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Synthesis, characterization, X-ray crystal structures and antibacterial activities of Schiff base ligands derived from allylamine and their Vanadium(IV), Cobalt(III), Nickel(II), Copper(II), Zinc(II) and Palladium(II) complexes

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Abstract

A new Schiff base ligand, HL^2 , and four new Schiff base complexes, NiL_2^1 , PdL_2^1 , NiL_2^2 and ZnL_2^2 , have been prepared and characterized by elemental analysis (CHN), FT-IR and UV-Vis spectroscopy. ¹H and ¹³C NMR techniques were employed for characterization of the ligand (HL^2) and the diamagnetic complexes (PdL_2^1 and ZnL_2^2). The molecular structures of PdL_2^1 , NiL_2^2 and ZnL_2^2 complexes were determined by the single crystal X-ray diffraction technique. The crystallographic data reveal that in these complexes the metal centers are four-coordinated by two phenolate oxygen and two imine nitrogen atoms of two Schiff base ligands. The geometry around the metal center in the PdL_2^1 and NiL_2^2 complexes is square-planar and for ZnL_2^2 it is a distorted tetrahedral.

In the end, five new (HL^2 , NiL_2^1 , PdL_2^1 , NiL_2^2 and ZnL_2^2) and six reported (HL^1 , VOL_2^1 , CoL_3^1 , CuL_2^1 , ZnL_2^1 and $Zn_2L_4^1$) Schiff base compounds were tested for their *in vitro* antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* as examples of Gram-positive and Gram-negative bacterial strains, respectively, by disc diffusion method.

Keywords: Schiff base, Crystal structure, Antibacterial activity

1. Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions [1-7]. The high stability potential of Schiff base complexes with different oxidation states extended the application of these compounds in a wide range.

The catalytic activity of Schiff base metal complexes has been analyzed critically in various reactions such as polymerization, oxidation, epoxidation, reduction of ketones, allylic alkylation and Michael addition reactions [4, 8-17].

Apart from the catalytic applications of Schiff base compounds, they are important class of compounds in medicinal and pharmaceutical fields. They show potential applications and properties such as anticancer, anticonvulsant, antitumor, antifungal, antibacterial, antitubercular, antioxidant, antimalarial, anti-inflammatory and anti-HIV activities [5, 18-28].

Although numerous Schiff base complexes with different structures have been synthesized and characterized, reports on Schiff base ligands and complexes derived from amines containing terminal allyl group are scanty [29, 30]. We have recently reported the synthesis and structural properties of a bidentate Schiff base ligand (**HL**¹) derived from salicylaldehyde and allylamine and its Vanadium(IV), Cobalt(III), Copper(II) and Zinc(II)) complexes [31]. Also, in another work, a new asymmetric Schiff base ligand derived from condensation of 2,3-dihydroxybenzaldehyde and allylamine and its Mo(VI) complex were prepared and characterized by single crystal X-ray analysis that showed special geometry called pseudo-scorpionate due to hydrogen interaction in terminal allyl group of the ligands [32-36]. In continuation of these studies, herein we report the synthesis, characterization and X-ray crystal structures of four new complexes, NiL¹₂, PdL¹₂, NiL²₂ and ZnL²₂, of the reported (**HL**¹) and new (bidentate Schiff base ligands (Schemes 1 and 2). In continuation, the antibacterial activities of Schiff base ligands, **HL**¹ and **HL**², and its mononuclear complexes, **VOL**¹₂, **CoL**¹₃, **CuL**¹₂, **ZnL**¹₂,

 NiL_{2}^{1} , PdL_{2}^{1} , NiL_{2}^{2} and ZnL_{2}^{2} , and also a related binuclear Zn(II) complex, $Zn_{2}L_{4}^{1}$, have been investigated for their *in vitro* antimicrobial activity against *Staphylococcus aureus* (ATCC 29737) and *Pseudomonas aeroginosa* (PTTC 1570) as examples of Gram-positive and Gram-negative bacterial strains, respectively, by disc diffusion method. The diffusion method is simple, yet is routinely used in hospital laboratories; it requires commercial disks, the medium used is Mueller-Hinton agar with 2% of glucose, and the diameter of the zone of inhibition is visually read 24 h after incubation at 37 °C. Antibacterial activity was estimated on the basis of the size of the zone of inhibition formed around the paper disks on the seeded agar plates.

