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Synthesis, spectroscopic and single crystal X-ray studies on three new mononuclear Ni(II) pincer type complexes: DFT calculations and their antimicrobial activities

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ABSTRACT

Three new mononuclear square planar Ni(II) complexes, containing pincer type tridentate Schiff base ligands, having general formula [(NiL_1(4-MePy)] (**1**), [(NiL_1(2-AzNp)] (**2**), and [(NiL_2(4-MePy)] (**3**) [where L_1 = anion of *N*-(2-hydroxy-3-methoxybenzylidene) benzoylhydrazide (HL_1), L_2 = anion of *N*-(2-hydroxy-3-methoxybenzylidene) thiosemicarbazide (HL_2), 4-MePy = 4-Methylpyridine and 2-AzNp = 2-Azanapthalene] have been synthesized and fully characterized by FT-IR, UV–visible, NMR, single crystal X-ray diffraction studies and elemental analysis. All the three complexes show square planar geometry around the nickel atom. The pincer type ligand occupies three coordination sites, while the fourth site is occupied by the monodentate nitrogen containing ligand. The Quantum chemical DFT calculations have also been carried out using DFT/B3LYP method and 6-311++G(d,p) basis set. The synthesized nickel complexes were screened for antimicrobial activities by agar well diffusion method against *E. coli* bacteria. Out of three complexes, [(NiL_2(4-MePy)] (**3**) only showed the antimicrobial activity against *E. coli* bacteria.

1. Introduction

In recent decade, multi-dentate Schiff bases and their metal complexes have allured a lot of attention of chemists not only because of their an assortment of applications in coordination chemistry [1], but also for their miscellaneous biological activities such as antifungal, antibacterial, analgesic, sedative, antipyretic and anti-inflammatory properties [2–8]. These are also in huge stipulate in catalysis [9–12], agriculture, analytical chemistry, dye polymer industry [13–15], luminescent probes [16] etc. Owing to multi-dentate nature of these ligands, they have been used in the synthesis of model complexes for the active sites of various enzymes. The contribution of metal ions in biological reactions is well known [17]. A perusal of the literature survey reveals that, presence of azomethine (-C=N-) linkage in Schiff bases and lone pair of electrons on a sp^2-hybridized orbital of nitrogen atom of the azomethine group is accountable for antimicrobial activities and plays a significant chemical and biological role [18]. Our persistent interest in transition metal complexes [19–21] and their diverse applications, has lead us to synthesis hydrazide and carbazide containing Schiff base ligands and their complexes. Recently, nickel has emerged as a striking transition metal for the development of catalysts in biological and industrial applications [22–24]. During the present studies, we have chosen two potential tridentate Schiff base ligands, *N*-(2-hydroxy-3-methoxybenzylidene) benzoylhydrazide (HL_1) and *N*-(2-hydroxy-3-methoxybenzylidene) thiosemicarbazide (HL_2). Both ligands contain two potentially dissociable acidic protons, *viz.* the phenolic *O–H* or *S–H* and the hydrazinic *N–H* protons. Herein, we describe the synthesis and characterization of three new complexes of general formula [(NiL_1(4-MePy)] (**1**), [(NiL_1(2-AzNp)] (**2**) and [(NiL_2(4-MePy)] (**3**) obtained by the reaction of nickel(II) acetate and the corresponding ligand and a monodentate co-ligand in methanol at room temperature. Keeping in mind the significance and development of new therapeutic reagents in biological field [25–27], all three

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complexes have been tested for their antibacterial activities against common bacteria *Escherichia coli* using agar well diffusion method. In addition to these the structural geometry and binding mode of ligands with Ni(II) in all complexes are presented by DFT calculations.

2. Experiment

2.1. Materials and physical measurements

All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification. The FT-IR spectra were recorded on a Perkin Elmer Spectrometer (Model: Cary 660) in the range of 400–4000 cm^{-1} using KBr pellets in which MCT used as a detector with scan number 20, and resolution 4 cm^{-1}. The UV visible spectra were obtained on an Agilent 8453 diode array spectrophotometer using DMF as solvent. Elemental analyses were carried out using a Heraeus CHN-Rapid elemental analyzer. The NMR spectra of complexes were recorded in $CDCl_3$ on a Bruker 75 AvIII HD-400 MHz spectrometer using TMS as the internal Standard.

2.2. Synthesis of N-(2-hydroxy-3-methoxybenzylidene) benzohydrazide (HL_1)

The Schiff base ligand HL_1 was synthesized by slight modification of the reported method [28]. A solution of benzoylhydrazine (0.1362 gm, 1 mmol) in ethanol (5 mL) was added to an ethanolic solution (5-mL) of *ortho*-vaniline (0.1522 gm, 1 mmol) at room temp. The resultant solution was heated to reflux for a period of 3–4 h to produce off-white solid. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. Yield: 0.233 g, 81%. Selected FT-IR (KBr), cm^{-1}: 3564 (NH), 3380 (OH), 2839-3062 (CH_{ar}), 1646 (C=O), 1596 (C=N), 1470 ($C{=}C_{ring}$).

2.3. Synthesis of N-(2-hydroxy-3-methoxybenzylidene) thiosemicarbazide (HL_2)

The Schiff base ligand HL_2 was synthesized by slight modification of the reported method [29]. A solution of thiosemicarbazide (0.091 g, 1 mmol) in ethanol (5 mL) was added to an ethanolic solution (5-mL) of *ortho*-vaniline (0.1522 gm, 1 mmol) at room temp. The resultant solution was heated to reflux for a period of 2–3 h to produce off-white solid. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. Yield: 0.185 g, 76%. m.p. 79-82 °C. Selected FT-IR (KBr), cm^{-1}: 3443 (NH), 3326, 3157 (NH_2), 3021 (OH), 1596 (C=N), 1045 (C=S).

2.4. Synthesis of complex [(NiL_1(4-MePy)] (**1**)

A solution of Schiff base ligand (HL_1) (0.144 mg, 0.50 mmol) in methanol (4 mL) was added drop-wise to a methanolic solution (4 ml) of $Ni(OAc)_2{\cdot}4H_2O$ (0.124 mg, 0.50 mmol) with constant stirring at room temperature. After stirring the solution for 10 min at room temperature, co-ligand 4-methylpyridine (0.048 ml, 0.50 mmol, dissolved in 2-mL methanol) was added *via* a syringe to the reaction. On addition of co-ligand, the color of solution had changed from greenish to dark-brown. After 6 h of stirring at rt, the resultant precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. The precipitate was re-crystallized from DMF. Suitable single crystals for X-ray crystallography were grown over a period of two weeks from a concentrated solution of the complex in DMF.

