Synthesis, Structural Characterization, Hirshfeld Surface Analysis, and Antibacterial Study of Pd(II) and Ni(II) Schiff Base Complexes Derived from Aliphatic Diamine

Nur Husnina Nasaruddin, Shahrul Nizam Ahmad,* Siti Syaida Sirat, Kong Wai Tan, Nurul Aili Zakaria, Siti Sarra Mohamad Nazam, Nor Mas Mira Abd Rahman, Nor Saadah Mohd Yusof, and Hadariah Bahron

ABSTRACT: A Schiff base bearing two methyl substituents, namely, 6,6′-(((1E,1′E)-((2,2-dimethylpropane-1,3-diyl) bis(azanylylidene)) bis(methanylylidene)) bis(2-methylphenol) [H₂AD1Me] was synthesized and characterized through physico-chemical and spectroscopic analyses. Then, the Schiff base was complexed with Pd(II) and Ni(II) to form [Pd(AD1Me)] and [Ni(AD1Me)], respectively. Both metal complexes were successfully obtained and characterized through several analyses, viz., melting point, elemental analysis, molar conductivity, magnetic susceptibility, FTIR, ¹H NMR, UV−vis, and single crystal X-ray diffraction. A quantitative analysis of the intermolecular interactions in the crystal structures has been performed using Hirshfeld surface analysis. Both metal complexes were crystallized in a monoclinic crystal system with the space group of P2₁/c. Additionally, the deprotonated phenolic oxygen atom (O1/O2) and azomethine nitrogen atom (N1/N2) of the ligand chelate the Pd(II) and Ni(II) ions, forming a slightly distorted square-planar complex containing three six-membered rings encircling the metal core with dsp³ hybridization. The shift of ν(C=ðN) to a higher frequency in FTIR by 26−28 cm⁻¹ indicated that the complexation to Pd(II) and Ni(II) through the azomethine N was established. It was further supported through the shifting of the azomethine proton signal to higher or lower chemical shifts with δ = 1.15 ppm in ¹H NMR. In addition, the shifting of the n−π* (C=ðN) band in UV−vis spectra with Δλ = 24−40 nm indicated the involvement of azomethine nitrogen in the complexation. All the compounds showed no significant antibacterial activity against three bacterial strains, namely, Staphylococcus aureus subsp. aureus Rosenbach (ATCC 6538), Streptococcus mutans Clarke (ATCC 700,610), and Proteus vulgaris (ATCC 6380), as the percent growth inhibition calculated was less than 90%.

1. INTRODUCTION

A condensation of primary amine and aldehyde or ketone in a specific solvent can easily produce a compound named a Schiff base.¹ Structurally, the carbonyl group (C=ðO) of the aldehyde or ketone is replaced by an imine or azomethine group.² To form metal complexes, the Schiff base ligand is added to a metal precursor in an appropriate ratio, along with suitable experimental conditions.³ Commonly, the multi-dentate Schiff bases coordinate to metals through the imine nitrogen and another nitrogen or oxygen atom from a proper functional group from its neighborhood.⁴ Due to their fascinating physical and chemical properties, Schiff base complexes that have synthetic sensitivity, selectivity, and flexibility have become important compounds in coordination chemistry.⁵

A Schiff base is a versatile pharmacophore that can be used for drug discovery and drug design. They play key roles in industrial, herbicidal, anticancer, antifungal, and antibacterial applications, especially when complexed with transition metals.⁶ ONNO tetradeinate Schiff bases have been widely prepared as supportive ligands in the coordination chemistry of d-block elements, as the compounds stabilize metal ions in various oxidation states.⁷ Palladium(II) and nickel(II) Schiff base complexes have been known for their biological potential in the treatment of various diseases.⁸−¹⁰ According to Kargar et al. (2022), the Ni(II) complex has found to be a good inhibitor for S. aureus, where the inhibition performance of the Ni(II) complex is as good as the antibiotic Erythromycin against Gram-positive bacterial strains.⁹ Besides, the Pd(II) Schiff base complex exhibited a slight activity against Gram-negative...
bacteria *P. aeruginosa* (ATCC 10145) and *S. sonnei* (ATCC 25931). Schiff bases with hydroxyl and azomethine chromophores tend to have hydrogen bonding with active centers of cells of the cell membrane, resulting in higher permeability. Based on antibacterial result reported by Kargar et al. (2022) and Rosnizam et al. (2022), both metal complexes were generally observed to be more pronounced than their parent ligands against the tested bacterial strains. The antibacterial activities of the metal complexes against various kinds of Gram-positive and Gram-negative bacterial strains are enhanced owing to the chelation process. This can be achieved through the delocalization of the π-electron density and sharing some of positive charges of the metals with the donor atoms. Additionally, the increased solubility, dipole moment, cell permeability, and enzymatic action of the complexes would be expected to result in their increased biological activity. The increased level of toxicity at the cell surface and the structural specificity of the metal complexes may damage biomolecules inside the cell or on the cell surface. This shows the synergistic relationship between metal and ligands in microbial growth inhibition.

