaces have been visually depicted over d_{norm} ranging from -0.0505 to 1.5908 (Figures 8 and 9) [30]. The interactions between the donor and acceptor atoms with distances shorter or longer than or equal to the sum of the van der Waals radii are shown in red, blue and white colors, respectively, in the three dimensional figures [35]. In the two dimensional fingerprint plots d_i and d_e are the

separations between the closest atoms inside and outside the surface and the scale is shown as the default view (Figures 9 and 10).

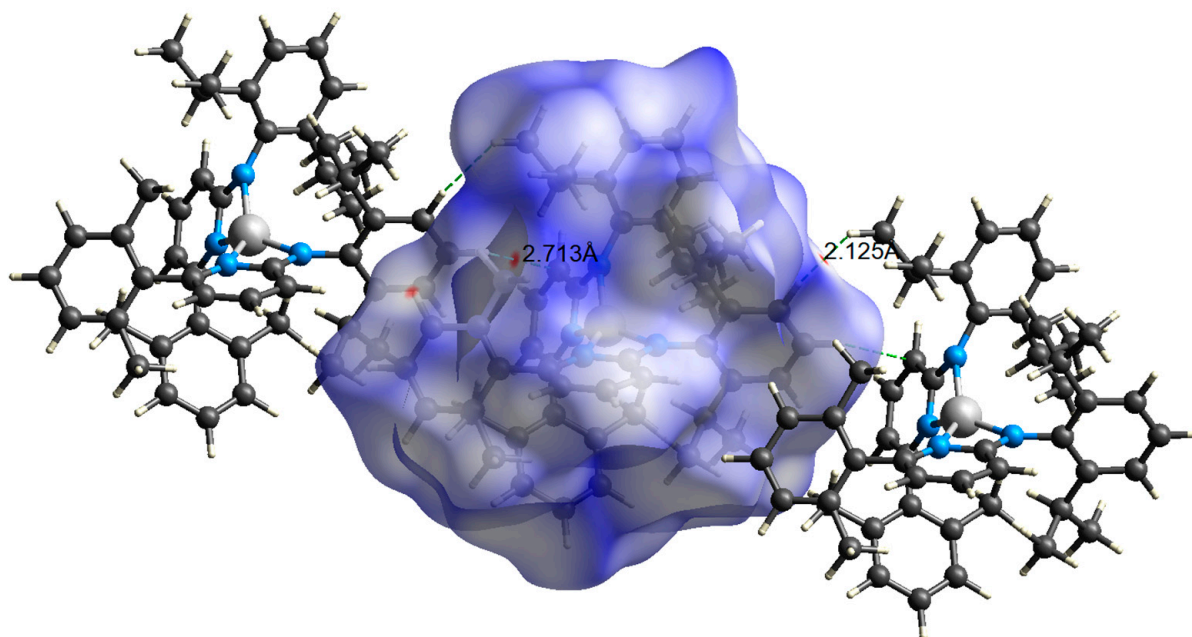


Figure 8. The three-dimensional view of the Hirshfeld surfaces of 3.