Yields: 0.230 gm, 73%. Anal. Calc. for $C_{21}H_{19}N_3NiO_3$: C, 60.04; H, 4.56; N, 10.00. Found: C, 60.24; H, 4.42; N, 10.24. Selected FT-IR (KBr), cm^{-1}: 2915 (CH_{ar}), 1579 (C=N), 1230 (C–O), 582 (Ni–O), ν(Ni–N) 473. UV–Vis [λ_{max}(nm), ε (L mol^{-1} cm^{-1})]: 303 (18400), 363 (18800), 413 (9800). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta = 8.56$ (s, 1H, H–CN), 7.84–8.00 (d, 3H, Ar *H*), 7.01–7.46 (m, 5H, Ar *H*), 6.96 (s, 1H, Ar *H*), 6.61–6.73 (d, 3H, Ar *H*), 3.81 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3).

2.5. Synthesis of [(NiL_1(2-AzNp)](**2**)

A solution of Schiff base ligand (HL_1) (0.144 mg, 0.50 mmol) in methanol (4 mL) was added drop-wise to a methanolic solution (4 ml) of $Ni(OAc)_2{\cdot}4H_2O$ (0.124 mg, 0.50 mmol) with constant stirring at room temperature. After stirring the solution for 10 min at room temperature, co-ligand 2-azanaphthalene (isoquinoline) (0.059 ml, 0.50 mmol, dissolved in 2-mL methanol) was added *via* a syringe to the reaction. On addition of co-ligand, the color of solution had changed from greenish to dark-brown. After 6 h of stirring at rt, the resultant precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. The precipitate was re-crystallized from DMF. Suitable single crystals for X-ray crystallography were grown over a period of two weeks from a concentrated solution of the complex in DMF.

Yields: 0.216 gm, 65%. Anal. Calc. for $C_{24}H_{19}N_3NiO_3$: C, 63.73; H, 4.71; N, 8.92; Found: C, 63.55; H, 4.84; N, 8.99. Selected FT-IR (KBr), cm^{-1}: 1580 (C=N), 1217 (C–O), 560 (Ni–O), 468 (Ni–N). UV–Vis [λ_{max}(nm), ε (L mol^{-1} cm^{-1})]: 309 (20900), 361 (19100), 414 (9600). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ = 9.44 (s, 1H, isoquinoline *H*), 8.61 (s, 1H, *H*–CN), 7.72–8.10 (m, 8H, Ar *H*), 7.34–7.37 (t, 2H, Ar *H*), 6.98 (d, 1H, Ar *H*), 6.75–6.77 (t, 2H, Ar *H*), 6.64 (t, 1H, Ar *H*), 3.89 (s, 3H, OCH_3).

2.6. Synthesis of [(NiL_2(4-MePy)] (**3**)

A solution of Schiff base ligand (HL_2) (0.113 mg, 0.50 mmol) in methanol (4 mL) was added drop-wise to a methanolic solution (4 ml) of $Ni(OAc)_2{\cdot}4H_2O$ (0.124 mg, 0.50 mmol) with constant stirring at room temperature. After stirring the solution for 10 min at room temperature, co-ligand 4-methylpyridine (0.048 ml, 0.50 mmol, dissolved in 2-mL methanol) was added *via* a syringe to the reaction. On addition of co-ligand, the color of solution had changed from greenish to dark-brown. After 6 h of stirring at rt, the resultant precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. The precipitate was re-crystallized from DMF. Suitable single crystals for X-ray crystallography were grown over a period of two weeks from a concentrated solution of the complex in DMF.

Yields: 0.198 gm, 70%. m.p: 195 °C. Anal. Calc. for $C_{15}H_{16}N_4NiO_2S$: C, 48.03; H, 4.30; N, 14.94; Found: C, 48.15; H, 4.41; N, 14.80. Selected FT-IR (KBr), cm^{-1}: 3362, 3265 (NH_2), 1530 (C=N), 1312 (C–O), 568 (Ni–O), 481 (Ni–N). UV–Vis [λ_{max}(nm), ε (L mol^{-1} cm^{-1})]: 297 (19700), 367 (16900), 415 (7300). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta = 8.61$ (s, 1H, *H*–CN), 7.79 (s, 1H, Ar *H*), 7.10–7.11 (m, 2H, Ar *H*), 6.83 (d, 1H, Ar *H*), 6.66 (d, 1H, Ar *H*), 6.48–6.57 (t, 2H, Ar *H*), 4.57 (s, 2H, –NH_2), 3.67 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3).

2.7. Crystallographic studies

Diffraction quality crystals of the complexes (1-3) were grown over a period of two weeks from a concentrated solution of the complex in DMF at room temperature and the structure of the complex have been elucidated by single-crystal X-ray diffraction. The X-ray diffraction intensity data were measured at 103 K with a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo K α radiation ($\lambda = 0.71073$ Å), with the SMART suite

of programs [30]. All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS [31]. Structural solution and refinement were carried out with the SHELXTL suite of programs [32]. The structures were refined (weighted least squares refinement on F^2) to convergence. All the non-hydrogen atoms in all the compounds were refined anisotropically till convergence is reached. Precise unit-cell parameters were determined by a least-squares fit of 2500 (1), 3662 (2) and 1053 (3) reflections of the highest intensity, chosen from the whole experiment. A summary of the crystallographic and refinement data of these three nickel complexes are given in Table 1.

2.8. Computational details

For supporting the experimental work, geometrical optimization calculation of three nickel complexes were carried out in Gaussian 09 program with DFT/B3LYP [33,34] method. The geometries of all the three complexes were optimized using 6-311++G(d,p) basis set [35,36] and the stationary point structures were visualized with the help of Gauss-View 5.0 program [37]. Using DFT calculations, the energy level HOMO and LUMO diagrams and molecular chemical stability of the Ni(II) complexes were determined.

2.9. Antimicrobial assays

The *in-vitro* antibacterial activity and MIC value of the synthesized nickel complexes were evaluated against *Escherichia coli* by agar well diffusion method [38].

2.9.1. Determination of minimum inhibitory concentrations (MIC)

Agar dilutions were mostly prepared in sterilized Petri dishes as it has advantage to test antimicrobial activity of several concentrations of the same compound on each plate. One can also get an overview idea about the MIC of the test compound. MIC is defined as the lowest concentration of an antimicrobial that will inhibit the visible growth of a microorganism after overnight incubation [39]. Nutritional Agar was made with the following components [40]:

After the setting of plates with the agar media, they were well dried at 37 °C in a laminar airflow under UV light. For preparing the stock, *Escherichia coli* ATCC 25922 (American Type Culture Collection, Rockville, MD) cultures were kept for 24 h at 36 °C±1 °C and the purity of cultures was checked after 8 h of incubation of *E. coli*. And then plates were washed out with stock. After 24 h of incubation, bacterial suspension (inoculums) was diluted with sterile physiological solution, for the diffusion and indirect bioautographic tests, to 10^8 CFU/mL (turbidity = McFarland barium sulfate standard 0.5) [41]. Plates inoculated with the *E. coli* had three 6 mm wells cut into the surface of the agar using a cork borer dipped in alcohol and flamed. The wells were filled with 0.5 ml of test compounds with different concentration solutions. All plates were incubated (35 °C) overnight [42]. After incubation, the diameters of any clear zones around the antimicrobial compound-containing wells were measured using calipers.

