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An analysis of spectroscopic signatures, DFT calculations and anti-bacterial activity of newly synthesized Cu(II) and Pd(II) complexes of 2-aminoquinolin-8-ol and 2-(naphthalen-1-ylmethyl)-4,5-dihydro-1*H*-imidazole

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Copper(II), palladium(II) complexes $[Cu(L1)_2]$ (**1**), $[Pd(L1)_2]$ (**2**), $[Cu(L2)_2Cl_2.H_2O]$ (**3**), $[Pd(L2)_2Cl_2]$ (**4**), of 2-aminoquinolin-8-ol (L1) and 2-(naphthalen-1-ylmethyl)-4,5-dihydro-1*H*-imidazole (L2) were synthesized and physico-chemically characterized by spectroscopic techniques like IR, UV-Visible and elemental analysis. The structures of the ligands and their complexes were optimized by density functional theory (DFT) method using B3LYP/6-311++G(d,p) basic set for L1 and L2 and B3LYP/LanL2DZ basic set for **1**, **2**, **3** and **4**, respectively. The bond lengths and bond angles of complexes were compared with the literature values which were in good agreement. The results revealed that **1**, **2** and **4** complexes were in square planar geometry and square pyramidal geometry for complex **3**. Frontier orbital analysis and global reactivity parameters were also computed at same basic set in the same phase. In addition, DOS and COOP analysis were also performed using Gauss Sum 3.0 programme for compound **4**. All the ligands and complexes were screened for anti-bacterial activity and the metal complexes exhibited highest anti-bacterial activity when compared to ligands.

Keywords: Cu(II), Pd(II) complexes, DFT studies, anti-bacterial activity.

Introduction

Copper(II) and palladium(II) complexes have been gaining significant attention due to their potentially beneficial pharmacological properties. Palladium complexes with aromatic *N*-containing ligands, such as pyridine, quinoline, pyrazole and 1,10-phenanthroline derivatives, have shown very promising anti-tumor characteristics[1–4]. On the other hand, Pd(II) complexes exhibited catalytic activity in carbon-carbon and carbon-nitrogen bond forming reactions[5]. Four coordinate palladium(II) complexes with square planar geometry and various *N*-heteroaromatic ligands are useful building blocks for producing interesting molecular structures[6]. As an important class of heterocyclic scaffolds, 2-imidazolines have attracted the attention from the chemists interested in natural products, pharmaceutical chemistry, synthetic organic chemistry, coordination chemistry and homogeneous catalysis[7].

8-Hydroxyquinoline (8-HQ) and derivatives are known to be the best chelating agents after EDTA and their derivatives owing to their guest modulated chromogenic and fluo-

rescent behaviour. Accordingly, they have been used in chromatography[8], detection of metal ions[9–11], preparation of organic light emitting diode devices[12,13], and electrochemical luminescence[14]. 8-HQ form stable five-membered stable chelate metal complexes of the type $M(HQ)^+$, $M(HQ)_2$ or $M(HQ)_3$ with divalent transition and post-transition metal ions including La(III)[15], Sm(III)[16], Gd(III)[17] and Yb(III)[18] quinolinolates.

In view of the above importance and applications, we herein disclose the synthesis, theoretical studies and antibacterial activity of novel Cu(II) and Pd(II) complexes of 2-aminoquinolin-8-ol and 2-(naphthalen-1-ylmethyl)-4,5-dihydro-1*H*-imidazole.

Results and discussion

The molar conductance (Λ_M) measurements of the complexes were carried out using DMF as the solvent at 10^{-3} *M* concentration reveals that non-electrolyte behaviour of the complexes. Colour, molar conductivity values, melting point and elemental analysis of the complexes were outlined in Table 1. All of these complexes are stable in air and polycrystalline in nature.

Table 1. Anti-bacterial activity of compounds (L1 and **1**, **2**; L2 and **3**, **4**)

Compd.	Bacteria tested	Diameter (mm) of compounds at concentrations (μg/mL)		
		250	125	63.5
L1	*S. aureus*	13	7	–
	E. coli	9	4	–
1	*S. aureus*	25	13	7
	E. coli	19	9	5
2	*S. aureus*	20	11	6
	E. coli	16	7	4
L2	*S. aureus*	10	6	–
	E. coli	7	4	–
3	*S. aureus*	27	14	8
	E. coli	19	10	6
4	*S. aureus*	25	12	5
	E. coli	18	8	4
Streptomycin (standard)	*S. aureus*	38	21	13
	E. coli	35	20	11

FT-IR spectra:

The strong absorption band at 3403 cm^{-1} assigned as stretching vibrational mode of the phenolic -OH group and the same mode disappears in vibrational spectra of complexes, which reflect the ligand coordinating with the metal ion through phenolic -OH group. The C=N stretching vibrational mode of the ligand was observed at 1643 cm^{-1}, wherein vibrational spectra of metal complexes for this mode shifted about 40–50 cm^{-1} which confirms that ligand coordinate with metals through quinoline ring nitrogen[19]. The phenolic C-O stretching vibration that appeared in ligand at 1266 cm^{-1} which shifted towards higher frequency by 20–25 cm^{-1} in the complexes. The positive shift of the vibrational mode suggests that coordination of the phenolate anions with the metal ions via de-protonation[20,21]. The above results reflect that 2-aminoquinolin-8-ol act as mono-anionic bidentate in nature which is coordinating through quinoline nitrogen as well as phenolic -OH group (Fig. 1).

