Journal of Metals, Materials and Minerals, 35(2), e2324, 2025

Mechanochemical synthesis of Ni(II)-tptz complexes with co-ligands: Spectroscopy, DFT, and biological studies

Deepak SENAPATI[1], Anulipsa PRIYADARSHINI[1], Debadutta SAMAL[1], P. Ramesh BABU[2], Satyanarayan SAHOO[3], Narayan CHANDRA BERA[1], Raghabendra SAMANTARAY[1], Jagannath PANDA[1,*], and Rojalin SAHU[1,*]

[1] *School of Applied Sciences, KIIT University, Bhubaneswar, 751024, Odisha, India*
[2] *Department of Engineering Chemistry, College of Engineering, Andhra University, Visakhapatnam, 530003, India*
[3] *P. G. Department of Chemistry, Berhampur University, Ganjam, 760007, Odisha, India*

***Corresponding author e-mail**: rsahufch@kiit.ac.in, jagannath.panda@kiit.ac.in

Received date:
20 February 2025
Revised date:
26 March 2025
Accepted date:
22 April 2025

Keywords:
Vibrational spectra;
Electronic spectra;
Ni (II) mixed ligand complexes;
DNA binding;
Antimicrobacterial study

Abstract

New mixed-ligand Ni(II) complexes [Ni(tptz)(1,10-phen)] (1), [Ni(tptz)(2-Mimd)$_2$] (2), and [Ni(tptz)Imd)$_2$] (3) were synthesized via a green, solvent-free mechanochemical approach using ball milling. The primary ligand used was 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz), with secondary ligands being 1,10-phenanthroline, 2-methyl imidazole, and imidazole, respectively. Structural characterization by IR, UV-Visible, photoluminescence spectroscopy, and powder X-ray diffraction, supported by DFT calculations, revealed a distorted square planar geometry for complex 1 and distorted tetrahedral geometries for complex-2 and complex-3. Notably, bathochromic shifts in the UV-Vis spectra confirm metal-ligand charge transfer transitions and extended π-delocalization. Powder XRD analysis determined average crystallite sizes of 17.86 nm (1), 25 nm (2), and 14.7 nm (3). DNA-binding studies against calf thymus DNA exhibited bathochromic and hypochromic shifts, indicating an intercalative binding mode. Antibacterial evaluation showed that complexe-2 and complex-3 exhibited enhanced activity against Bacillus subtilis and Escherichia coli, with inhibition zones up to 16 mm, compared to their uncoordinated ligands. These results highlight the potential of Ni(II) coordination complexes as bioactive agents.

1. Introduction

Transition metal complexes have been used as therapeutics to treat cancer, diabetes, lymphomas, infection, and neurological disorders. These metals have variable oxidation states and may interact with many negative, neutral molecules. Due to this unique property, medicinal inorganic chemistry research has started to develop Metallo-drugs with significant therapeutic as well as diagnostic applications. Many metal complexes are already in use for these purposes and this has stimulated further research in this direction. Mixed ligand metal complexes are very important in biological processes because these are used as models for biochemical reactions [1], activation of enzymes [2], storage and transport of active substances through membranes [3]. These complexes are also active against pathogenic microorganisms [4]. Mixed ligand metal complexes have gained considerable research interest because these are having valuable properties such as antifungal, antibacterial, anticancer properties [5-8], magnetic exchange [9,10], electrical conductivity [11], photoluminescence [12], and nonlinear optical property [13,14]. Metallodrugs having Ni as the metal center has extensive applications in pharmacology such as antimicrobial [15, 16], antioxidant [17,18], antiviral [19], antifungal [20], antimycobacterial [21], anti-inflammatory [22], anti-ischemic [23], antiparasitic [24], antithrombolytic [25], enzymatic treatments [26] anticancer agents [27] owing to their biological role and synergistic action with other medicines.

2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) is a versatile neutral N-donor ligand which can function simultaneously as a tridentate as well as bidentate ligand in coordination chemistry [28]. It has been used as an efficient spacer for supramolecular complexes [29]. The metal complexes of tptz have been screened for magnetic [30], optical [31], antitumor [32], antibacterial [33], catalytic [34] properties. The aim of this study was the mechanochemical synthesis of three mixed ligand Ni(II) complexes using tptz as the primary ligand and imidazole/2-methyl imidazole/1,10 phenanthroline as secondary ligand. These complexes are characterized by different spectroscopic methods and screened for their antibacterial activities against *Bacillus subtilis* and *Escherichia coli*. DNA binding study of these complexes has been carried out against Calf thymus DNA with the help of UV-Vis spectroscopy.