3. Results and discussion

Two Schiff base ligands HL_1 and HL_2 were synthesized by modification of the reported methods [28,29]. Both ligands were obtained as off-white crystalline solid in good yields (76 and 81%) on heating an ethanolic solution of corresponding reactants just for 2–4 h. The synthesis of nickel complexes is outlined in Scheme 1. All three complexes were obtained as dark-brown crystalline solids in high yields (65–75%). The complexes were found to be air stable, soluble in common organic solvents such as MeOH, CH_3COCH_3, Et_2O, $CHCl_3$, CH_2Cl_2, CH_3CN, DMF and DMSO and insoluble in water and benzene. All complexes were fully characterized by various spectroscopic techniques like FT-IR, UV–visible, ^{1}H NMR, elemental analysis. The solid state structures of complexes [(NiL_1(4-MePy)] (**1**), [(NiL_1(2-AzNp)] (**2**) and [(NiL_2(4-MePy)] (**3**) were determined by single crystal X-ray diffraction analysis.

3.1. Single crystal X-Ray studies

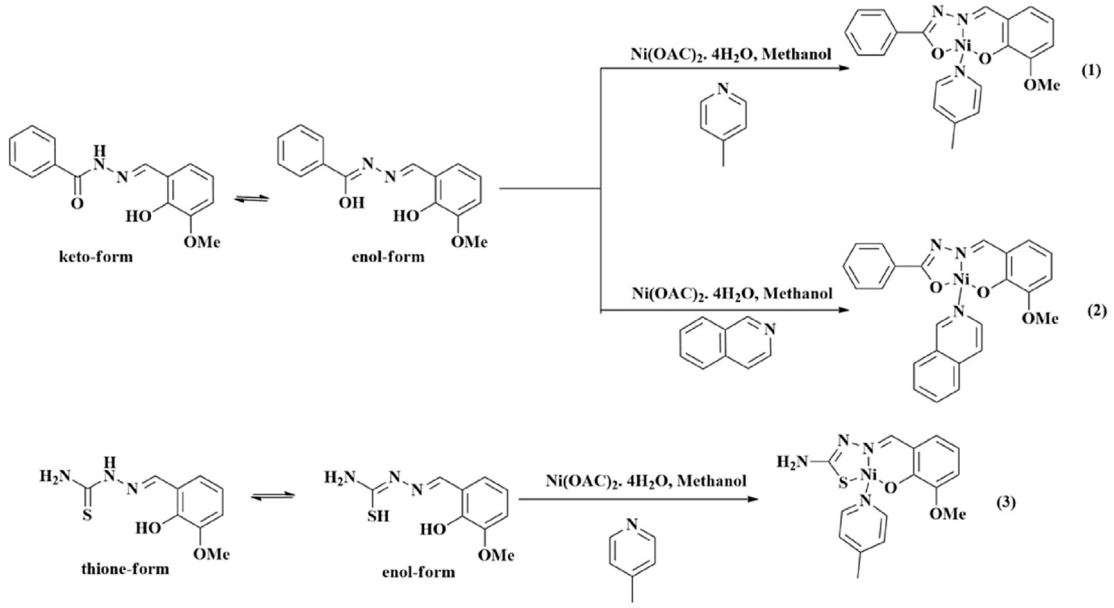
The proposed structures of three nickel(II) complexes 1, 2 and 3

Table 1
Crystallographic and refinement data for [(NiL_1(4-MePy)] (1), [(NiL_1(2-AzNp)] (2) and [(NiL_2(4-MePy)] (3) complexes.

Complex	[(NiL_1 (4-MePy)]	[(NiL_1 (2-AzNp)]	[(NiL_2 (4-MePy)]
CCDC deposition number	1470164	1477281	1477282
Chemical formula	$C_{21}H_{19}N_3NiO_3$	$C_{24}H_{19}N_3NiO_3$	$C_{15}H_{16}N_4NiO_2S$
Formula weight	420.10 g/mol	456.13 g/mol	375.09 g/mol
Temperature	103 (2) K	103 (2) K	103 (2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.060 × 0.140 × 0.160 mm	0.040 × 0.220 × 0.400 mm	0.140 × 0.180 × 0.320 mm
Crystal habit	red plate	red plate	red block
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*P b c a*	*P b c a*	*P 1 21/c 1*
Unit cell dimensions			
a (Å)	21.1983 (14)	8.8501 (7)	10.792 (2)
b (Å)	14.0989 (8)	17.0214 (15)	9.655 (2)
c (Å)	25.1003 (15)	26.151 (2)	15.556 (4)
α (°)	90	90	90°
β (°)	90	90	101.932 (12)°
γ (°)	90	90	90°
V (Å^3)	7501.8 (8)	3939.4 (6) Å^3	1585.9 (7)
Z	16	8	4
Density (calculated)	1.488 g/cm^3	1.538 g/cm^3	1.571 g/cm^3
Absorption coefficient	1.062 mm^{-1}	1.018 mm^{-1}	1.369 mm^{-1}
F (000)	3488	1888	776
R_{int}	0.1184	0.0866	0.0879
R_1[I > 2δ(I)]	0.0652	0.0501	0.0811
wR_2 (all data)	0.2435	0.1106	0.2236
Largest diff. peak and hole	1.519 and −0.715 eÅ^{-3}	0.552 and −0.685 eÅ^{-3}	1.332 and −0.579 eÅ^{-3}
R.M.S. deviation from mean	0.158 eÅ^{-3}	0.089 eÅ^{-3}	0.143 eÅ^{-3}