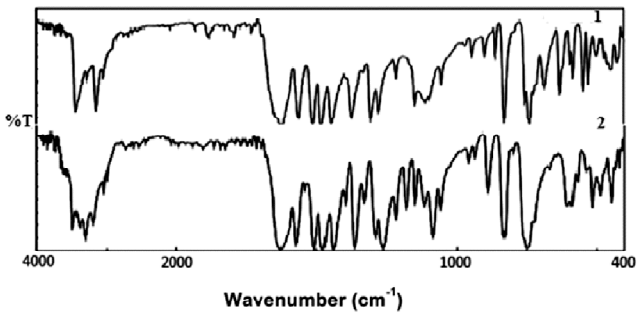

Fig. 1. FT-IR spectrum of $[Cu(L1)_2]$ (**1**) and $[Pd(L1)_2]$ (**2**).

The vibrational mode at 1604 cm^{-1} was assigned to stretching vibrational mode of ν(C=N) group of L2. This mode shifted towards lower frequencies around 30–40 cm^{-1} after complexation with metal ions which is a explicit evidence for coordination of the imidazoline ring through the C=N group. This was further supported by the new band at 547–532 cm^{-1} in the complexes assigned to M-N[22–24]. In addition to this, copper complex spectra showed 3422 cm^{-1} indicating the presence of coordinated water molecule[25,26]. The non-ligand bands at 450 to 412 cm^{-1} region were assigned to ν(M-Cl) stretching modes[22–24]. The above results unequivocal shows that 2-(1-napthylmethyl)-2-imidazole (L2) ligand act as a neutral monodentate, coordinate to Cu(II) and Pd(II) metal ions through C=N group of immdazoline ring.

UV-Visible spectra:

The UV-Visible spectra of 2-aminoquinolin-8-ol (L1) have broad band around 25773 cm^{-1} due to intra-ligand transi-

tions. The Cu(II) and Pd(II) complexes showed corresponding intra-ligand transitions in the region 24875 cm^{-1}. The Cu(II) complex displayed a strong intense band around 21321 cm^{-1} and assigned to the ligand to metal charge transfer transition (LMCT) or alternatively called as metal reduced charge transfer spectra. The bands in 25000–21052 cm^{-1} range was assigned to phenoxy O→Cu transitions. The spectra of the copper complex exhibited weak band centred around 16694 cm^{-1}. For a copper(II) square planar complex with $d_{x^2-y^2}$ ground state, three transitions are possible $d_{z^2} \leftarrow d_{x^2-y^2}$, $d_{xy} \leftarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \leftarrow d_{x^2-y^2}$ ($^2A_{1g} \leftarrow {}^2B_{1g}$, $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$) and it was difficult to resolve it in to three bands. Owing to four lower orbitals were closer together in energy that individual transitions cannot be distinguished resulting in a single absorption band[27,28].

The UV-Visible spectra of Pd(II) complex (**2**) reveals the spin allowed *d-d* transitions observed at 16393 cm^{-1}, corresponding to the transitions from the three lower lying '*d*' levels to the empty $d_{x^2-y^2}$ orbitals. The ground state $^1A_{1g}$ and the excited states corresponding to the above transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g which are in the order of increasing energy. The Pd(II) complex demonstrated charge transfer transition band merge with high intensity intra-ligand absorption at 23923 cm^{-1}. The electronic spectra of this complex support a square planar geometry around the Pd(II) ion[29] (Fig. 2).

Anti-bacterial activity:

The synthesized compounds were screened for anti-bacterial activities against test bacteria *S. aureus* (Gram-positive) and *E. coli* (Gram-negative) at different concentrations

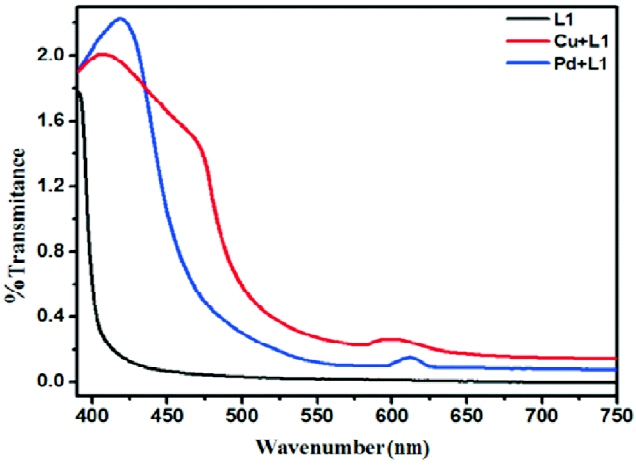

Fig. 2. UV-Visible spectra of L1 and it's complexes (**1**) and (**2**).

by disc diffusion technique[30,31]. The tested compounds in calculated quantities were dissolved in DMF to get concentrations of 250, 125 µg mL^{-1} of compounds. The disc of Whatmann No. 1 filter paper having the diameter 5.00 mm each containing (1.5 mg cm^{-1}) of compounds were placed at four equidistant places at a distance of 2 cm^{-1} from the centre in the inoculated petriplates. Filter paper disc treated with DMF served as control and streptomycin used as a standard drug. All determinations were made in duplicate for each of the compounds. Averages of two independent readings for each compound were recorded. These petriplates were kept in refrigerator for 24 h for pre-diffusion. Finally, petriplates were incubated at 30°C for 24 h.