The Hirshfeld surface analysis was developed in an attempt to categorize the space that a molecule occupies within a crystal in order to divide the crystal electron density into molecular fragments. Moreover, Hirshfeld surface studies are significant for understanding the interactions between molecules in a crystal structure, helping in the design and development of new materials. The noncovalent interactions that are vital when describing the assembling of the molecules into a single crystal can also be revealed through Hirshfeld surface analysis. Therefore, the preparation of new Schiff bases and their metal complexes along with computational exploration is a significant research endeavor.

We report the synthesis and characterization of a Schiff base, H₂AD1Me, and its palladium(II) complex, [Pd(AD1Me)] and nickel(II) complex, [Ni(AD1Me)] (Scheme 1). The molecular structures of all compounds were elucidated through elemental analysis, magnetic susceptibility, molar conductivity, FTIR, 'H NMR, UV–vis analysis, and single crystal X-ray diffraction. Hirshfeld surface analysis and preliminary results of antibacterial studies of the synthesized compounds are also reported herein.

### 2. RESULTS AND DISCUSSION

#### 2.1. Single Crystal X-ray Analysis

Orange and green crystals of [Pd(AD1Me)] and [Ni(AD1Me)] were obtained through slow evaporation from acetonitrile at room temperature. The crystal structures of [Pd(AD1Me)] and [Ni(AD1Me)] with assigned atom-numbering schemes are shown in Figure 1(a) and (b), respectively. Both metal complexes were crystallized in a monoclinic crystal system with the space group of *P*2₁/c. The crystal data and structure refinement parameters of [Pd(AD1Me)] and [Ni(AD1Me)] are tabulated in Table 1.

The presence of Schiff base at [Pd(AD1Me)] was confirmed by C=N bond lengths of 1.295 (13) and 1.296 (12) Å of C7–N1 and C13–N2, respectively. On the other hand, in the case of [Ni(AD1Me)], the formation of a Schiff base was confirmed by C7–N1 and C13–N2 bonds with bond lengths of 1.293 (6) and 1.275 (8) Å, respectively. The value is in agreement with the previously reported analogous Pd(II) complex.

![Scheme 1. Synthesis of H₂AD1Me, [Pd(AD1Me)], and [Ni(AD1Me)]](https://example.com/scheme1.png)

![Figure 1. Crystal structures of (a) [Pd(AD1Me)] and (b) [Ni(AD1Me)] with the atom numbering scheme drawn at 50% probability ellipsoid level.](https://example.com/fig1.png)
Table 1. Crystallographic Data Summary for [Pd(AD1Me)] and [Ni(AD1Me)]

| Compound                        | [Pd(AD1Me)]                  | [Ni(AD1Me)]                  |
|---------------------------------|------------------------------|------------------------------|
| CCDC number                     | 2182057                      | 2182056                      |
| Empirical formula               | C_{11}H_{10}N_{2}O_{2}Pd     | C_{11}H_{10}N_{2}O_{2}Ni     |
| Formula weight                  | 442.82                       | 395.13                       |
| Temperature/K                   | 298                          | 293(2)                       |
| Crystal system                  | Monoclinic                   | Monoclinic                   |
| Space group                     | P2_1/c                       | P2_1/c                       |
| a/Å                             | 10.4388(13)                  | 9.6754(4)                    |
| b/Å                             | 15.5627(11)                  | 17.4279(7)                   |
| c/Å                             | 12.1489(8)                   | 11.3622(4)                   |
| α/°                             | 90                           | 90                           |
| β/°                             | 171.60(5)                    | 92.30(3)                     |
| γ/°                             | 97.818(4)                    | 98.184(4)                    |
| Volume/Å³                       | 1938.1(3)                    | 1898.10(14)                  |
| Z                               | 4                            | 4                            |
| ρ_{calc}/g/cm³                  | 1.518                        | 1.383                        |
| μ/mm⁻¹                          | 0.974                        | 1.039                        |
| F(000)                          | 904.0                        | 832.0                        |
| Crystal size/mm³                | 0.5 × 0.5 × 0.5              | 0.2 × 0.2 × 0.2              |
| Radiation                       | MoKα (λ = 0.71073)           | MoKα (λ = 0.71073)           |
| θ range for data collection/°   | 6.682 to 59.474              | 6.99 to 54.988               |
| Index ranges                    | −13/14, −20/21, −11/16       | −12/10, −19/22, −11/14       |
| Reflections collected           | 8442                         | 8009                         |
| Independent reflections         | 4656                         | 4258                         |
| Data/restraints/parameters      | 4656/234/239                 | 4258/234/239                 |
| Goodness-of-fit on F²           | 1.059                        | 1.041                        |
| Final R indexes [1 ≥ 2σ (I)]    | R1 = 0.0756, wR2 = 0.1757    | R1 = 0.0720, wR2 = 0.2085    |
| Final R indexes [all data]      | R1 = 0.1273, wR2 = 0.2234    | R1 = 0.0960, wR2 = 0.2370    |
| Largest diff. peak/hole/e Å⁻³   | 0.75/−0.99                   | 1.690/−0.814                 |