Ingredients	Peptic digest of animal tissue	Sodium chloride	Beef extract	Yeast extract	Agar	Final pH at 25 °C
gL^{-1}	5	5	1.5	1.5	15	7.4 ± 0.2

based on the above techniques were unambiguously confirmed by X-ray diffraction studies. The ORTEP representations of three nickel (II) complexes including the atom numbering scheme are shown in Fig. 1. Molecular structures of these complexes revealed that the nickel atoms in all complexes have distorted square planar coordination geometry. Distortion is mainly caused by the presence of the double deprotonated tridentate Schiff base ligand, which forms one five-membered and one six-membered chelating ring with nickel atom. The neutral complexes contain one Ni(II) ion with four coordination number legated to one tridentate Schiff base ligand and the appropriate amine *i.e.* coligand, and have similar structures. This coordination is fulfilled by one nitrogen and two phenolic oxygen atoms from the tridentate Schiff base ligands (L_1), with one nitrogen atoms from 4-methylpyridine (1) and 2-azanapthalene molecule (2). In case of complex 3, the nickel is coordinated by one nitrogen, one phenolic oxygen atom and one thionate sulphur atom from the tridentate Schiff base ligand (L_2) along with one nitrogen atom of 4-methylpyridine. The selected bond lengths and bond angles are listed in Table 2. The N(1)-Ni(1)-O(1), N(1)-Ni(1)-O(2) and N(1)-Ni(1)-N(3) chelate bite angles of the complexes **1** and **2** are in the range of 83.7(2)° - 95.2(2)°, 83.61(10)° - 94.62(10)° and 174.6(2)° - 174.88(11)° respectively. While the N(1)-Ni(1)-O(1) and O(1)-Ni(1)-S(1) chelate bite angles are 95.8(2)° and 169.69(17)° respectively for complex 3. The Ni—O and Ni—N bond lengths in all three complexes (1-3) are in the range of 1.807(5)-1.868(5) Å and 1.819(5)-1.952(3) Å respectively which are in close agreement with the values reported for other nickel(II) complexes [43,44]. The Ni—S bond length of complex 3 is 2.145(2) Å, is nearly similar to



Scheme 1. Preparation of nickel(II) complexes of Schiff base ligands.

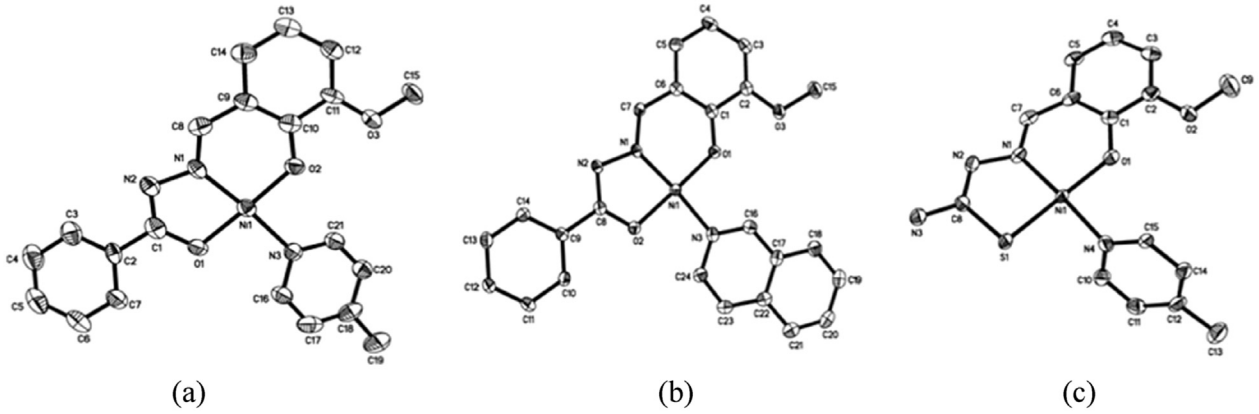


Fig. 1. ORTEP diagram of (a) [(NiL_1(4-MePy)] (1), (b) [(NiL_1(2-AzNp)] (2) and (c) [(NiL_2(4-MePy)] (3) complexes with the atom labeling scheme (Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity).

Table 2
Selected bond distances (Å) and bond angles (°) for [(NiL_1(4-MePy)] (1), [(NiL_1(2-AzNp)] (2) and [(NiL_2(4-MePy)] (3) complexes.

	[(NiL_1(4-MePy)]	[(NiL_1(2-AzNp)]	[(NiL_2(4-MePy)]
Bond distances			
Ni(1)–N(1)	1.826 (6)	1.823 (3)	1.860 (5)
Ni(1)–N(3)	1.934 (6)	1.952 (3)	–
Ni(1)–N(4)	–	–	1.922 (6)
Ni(1)–O(1)	1.833 (5)	1.824 (2)	1.868 (5)
Ni(1)–O(2)	1.828 (5)	1.851 (2)	–
Ni(2)–O(4)	1.828 (5)	–	–
Ni(2)–O(5)	1.807 (5)	-	-
Ni(1)–S(1)	–	-	2.145 (2)
Bond angles			
N(1)–Ni(1)–O(1)	83.7 (2)	94.62 (10)	95.8 (2)
N(1)–Ni(1)–O(2)	95.2 (2)	83.61 (10)	-
O(2)–Ni(1)–O(1)	175.4 (2)	177.80 (10)	-
N(1)–Ni(1)–N(3)	174.6 (2)	174.88 (11)	-
N1–Ni1–N4	–	–	169.2 (2)
O(2)–Ni(1)–N(3)	89.9 (2)	91.35 (10)	-
O(1)–Ni(1)–N(3)	91.1 (2)	90.44 (10)	-
N(1)–Ni(1)–S(1)	–	-	86.97 (18)
O(1)–Ni(1)–S(1)	–	-	169.69 (17)

previously reported Ni(II) complex published by I. Kilic-cikla et al. [45]. Packing of molecules of **1**–**3** is shown in ESI Fig. S1, Fig. S2 and Fig. S3 respectively.

3.2. Computational study

Quantum chemical DFT calculations of all the nickel(II) complexes were performed in Gaussian 09 program using DFT/B3LYP method with 6–311++G(d,p) basis set. The energy of the molecules was calculated by simply optimization of complex structures and the optimized structures of all three complexes were shown in ESI Fig. S4. The optimized structures are at global minima was confirmed by lack of imaginary vibration in frequency calculation and from this result it may be concluded that the obtained structures to be local minima on the potential energy surfaces. Frontier molecular orbital (FMO) play an important role in determining the reactivity of compounds. The HOMO and LUMO contours of complexes [(NiL_1(4-MePy)] (**1**), [(NiL_1(2-AzNp)] (**2**) and [(NiL_2(4-MePy)] (**3**) are shown in Fig. 2. HOMO generally behaved as an electron donor and LUMO as an electron acceptor. In all the three complexes, Schiff base ligand contained HOMO orbital around it while heterocyclic aromatic co-ligand contained LUMO orbital. Aromatic rings, especially heterocyclic bases, are suitable electrophilic sites while the oxygen of methoxy moiety and nitrogen and sulphur of hydrazine are potential negative sites. The interaction of ligand with the metal is confirmed by availability of these sites. Molecular chemical stability of the complexes was determined by the difference of energy between HOMO and LUMO. Complex which contained larger energy difference have a lower chemical reactivity. A suitable cavity was formed for encapsulating Ni(II) by both the ligands in presence of two co-ligand such as 4-methylpyridine or 2-azanapthalene. The computed optimization energy values of the three Ni(II) complexes [(NiL_1(4-MePy)] (**1**), [(NiL_2(4-MePy)] (**2**) and [(NiL_1(2-AzNp)] (**3**) were −73740.62 eV, −76851.78 eV and −70401.27 eV respectively (Fig. 2). The metal binding energy of all three metal complexes **1**, **2** and **3** were found to be −41006.66 eV, −41006.20 eV and −33661.55 eV, respectively. It may be concluded that the higher the binding energy of the complex, the greater will be the stability. Since, complex 1 has highest metal binding energy among the three complexes, it is likely to have the highest stability.