2. Materials and methods

2,4,6-tris-(2-pyridyl)-1,3,5-triazine (tptz) was procured from Merck and used without purification. All the materials were of commercial reagent grade and used without further purification. Tris HCl and agar gel from HiMedia, Double-stranded Calf thymus

DNA (molecular biology grade), were procured from Sigma–Aldrich and stored at –4°C. Doubly distilled water was used for DNA binding studies. IR spectra were recorded in the 4000 cm^{-1} to 400 cm^{-1} range on a FT-IR Thermo Fisher Spectrophotometer using KBr pellets. Photoluminescence spectra were recorded by using Shimadzu Spectrophotofluorometer (RF-5301 PC) equipped with source of Xenon discharge lamp (solid sample in glass slide with tape). Electronic absorption spectra were recorded on Shimadzu UV–Vis double-beam spectrophotometer.

2.1 Mechanochemical synthesis of complexes [1-3]

A fixed amount of 0.027 g of $Ni(NO_3)_2$ was added to 0.062 g of tptz with varying amounts of 1,10-phenanthroline (0.035 g), 2-methyl imidazole (0.015 g) and Imidazole (0.013 g) during grinding in a planetary ball mill for 30 min at a speed of 2600 rpm to synthesize the complexes. From quantum mechanical and experimental data, the complexes are assigned with the formulae as [Ni(tptz)(1,10-phen)] (1), [Ni(tptz)(2-Mimd)$_2$] (2) and [Ni(tptz)(Imd)$_2$] (3).

2.2 Computational details

The widely used hybrid functional B3LYP [35] method based on DFT has been applied to optimize the geometry of the complexes [1-3] without symmetry restriction. The hybrid B3LYP methods that combine an exchange-correlation functional with some exact exchange contribution yield a very reasonable accuracy even for transition metal coordination complexes [36]. The IR spectra of these complexes along with vibrational frequencies are also calculated using the B3LYP method. A double-zeta split-valence basis set, 6-31+G*, was employed for all atoms [37]. All calculations were performed using the Gaussian 09 suite of quantum chemistry programs, and the optimized molecular structures and IR spectra were visualized using Chemcraft software [38].

2.3 DNA binding experiments

DNA binding experiments of the complexes with CT-DNA were carried out in 5 mM Tris-HCl/NaCl buffer and adjusted to pH 7.2 with HCl using an aqueous solution of metal complexes. The solution of CT-DNA was absolutely free from protein contamination which was confirmed by the ratio of UV absorbance at 260 nm and 280 nm and it was 1.89 [39]. Absorption titration experiment was carried out with fixed concentrations of complexes (1-3) while gradually increasing the concentrations of (10, 20, 30, 40 and 50 µL) CT-DNA stock solution.

2.4 Anti-microbial activity

The ligand tptz, co-ligands (1,10-phenanthroline/imidazole/2-methyl imidazole) and metal complexes were investigated for anti-microbial activity against one Gram-positive (*Bacillus subtilis* ATCC 6633) and one Gram-negative (*Escherichia coli* ATCC 35218) bacteria by using disc-agar diffusion method. DMSO was used as a controller and ampicillin was used as standard antibacterial reference. Using sterile cork borer of 6 mm diameter, wells were bored into seeded agar plates and they were loaded with 100 µL volume of the test substances with a concentration of 500 mg·mL^{-1} reconstituted in dimethylsulphoxide (DMSO). Antibacterial activity was calculated by measuring the diameter of the zone of inhibition against the bacteria (*Escherichia coli*) and (*Bacillus subtilis*). All the plates were incubated at 37°C for 24 h. The inhibition zone diameters around each disc were measured in mm.