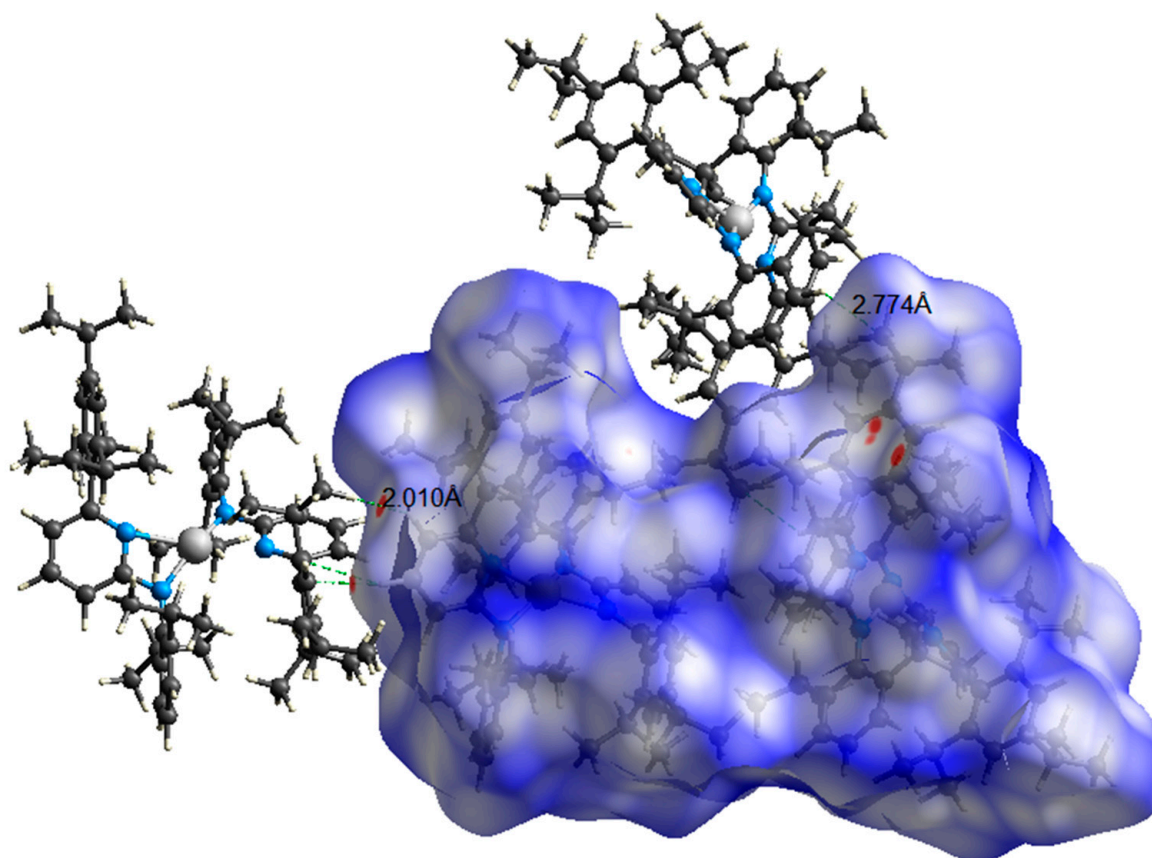


Figure 9. The three-dimensional view of the Hirshfeld surfaces of 4.