3.3. FT-IR spectra of the complexes

The FT-IR spectrum of the ligand HL_1 exhibited a broad band at 3380 cm^{-1} and a weak band at 3564 cm^{-1} due to ν OH and ν NH groups, respectively. Interestingly, HL_1 exhibited a sharp and high

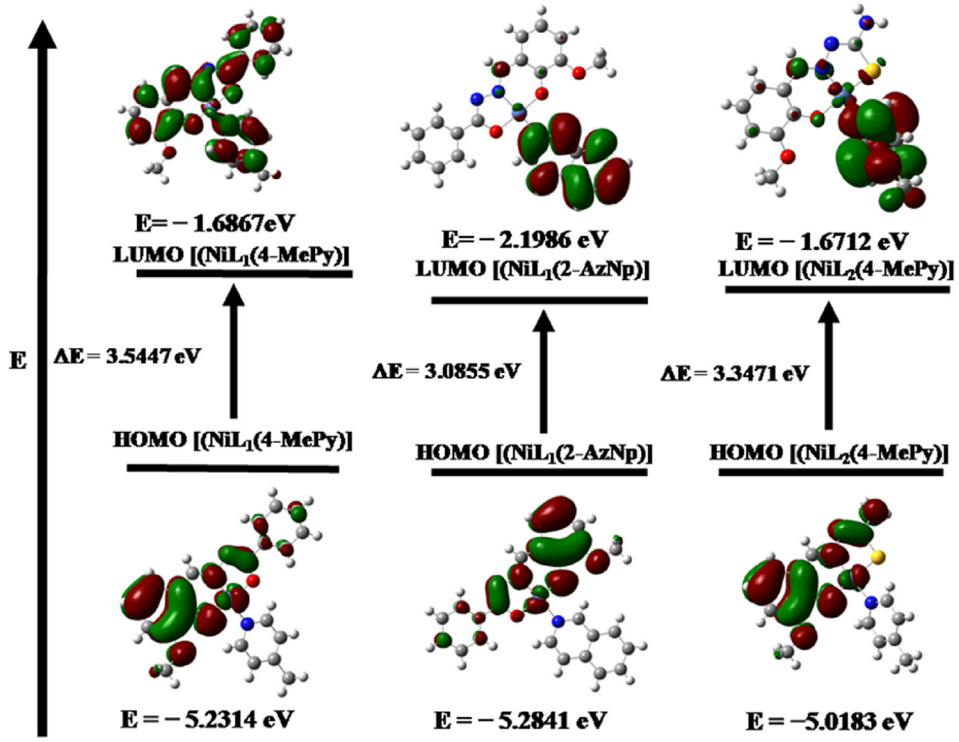


Fig. 2. Energy level HOMO and LUMO diagrams of Ni(II) complexes.

intensity band at 1646 cm^{-1} due to ν C=O. The presence of ν NH at 3564 cm^{-1} and ν C=O at 1646 cm^{-1} clearly indicated that the ligand HL_1 existed predominantly in keto form in the solid state [28]. The FT-IR spectrum of the HL_1 ligand also showed an intense band at around 1596 cm^{-1} due to the azomethine group ν (C=N). The FT-IR spectra of the nickel(II) complexes (**1**) and (**2**) are given in Fig. S5 and Fig. S6 (Supporting information). The FT-IR spectra of complexes (**1**) and (**2**) exhibited bands at 1579 cm^{-1} and 1580 cm^{-1} assignable to ν (C=N) stretching frequency, respectively. A comparison of the FT-IR of the free ligand HL_1 and complexes clearly indicated that the C=N stretching frequency were shifted to lower wave number by 17 cm^{-1} and 16 cm^{-1}, in complex (**1**) and (**2**), respectively. The shifting of azomethine stretching frequency to lower wave number may be taken as evidence for the coordination of the nitrogen atom to the metal [46]. The disappearance of ν OH peak and appearance of a peak at 582 cm^{-1} and 560 cm^{-1} (Ni–O) in the FT-IR spectra of complex (**1**) and (**2**), respectively, supports the formation of complexes (**1**) and (**2**) [47].

The FT-IR spectrum of the free ligand (HL_2), showed an intense band at 3443 cm^{-1} and 1045 cm^{-1} assignable to ν (*N*–H) and ν(C=S) groups, respectively. It confirms the presence of the thione form of ligand in the solid state. The FT-IR spectrum of the HL_2 ligand also showed an intense band at around 1590 cm^{-1} due to the ν (C=N) stretching frequency. The bands at 3331 cm^{-1} and 3157-3326 cm^{-1} were assigned to the ν OH and ν NH_2 vibrations of the ligand. The FT-IR spectra of complex (**3**) showed a band at 1584 cm^{-1} assignable to ν (C=N) group. A comparison of the FT-IR of the free ligand HL_2 and complex (**3**) indicated that the C=N stretching frequency were shifted to lower wave number by 6 cm^{-1} (Fig. S7) which confirmed the coordination of the nitrogen atom to the metal. The disappearance of ν OH stretching frequency and the appearance of a peak at 588 cm^{-1} (Ni–O) in FT-IR of the complex support the formation of the complex (**3**) [48].

Theoretical FT-IR spectra of all complexes, calculated with DFT/B3LYP method using a 6-311++G(d,p) basis set, exhibited more similarities with the experimental FT-IR spectra as shown in Figs. S8–S10. The calculated vibrational frequencies and experimental FT-IR frequencies are presented in Table 1S. These values were found in good agreement with observed group frequencies.

3.4. UV–visible spectra of the complexes

The electronic spectra of nickel(II) complexes were recorded in DMF solutions (10^{-4} M) in the range of 270–800 nm. Each of the complexes displayed three strong absorption bands in the region 297–309 nm, 360–367 nm and 412–417 nm [49] (Supporting information, Figs. S11–S13). The strong and high energy peaks in the regions 297–309 nm were attributed to the intra-ligand transition. The n-π^* transition corresponding to the azomethine groups observed in the range of 360–367 nm have been attributed to ligand to metal charge transfer (LMCT) transition ($^3A_{2g} \rightarrow {}^3T_{2g}$) and the shoulder at 412–417 nm to forbidden ($^3A_{2g} \rightarrow {}^3T_{1g}$) transition [50,51].