The results revealed that all the metal complexes showed higher activity than free ligands. In specific, L2 metal complexes exhibited highest activity than the other compounds (Table 1).

The electronic spectrum of (L2) consists of a broad band at 32467 cm^{-1} which is intra-ligand transitions. The intra-ligand transition of Cu(II) complexes contains these bands in the region 30959 cm^{-1}. These broad band can be regarded as a combination of $n \rightarrow \pi^*$ transitions and $\pi \rightarrow \pi^*$ of naphthalene ring and C=N, respectively[32]. The charge transfer high intensity band was observed at 21739 cm^{-1}, and their broadness can be explained due to N→Cu LMCT transitions[33]. This exhibited a broad peak 15552 cm^{-1} which is characteristic to Cu(II) complex with a square pyramidal geometry[29,34]. Hence, the transition is characteristic of a Cu(II) ion with the single electron residing in the $d_{x^2-y^2}$ orbital. The broadness of the band does not permit its resolution into various components.

The Pd(II) complexes exhibit three spin allowed *d-d* transitions from lower lying *d*-levels to the empty $d_{x^2-y^2}$ orbital. Although, other two electronic transitions were also observed but their intensities were very weak and therefore, neglected. The complex showed the absorption bands at 16583 cm^{-1} corresponding to *d-d* transition[29]. Moreover, the complex with high intensity intra-ligand and charge transfer absorption bands were also observed at 34129 cm^{-1} and 28571 cm^{-1} transition, respectively. These absorption bands suggest that the complexes possess D_{4h} symmetry and square planar geometry (Fig. 3).

Magnetic susceptibility measurements:

The magnetic susceptibility measurements for titled com-

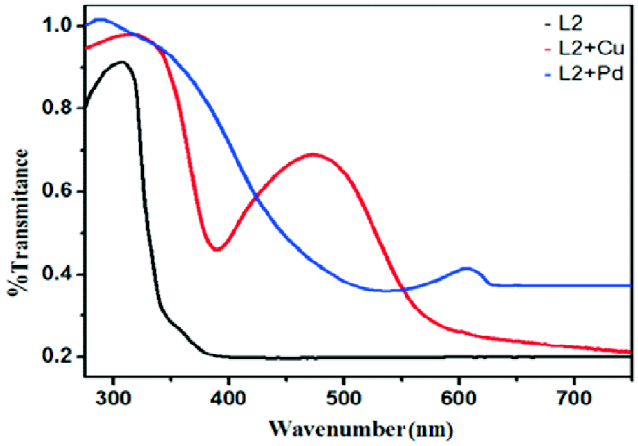

Fig. 3. UV-Visible spectra of L2 and it's complexes (**3**) and (**4**).

pounds measured at room temperature, the values for **1**, **3** complexes are1.88–1.95 B.M. (where μ_{eff} is the effective magnetic moment) is higher than that expected for the spin only value (1.73 B.M.)[35] which indicates that absence of any metal-metal interactions and also support the possibility of these complexes in square planar (**1**) and square pyramidal geometry (**2**) (Table 2). Magnetic susceptibility measurements of Pd(II) complexes (**2**, **4**) were reflect that low spin, diamagnetic complexes[36].

Theoretical studies:

The optimized geometrical (Fig. 4) parameters were tabulated in Tables 3 and 4. The geometrical parameters of **1** and **2** complexes of the L1 in Table 3; the bond lengths are Pd(39)-N(30), Pd(39)-O(38) as 2.05, 2.04 Å and Cu(29)-N(32), Cu(29)-O(30) as 2.00, 1.94 Å respectively, whereas reported values were 2.0, 1.98 Å and 1.97, 1.91 Å for the similar derivatives. The bond angles were O(37)-Pd(39)-N(29) and O(30)-Cu(29)-N(33) 82.10° and 83.95° were in accordance with reported values 81.95° and 93.88°. For the **2** and **4** complexes (Table 4) the bond lengths are Pd(1)-N(6), Pd(1)-Cl(57) as 2.02, 2.42 Å and Cu(1)-N(4), Cu(1)-Cl(3) as 1.95, 2.42 Å respectively and reported values as 2.01, 2.32 Å and 1.99, 2.61 Å for similar derivatives. The bond angles for N(6)-Pd(1)-Cl(57) and N(6)-Cu(1)-Cl(57) are 90.96° and 91.51°, shows good in mutual agreement.