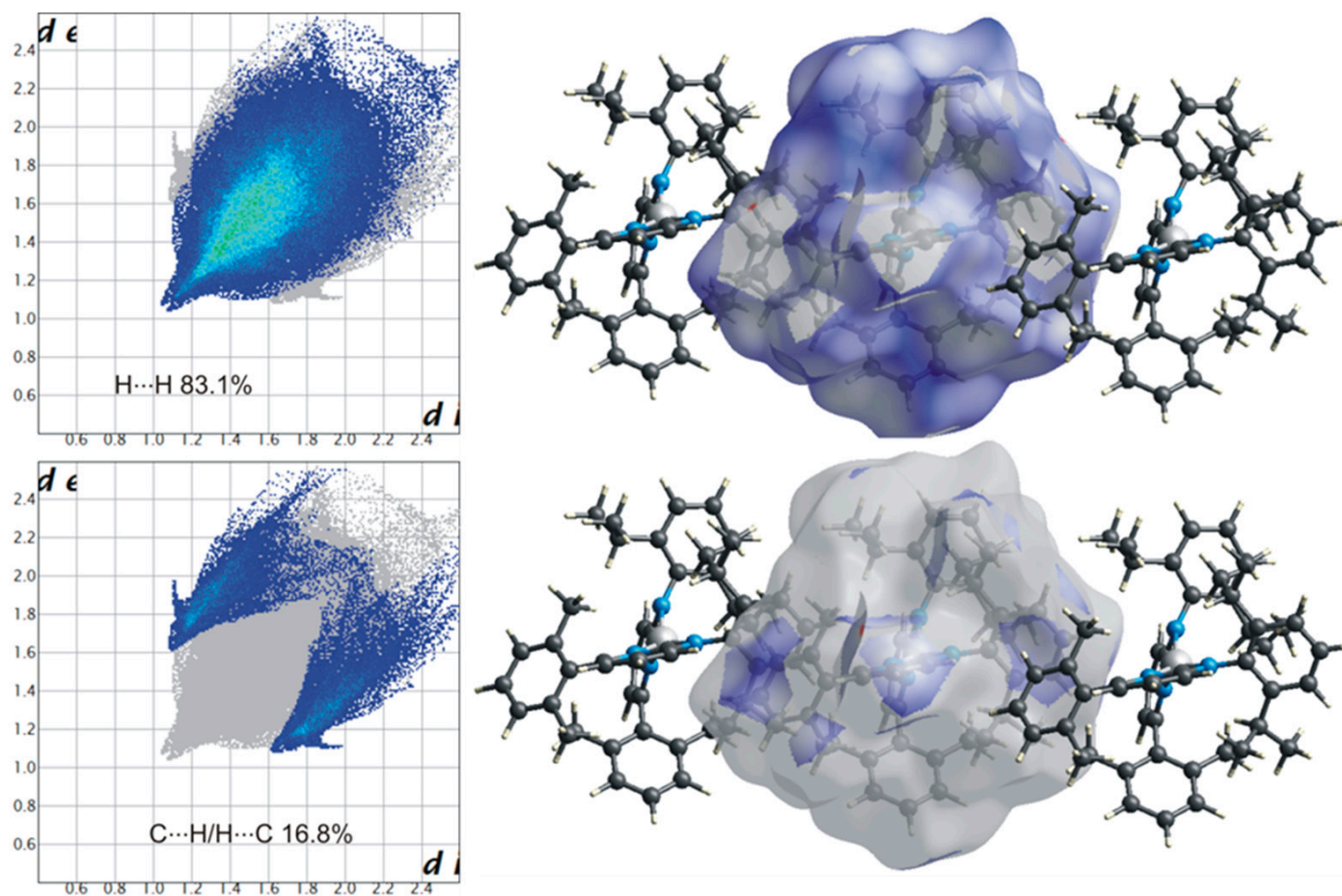


Figure 10. Two-dimensional fingerprint plots along with the specified percentage contribution for each intermolecular contact in **3**.

The shortest contacts that can be seen as red spots in **3** are the $\text{H} \cdots \text{H}$ between the H atoms of the isopropyl and aromatic ring of aniline (2.125 Å) and $\text{C-H} \cdots \pi$ -interactions (2.713 Å) between the aromatic rings of aniline and pyridine groups [Figure 8]. Such red spots in **4** are due to $\text{H} \cdots \text{H}$ contacts (2.010 Å) between isopropyl group and pyridine ring. The closest observed $\text{C-H} \cdots \pi$ -interactions (2.774 Å) in **4** are between the isopropyl group and aromatic ring of aniline [Figure 9].

The two-dimensional fingerprint plots clearly show that in both complexes the most significant contributions to the Hirshfeld surfaces are due to the $\text{H} \cdots \text{H}$ contacts, accounting for 83.1% and 93.1%. The endpoints indicating the origin and fitting to $d_e = d_i$ clearly show that the minimum $\text{H} \cdots \text{H}$ contacts in **4** ($\cong 1.0$ Å) are comprehensively shorter than in **3** ($\cong 1.15$ Å) (Figures 10 and 11). Other dominant contacts that appear as symmetric pair of wings are due $\text{H} \cdots \text{C}/\text{C} \cdots \text{H}$ π -interactions (16.8% and 6.6%, respectively) with nearly identical contact distances [$d_e + d_i \cong 3.2$ Å (**3**) 3.3 Å (**4**)]. The $\text{H} \cdots \text{H}$ interactions are more dominant in **4** than those in **3** and the $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ π -contacts in **3** are more than the twice of **4**.