3.5. ^1H NMR spectra

The ^1H NMR spectra of the complex [(NiL_1(4-MePy)] in $CDCl_3$ at room temperature showed a sharp singlet at δ 8.56 due to C–*H* of azomethine. The absence of O*H* protons in the ^1H NMR of the complex indicated the de-protonation of the hydroxy group and coordination of the oxygen atom to the metal. Multiplet resonances observed in the range δ 6.6–8.0 were assigned to the aromatic protons. The ^1H NMR of Complexes [(NiL_1(2-AzNp)] (**2**) and [(NiL_2(4-MePy)] (**3**), exhibited the azomethine proton (*H*C=N-) signal at δ 8.61 and 9.44, respectively. In all three complexes, the –OCH_3 of *ortho*-vaniline were observed in the range of δ 3.67 to 3.90. The –CH_3 protons of the co-ligand 4-methylpyridine were observed as singlet at δ 2.30 and 2.50, in complex **1** and complex (**3**), respectively. However, the complex (**3**) exhibited a signal at δ 4.57 for two protons of the –NH_2 group. It is obvious from the ^1H NMR of complex (**3**), that no de-protonation of the NH_2 group of thiosemicarbazide moiety had occurred, confirming the non-participation of the NH_2 group in coordination. The fact that the –NH_2 group remained intact is unambiguously supported by single crystal structure of the complex (**3**) [Fig. 1(c)]. The ^1H NMR spectra of all three complexes are given in Fig. S14-Fig. S16 (Supporting information), respectively.

3.6. Antimicrobial activity

In order to study the potential biological properties of the synthesized nickel complexes, the antibacterial properties were studied. As the test complexes were insoluble in water, we used 5% DMSO solution to make a homogeneous aqueous solution. The effect of 5% DMSO on the growth of *E. coli* is negligible and it is reported that at 5% DMSO, only a slight reduction in growth rate was observed over a 6 h [52]. Since aqueous solutions of DMSO were known to be alkaline, the pH was carefully monitored each and

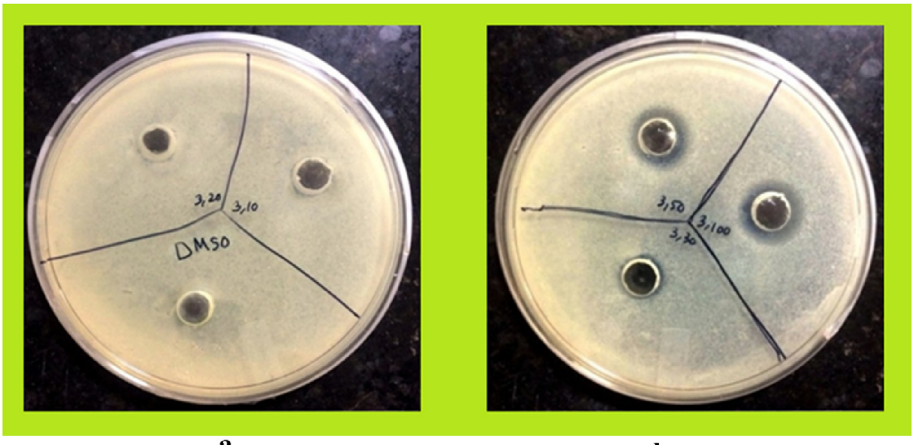


Fig. 3. (a) Control 5% DMSO, 10 ppm and 20 ppm concentration of the [(NiL_2(4-MePy)] (3) complex shows no significant antimicrobial effect on *E. coli*. (b) 30 ppm, 50 ppm and 100 ppm shows increasing inhibition zone for the antimicrobial effect of the test compound.

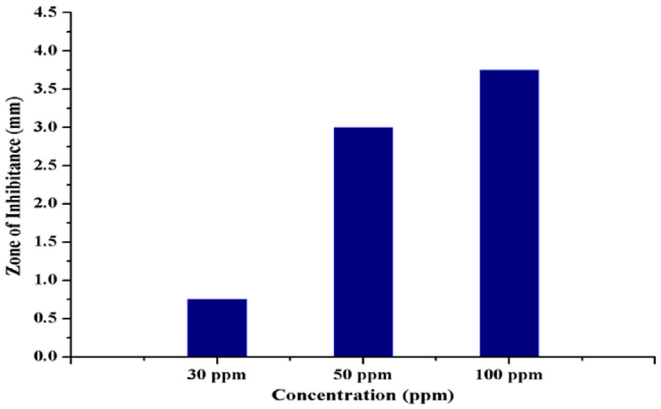


Fig. 4. Inhibition on *E. Coli* bacteria at different concentration of [(NiL_2(4-MePy)] (3) complex at concentration 30, 50 and 100 ppm.

every time [53]. A control study was done with 5% DMSO without the addition of any compound to eliminate the effect of DMSO on bacterial growth inhibition. The study shows that MIC value of the test compound must be between 20 and 30 ppm and more precisely around 30 ppm. Control 5% DMSO has no significant effect on the growth of *E. coli*. Based upon observations, it was concluded that the complex (**3**) have significant antimicrobial activity over 30 ppm of concentration. These observations are more or less similar to the earlier report [54] of bioactivities of other Ni(II) complexes. The result for the antimicrobial activity of complex (**3**) against *E. coli* bacteria is shown in Fig. 3. The inhibition zone on *E. coli* bacteria at different concentration 30, 50 and 100 ppm of [(NiL_2(4-MePy)] (**3**) complex are shown in Fig. 4. The rest two complexes are non toxic and eco-friendly in nature.

4. Conclusion

Three new heteroleptic nickel(II) complexes containing pincer type of Schiff base ligand have been synthesized and characterized by various spectroscopic techniques. The structures of all three complexes (**1**), (**2**) and (**3**) were unambiguously confirmed by single crystal X-ray diffraction studies. All complexes possess a square planar geometry in which three coordination site are occupied by a pincer type Schiff base ligand and the forth site by a nitrogen atom of a co-ligand. The quantum chemical DFT calculations supplemented the structures of the complexes and the binding motif of ligands. Antimicrobial studies indicated that complex [(NiL_2(4-MePy)] (**3**) was effective against *E. coli* bacteria at minimum inhibitory concentration of 30 ppm.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.03.114.