2. Experimental section

2.1. Chemicals and instrumentation

All the chemicals were purchased from Merck Co. and used without further purification. The FT-IR spectrum was recorded on a JASCO, FT/IR-6300 spectrometer (4000–400 cm⁻¹) in KBr pellets. The elemental analysis was performed on Leco, CHNS-932 and Perkin-Elmer 7300 DV elemental analyzers. VOL_{2}^{1} , CoL_{3}^{1} , CuL_{2}^{1} , ZnL_{2}^{1} and $Zn_{2}L_{4}^{1}$ were prepared according to literature methods [29, 31].

2.2. Crystal structure determination

X-ray data for PdL_{2}^{1} , NiL_{2}^{2} and ZnL_{2}^{2} complexes were collected on a STOE IPDS-II diffractometer with graphite monochromated Mo-K α radiation. For NiL_{2}^{2} the crystals were green and for PdL_{2}^{1} and ZnL_{2}^{2} complexes, the crystals were yellow. A high-quality piece of crystal was chosen in each case using a polarizing microscope and they were mounted on a glass fiber, then used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement. Data were collected at a temperature of 298(2) in a series of ω scans in 1° oscillations and integrated using the Stöe X-AREA [37] software package. A numerical absorption correction was applied using the X-RED [38] and X-SHAPE [39] software's. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods using SIR2004 [40]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [41]. All hydrogen atoms were added at ideal positions and constrained to ride on their parent atoms. Crystallographic data for complexes are listed in Table 1. Selected bond distances and angles are summarized in Table 2.

2.3. Synthesis of Schiff-base ligand (HL²)

Allylamine (10 mmol) was dissolved in 30 ml of absolute methanol or chloroform and added slowly to a stirred solution 2-hydroxy-5-methylbenzaldehyde (10 mmol) in 30 ml of absolute methanol or chloroform at ambient temperature. The color immediately changed to yellow. The mixture was then stirred for 2h at ambient temperature before removal of solvent under vacuum. The result was yellow oil. Anal. Calc. for $C_{11}H_{13}ON$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.33; H, 7.43; N, 8.04. Selected IR data (KBr,cm⁻¹): 1631(vC=N), 1328 (vC-O).

2.4. Preparation of complexes (NiL¹₂, NiL²₂, ZnL²₂ and PdL¹₂)

A MeOH (or EtOH) solution (20 ml) of allylamine (6 mmol) was added dropwise to a MeOH solution (20 ml) of the salicylaldehyde (for preparation of NiL_2^1 and PdL_2^1) or 2-hydroxy-5methylbenzaldehyde (for preparation of NiL_2^2 and ZnL_2^2) (6 mmol). The yellow solution was stirred for 2h at ambient temperature. Then a solution of triethylamine (8 mmol) in absolute MeOH (5 ml) was added to the solution. The solution was essentially dark yellow at this time. The mixture was stirred for 10 min, and then a solution of appropriate metal salt (3 mmol $Zn(NO_3)_2.6H_2O$, NiCl₂.6H₂O or Pd(OAc)₂) in absolute MeOH (20 ml) was added dropwise.

NiL¹₂: Upon addition of NiCl₂, the color of solution changed to green. The resulting solution was stirred for 12h at ambient temperature. After concentration at room temperature, the green precipitate was collected by filtration. The typical yield was 93%. Anal. calc. for $C_{20}H_{20}N_2O_2Ni$: C: 63.37, H: 5.32, N: 7.39. Found: C: 63.36, H: 5.35, N: 7.37. Selected IR data (KBr, cm⁻¹): 1609 (vC=N), 1326 (vC-O).

 NiL_2^2 : Upon addition of NiCl₂, the color of solution changed to green. The resulting solution was stirred for 12h at ambient temperature. The green solution was slowly evaporated to dryness at room temperature to yield a green solid which was purified by washing with 50 ml of cold methanol and the obtained green precipitate was dried in air. Appropriate single crystals for X-ray crystallography were obtained directly from the reaction mixture. The typical yield was 89%. Anal. calc. for C₂₂H₂₄N₂O₂Ni: C: 64.90, H: 5.94, N: 6.88. Found: C: 64.86, H: 5.91, N: 6.90. Selected IR data (KBr,cm⁻¹): 1617(vC=N), 1329 (vC-O).