Based on Figure 1, Pd(II) and Ni(II) ions are chelated via the deprotonated phenolic oxygen atom (O1/O2) and azomethine nitrogen atom (N1/N2) of the ligand, forming a slightly distorted square-planar complex, resulting in three six-membered rings encircling the metal core. In [Pd(AD1Me)], the O1−Pd1−O2, O1−Pd1−N1, N1−Pd1−N2, and O1−Pd1−N2 bond angles are 79.3(3)°, 92.9(3)°, 95.5(3)°, and 171.6(3)°, respectively. The Pd1−N1, Pd1−N2, Pd1−O1, and Pd1−O2 bond lengths are 1.998(6), 2.000(8), 1.977(7), and 1.987(5) Å, respectively. The bond angle and bond length are in close agreement with the previously reported complexes.16,17

Meanwhile, in the coordination sphere of Ni(II), Ni−N and Ni−O bond lengths range from 1.869(5) to 1.884(4) Å and 1.830(4) to 1.844(4) Å, respectively, whereas bond angles range from 82.03(16)° to 165.98(19)°. It shows that the Ni−O bond is slightly longer than Ni−O which indicates strong interactions between O and Ni.18 The bond lengths and bond angles are in good agreement with the previously reported Ni(II) complexes with the ONNO Schiff base ligand.19 In addition, the bond lengths of Ni–O and Ni–N are slightly shorter than the Pd–O and Pd–N bonds, reflecting the greater bond strength of the former. In the [Pd(AD1Me)] complex, only C−H−O weak hydrogen bonds are stabilizing the structure; no hydrogen bond interaction appeared in [Ni(AD1Me)] (Table 3).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of [Pd(AD1Me)] and [Ni(AD1Me)]

| Bond lengths (Å) Bond angles (deg) |
|-----------------------------------|-----------------------------------|
| Pd1−O1                            | Ni1−O1                            |
| 1.977(7)                           | 1.830(4)                           |
| Pd1−O2                            | Ni1−O2                            |
| 1.987(5)                           | 1.844(4)                           |
| Pd1−N1                            | Ni1−N1                            |
| 1.998(6)                           | 1.884(4)                           |
| Pd1−N2                            | Ni1−N2                            |
| 2.000(8)                           | 1.869(5)                           |
| O1−C1                             | O1−C1                             |
| 1.285(12)                          | 1.315(6)                           |
| O2−C1                             | O2−C1                             |
| 1.312(12)                          | 1.306(6)                           |
| N1−C7                             | N1−C7                             |
| 1.295(13)                          | 1.296(13)                          |
| N1−C8                             | N1−C8                             |
| 1.476(10)                          | 1.463(7)                           |
| N2−C12                            | N2−C12                            |
| 1.486(11)                          | 1.568(10)                          |
| N2−C15                            | N2−C15                            |
| 1.296(12)                          | 1.275(8)                           |

Table 3. Hydrogen Bond Interactions

| Bond | Bond length (Å) | Bond angle (deg) |
|------|-----------------|-----------------|
| D−H−A| H8B−O2          | 0.97            |
| D−H−A| C8−H20A          | 0.96            |

From the largest angle values stated in Table 2, the structural parameter τ value can be calculated to determine the geometry of the complexes for four-coordinated compounds; the possible geometry could be either tetrahedral or square planar. The formula to calculate the τ value is τ = [(360° − (α + β))/141°], where the α and β represent the largest angles around the metal center.20 The perfect tetrahedron and square planar geometries are represented by the τ value of 0 and 1, respectively.20 For this study, the calculated value of τ for both Pd(II) and Ni(II) complexes is 0.116 and 0.211, respectively. The results show that both complexes have a distorted square planar geometry with dsp² hybridization,11 which is consistent with the diamagnetic property revealed through the magnetic susceptibility measurement.