3. Results and discussion

3.1 Structural description

Selected bond lengths and bond angles of the complexes (1-3) were calculated at B3LYP/6-31+G* level is summarized in Table 1-3 and their structures are shown in Figure 1(a-c). The optimized geometry of [Ni(tptz)(1,10-phen)] (complex-1) gives a distorted square planar structure with four Ni-coordination: two with tptz moiety and two with 1,10 phenanthroline but in [Ni(tptz)(2-Mimd)$_2$] (complex-2) and [Ni(tptz)(Imd)$_2$] (complex-3) complexes, Ni has five coordination out of which two with individual Imidazole moiety and three with tptz which leads to distorted tetrahedral geometry. In complex-1, Ni is coordinated with two nitrogens of same phenanthroline, therefore due to the steric effect Ni is bonded with only pyridyl groups of tptz moiety and converged to a distorted square planer structure. The bond length of Ni with phenanthroline moiety in complex-1 varies from 1.78 Å to 1.97 Å and two bond lengths with tptz varies from 1.918 Å to 1.953 Å. The bond angle of phenanthroline-Ni (N1-Ni-N2) is 92.58°, tptz-Ni (N3-Ni-N5) is 83.03°, and the bond angle of phenanthroline-Ni-tptz varies from 107.86° (N1-Ni-N5) to 108.07° (N2-Ni-N3). The experimental value of Ni-phenanthroline bond length of complex [Ni-(phen)$_3$] [40] varies from 2.081 Å to 2.095 Å which is a maximum 0.2 Å from of our calculated value for 4 coordinated Phen-Ni-tptz complex and the experimental bond angle for N(phen)-Ni-N(Phen) is around 80° which agrees very well with our theoretical value ~83.03°.

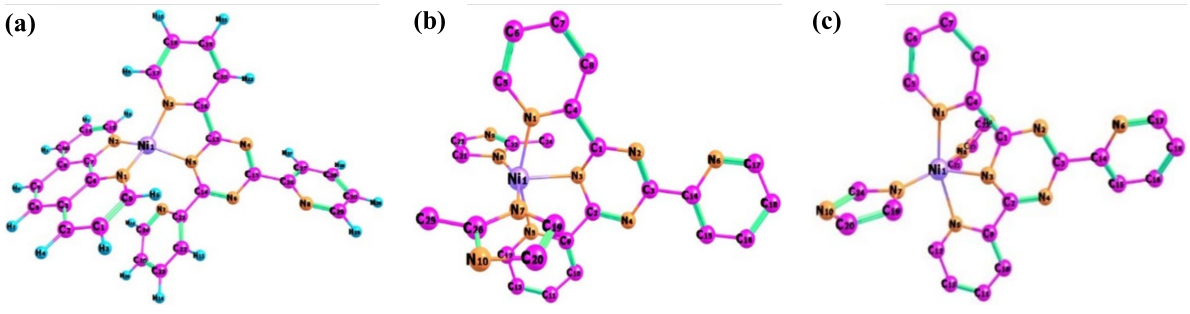

Figure 1. Optimized DFT based hybrid B3LYP structure of (a) complex-1, (b) complex-2 and (c) complex-3.

Table 1. Optimized bond distances (Å) and bond angles (°) for [Ni (tptz)(1,10-phen)] (1).

Structural parameters of complex-1			
Bond	**Length (Å)**	**Bond**	**Angle (°)**
Ni1-N1	1.78	N1-Ni1-N2	92.58
Ni1-N2	1.97	N2-Ni1-N3	108.07
Ni1-N3	1.91	N3-Ni1-N5	83.03
Ni1-N5	1.96	N1-Ni1-N5	107.86
N1-C4	1.39	C4-N1-C5	117.36
N1-C5	1.35	C7-N2-C12	118.06
N2-C7	1.39	C16-N3-C17	117.54
N2-C12	1.33	C13-N5-C14	114.91
N3-C16	1.37	C13-N4-C15	116.83
N3-C17	1.35	C14-N6-C15	116.88
N5-C13	1.37	C26-N8-C29	118.44
N5-C14	1.35	C21-N7-C24	118.32

Table 2. Optimized bond distances (Å) and bond angles (°) for [Ni(tptz)(2-Mimd)$_2$] (2).