ZnL²₂:

After adding of $Zn(NO_3)_2.6H_2O$, the resulting solution was stirred for 12h at ambient temperature. The yellow solution was slowly evaporated to dryness at room temperature to yield a yellow solid which was purified by washing with 50 ml of cold methanol. Appropriate single crystals for X-ray crystallography were obtained directly from the reaction mixture. The typical yield was 84%. Anal.

calc. for C₂₂H₂₄N₂O₂Zn: C: 63.85, H: 5.85, N: 6.77. Found: C: 63.88, H: 5.83, N: 6.76. Selected IR data (KBr,cm⁻¹): 1619 (vC=N), 1322 (vC-O).

 PdL_{2}^{1} : Prepared in a similar manner to NiL_{2}^{1} but the resulting green solution after adding $Pd(OAc)_{2}$ (3 mmol) was refluxed for 12h. After concentration at room temperature, green precipitate was collected by filtration and purified by washing with cold methanol. Recrystallization from $CH_{2}Cl_{2}$ yielded single crystals of PdL_{2}^{1} suitable for X-ray crystallography. The typical yield was 82%. Anal. calc. for $C_{20}H_{20}N_{2}O_{2}Pd$: C: 56.28, H: 4.72, N: 6.56. Found: C: 56.35, H: 4.73, N: 6.62. Selected IR data (KBr,cm⁻¹): 1622 (vC=N), 1320 (vC-O).

2.5. Antibacterial studies

The antibacterial activity of compounds were tested on *Staphylococcus aureus* ATTC 29737 and *Pseudomonas aeroginosa* PTTC 1570 (Persian type culture collection) by comparison based on diameter of inhibition zone using the standard Kirby–Bauer disc diffusion assay (KBDD method). The bacterial species (*Staphylococcus aureus* and *Pseudomonas aeroginosa*) were stored in a refrigerator. Nutrient agar powder (1.8 g) was dissolved in 50 ml of water, sterilized by autoclaving at 115 °C for 20 min, cooled in a disinfected laminar hood and 100 μ l of culture of each organism was seeded in agar plates using the pour plate technique. The compound was placed on top of the agar and the plates and incubated at 37 °C overnight. The zones around each disc were measured with a ruler.

3. Results and discussion

3.1. IR spectra

The formation of Schiff base ligand, HL^2 , is evidenced by the presence of a strong IR band at 1631 cm⁻¹ due to v(C=N), while no bands attributable to v(C=O) or to v(NH₂) have been detected [31, 42]. A comparison of the spectra of the free ligands, HL^1 [31] and HL^2 , and its Ni(II), Zn(II) and Pd(II) complexes, NiL¹₂, PdL¹₂, NiL²₂ and ZnL²₂, indicated that the ligands were coordinated to the metal centers. Coordination of the azomethine nitrogen to the metals was suggested by the shift of the C=N band to lower frequencies in the IR spectra of the zinc, nickel and palladium complexes compared with the Schiff base ligands. Formation of M–N bonds leading to weakening of C=N band and this can be explained by the donation of electrons from the nitrogen atom to the empty d-orbitals of the metal atom [4]. Additional support for the formation of the Ni(II) Zn(II) and Pd(II) complexes were provided by the existence of weak intensity bands at ~ 480 cm⁻¹ attributed to the formation of M–N and M–O bonds [14].

3.2. NMR study

The ¹H NMR and ¹³C NMR spectra of the Schiff base ligand, HL^2 , and diamagnetic complexes, PdL_2^1 and ZnL_2^2 , were measured in CDCl₃, with TMS as internal standard. The data is depicted in Figs. 1 and 2 and spectra in Figs. S1-S7. The ¹H and ¹³C NMR were run immediately after dissolving in CDCl₃ and gave the expected simple spectra, indicating the integrity of Schiff base ligand and complexes. The spectra for ligand and complexes obtained after 12, 24, 48 and 120 h were similar to the initial spectra indicating that Pd(II) and Zn(II) complexes are stable in deuterated chloroform.