Table 2. Magnetic moment and UV-Visible spectra values for ligands and complexes

Sr. No.	Compd.	μ_{eff} (B.M.)	λ_{max}
1.	L1	–	32467
2.	**1**	1.88	30959, 21739, 15552
3.	**2**	Diamagnetic	34129, 28571, 16583
4.	L2	–	25773
5.	**3**	1.95	24875, 21321, 16694
6.	**4**	Diamagnetic	23923, 16393

Analysis of Frontier orbitals and Global reactivity parameters:

The complexes **1** and **2** shows, HOMO orbital confirmed over metal and partially on ligand, LUMO orbital confirmed over ligand, this reflect that there is charge transfer between metal and ligand. The HOMO-LUMO orbital analysis of ligand L2 show that the HOMO orbital confirmed over imidazoline

Table 3. Elemental analysis data and physical properties of the ligands and Cu(II) and Pd(II) complexes

Sr. No.	Compd.	Colour	Molar conductance (Ω^{-1} cm^2 mol^{-1})	M.p. (°C)	Analytical data (%): Found (Calcd.) M	C	H	N
1.	$C_9H_8N_2O$ (L1)	Pale yellow	_	156	_	67.45	5.01	17.41
						(67.39)	(5.06)	(17.49)
2.	$[Cu(L1)_2]$	Green	8.63	251	16.59	56.58	3.76	14.64
	$C_{18}H_{14}CuN_4O_2$ (**1**)				(16.64)	(56.61)	(3.70)	(14.67)
3.	$[Pd(L1)_2]$	Yellow	5.21	>300	24.89	50.78	3.29	13.07
	$C_{18}H_{14}N4O_2Pd$ (**2**)				(25.05)	(50.90)	(3.32)	(13.19)
4.	$C_{14}H_{14}N_2$ (L2)	White	_	253	_	79.97	6.71	13.32
						(80.03)	(6.75)	(13.25)
5.	$[Cu(L2)_2Cl_2.H_2O]$	Green	3.10	>300	10.99	58.71	5.23	9.74
	$C_{28}H_{30}Cl_2CuN_4O$ (**3**)				(11.09)	(58.69)	(5.28)	(9.78)
6.	$[Pd(L2)_2Cl_2]$	Yellow	5.12	285	17.73	56.21	4.69	9.41
	$C_{28}H_{28}Cl_2N_4Pd$ (**4**)				(17.80)	(56.25)	(4.72)	(9.37)

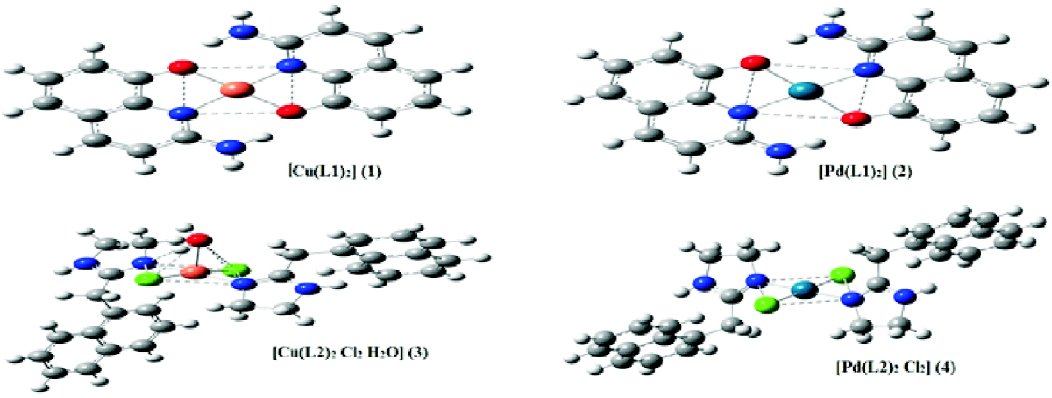

Fig. 4. Optimized structures of $[Cu(L1)_2]$ (**1**), $[Pd(L1)_2]$ (**2**), $[Cu(L2)_2Cl_2.H_2O]$ (**3**) and $[Pd(L2)_2Cl_2]$ (**4**).

Table 4. Comparison of bond length (Å) and bond angles (°) of $[Pd(L1)_2]$ and $[Cu(L1)_2]$ with literature values

Bond length (Å)	$[Pd(L1)_2]$	Ref.[37]	Bond length (Å)	$[Cu(L1)_2]$	Ref.[38,39]
Pd(39)-N(30)	2.05536	2.076	Cu(29)-N(32)	2.00796	1.974
Pd(39)-O(38)	2.04419	1.986	Cu(29)-O(30)	1.94664	1.919
C(19)-O(38)	1.36479	–	C(29)-O(31)	1.35522	–
C(31)-N(26)	1.36230	–	C(29)-N(34)	1.35650	–
Bond angle (°)			Bond angle (°)		
O(37)-Pd(39)-O(38)	179.99791	–	O(30)-Cu(29)-O(31)	179.99938	–
N(29)-Pd(39)-N(30)	179.99110	–	N(32)-Cu(29)-N(33)	180.00000	–
O(37)-Pd(39)-N(29)	82.10385	81.95	O(30)-Cu(29)-N(33)	83.95166	83.88