Structural parameters of complex-2			
Bond	**Length (Å)**	**Bond**	**Angle (°)**
Ni1-N1	2.01	N1-Ni1-N3	77.74
Ni1-N7	1.92	N7-Ni1-N3	96.16
Ni1-N3	2.12	N7-Ni1-N8	157.29
Ni1-N5	2.01	N7-Ni1-N1	91.13
Ni1-N8	1.33	N7-Ni1-N5	90.16
N1-C5	1.33	N8-Ni1-N1	93.91
N1-C4	1.36	N1-Ni1-N5	155.24
N3-C1	1.33	N8-Ni-N5	93.79
N3-C2	1.33	N8-Ni-N3	106.53
N5-C12	1.33	N3-Ni1-N5	77.51
N5-C9	1.36	C1-N3-C2	116.45
N7-C19	1.38	C2-N4-C3	114.77
N7-C26	1.36	C1-N2-C3	114.62
N8-C22	1.36	C4-N1-C5	118.62
N8-C21	1.38	C9-N5-C12	118.66
		C14-N6-C17	117.83
		C21-N8-C22	105.12
		C19-N7-C26	104.92
		C22-N9-C23	105.12
		C20-N10-C26	104.94

Table 3. Optimized bond distances (Å) and bond angles (°) for [[Ni(tptz)(Imd)$_2$] (3).

Structural parameters of complex-2			
Bond	**Length (Å)**	**Bond**	**Angle (°)**
Ni1-N1	2.01	N1-Ni1-N3	77.54
Ni1-N7	1.89	N3-Ni1-N5	77.40
Ni1-N3	2.16	N1-Ni1-N5	154.94
Ni1-N5	2.00	N7-Ni1-N5	92.58
Ni1-N8	1.91	N7-Ni1-N1	92.21
N1-C5	1.33	N7-Ni1-N3	101.95
N1-C4	1.36	N8-Ni1-N1	92.73
N3-C1	1.33	N8-Ni1-N3	96.38
N3-C2	1.33	N8-Ni1-N5	90.39
N5-C12	1.33	C1-N3-C2	115.47
N5-C9	1.36	C2-N4-C3	114.81
N7-C19	1.37	C1-N2-C3	114.68
N7-C24	1.36	C4-N1-C5	118.64
N8-C22	1.36	C9-N5-C12	118.70
N8-C21	1.38	C14-N6-C17	117.77
		C21-N8-C22	104.28
		C19-N7-C24	104.95
		C22-N9-C23	104.26
		C20-N10-C24	104.21

In 2 and 3 complexes, both the pyridyl groups of tptz are bonded with Ni atom and converged to a distorted tetrahedral geometry with a little shift of Ni atom from the tptz plane. The bond lengths of 2-methyl Imidazole and Ni of complex-2 and Imidazole-Ni of complex-3 varies from 1.89 Å to 1.92 Å but the bond angle of 2-methyl imidazole-Ni-2-methyl imidazole (N7-Ni-N8) of 2 and that of imidazole-Ni-imidazole (N7-Ni-N8) of complex-3 vary from 157.29° to 161.63°. In tptz part the bond length of Ni-N (tptz) of complex-2 varies from 2.01 Å to 2.12Å and in complex-3, it varies from 2.0 Å to 2.16 Å. The bond angle of 2-Methyl Imidazole-Ni-N(tptz) of complex-2 and Imidazole-Ni-N(tptz) ($N_{7/8}$-Ni-$N_{1/3/5}$) varies from around 91° to 106°. The N7-Ni-N3 bond angle for both complex-2 and complex-3 are little higher than that of $N_{7/8}$-Ni-$N_{1/5}$ which clearly indicates the displacement of Ni atom from tptz. The bond length of Ni-N(tptz) of complex-1 is about 1.91 Å and 1.96 Å and that for complex-2 and complex-3 are little elongated to 2.12 Å and 2.16 Å respectively. Recent crystallographic data on bond length of Ni-tptz part in [Ni-(tptz)Cl(H_2O)$_2$] and [Ni-(tptz)Cl_2(H_2O)] complexes 1.987 Å to 2.17 Å which is very close to our calculated value with a maximum deviation ~0.05 Å and also for angle of N1-Ni-N3 and N3-Ni-N5 for both the Ni-tptz complex varies from 76.67° to 77.05° and N1-Ni-N5 is about 153.12° to 153.39° which agree very well with our calculated value ~77.5° and ~155° respectively [41]. The same geometrical parameters reported in a recent article on Ni(tptz)$_2$ and Ni-(tptz)(CH_3OH)Cl_2 also support our calculated values [42].