The packing diagram for [Pd(AD1Me)] is shown in Figure 2. The molecules are stabilized by van der Waals interaction leading to the formation of a linear chain along the a-axis. The packing diagram for [Ni(AD1Me)] is shown in Figure 3. The molecules are stabilized by van der Waals interaction leading to the formation of a herringbone motif when viewed along the c-axis.

2.2. Physicochemical and Spectroscopic Characterization. A sticky yellow liquid, H₂AD1Me, was obtained through a conventional synthesis of a 2:1 molar ratio mixture of 3-methylsalicylaldehyde with 2,2-dimethyl-1,3-propanediamine. The Schiff base was then reacted with metal acetyl salt to form Pd(II) and Ni(II) complexes. Both metal complexes
afforded a medium to high yield which is 66% and 74% for [Ni(AD1Me)] and [Pd(AD1Me)], respectively. According to the elemental analysis of C, H, and N for both complexes, the experimental values were in accordance with the calculated values of the proposed structure (Table 4). Besides, the low molar conductivity values of 1 × 10⁻³ M Pd(II) and Ni(II) complexes in MeCN, 2 and 0 Ω⁻¹ cm² mol⁻¹, respectively, indicated their nonelectrolytic nature, with the absence of any counterions. 21,22 The diamagnetic properties of both metal complexes as indicated through magnetic susceptibility values suggested their square planar geometry.

All compounds are reported to have a high percent of atom economy in the range of 67.28–90.38%, suggesting that most of the starting materials or reactants were effectively used with minimum waste produced (Table 5). The concept of atom economy can be used to define new pollution prevention benchmarks and can be applied to any synthesis as it measures the greenness of the chemical reaction.23

Table 5. Percent Atom Economy of H₂AD1Me, [Pd(AD1Me)], and [Ni(AD1Me)]

| Compounds    | Chemical formula | Mass of atoms in reactants | Mass of atoms of products | % Atom economy |
|--------------|------------------|----------------------------|---------------------------|---------------|
| H₂AD1Me      | C₂₁H₂₂N₂O₂       | 734.48 g/mol               | 338.44 g/mol              | 90.38%        |
| [Pd(AD1Me)]  | C₂₁H₂₂N₂O₂Pd     | 562.94 g/mol               | 442.85 g/mol              | 78.67%        |
| [Ni(AD1Me)]  | C₂₁H₂₄N₂O₂Ni     | 587.28 g/mol               | 395.12 g/mol              | 67.28%        |

The significant FTIR data of H₂AD1Me, [Pd(AD1Me)], and [Ni(AD1Me)] are listed in Table 6. The IR spectrum of

Table 6. IR Data of H₂AD1Me, [Pd(AD1Me)], and [Ni(AD1Me)]

| Compound     | ν(C=N) (s) | ν(C−N) (m) | ν(C=O) (phenol) | ν(M−N) (w) | ν(M−O) (w) |
|--------------|------------|------------|-----------------|------------|------------|
| H₂AD1Me      | 1636 (s)   | 1338 (m)   | 1273 (s)        | -          | -          |
| [Pd(AD1Me)]  | 1608 (s)   | 1331 (m)   | 1227 (s)        | 568 (w)    | 473 (w)    |
| [Ni(AD1Me)]  | 1610 (s)   | 1325 (m)   | 1234 (s)        | 545 (w)    | 466 (w)    |

“Note: br - broad; s - strong; m - medium; w - weak.

the ligand H₂AD1Me exhibited a strong band at 1636 cm⁻¹ assignable to the azomethine ν(C=N) group.24,25 Upon complexation, the ν(C=N) and ν(C−N) shifted to lower frequencies by of 26–28 cm⁻¹ and 7–13 cm⁻¹, respectively, a strong indicator that imine nitrogen is involved in coordination with metal ions.3 This was also supported by the appearance of new peaks of 568 and 545 cm⁻¹ assignable to ν(Pd=N) and ν(Ni−N), respectively.1,26 Meanwhile, the absence of ν(OH) indicated the coordination of phenolic oxygen to the metal center. The shifting of ν(C=O) to a lower frequency and the appearance of new peak ν(M−O) in the IR spectra of both metal complexes reinforce the participation of the phenolic oxygen in the complexation. The appearance of new peaks ν(Pd−O) and ν(Ni−O) at 473 and 466 cm⁻¹, respectively, are in agreement with the previously reported values.