The ¹H NMR spectrum of HL^2 shows one singlet peak at 8.31 ppm corresponding to the imine proton (CH=N), and an almost broad O-H signal at 13.22 ppm. The ¹H NMR spectra of the complexes are almost similar to that of the ligands with slight shift to lower fields. The signal for the imine proton in the Pd(II) and Zn(II) complexes appears at 7.56 and 8.12, respectively, and this is shifted upfield with

respect to the corresponding signal in the free ligand, indicating that the metal-nitrogen bond is retained in solution. Phenolic-OH signals of Schiff base ligands, (**HL**¹:11.1 ppm and **HL**²:13.2 ppm) disappears in spectra of their complexes, indicating that OH protons are removed completely upon coordination.

The ¹³C NMR spectra of Schiff base ligand, Pd(II) and Zn(II) complexes, show one peak at 165.7, 162.6 and 171.3 ppm corresponding to the imine carbon atom of HL^2 , PdL_2^1 and ZnL_2^2 , respectively.

3.3. X-Ray diffraction studies

3.3.1. Structure description of PdL¹₂ and NiL²₂

The molecular structure of PdL_2^1 and NiL_2^2 are shown in Figures 3 and 4, respectively. The crystallographic data and selected bond lengths and angles are collected in Tables 1 and 2. In the solid state, PdL_2^1 and NiL_2^2 are placed in a crystallographic center of symmetry that is right in the middle point of the M(II) in a planar-transoid conformation (Figs. 3 and 4). The molecular unit is centrosymmetric and is made up of equivalent halves. The crystallographic data reveal that the Ni(II) and Pd(II) complexes are four-coordinated by two phenolate oxygen and two imine nitrogen atoms of two Schiff base ligands. The Schiff base ligands are arranged with respect to each other in a *trans* orientation such that one allyl substituent lies above the [MO₂N₂] plane and the other below (Fig. S8.). In NiL_2^2 complex, the chelate rings have the envelope form and the structure is the step configuration, while the configuration in PdL_2^1 complex is planar [4]. The C=N bond distance is 1.284(4) (N1=C7) for PdL_2^1 and 1.285(5)Å (N1=C7) for NiL_2^2 , which are consistent with a slight elongation of the C—N double bond when coordinated to a metal center [31]. Examination of the main metal–ligand distances in Ni(II) and Pd(II) complexes shows that the M…N distance [1.928(3) Å for NiL_2^2 , 2.017(2) Å for PdL_2^1 is longer than the M…O distance [1.837(3) Å for NiL_2^2 , 1.981(2) Å for PdL_2^1 . The bond

angles O–M–N [O(1)–M(1)–N(1) = 92.53(12)° [NiL²₂] and 91.90(10)° [PdL¹₂]; O(1)—M(1)–N(1A) = 87.47(12)° [NiL²₂] and 88.10(10)° [PdL¹₂] are close to 90°. These distances and angles are similar to those seen in related complexes [4, 31]. The C=C distance [1.278(8) Å for NiL²₂ and 1.294(2) Å for PdL¹₂] is well within the range expected for double bonds found in allyl derivatives [29, 31]. Although there are no classical hydrogen bonds in structure of PdL¹₂ and NiL²₂, but two intramolecular C–H…O contacts are observed in the solid state (Figs. 3, 4; Table 3). Also, there are intermolecular C–H…T interactions in NiL²₂ complex (Fig. 5). Special structures of molecular assemblies can be formed and controlled by various kinds of hydrogen bonding, even by C–H… π interactions that are considerably weaker than classical H bonding. These C–H/ π interactions also play notable structure-stabilizing roles in structures. Here C–H… π edge-to-face interactions are present between CH groups with H… π distance of 2.96 Å for C(5)—H(5) …Cg(1) and 2.90 Å for C(10)—H(10B)…Cg(1) [Cg(1) is centroid for C(1)/C(6) ring].

3.3.2. Structure description of ZnL²₂

An ORTEP view of \mathbf{ZnL}_{2}^{2} with the atom-numbering scheme is presented in Fig. 6 and the crystallographic data and selected bond lengths and angles are collected in Tables 1 and 2. The asymmetric unit of \mathbf{ZnL}_{2} consists of two independent Schiff base complexes with slightly different bond lengths and angles. The crystallographic data reveal that the metal center is four-coordinated by two phenolate oxygen and two imine nitrogen atoms of two Schiff base ligands. The geometry around the metal center is distorted tetrahedral, with $P2_{1}/c$, space group. The ligands coordinate to the metal center in *cis* geometry with respect to each other.