3.2 IR spectral studies and DFT calculations

To determine the chelation sites of the ligands as well as co-ligands that may coordinate to the metal center, the IR spectra of mixed ligand metal complexes Figure 2(a-c) were compared with free ligands/co-ligands. There is a significant change in the position and/or intensities of these peaks after coordination. All the significant peaks are also supported by calculated values depicted in Figure 3(a-c) and it is summarized in Table 4. The strong band of C=C appears around 1590 cm^{-1} to 1525 cm^{-1} of the ligands and co-ligands have been shifted to lower wave number in the ranges between (1579 cm^{-1} to 1529 cm^{-1}) [32]. The intense peak at 1660 cm^{-1} in the ligand tptz which is assigned to C=N has been shifted to lower wave lengths (1625 cm^{-1} to 1611 cm^{-1}) in the complexes.

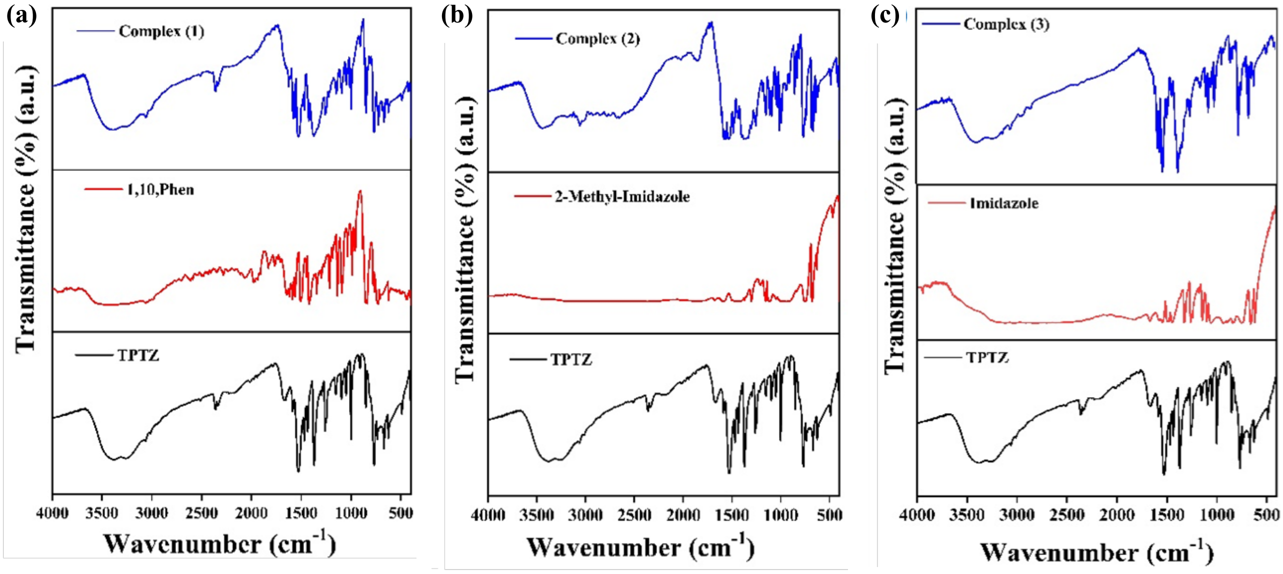

Figure 2. FT-IR spectra of (a) complex-1, (b) complex-2, and (c) complex-3 (Experimental).

Table 4. The observed FT-IR calculated frequencies (cm^{-1}) computed by DFT/B3LYP and Experimental.

Sl No.	Complexes	Vibrational assignments	Experimental frequency [cm^{-1}]	B3LYP calculated frequency [cm^{-1}]
1	1	C=N	1625 to 1611	1630
2		C=C	1590 to 1525	1539
3		C-C	1484 to 1255	1413, 1472
4		N-Ni-N	600 to 800	1000, 740
1	2	C=N	1611.87	1631
2		C=C	1533.47	1504
3		C-C	1484 to 1255	1393
4		N-Ni-N	600 to 800	697
1	3	C=N	1611.89	1586
2		C=C	1533.35	1425
3		C-C	1484 to 1255	1498
4		N-Ni-N	600 to 800	767
		C-H	2900 to 3150	3176

This shift has been occurred due to co-ordination of N-atom of the tptz to Ni(II) [32]. There are several other bands at 800 cm^{-1} to 600 cm^{-1} which is the significant peak due to the coordination of the pyridine ring with Ni(II) [43]. Further few new peaks in the range of 2900 cm^{-1} to 3150 cm^{-1} are appeared and are slightly shifted as compared to the unbound ligands owing to absorptions of C–H stretching and bending vibrations of the aromatic hydrogen atoms [44].