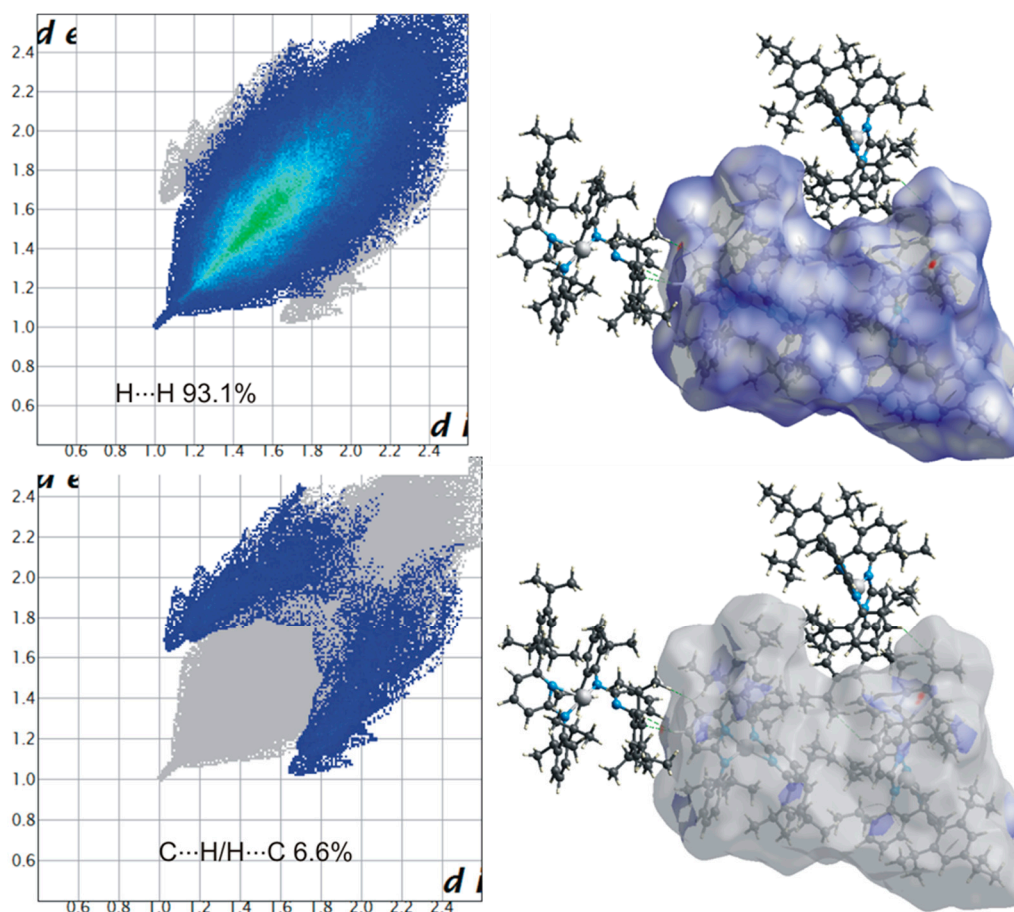


Figure 11. Two-dimensional fingerprint plots along with the specified percentage contribution for each intermolecular contact in **4**.

4. Conclusions

Applying appropriate steric bulk and stoichiometry first mononuclear Zn complexes of aminopyridinate ligands were synthesized adopting alkane as well as amine elimination routes. NMR studies show that bis(aminopyridinate) Zn complexes are the selective products. Steric consequences are attributed to the *cisoid* or *transoid* arrangement as well as the non-bridging κ^2 -coordination of the two ligands in these rare examples of homoleptic complexes. Hirshfeld surface analyses show that intermolecular $H \cdots H$ contacts and $H \cdots C/C \cdots H$ π -interactions dominate the crystal packing.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst15090821/s1>, NMR spectra (Figures S1–S4) and Supplementary crystallographic data can be obtained online free of charge via <https://www.ccdc.cam.ac.uk/structures> (accessed on 9 August 2025).

Author Contributions: Conceptualization, A.N.; methodology, A.N. and S.Q.; software, A.N.; validation, A.N. and S.Q.; formal analysis, A.N. and S.Q.; investigation, A.N. and S.Q.; resources, A.N.; writing—A.N.; writing—review and editing, A.N. and S.Q.; visualization, A.N.; supervision, A.N.; project administration, A.N.; funding acquisition, A.N. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Deanship of Scientific Research, Vice Presidency for Graduate Studies and Scientific Research, King Faisal University, Saudi Arabia [Grant No. KFU252850].

Data Availability Statement: Supplementary crystallographic data can be obtained online free of charge via <https://www.ccdc.cam.ac.uk/structures> (accessed on 9 August 2025).

Acknowledgments: We acknowledge the unconditional and sincere support of Rhett Kempe, Inorganic Chemistry II—Catalyst Design, Sustainable Chemistry Centre, University of Bayreuth, to access the research facilities and Andre Dickert for re-refinement of the crystal data.

Conflicts of Interest: The authors declare no conflicts of interest.

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