The C=N bond distances for two independent molecules are 1.276(6) Å (N1=C7), 1.287(6) Å (N2=C18), 1.286(8) Å (N3=C29) and 1.302(8) Å (N4=C40) which are consistent with a slight 10

elongation of the C—N double bond when coordinated to a metal center [29,31]. The C–O bond distance exhibit values between 1.313(7) until 1.328(6) Å [(C(1)-(O1): 1.314(6): (C(12)-(O2): 1.328(6) ; (C(23)-(O3): 1.321(7); (C(34)-(O4): 1.313(7)] in \mathbf{ZnL}_{2}^{2} complex, which is nearer to a C–O single bond than to a C–O double bond distance. These distances prove that the ligand coordinates to the Zn(II) in enolate form [29,31].

Surprisingly, we can see the big difference in geometry around Zn(II) in ZnL_2^1 and ZnL_2^2 complexes. As depicted in Fig. 6, The geometry around the Zn(II) center in ZnL_2^2 complex is distorted tetrahedral. But, as previously reported by our group [31], the geometry around the Zn(II) center for ZnL_2^1 complex is square planer. The only difference between ZnL_2^1 complex and ZnL_2^2 complex is use of 2hydroxy-5-methylbenzaldehyde instead of salicylaldehyde in synthesis of ZnL_2^2 complex. In order to justify such structures, the investigating of steric and electronic factors in these two complexes is necessary. As shown in Fig. 6, the methyl group of HL^2 Schiff base ligand is very far from Zn(II)center. For this reason, we don't have any steric hindrance on behalf of methyl group in ZnL_2^2 complex for changing of the structure of square planar to distorted tetrahedral. Then, the only effective parameter for this change is electronic factor,

3.4. Electronic spectra

Electronic spectra of the free Schiff base ligands and their complexes were recorded in a MeOH solution and are shown in Fig. 7. Based on literature data recorded for benzene [43] and similar Schiff bases in different solvents [44], all UV spectra of Schiff bases and their complexes exhibit two main bands. The first intense and lower wavelength bands in the 215–270 nm region have molar extinction coefficient values greater than one thousand and are attributed to intra-ring $\pi \rightarrow \pi^*$ transitions of the phenolic ring that in the complexes are significantly shifted relative to the free ligand as a result

of the coordination of the heavy metal core. The second bands at the 270–400 nm range involve the azomethine $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions that for **HL**² and its complexes shift to lower wavelengths. In the Ni(II) and Pd(II) complexes, the band around 400 nm may be due to LMCT (O/N(p) \rightarrow M(d)) transition. In these two complexes with d⁸ square planar structure, it is expected to show three spin-allowed d–d transition bands corresponding to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$, ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$, while the tailing of CT bands that appeared at ~ 400 nm toward the visible region cause the disappearance of these bands [4, 45].

3.5. Antibacterial results

Schiff base ligand and its metal complexes were evaluated for their *in vitro* antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* as examples of Gram-positive bacteria and Gram-negative bacteria, respectively. The disk- diffusion method was carried out to evaluate the antibacterial activity of compounds (Fig. S9). All compounds were used as powder in antibacterial activity test except the Schiff base ligands that were used as oil. The results of the antimicrobial activity of the Schiff base ligand and complexes against tested bacteria are shown in Table 4. From the results, we can conclude that:

- 1. On comparing the activity of the tested complexes with Schiff base ligands, the obtained data indicated that the activity of HL^1 is less than its complexes, while the activity of HL^2 is partly more than its complexes.
- 2. All the tested compounds, except CoL_{3}^{1} , CuL_{2}^{1} and PdL_{2}^{1} are found to have biological activity against *E. coli*.
- 3. All the tested compounds, except CoL_{3}^{1} and PdL_{2}^{1} are found to have biological activity against *S*. *aureus*.