Based on the ¹H NMR spectrum of H₂AD1Me, the phenolic and azomethine protons were observed at 13.79 and 8.33 ppm, respectively. Upon complexation, the peak of the phenolic proton was absent in both spectra of the complexes suggesting the deprotonation of the phenolic proton.27,28 Another key piece of evidence of the complexation of ligands with metals is the slight upfield and downfield shifts of signals of azomethine protons at 7.90 and 9.48 ppm for [Pd(AD1Me)] and [Ni(AD1Me)], respectively, denoting a significant shielding.

Afforded a medium to high yield which is 66% and 74% for [Ni(AD1Me)] and [Pd(AD1Me)], respectively. According to the elemental analysis of C, H, and N for both complexes, the experimental values were in accordance with the calculated values of the proposed structure (Table 4). Besides, the low molar conductivity values of 1 × 10⁻³ M Pd(II) and Ni(II) complexes in MeCN, 2 and 0 Ω⁻¹ cm² mol⁻¹, respectively, indicated their nonelectrolytic nature, with the absence of any counterions. 21,22 The diamagnetic properties of both metal complexes as indicated through magnetic susceptibility values suggested their square planar geometry.

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and deshielding effect. This shifting was previously observed by Gondia and Sharma (2018). As a result, the binding sites available for coordination with palladium and nickel are phenolic oxygen and azomethine nitrogen. The methyl protons signal was seen at 2.29 ppm in the spectrum of H$_2$AD1Me which corresponds to the previously reported value. The signal was experiencing some shifting upon the complexation to the metal center.

The UV–vis spectroscopy data and spectra of the free ligand and its Pd(II) and Ni(II) complexes are shown in Table 7 and Figure 4, respectively. The electronic transitions in H$_2$AD1Me and its Pd(II) and Ni(II) complexes are shown in Table 7 and Figure 4, respectively. The electronic transitions in H$_2$AD1Me resulted in three main characteristic absorption bands, i.e., π−π*(C=C), π−π*(C=N), and n−π*(C=C=N). The π−π*(C=C) band of ligand was observed at 219 nm, and the band shifted to higher wavelengths in the complexes, appearing at 242 and 248 nm for Pd(II) and Ni(II) complexes, respectively. Besides, the π−π*(C=N) band at 261 nm underwent a bathochromic shift, appearing at 287 and 266 nm. The n−π* transitions of imine of the complexes shifted to a higher wavelength, possibly due to the coordination of the nitrogen atom of the imine group to the metal ion. The fact that these three bands have shifted to longer wavelengths corroborated the complexation of the ligand and the metal center. The presence of a new peak at 421 nm in the Ni(II) complex spectrum is assigned as a d−d band of square planar, and it is in agreement with the geometry reported in the single crystal XRD section. These findings are consistent with the IR and $^1$H NMR data as previously discussed.

### 2.3. Hirshfeld Surface Analysis

Hirshfeld surface analysis was performed to visualize and quantify the differences and the similarities of intermolecular contacts across the crystal structures of [Pd(AD1Me)] and [Ni(AD1Me)]. The Hirshfeld surface analysis provides significant information on the quantitative ratios of atom–atom short contacts with the potential to form weak hydrogen bond intermolecular interactions and the locations of these interactions. Figure 5 displays surfaces which have been mapped over $d_{norm}$ for [Pd(AD1Me)] and [Ni(AD1Me)]. The dark red spots on the $d_{norm}$ of [Pd(AD1Me)] indicate the presence of C8–H8B···O2 interactions, while there is no strong hydrogen bond interaction presented for [Ni(AD1Me)] as stated in Table 8. The other interactions observed for both complexes appeared as smaller bright red spots indicating weaker and longer contacts on the Hirshfeld surfaces mapped on the $d_{norm}$. The 2D fingerprint plots for [Pd(AD1Me)] and [Ni(AD1Me)] are shown in Figure 6 demonstrated that H···H contacts are the largest contribution to the total Hirshfeld surface. These account for 63.4% ([Pd(AD1Me)]) and 63% ([Ni(AD1Me)]) at the range of $d_e + d_i \approx 2.2$ and 2.0 Å, respectively. Probably,