ring and partially on entire molecule and the LUMO orbital confirmed over whole molecule other than imidazole ring, this reflect that charge transfer between imidazole and naphthalene rings. The global reactivity parameters for the investigated compounds were calculated; ionization potential (I) = $-E_{HOMO}$, electron affinity (A) = E_{LUMO}, electronegativity (χ) = ($I + A$)/2, global hardness (η) = ($I - A$)/2, chemical potential (μ) = ($I + A$)/2, chemical softness (ν) = 1/η and electrophilicity index (ω) = $\mu^2/2\eta$[41,42], and shown in Table 4. An electronic system with a larger HOMO-LUMO gap should be less reactive when compared to one having a smaller gap and also this energy reflect on biological activity of the compound.

The analysis density of states has prevailed importance in explanation of group contributions to electronic state energies. In the present study, complex **4** taken as a model and it can be fragmented to four parts which were labelled as Pd, naphthalene ring, naphthalene ring 2 and Cl. A Density of states (DOS) spectrum is a representation of the number of energy levels in a section along the energy axis of width dE. Partial density of states (DOS) and overlap population density of states (OPDOS) in terms of Mullikan population analysis were calculated using the Gauss Sum program. They provide a pictorial representation of the MO compositions and their contributions to chemical bonding. The DOS diagram for complex **4** was shown in Fig. 5. The DOS plot mainly represents the composition of the fragment orbitals contributing to the molecular orbitals. From the DOS plots, one can see the HOMO has d Pd and p Cl character and the LUMO is composed of d Pd and π^* orbital of the imidazole ligand. The OPDOS gives an indication of the bonding, non-bonding, and anti-bonding characteristics with respect to the particular fragments. A positive value in the OPDOS plot means a bonding interaction, while a negative value represents an anti-bonding interaction, and a near zero value indicates a non-bonding interaction. At the same time, an analysis of the OPDOS diagram allows us to determine the donor-acceptor properties of the ligands. At the same time, an analysis of the OPDOS diagram allows us to determine the donor-

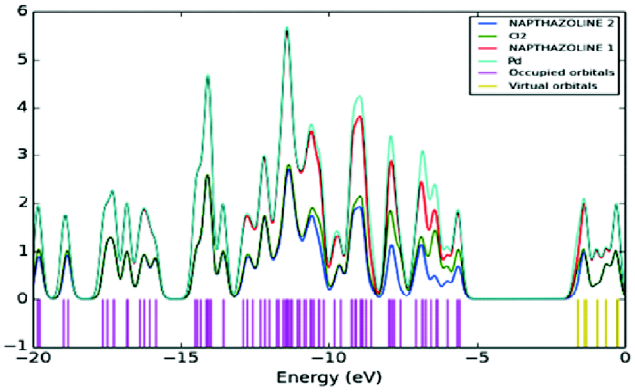

Fig. 5. Pictorial representation of OPDOS spectra of $[Pd(L2)_2Cl_2]$ (**4**).

acceptor properties of the ligands. It may be concluded that the imidazole ligand have strong σ-donor and π-acceptor properties which was consistent with the charges on the palladium atoms given above.

Experimental

The reagents and solvents used for the synthesis were procured from commercial AnalaR grade source and used as such without further purification. 2-Aminoquinolin-8-ol (L1)[43] and 2-(1-napthylmethyl)-2-imidazole (L2)[44] were synthesized according to the procedure described in literature. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX-300 MHz spectrometer operating at room temperature in $CDCl_3$ and DMSO-d_6 as solvents. The chemical shift values (δ) were reported in parts per million (ppm) using tertramethyl silane (TMS) as an internal standard. FT-IR spectra were recorded on Perkin-Elmer Spectrum one in the form of KBr discs in the range 4000–500 cm^{-1}. Elemental analysis was carried out using Flash-2000 Organic Elemental Analyzer. Electronic spectra of titled compounds were recorded using Shimadzu UV-1800 spectrophotometer. Molar conductance measurements were carried out by ELICO (CM82T) Conductivity Bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as a calibrant.

Synthesis of ligands:

2-Aminoquinolin-8-ol (L1):

Crystalline yellow. Yield: 53.5%; m.p. 157–160°C; UV-Vis [λ_{max} (cm^{-1})]: 32467; FT-IR (KBr, cm^{-1}): 3403, 3305, 3103, 3071, 1633, 1620, 1576, 1513, 1486, 1387, 1078, 982, 951, 930, 880, 835, 803, 742, 712; ^{1}H NMR (300 MHz, DMSO-d_6) δ, ppm: 6.41 (brs, 2H, NH_2), 6.80 (d, 1H, H-C(3)), 6.88 (d, 1H, H-C(7)), 7.00 (t, 1H, H-C(6)), 7.10 (d, 1H, H-C(5)), 7.87 (d, 1H, H-C(4)) (Fig. S1); ^{13}C NMR (300 MHz, DMSO-d_6) δ, ppm: 110.5, 112.8, 117.6, 121.5, 122.8, 137.1, 137.4, 150.0, 157.0; LC-MS *m/z*: 161.0 [M+H]$^+$; Anal. Found (Calcd.) for $C_9H_8N_2O$: C, 67.45 (67.39); H, 5.01 (5.06); N, 17.41 (17.49).