- 4. Ni(II) complex, NiL_{2}^{1} , appears to have a higher activity than all the other metal complexes.
- 5. There are not lack of growth of *S. aureus* and *E. coli* around the VOL¹₂ complex, but 15 mm after the VOL¹₂ complex, we can see a zone with very weak growth of bacteria (Fig. S9).
- Although monometallic and bimetallic Zn(II) complexes prepared from HL¹ ligand, ZnL¹₂ and Zn₂L¹₄, are found to have no biological activity against *S. aureus* until 20 mm of samples, but 20 mm after the samples another zone can be seen that the growth of bacteria is greatly reduced (Fig. S9).
- 7. The tested ligands and complexes have almost similar inhibitory against Gram-positive and Gramnegative bacteria.

4. Conclusion

In this study, a new Schiff base ligand, HL^2 , and four new Schiff base complexes, NiL_2^1 , PdL_2^1 , NiL_2^2 and ZnL_2^2 , have been prepared and characterized. The molecular structures of PdL_2^1 , NiL_2^2 and ZnL_2^2 complexes were determined by the single crystal X-ray diffraction technique. The crystallographic data reveal that in all the complexes the metal centers are four-coordinated by two phenolate oxygen and two imine nitrogen atoms of two Schiff base ligands. The geometry around the metal center in the PdL_2^1 and NiL_2^2 complexes is square-planar and for ZnL_2^2 it is a distorted tetrahedral.

The new synthesized Schiff base ligand and complexes, HL^2 , NiL^1_2 , PdL^1_2 , NiL^2_2 and ZnL^2_2 , along with reported Schiff base ligand and complexes, HL^1 , VOL^1_2 , CoL^1_3 , CuL^1_2 , ZnL^1_2 , $Zn_2L^1_4$, were assayed for their *in vitro* antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* as examples of Gram-positive and Gram-negative bacterial strains, respectively, by using disc diffusion method.

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Appendix A. Supplementary data

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 1449477, 1449478 and 1449479 for NiL_{2}^{2} , PdL_{2}^{1} and ZnL_{2}^{2} , respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033 or e-mail: <u>deposit@ccdc.cam.ac.uk</u>).

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Scheme 2. Synthetic routes for the preparation of Schiff base ligands and complexes



Fig. 1. ¹H NMR and ¹³C NMR data for PdL¹₂

s, singlet; d, doublet; t, triplet; m, multiplet

	H ₁₁ H ₁₁	H_{5} H_{5} $C_{5} = C_{6}$ C_{4} C_{5}	$H_{10}t$ $H_{8}a$ $H_{8}b$	с ₁₀ —H ₁₀ а H ₉	9
	H ₁₁	\mathbf{c}_{3} \mathbf{c}_{2}	2	¹³ CNMR	
	HL ²	ZnL^{2}		HL ²	ZnL_{2}^{2}
H ₇	8.31 (s)	8.12 (s)	C ₇	165.7	171.3
H_3	7.14 (d of d)	7.14 (d of d) 🦱	C_8	61.4	62.7
H_5	7.07 (d)	6.88 (d)	C ₁₁	20.4	20.2
H_2	6.92 (d)	6.78 (d)	C_{9}, C_{10}, C_{ar}	158.9, 134.9,	165.6, 136.5,
H_9	6.05 (m)	5.86 (m)		133.1, 131.4,	134.9, 133.4,
H_{10b}, H_{10a}	5.28, 5.23,	5.18, 5.13,		127.6, 118.5,	133.1, 131.3,
	5.21, 5.19 (4q)	5.11, 5.08 (4q)		116.8, 116.4	122.9, 119.4
H_{8a}, H_{8b}	4.25, 4.23(2d)	4.14(d)			
H ₁₁	2.32(s)	2.25(s)			
OH	13.22(s)	2			

Fig. 2. ¹H NMR and ¹³C NMR data for HL² and ZnL²₂

s, singlet; d, doublet; q, quartet; m, multiplet



Fig. 3. ORTEP representation of PdL_{2}^{1} . Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.



Fig. 4. ORTEP representation of NiL_{2}^{2} . Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.