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**Table 7. $^1$H NMR Data of H$_2$AD1Me, [Pd(AD1Me)], and [Ni(AD1Me)]**

| Compounds     | C$^2$−OH | HC$^2$=N | C$^2$−H (Ar) | C$^3$−H (Ar) | C$^3$−H (Ar) | N−C$^3$H$_2$ | C$^3$−H$_3$ | Ar−CH$_3$ |
|---------------|----------|----------|-------------|-------------|-------------|-------------|-------------|-----------|
| H$_2$AD1Me    | 13.79 (s, 2H) | 8.33 (s, 2H) | 7.11 (d, 2H) | 6.80 (t, 2H) | 7.19 (d, 2H) | 3.50 (s, 4H) | 1.09 (s, 6H) | 2.29 (s, 6H) |
| [Pd(AD1Me)]  | –        | 7.90 (s, 2H) | 7.15 (m, 2H) | 6.43 (dd, 2H, 6.92, 7.92 Hz) | 7.15 (m, 2H) | N.D. | 1.00 (s, 6H) | 2.14 (s, 6H) |
| [Ni(AD1Me)]  | –        | 9.48 (s, 2H) | 7.15 (d, 2H) | 6.30 (t, 2H) | 8.11 (d, 2H) | N.D. | 1.21 (s, 6H) | 2.32 (s, 6H) |

*Note: s - singlet; d - doublet; t - triplet; dt - doublet of triplet; dd - doublet of doublet; m - multiplet.*

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**Figure 4. UV–vis spectra of H$_2$AD1Me and its metal complexes.**

**Figure 5. Hirshfeld surfaces mapped with $d_{norm}$ for (a) [Pd(AD1Me)] and (b) [Ni(AD1Me)].**
the large hydrogen content on both complexes contributed to these interactions and is the result of attractive dispersion forces. The second large contribution is the C⋯H/H⋯C contacts presented as a pair of Batman masks with the tips at $d_e + d_i \approx 3.2 \text{ Å}$ for both complexes. The contribution of the O⋯H/H⋯O contacts appear as a diffuse shape for both complexes with $d_e + d_i \approx 2.8 \text{ Å}$. The C⋯C contacts show an inferior contribution for [Pd(AD1Me)] and [Ni(AD1Me)] with 2.2% and 2.4%, respectively. The others weak contacts (Pd⋯H/H⋯Pd, Ni⋯H/H⋯Ni) are identified with a minor density of scattered points in 2D fingerprint plots. The presence of these contacts provides further stabilization in crystal structures of [Pd(AD1Me)] and [Ni(AD1Me)].

2.4. Antibacterial Study. The antibacterial activity screening test was conducted according to previously reported procedure. Both metal complexes and their parent ligand were screened against two Gram-positive bacteria, *Staphylococcus aureus* subsp. *aureus* Rosenbach (ATCC 6538) and *Streptococcus mutans* Clarke (ATCC 700,610) and a Gram-negative bacterium, *Proteus vulgaris* (ATCC 6380). The percent growth inhibition is tabulated in Table 9. The assay’s
validity was demonstrated by the strains’ susceptibility to ampicillin antibiotics, and DMSO was used as a control.

Table 9. Antibacterial Screening of H$_2$AD1Me and Its Metal Complexes Express in % Growth Inhibition$^a$

| Test bacteria/compound | % Growth inhibition |
|------------------------|---------------------|
|                        | H$_2$AD1Me [Pd(AD1Me)] [Ni(AD1Me)] |
| Staphylococcus aureus subs. aureus Rosenbach (ATCC 6538) | −30.33 22.83 −6.38 |
| Streptococcus mutans Clarke (ATCC 700,610) | −30.33 53.12 −35.46 |
| Proteus vulgaris (ATCC 6380) | −29.45 10.06 30.47 |

$^a$Note: Std. drug: Ampicillin (100 μM), with >99.35% growth inhibition; Negative control: Untreated bacteria; Solvent control: <1% of DMSO; Sterility control: Mueller Hinton Broth; Positive inhibition/Active >90% growth inhibition.

The parent ligand, H$_2$AD1Me was having a negative value of % growth inhibition in both Gram-positive and Gram-negative bacteria. However, a positive value of percent growth inhibition was observed for [Pd(AD1Me)] against all three bacteria strains and [Ni(AD1Me)] against Proteus vulgaris. The negative value indicated the non-antibacterial properties of the compounds. Although the [Pd(AD1Me)] showed a positive value of percent growth inhibition against all bacteria strains, the compound is still considered a negative inhibitor. The incremental value of % growth inhibition can be observed when metal complexes have been screened against all bacteria strains except for [Ni(AD1Me)] against the Streptococcus mutans Clarke (ATCC 700,610). In this result, it shows that the Pd(II) complex has a good potential as bacterial inhibitor compared to its ligand, H$_2$AD1Me.