2-(Naphthalen-1-ylmethyl)-4,5-dihydro-1H-imidazole (L2):

White solid. Yield: 78%; m.p. 253–255°C; UV-Vis [λ_{max} (cm^{-1})]: 25773; FT-IR (KBr, cm^{-1}): 3299, 3197, 2957, 2910, 1604, 1593, 1277, 1110; ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 3.50 (s, 4H), 4.03 (s, 2H), 4.28 (s, 1H), 7.26–7.43 (m, 2H), 7.47–7.55 (m, 2H), 7.79 (d, 1H), 7.86 (d, 1H), 8.12 (d, 1H) (Fig. S2); ^{13}C NMR (300 MHz, $CDCl_3$) δ, ppm: 34, 49, 123, 126, 127, 132, 133, 163; LC-MS *m/z*: 211 [M+H]$^+$; Anal. Found (Calcd.) for $C_{14}H_{14}N_2$: C, 79.97 (80.03); H, 6.71 (6.75); N, 13.32 (13.25).

Synthesis of complexes:

*General procedure for preparation of **1** and **2** complexes:*

A solution of 2-aminoquinolin-8-ol (L1) (2 mol) in a mixture of methanol (5 mL) and chloroform (5 mL) was added drop wise to 10 mL methanolic solution of metal salt ($CuCl_2.2H_2O$ and Na_2PdCl_4 (1 mol)). The reaction mixture was allowed to stir for 3–4 h at ambient temperature. The resulting precipitate was filtered and washed with cold methanol (5 mL×3) followed by diethyl ether (5 mL×3). The solid

Table 5. Comparison of bond length (Å) and bond angles (°) of $[Pd(L2)_2]$ and $[Cu(L2)_2]$ with literature values

Bond length (Å)	$[Pd(L2)Cl_2]$	Ref.[37]	Bond length (Å)	$[Cu(L2)Cl_2.H_2O]$	Ref.[40]
Pd(1)-N(6)	2.0295	2.014	Cu(1)-N(4)	1.95484	1.997
Pd(1)-Cl(57)	2.4288	2.321	Cu(1)-Cl(3)	2.42679	2.6146
Bond angle (°)			Bond angle (°)		
Cl(57)-Pd(1)-Cl(58)	179.9937	–	Cl(57)-Pd(1)-Cl(58)	171.29003	–
N(2)-Pd(1)-N(6)	179.9973	–	N(2)-Pd(1)-N(6)	174.07661	–
N(6)-Pd(1)-Cl(57)	90.9628	90.27	N(6)-Pd(1)-Cl(57)	91.51148	92.25

was dried over P_4O_{10} under vacuum gave complexes **1** and **2**.

$[Cu(C_{18}H_{14}N_4O_2)]$ (**1**): Green solid. Yield: 65%; m.p. 251–253°C; UV-Vis [λ_{max} (cm^{-1})]: 30959, 21739 and 15552; FT-IR (KBr, cm^{-1}): 3399, 3149, 3056, 1622, 1562, 1512, 1305, 1110, 626, 393; Anal. Found (Calcd.): Cu, 16.59 (16.64); C, 56.58 (56.61); H, 3.76 (3.70); N, 14.64 (14.67).

$[Pd(L1)_2]$ (**2**): Yellow crystalline solid. Yield: 71%; m.p. 300–302°C; UV-Vis [λ_{max} (cm^{-1})]: 34129, 28571, 16583; FT-IR (KBr, cm^{-1}): 3383, 3308, 3196, 3046, 1628, 1573, 1548, 1508, 1298, 1112, 659, 447; ^{1}H NMR (300 MHz, DMSO-d_6) δ, ppm: 6.49 (brs, 2H, NH_2), 6.83 (d, 1H, H-C(3)), 6.99 (d, 1H, H-C(7)), 7.15 (t, 1H, H-C(6)), 7.24 (t, 1H, H-C(5)), 7.98 (d, 1H, H-C(4)); Anal. Found (Calcd.): Pd, 24.89 (25.05); C, 50.78 (50.90); H, 3.29 (3.32); N, 13.07 (13.19).

*General procedure for preparation of **3** and **4** complexes:*

A solution of 2-(1-napthylmethyl)-2-imidazole (L2) (2 mol) in 10 mL of dry methanol was added drop wise to 10 mL methanolic solution of respective metal salt (Na_2PdCl_4 and $CuCl_2.2H_2O$ (1 mol) at ambient conditions. The reaction mixture was allowed to stir for 3–4 h. The precipitate was filtered and washed with cold methanol (10 mL×2), followed by diethyl ether (5 mL×2). The solid was dried over P_4O_{10} in vacuum to afford the complex **3** and **4**.