$\Lambda - H(I) \dots Cg(J)^*$	HCg	ACg	л—н…Сg	Symmetry codes	
$C(5) - H(5) \dots Cg(1)$	2.96	3.670(4)	134	-X,-1/2+Y,1/2-Z	
C(10)—H(10B)Cg(1)	2.90	3.681(7)	142	1+X,Y,Z	
$*C_{2}(1), C(1)/C(6)$ min 2					

Cg(1): C(1)/C(6) ring

Fig. 5. Illustration of C—H... π interactions in molecular structure of NiL²₂



Fig. 6. ORTEP representation of \mathbf{ZnL}_{2}^{2} . Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



Fig. 7. Electronic spectra of Schiff base ligands and complexes (A: HL^1 , B: VOL^1_2 , C: CoL^1_3 , D: NiL^1_2 , E: ZnL^1_2 , F: CuL^1_2 , G: PdL^1_2 , H: HL^2 , I: NiL^2_2 and J: ZnL^2_2)

Table 1	Crystal	data and	structure	refinement	details	of PdL ¹ ₂ ,	ZnL_{2}^{2} and	$1 \operatorname{NiL}^2_2$.

	PdL ¹ ₂	ZnL ² ₂	NiL ² ₂
Empirical formula	$C_{20}H_{20}N_2O_2Pd$	$C_{22}H_{24}N_2O_2Zn$	$C_{22}H_{24}N_2O_2Ni$
Formula weight	426.78	413.80	407.14
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_1/c$
Unit cell (Å, °)			
a	9.1663(9)	13.830(3)	8.7116(17)
b	5.3797(5)	13.282(3)	5.8886(12)
c	18.5168(18)	23.576(5)	19.249(4)
β	90.995(5)	102.39(3)	93.67(3)
Volume (Å ³)	912.96(15)	4229.7(17)	985.4(3)
Z	2	8	2
Calculated density (Mg/m ³)	1.552	1.300	1.372
Absorption coefficient (mm ⁻¹)	1.031	1.179	1.003
F(000)	432	1728	428
θ range for data collection (°)	2.20 to 27.10	2.56 to 27.00	3.06 to 25.00
Index ranges	$-11 \le h \le 11$	-15≤ h ≤17	$-8 \le h \le 10$
	-6≤ k ≤6	-16≤ k ≤16	-7≤ k ≤7
	23≤1 <i>≤</i> 23	-30≤1 <i>≤</i> 30	-22≤1≤22
Reflections collected	13167	28537	5191
Independent reflections	13167 $[R_{(int)} = 0.0465]$	9222 $[R_{(int)} = 0.1613]$	$1704 [R_{(int)} = 0.1445]$
Data Completeness (%)	99.5	99.9	98.6
Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
	on F^2	on F^2	on F^2
Data / restraints / parameters	2002 / 1 / 115	9222 / 6 / 500	1704 / 0 / 125
Goodness-of-fit on F^2	1.072	0.806	1.047
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0326$	$R_1 = 0.0688$	$R_1 = 0.0711$
	$wR_2 = 0.0788$	$wR_2 = 0.1576$	$wR_2 = 0.1815$
R indices (all data)	$R_1 = 0.0505$	$R_1 = 0.1481$	$R_1 = 0.0775$
	$wR_2 = 0.0886$	$wR_2 = 0.1813$	$wR_2 = 0.1890$
Largest diff. peak and hole	0.625 and -0.433	1.132 and -1.321	1.221 and -1.564
(e.Å ⁻³)			