In previous study, Kargar et al. (2021) and PrabhuKumar et al. (2022) have reported that the Ni(II) and Pd(II) Schiff base complexes showed a slight increase in the antibacterial activity over the free ligand. The enhancement in the activities against bacterial pathogens can be assumed based on Overtone’s concept and Tweedy’s chelation theory.$^{12,35}$ The decrease in the number of active bacterial cells on the treatment with these compounds could be attributed based on cell permeability and lipophilicity. The lipophilic character of the metal chelate is increased as the chelation reduced the polarity of the metal ions. Hence, the permeation become more efficient through the lipid layer of the microorganism, destroying them more forcefully.$^{12}$

In this research work, the absence of interactions between the molecule and the pathogen-specific protein in the bacteria rendered the compound incapable of inhibiting the tested microbial strains. Although the precise mechanism is not understood, the antibacterial properties exerted by the compounds may be influenced by the hetero atoms. In addition, the free groups from ligand could increase the lipophilicity of the compounds, thereby facilitating their permeation through the lipid bilayer of the microorganisms more efficiently, resulting in complexes with pronounced biological activity.$^{36}$ Comparatively, [Pd(AD1Me)] and [Ni(AD1Me)] studied possessed no uncoordinated donor atoms, which may have contributed to their inability to inhibit the bacterial growth. However, the mode of action of palladium ions and nickel ions is not fully clear. The complex formation of these ions with cellular components and the oxidation state of the compounds can also likely be the fundamental role.$^{37}$ Further investigation is required to understand the mechanism involved.

3. CONCLUSIONS

The new tetradentate Schiff base and its Pd(II) and Ni(II) complexes have been prepared via condensation reaction. The formation of the Schiff base and its metal complexes was verified through the physicochemical and spectroscopic analysis. The shifting of significant peaks in FTIR, $^1$H NMR, and UV–vis indicated that the complexation had taken place through the deprotonation of phenolic proton and shifting of azomethine nitrogen. Based on single-crystal X-ray diffraction, it can be concluded that the ligand coordinated to Pd(II) and Ni(II) ions through ONNO donor atoms and the [Pd(AD1Me)] and [Ni(AD1Me)] adopted distorted square planar geometry. The Hirshfeld surface analysis revealed H···H contacts in the crystal structure of [Pd(AD1Me)] and [Ni(AD1Me)], contributing to their stability. The closest interactions between Pd(II) complex units are H···H (63.4%), C···H (22.7%), and O···H (8.1%). Meanwhile, those for the Ni(II) complex are H···H (63.0%), C···H (23.2%), and O···H (7.4%). Although the [Pd(AD1Me)] showed a positive value of percent growth inhibition against all bacteria strains compared to the ligand and [Ni(AD1Me)], the compound is still considered a negative inhibitor likely owing to the absence of interactions between the molecule and the pathogen-specific protein in the bacteria.

4. EXPERIMENTAL SECTION

4.1. Materials and Instrumentation. Chemicals and solvents used in this work were 2,2-dimethyl-1,3-propanedi-amine (DMPD), 3-methylsalicylaldehye, palladium (II) acetate, nickel(II) acetate tetrahydrate, acetonitrile, and ethanol. All chemicals and reagents used in the synthesis were of analytical grade and procured from Sigma-Aldrich and Merck. The solvents for the synthesis of ligands and complexes were used without further purification. All glassware was washed, rinsed with acetone, and dried in a 50 °C drying cabinet before use.