References

[1] A.D. Garnovski, A.L. Nivorozhkin, V.I. Minkin, Ligand environment and the structure of schiff base adducts and tetracoordinated metal-chelates, Coord. Chem. Rev. 126 (1993) 1–69.
[2] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, Coordination compounds of copper, nickel and iron with Schiff bases derived from hydroxynaphthaldehydes and salicylaldehydes, Coord. Chem. Rev. 119 (1992) 67–88.
[3] M. Du, X.J. Zhao, J.H. Guo, X.H. Bu, J. Ribas, Towards the design of linear homotrinuclear metal complexes based on a new phenol-functionalised diazamesocyclic ligand: structural analysis and magnetism, Eur. J. Inorg. Chem. (2005) 294–304.
[4] S.C. Bhatia, J.M. Bindlish, A.R. Saini, P.C. Jain, Crystal and molecular structure of bis(*N*-allylsalicylideneiminato)-nickel(II) and -copper(II), J. Chem. Soc. Dalton Trans. (1981) 1773–1779.
[5] S. Leininger, B. Olenyuk, P.J. Stang, Self-assembly of discrete cyclic nanostructures mediated by transition metals, Chem. Rev. 100 (2000) 853–908.
[6] S. Chandra, X. Sangeetika, EPR, magnetic and spectral studies of copper(II) and nickel(II) complexes of schiff base macrocyclic ligand derived from thiosemicarbazide and glyoxal, Spectrochim. Acta, Part A 60 (2004) 147–153.
[7] E.I. Solomon, R.K. Szilagyi, S.D. George, L. Basumallick, Electronic structures of metal sites in proteins and models: contributions to function in blue copper proteins, Chem. Rev. 104 (2004) 419–458.
[8] C.R. Choudhury, S.K. Dey, R. Karmakar, C.D. Wu, C.Z. Lu, M.S. ElFallah, S. Mitra, First report of singly phenoxo-bridged copper(II) dimeric complexes: synthesis, crystal structure and low-temperature magnetic behaviour study, New J. Chem. 27 (2003) 1360–1366.
[9] S. Kumar, D.N. Dhar, Applications of metal complexes of Schiff bases- A review, J. Sci. Ind. Res. 68 (2009) 181–187.
[10] G. Grivani, A. Ghavami, M. Kucerakova, M. Dusek, A.D. Khalaji, Synthesis, characterization, crystal structure determination, thermal study and catalytic activity of a new oxidovanadium Schiff base complex, J. Mol. Struct. 1076 (2014) 326–332.
[11] P. Pattanayaka, J.L. Pratiharb, D. Patrac, P. Brandaod, V. Felix, Synthesis, crystal structure, spectral properties and catalytic activity of binuclear copper(II), mononuclear nickel(II) and cobalt(III) complexes containing Schiff base ligand, Inorg. Chim. Acta 418 (2014) 171–179.
[12] A. Ghaffari, M. Behzad, M. Pooyan, H. Amiri, G. Bruno, Crystal structures and catalytic performance of three new methoxy substituted salen type nickel(II) Schiff base complexes derived from *meso*-1,2-diphenyl-1,2-ethylenediamine, J. Mol. Struct. 1063 (2014) 1–7.
[13] L. Li, L.K. Yang, Z.K. Chen, Y.Y. Huang, B. Fu, J.L. Du, Synthesis and characterization of multifunctional Schiff base and Cu(II) complex: degradation of organic dyes and an optical property investigation, Inorg. Chem. Commun. 50 (2014) 62–64.
[14] H.T. Fan, J. Liu, D. Sui, H. Yao, F. Yan, T. Sun, Use of polymer-bound Schiff base as a new liquid binding agent of diffusive gradients in thin-films for the measurement of labile Cu^{2+}, Cd^{2+} and Pb^{2+}, J. Hazard. Mater 260 (2013) 762–769.
[15] A. Masuya, C. Igarashi, M. Kanesato, H. Hoshino, N. Iki, One-pot synthesis and structural characterization of a Tb(III) coordination polymer based on a tripodal Schiff base ligand adopting an *exo*-bridging coordination mode, Polyhedron 85 (2015) 76.
[16] P. Wu, D. Ma, C. Leung, S. Yan, N. Zhu, R. Abagyan, C. Che, Stabilization of G-quadruplex DNA with platinum(II) Schiff base complexes: luminescent probe and down-regulation of c-*myc* oncogene expression, Chem. Eur. J. 15 (2009) 13008–13021.
[17] H.A. Ali, M.D. Darawsheh, E. Rappocciolo, Synthesis, crystal structure, spectroscopic and biological properties of mixed ligand complexes of zinc(II) valproate with 1,10-phenanthroline and 2-aminomethylpyridine, Polyhedron 61 (2013) 235–241.
[18] Y. Mohini, R.B.N. Prasad, M.S.L. Karuna, Y. Poornachandra, C.G. Kumar, Synthesis, antimicrobial and anti-biofilm activities of novel Schiff base analogues derived from methyl-12-aminooctadec-9-enoate, Bioorg. Med. Chem. Lett. 24 (2014) 5224–5227.
[19] S. Layek, S. Kumari, Anuradha, B. Agrahari, R. Ganguly, D.D. Pathak, Synthesis, characterization and crystal structure of a diketone based Cu(II) complex and its catalytic activity for the synthesis of 1,2,3-triazoles, Inorg. Chim. Acta 453 (2016) 735–741.
[20] Anuradha, S. Kumari, S. Layek, D.D. Pathak, Chitosan supported Zn(II) mixed ligand complexes as heterogeneous catalysts for one-pot synthesis of amides from ketones *via* Beckmann rearrangement, J. Mol. Struct. 1130 (2017) 368–373.
[21] B. Agrahari, S. Layek, S. Kumari, Anuradha, R. Ganguly, D.D. Pathak, Synthesis, characterization and crystal structure of Cu(II) complex of trans-cyclohexane-1,2-diamine:Application in synthesis of symmetrical biaryls, J. Mol. Struct. 1134 (2017) 85–90.
[22] D. Nakane, Y.W. Tsutsui, Y. Funahashi, T. Hatanaka, T. Ozawa, H. Masuda, A novel square-planar Ni(II) complex with an amino-carboxamido-dithiolato-type ligand as an active-site model of NiSOD, Inorg. Chem. 53 (2014) 6512.
[23] D. Nakane, S. Kuwasako, M. Tsuge, M. Kubo, Y. Funahashi, T. Ozawa, T. Ogurab, H. Masuda, A square-planar Ni(II) complex with an N_2S_2 donor set similar to the active centre of nickel-containing superoxide dismutase and its reaction with superoxide, Chem. Commun. 46 (2010) 2142–2144.
[24] F. Meyer, H. Kozlowski, in: J.A. Mc Cleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry ii: from Biology to Nanotechnology, vol. 6, Elsevier, Oxford, 2004, p. 247.
[25] M.A. Ali, M.H. Kadir, M. Nazimuddin, S.M.M. Majumder, M.T.H. Tarafder,