$[Cu(C_{28}H_{30}Cl_2N_4O)]$ (**3**): Green solid. Yield: 55%; m.p. 300–302°C; UV-Vis [λ_{max} (cm^{-1})]: 24875, 21321, 16694; FT-IR (KBr, cm^{-1}): 3393, 3343, 3000, 2948, 2868, 1567, 1220, 1080; Anal. Found (Calcd.): Cu, 10.99 (11.09); C, 58.71 (58.69); H, 5.23 (5.28); N, 9.74 (9.78).

$[Pd(L2)_2Cl_2]$ (**4**): Yellow solid. Yield: 63%; m.p. 285–287°C; UV-Vis [λ_{max} (cm^{-1})]: 23923, 16393; FT-IR (KBr, ν cm^{-1}): 3286, 3184, 2932, 2845, 1577, 1203, 1045, 547, 450; ^{1}H NMR (300 MHz, DMSO-d_6) δ, ppm: 3.56 (t, 2H), 3.83 (t, 2H), 4.08 (s, 2H), 4.35 (s, 1H), 7.50–7.63 (m, 2H), 7.71–7.84 (m, 2H), 7.80 (d, 1H), 7.88 (d, 1H), 8.23 (d, 1H); Anal. Found (Calcd.): Pd, 17.73 (17.80); C, 56.21 (56.25); H, 4.69 (4.72); N, 9.41 (9.37).

Computational details:

The structures of ligands and metal complexes were optimized at ground state in gas phase by using DFT/B3LYP[45,46] method with 6-311G(d,p) and LanL2DZ[47] basic sets, respectively using Gaussian 09W[48] programme and results were visualized by Gauss View 5.0[49] programme. Gauss Sum 3.0[50] programme was used to calculate group contributions to the molecular orbitals and to prepare the partial density of states (DOS) and overlap population density of states (OPDOS) spectra, which accept Gaussian out file as input. The PDOS and OPDOS spectra were created by convoluting the molecular orbital information with Gaussian curves of unit height and FWHM of 0.3 eV.

Table 6. Values of ionization potential (*I*), electron affinity (*A*), electronegativity (χ), global hardness (η), chemical potential (μ), chemical softness (ν) and electrophilicity index (ω) for titled compounds

Parameter/ Compd.	*I*	*A*	χ	η	μ	ν	ω
L1	8.40	0.34	4.19	4.02	–4.19	0.24	2.18
1	5.23	1.58	3.41	1.82	–3.41	0.54	3.19
2	5.09	1.64	3.36	1.72	–3.36	0.58	3.28
L2	5.99	1.37	3.68	2.30	–3.68	0.43	2.94
3	5.85	1.20	3.53	2.32	–3.53	0.43	2.68
4	5.81	1.75	3.78	2.02	–3.78	0.49	3.53

Conclusion

The current manuscript describes the synthesis, spectroscopic characterization, and anti-bacterial activity of Cu(II) and Pd(II) metal complexes of (L1) and (L2). DFT calculation were carried out for the structure optimization of ligand and metal complexes by using B3LYP/6-31++G(d,p) and B3LYP/LanL2DZ, respectively. The geometrical parameters of the titled compounds were good in agreement with reported values. The anti-bacterial activity of the complexes shown higher activities compared to ligands. Highest activity was displayed in case of copper complexes. This study could be useful in designing novel anti-bacterial metal-based drugs.

References

1. D. Kovala-Demertzi, M. A. Demertzis, E. Filiou, A. A. Pantazaki, P. N. Yadav, J. R. Miller, Y. Zheng and D. A. Kyriakidis, *Biometals*, 2013, **16**, 411.
2. E. Budizisz, U. Krajewska, M. Rozalski, A. Szulawska, M. Czyz and B. Nawrot, *Eur. J. Pharmacol*., 2004, **502**, 59.
3. J. Kuduk-Jaworska, A. Puszko, M. Kibiak and M. Pelczynska, *J. Inorg. Biochem.*, 2004, **98**, 1447.
4. E. Budzisz, M. Miernicka, I. P. Lorenz, P. Mayer, U. Krajewska and M. Rozalki, *Polyhedron*, 2009, **28**, 637.
5. N. Andrade Lopez, J. G. Alvarado Rodrýguez, S. Gonzalez Montiel, M. G. Rodrýguez Mendez and M. E. Paez Hernandez, *Polyhedron*, 2007, **26**, 4825.
6. L. Ma, R. C. Smith and J. D. Protasiewicz, *Inorg. Chim. Acta*, 2005, **358**, 3478.