The melting points of the synthesized compounds were determined using a Buchi Melting Point M-560 apparatus. The elemental analysis (CHN) was carried out using a Thermo Scientific Flash 2000 Elemental Analyzer. The chemical structures of Schiff base and Pd(II) and Ni(II) complexes were characterized through FTIR, $^1$H NMR, and UV–vis spectroscopic analyses. FTIR spectra were recorded in the 400–4000 cm$^{-1}$ range, using a PerkinElmer Spectrum One FTIR spectrometer with samples prepared using the standard KBr pellet technique. The proton NMR spectra of the Schiff base and metal complexes were recorded in CDCl$_3$ and DMSO-$d_6$, respectively, using TMS as the internal standard, on a Bruker Varian-300 MHz NMR spectrometer ($^1$H NMR). Electronic absorption spectra were recorded at room temperature on a PerkinElmer UV–vis Lambda 35 spectrophotometer, in the range of 200 to 700 nm, using 1 $\times$ 10$^{-4}$ M acetonitrile (MeCN) solution in a quartz cell. The molar conductivity of the 1 $\times$ 10$^{-3}$ M metal complexes solution was measured using a Mettler Toledo Inlab 730 conductivity meter. The magnetic susceptibility reading of the metal complexes was measured using Sherwood Auto magnetic susceptibility balance.
4.2. Synthesis of Schiff Base and Metal Complexes.
4.2.1. Synthesis of 6,6′-[(1E,1′E)-((2,2-Dimethylpropane-1,3-diyl) bis(azanylylidene)) bis(methanylylidene)) bis(2-methylphenol) \([H_2AD1Me]\), 0.1025 g (1 mmol) of 2,2-dimethyl-1,3-propanediamine dissolved in 10 mL ethanol was slowly added to 5 mL ethanolic solution containing 0.2729 g (2 mmol) 3-methylysalicylaldehyde with continuous stirring. After 2 h stirring, the reaction mixture was allowed to cool at room temperature. Since there was no precipitate formed, the solvent was reduced to half of its initial volume through rotatory evaporation. The mixture was chilled at 3 °C for 3 weeks. However, only the yellow sticky liquid was obtained. No yield was calculated.

4.2.2. Synthesis of \([Pd(AD1Me)]\). The metal complex was synthesized, with a metal-to-ligand ratio of 1:1, using the previously revealed method. 0.225 g (1 mmol) acetonitrile solution of \(Pd(CH_2COO)_2 \cdot 4H_2O\) was added into the liquid of \(H_2AD1Me\). The solution was refluxed for 4 h and then cooled to room temperature and chilled overnight. The yellow precipitate was filtered off, washed with cold MeCN, and air-dried. The orange cube single crystal of \([Pd(AD1Me)]\) was produced from recrystallization in a minimum amount of MeCN. Yield: 66%.

4.2.3. Synthesis of \([Ni(AD1Me)]\). 0.249 g (1 mmol) ethanolic solution of \(Ni(CH_2COO)_2 \cdot 4H_2O\) was added into the liquid of \(H_2AD1Me\). The solution was refluxed for 4 h and then cooled to room temperature and chilled overnight. The dark green precipitate was filtered off, washed with cold EtOH, and air-dried. Green cube single crystal \([Ni(AD1Me)]\) was produced from recrystallization in a minimum amount of EtOH. Yield: 74%.

4.3. X-ray Single-Crystal Crystallography. The intensity data and unit cell parameters of both suitable single crystals were collected on an Agilent Technologies SuperNova Dual diffractometer equipped with a MoKα X-ray source \(\left(\lambda = 0.71073 \text{ Å} \right)\). CrysAlisPro software was used for data acquisition, cell refinement data reduction, and absorption corrections on the data. The structures were solved with direct methods and refined with least-squares refinements by using SHELXL97. Material for publication was prepared using PUBLICIF and molecular graphics were drawn using Platon and Mercury 3.7. The crystallographic data for \([Pd(AD1Me)]\) and \([Ni(AD1Me)]\) can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+ 44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk.

4.4. Hirshfeld Surface Analysis. Hirshfeld surface analysis was performed by CrystalExplorer 17.5. The structural input file was obtained in CIF format. Hirshfeld surface distance from the nearest nucleus inside and outside the surface was measured and represented by \(d_s\) and \(d_i\), respectively. A normalized contact distance was represented as \(d_{\text{norm}}\).

4.5. Antibacterial Screening. The screening of antibacterial activity was carried out according to the procedure reported by Rosnizam et al. and tested against several selected bacterial strains: \(Staphylococcus aureus\) subsp. \(aureus\) Rosenbach (ATCC 6538), \(Streptococcus mutans\) Clarke (ATCC 700,610), and \(Proteus vulgaris\) (ATCC 6380). To reach a final concentration of 100 μM, 50 μL of adjusted inoculum (10⁶ CFU/mL) was transferred into the microtiter plate, followed by 50 μL of the tested compounds. A microtiter plate with sterile Mueller Hinton broth (MHB) in place of the inoculum was also prepared at the same time. This served as the blank control for the samples. Both microtiter plates were incubated for 24 h at 37 °C. Then, a microplate reader was used to take an absorbance reading at 600 nm after the incubation. The percentage of cell growth inhibition was then calculated. The results were compared to the standard drug (ampicillin), and a positive inhibition was defined as percent inhibition of more than 90%. All assays were carried out in three independent replicates. The minimum inhibitory concentration (MIC) was subsequently determined following a positive inhibition. MHB was used to make 2-fold dilutions of both the test compounds and the standard drug. The results were written down in μM.
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