M.A. Khair, Synthesis, Characterization and antifungal properties of some 4-coordinated nickel(II) and 5-coordinated copper(II) complexes containing tridentate thiosemicarbazones and heterocyclic bases, Indian J. Chem. Sec. A 27 (1988) 1064–1067.
[26] M.T. Behnamfar, H. Hadadzadeh, J. Simpson, F. Darabi, A. Shahpiri, T. Khayamian, M. Ebrahimi, H.A. Rudbari, M. Salimi, Experimental and molecular modeling studies of the interaction of the polypyridyl Fe(II) and Fe(III) complexes with DNA and BSA, Spectrochim. Acta, Part A 134 (2015) 502–516.
[27] N. Shahabadi, S. Kashanian, F. Darabi, DNA binding and DNA cleavage studies of a water soluble cobalt(II) complex containing dinitrogen Schiff base ligand: the effect of metal on the mode of binding, Eur. J. Med. Chem. 45 (2010) 4239–4245.
[28] S.Y. Ebrahimipour, I. Sheikhshoaie, M. Mohamadi, S. Suarez, R. Baggio, M. Khaleghi, M.T. Mahani, A. Mostafavi, Synthesis, characterization, X-ray crystal structure, DFT calculation, DNA binding, and antimicrobial assays of two new mixed-ligand copper(II) complexes, Spectrochim. Acta Part A 142 (2015) 410–422.
[29] Y.Y. Sun, Y.W. Zhang, G. Zhang, L. Cheng, *catena*-Poly[[triaquazinc(II)]-μ-1*H*-1,2,4-triazole-3,5-dicarboxylato], Acta Cryst. E 64 (2008) 1113.
[30] SMART Version 5.628, Bruker AXS Inc., Madison, WI, USA, 2001.
[31] G.M. Sheldrick, SADABS, University of Gottingen, Gottingen, Germany, 1996.
[32] SHELXTL Version 5.1, Bruker AXS Inc., Madison, WI, USA, 1997.
[33] R.D. Dennington, T.A. Keith, J.M. Millam, Gauss- View 5.0, Gaussian, Inc., Wallingford, CT, 2009.
[34] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648.
[35] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B Condens. Matter 37 (1988) 785.
[36] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A 38 (1988) 3098.
[37] C. Kumari, D. Sain, A. Kumar, S. Debnath, P. Saha, S. Dey, A real time colorimetric 'two in one' kit for tracking ppb levels of uric acid and Hg^{2+} in live HeLa S_3 cells and Hg^{2+} induced keto-enol tautomerism, RSC Adv. 6 (2016) 62990–62998.
[38] M. Balouiri, M. Sadiki, S.K. Ibnsouda, Methods for *in vitro* evaluating antimicrobial activity: a review, J. Pharm. Anal. 6 (2016) 71–79.
[39] J.M. Andrews, Determination of minimum inhibitory concentrations, J. Antimicrob. Chemother. 48 (2014) 5–16.
[40] N. Srivastava, M. Mukhopadhyay, Bioprocess Biosyst. Eng. 38 (2015) 1723.
[41] C. Valgas, S.M. Souza, E.F.A. Smania, A. Smania, Screening methods to determine antibacterial activity of natural products, Braz. J. Microbiol. 38 (2007) 369–380.
[42] I.A. Holder, S.T. Boyce, Agar well diffusion assay testing of bacterial susceptibility to various antimicrobials in concentrations non-toxic for human cells in culture, Burns 20 (1994) 426–429.
[43] Saswati, R. Dinda, C.S. Schmiesing, E. Sinn, Y.P. Patil, M. Nethaji, H.S. Evans, R. Acharyya, Mixed-ligand nickel(II) thiosemicarbazone complexes: synthesis, characterization and biological evaluation, Polyhedron 50 (2013) 354–363.
[44] S. Saha, S. Jana, S. Gupta, A. Ghosh, H.P. Nayek, Syntheses, structures and biological activities of square planar Ni(II), Cu(II) complexes, Polyhedron 107 (2016) 183–189.
[45] I.K. Cikla, S. Guveli, M. Yavuz, T.B. Demirci, B. Ulkuseven, 5-Methyl-2-hydroxyacetophenone-thiosemicarbazone and its nickel(II) complex: crystallographic, spectroscopic (IR, NMR and UV) and DFT studies, Polyhedron 105 (2016) 104–114.
[46] A. Bhattacharya, J.P. Naskar, P. Saha, R. Ganguly, B. Saha, S.T. Choudhury, S. Chowdhury, A new oxorhenium(V) complex with benzothiazole derived ligand: relative stability and global chemical reactivity indices, Inorg. Chim. Acta 447 (2016) 168–175.
[47] M.M. Tamizha, B. Varghese, A. Endoc, R. Karvembua, NMR (1D and 2D) and X-ray crystallographic studies of Ni(II) complex with *N*-(2-mercaptophenyl)-4-methoxysalicylideneimine and triphenylphosphine, Spectrochim. Acta, Part A 77 (2010) 411–418.
[48] M.S. Mohamad, Some transition metal complexes with new Schiff base ligand hexadentate, Acta Chim. Pharm. Indica 3 (2013) 140–148.
[49] G. Kalaiarasi, C. Umadevi, A. Shanmugapriya, P. Kalaivani, F. Dallemer, R. Prabhakaran, DNA(CT), protein(BSA) binding studies, anti-oxidant and cytotoxicity studies of new binuclear Ni(II) complexes containing 4(N)-substituted thiosemicarbazones, Inorg. Chim. Acta 453 (2016) 547–558.
[50] S. Priyarega, P. Kalaivani, R. Prabhakaran, T. Hashimoto, A. Endo, K. Natarajan, Nickel(II) complexes containing thiosemicarbazone and triphenylphosphine: synthesis, spectroscopy, crystallography and catalytic activity, J. Mol. Struct. 1002 (2011) 58–62.
[51] R. Prabhakaran, P. Kalaivani, P. Poornima, F. Dallemer, G. Paramaguru, V. Vijaya Padma, R. Renganathan, R. Huang, K. Natarajan, One pot synthesis of structurally different mono and dimeric Ni(II) thiosemicarbazone complexes and *N*-arylation on a coordinated ligand: a comparative biological study, Dalton Trans. 41 (2012) 9323–9336.
[52] H.C. Ansel, W.P. Norred, I.L. Roth, Antimicrobial activity of dimethyl sulfoxide against *Escherichia coli, Pseudomonas aeruginosa*, and *Bacillus megaterium*, J. Pharm. Sci. 58 (1969) 836–839.
[53] H. Basch, H.H. Gadebusch, In vitro antimicrobial activity of dimethylsulfoxide, Appl. Microbiol. 16 (1968) 1953–1954.
[54] M. Alexiou, I. Tsivikas, C.D. Samara, A.A. Pantazaki, P. Trikalitis, N. Lalioti, D.A. Kyriakidis, D.P. Kessissoglou, High nuclearity nickel compounds with three, four or five metal atoms showing antibacterial activity, J. Inorg. Biochem. 93 (2003) 256–264.