7. Han Liu and Da Ming Du, *Adv. Synth. Catal*., 2009, **351**, 489.
8. M. A. Marshall and H. A. Mottola, *Anal. Chem.*, 1985, **57**, 375.
9. R. T. Bronson, M. Montalti, L. Prodi, N. Zaccheroni, R. D. Lamb, N. K. Dalley, R. M. Izatt, J. S. Bradshaw and P. B. Savage, *Tetrahedron*, 2009, **60**, 11139.
10. J. S. Youk, Y. H. Kim, E. J. Kim, N. J. Youn and S. K. Chang, *Bull. Korean Chem. Soc.*, 2004, **25**, 869.
11. R. T. Bronson, J. S. Bradshaw, P. B. Savage, S. Fuangswasdi, S. C. Lee, K. E. Krakowiak and R. M. Izatt, *J. Org. Chem*., 2001, **66**, 4752.
12. S. Wang, *Coord. Chem. Rev*., 2001, **215**, 79.
13. C. H. Chen and J. Shi, *Coord. Chem. Rev.*, 1998, **171**, 3.
14. E. M. Gross, J. D. Anderson, A. F. Slaterbeck, S. Thayumanavan, S. Barlow, Y. Zhang, S. R. Marder, H. K. Hall, M. FloreNabor, J. F. Wang, E. A. Mash, N. R. Armstrong and R. M. Wightman, *J. Am. Chem. Soc.*, 2000, **122**, 4972.
15. M. A. Katkova, Y. A. Kurskii, G. K. Fukin, A. S. Averyushkin, A. N. Artamonov and A. G. Vitukhnovsky, *Inorg. Chim. Acta*, 2005, **358**, 3625.
16. F. G. Yuan, Q. S. Liu and L. H. Weng, *Chin. J. Chem*., 2002, **20**, 1612.
17. F. Artizzu, K. Bernot, A. Caneschi, E. Coronado, J. M. Clemente-Juan, L. Marchiò and M. L. Mercuri, *Eur. J. Inorg. Chem*., 2008, **24**, 3820.
18. A. Lbecht, M. Osetska, O. Fröhlich and R. Bünzli, *J. Am. Chem. Soc.*, 2007, **129**, 14178.
19. S. Chandra and Anil Kumar, *Spectrochim. Acta, Part A*, 2007, **67**, 697.
20. V. D. Bhat and A. Ray, *Synth. Met*., 1998, **92**, 115.
21. B. Srinivas, N. Arulsamy and P. S. Zacharias, *Polyhedron*, 1991, **10**, 731.
22. S. Chandra and A. K. Sharma, *Spectrochim. Acta, Part A*, 2009, **72**, 851.
23. S. Chandra and S. Raizada, *Spectrochim. Acta, Part A*, 2008, **69**, 816.
24. D. Harikishore Kumar Reddy, Y. Harinath, Y. Suneetha, K. Seshaiah and A. V. R. Reddy, *Inorg. Nano-Met. Chem*., 2011, **41**, 287.
25. S. Chandra, Sangeetika and S. D. Sharma, *Spectrochim. Acta, Part A*, 2003, **59**, 755.
26. N. Turan and M. Sekerci, *Synth. React. Inorg. Met. Org. Chem. and Nano. Met. Chem.*, 2009, **39**, 651.
27. R. P. John, A. Sreekanth, V. Rajakannan, T. A. Ajith and M. R. P. Kurup, *Polyhedron*, 1991, **23**, 2549.
28. B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev*., 1970, **5**, 143.
29. A. B. P. Lever, "Inorganic Electronic Spectroscopy", 2nd ed., Elsevier, Amsterdam, 1984.
30. J. R. Anacona and G. D. Sillva, *J. Chil. Chem. Soc.*, 2005, **50**, 447.
31. S. Znanovic, S. Chi and A. F. Draughan, *J. Food Sci*., 2005, **70**, M45.
32. C. R. K. Rao and P. S. Zacharias, *Polyhedron*, 1997, **16**, 1201.
33. H. Sacconi and G. Speroni, *J. Am. Chem. Soc*., 1965, **87**, 3102.
34. J. I. Tanaka, K. Itoh and J. I. Setsune, *Z. Kristallogr. NCS*, 2003, **218**, 333.
35. K. K. H. Yusuff and C. Krishnakumar, *Synth. React. Inorg. Het. Org. Chem.*, 1993, **23**, 695.
36. S. Mehmet, *Turk. J. Chem*., 2001, **25**, 181.
37. J. G. Malecki, A. Maron, I. Gryca and M. Serda, *Mandeleev Commun.*, 2014, **24**, 26.
38. I. Potocnak and P. Vrance, *Monatsheftefür Chemie*, 2012, **143**, 217.
39. M. D. Vaira, C. Bazzicalupi, B. Bruni and P. Zata, *Inorg. Chem*., 2004, **43**, 3795.
40. B. M. Ociepa, E. R. Sokołowska and D. Michalska, *J. Mol. Struct.*, 2012, **1028**, 49.
41. R. Parr, L. Szentpaly and S. Liu, *J. Am. Chem. Soc*., 1999, **121**, 1922.
42. P. K. Chattaraj and U. Sarkar Roy, *Chem. Rev.*, 2006, **106**, 2065.
43. T. Storz, *Organic Proc. Res. and Develop*., 2004, **8**, 663.
44. Adlof Sonn, Immidazoline, JP06345737 1939.
45. A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648.
46. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
47. P. J. Hay, *J. Phys. Chem. A*, 2002, **106**, 1634.
48. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, Ochterski, J. W. Ayala, P. Y., K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 09, Revision B.01. Gaussian, Inc., Wallingford CT, 2010.
49. R. Dennington, T. Keith and J. Millam, Gaussview, version 5, Semichem Inc., ShawneeMission, KS, 2009.
50. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comp. Chem.*, 2008, **29**, 839.