	NiL ² ₂	PdL_{2}^{1}		ZnL ² ₂
M(1)*—O(1)	1.837(3)	1.981(2)	Zn(1)-O(1)	1.911(4)
M(1) - N(1)	1.928(3)	2.017(2)	Zn(1)-O(2)	1.921(4)
N(1)-C(7)	1.285(5)	1.284(4)	Zn(1)-N(1)	1.995(4)
C(9)-C(10)	1.278(8)	1.294(2)	Zn(1)-N(2)	2.011(4)
			Zn(2)-O(3)	1.916(4)
O(1)-M(1)-O(1A)	180.00(10)	180.000(1)	Zn(2)-O(4)	1.921(4)
O(1)-M(1)-N(1)	92.53(12)	91.90(10)	Zn(2)-N(4)	2.004(5)
N(1)-M(1)-N(1A)	180.00(17)	180.00(13)	Zn(2)-N(3)	2.007(5)
C(1)-O(1)-M(1)	128.4(2)	126.4(2)	N(1)-C(7)	1.276(6)
C(7)-N(1)-M(1)	124.3(2)	123.3(2)	N(2)-C(18)	1.287(6)
C(8)-N(1)-M(1)	120.6(2)	119.7(2)	N(3)-C(29)	1.286(8)
O(1)-M(1)-N(1A)	87.47(12)	88.10(10)	N(4)-C(40)	1.302(8)
			O(1)- $Zn(1)$ - $O(2)$	112.99(15)
			O(1)- $Zn(1)$ - $N(1)$	97.01(16)
			O(2)- $Zn(1)$ - $N(1)$	120.20(18)
			O(1)- $Zn(1)$ - $N(2)$	117.48(18)
			O(2)-Zn(1)-N(2)	96.83(15)
			N(1)- $Zn(1)$ - $N(2)$	113.78(17)
			O(3)-Zn(2)-O(4)	111.58(17)
			O(3)-Zn(2)-N(4)	121.38(19)
			O(4)-Zn(2)-N(4)	96.1(2)
			O(3)-Zn(2)-N(3)	96.2(2)
			O(4)-Zn(2)-N(3)	123.3(2)
			N(4)- $Zn(2)$ - $N(3)$	110.3(2)

Table 2 Selected bond distances (Å) and angles (°) for PdL_2^1 , NiL_2^2 and ZnL_2^2

* M = Ni for NiL_2^2 and Pd for PdL_2^1 . Symmetry transformations used to generate equivalent atoms: 1 -x+2,-y,- z+2 (for NiL_2^2) and 1 -x+1,-y+2,-z+2 (for PdL_2^1)

	D—HA	D—H	HA	DA	D—HA	Symmetry codes
PdL ¹ ₂	C(8)—H(8A)O(1A)	0.97	2.28	2.792(5)	112	1-x,-y,-z
NiL ² ₂	C(8)—H(8B)O(1A)	0.97	2.20	2.712(5)	112	-x,2-y,-z

Table 3. Intramolecular hydrogen bond geometries (Å,°) for PdL_{2}^{1} and NiL_{2}^{2}

Table 4 Antimicrobial activities of Schiff base ligands and complexes

	Sample	The inoculated sample (mgr)	The diameter of inhibition zone (mm)	Description
	HL^{1} NiL^{1}_{2} PdL^{1}_{2} VOL^{1}	one drop 620	27 15 0	
	VOL ⁻ 2	2000	0	after the complex, we can see a zone with very weak growth of bacteria
SI	CoL ¹	580	0	arer the complex, we can see a zone with very weak growth of bacteria.
ıreı	CuL_{2}^{1}	380	10	
an	$\operatorname{ZnL}_{2}^{1}$	460	4	There are not lack of growth of bacteria around the complex, but 20 mm
S.	$Zn_2L_4^1$	700	11	after the complex, we can see a zone with very weak growth of bacteria. There are not lack of growth of bacteria around the complex, but 20 mm after the complex, we can see a zone with very weak growth of bacteria.
	HL^2		2	
	NiL_{2}^{2}		7	
	ZnL_{2}^{2}		2.5	
	HL	one drop	38	
	NiL_2	800	10	
			0	
	VOL ¹ ₂	2500	0	There are not lack of growth of bacteria around the complex, but 20 mm
ili	Col ¹	560	0	after the complex, we can see a zone with very weak growth of bacteria.
3	CuL_3 CuL^1	330	0	
E		960	6	
	$Zn_2L_4^2$	820	3	Y
	HL^2		2.5	
	NiL_{2}^{2}		12	Y
	ZnL ² ₂		4	
	7			

Highlights:

- Synthesis and characterization of a new bidentate Schiff base ligand (HL²) and four new Schiff base complexes (NiL¹₂, PdL¹₂, NiL²₂ and ZnL²₂).
- Determination of molecular structures of PdL¹₂, NiL²₂ and ZnL²₂ complexes by the single crystal X-ray diffraction technique.
- Investigation of antimicrobial activity of reported (HL¹, VOL¹₂, CoL¹₃, CuL¹₂, ZnL¹₂ and Zn₂L¹₄) and new (HL², NiL¹₂, PdL¹₂, NiL²₂ and ZnL²₂) Schiff base compounds.

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