3.3 Powder X-ray diffraction

The powder X-ray diffraction study has been carried out for complex-1 to complex-3 and there are peaks at 2θ = 29.01 and 32.32 positions which corresponds to the presence of nickel metal ion [45]. The other peaks at 2θ = 15 to 25 correspond to the presence of ligand and co- ligands. In the complex-1 to complex-3, there are some new diffraction peaks have occurred which suggest the formation of metal chelates Figure 4(a-c). The crystallite size of the complex-1 to complex-3 has been determined by using Scherrer's equation ($D = 0.9\ k/\beta\cos\theta$) and it was found to be 17.86 nm, 25 nm, and 14.7 nm, respectively [46,47].

3.4 UV-Vis and photoluminescence spectroscopy

The electronic spectrum of tptz and the complexes were measured in methanol and shown in Figure 5(a-c). The λ_{max} values of the ligand, co-ligands and the complexes were listed in Table 5. The free ligand tptz in methanol shows a band at 282 nm which is attributed to π-π* or n-π* transitions with in the triazine and pyridine rings. Upon coordination with Ni(II), a bathochromic shift of approximately 10 nm is observed in all Ni(II) complexes. This red shift, primarily due to metal-ligand coordination, which leads to a reduction in the HOMO-LUMO energy gap, stabilization of the excited states through strong ligand field effects, and contributions from charge transfer transitions (MLCT/ LMCT) as well as increased π-electron delocalization. All spectral measurements were performed in methanol under identical conditions, minimizing the influence of solvent effects. Therefore, the observed bathochromic shift can be attributed predominantly to electronic changes induced by complex formation [48,26].

The photoluminescence spectra of the complexes were measured in methanol with an excitation wave length 271 nm at room temperature and are depicted in Figure 6(a-c). It has been observed that the photoluminescence intensities for the complexes are higher than that of uncoordinated tptz ligand. This may happen due to the rigidity of the bound ligand in the complexes as compared to the unbound ligand [49]. The enhancement of intensity in the complexes arises due to Ni(II) coordination with the ligands [50]. Intraligand emission (π-π*) of tptz appeared at around 543.97 nm [51].

3.5 DNA binding

The absorption spectra of the complexes in the presence of CT-DNA are given in Figure 7(a-c). There are two well-resolved bands at approximately 272 nm and 291 nm for complex-1, 250 nm and 291 nm for complex-2, 251 nm and 291 nm for complex-3 respectively. From this figure, it is confirmed that with increasing concentration of DNA, bathochromic as well as hypochromic shifts occurred in all complexes. This indicates that the complexes bind to CT-DNA through intercalation as the intercalative binding of Schiff base complexes with Ct-DNA is driven by π-π stacking interactions, hydrogen bonding, electrostatic attractions, and hydrophobic effects, leading to hypochromic and bathochromic shifts in the absorption spectrum [52].

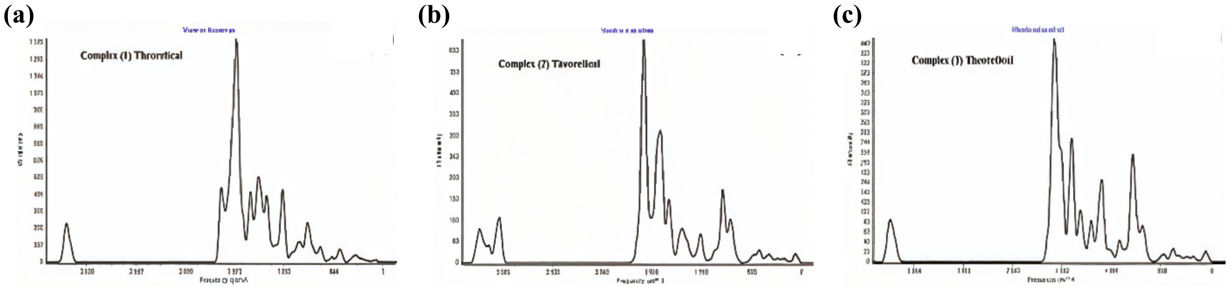

Figure 3. FT-IR spectra of (a) complex-1, (b) complex-2, and (c) complex-3 (Theoretical).

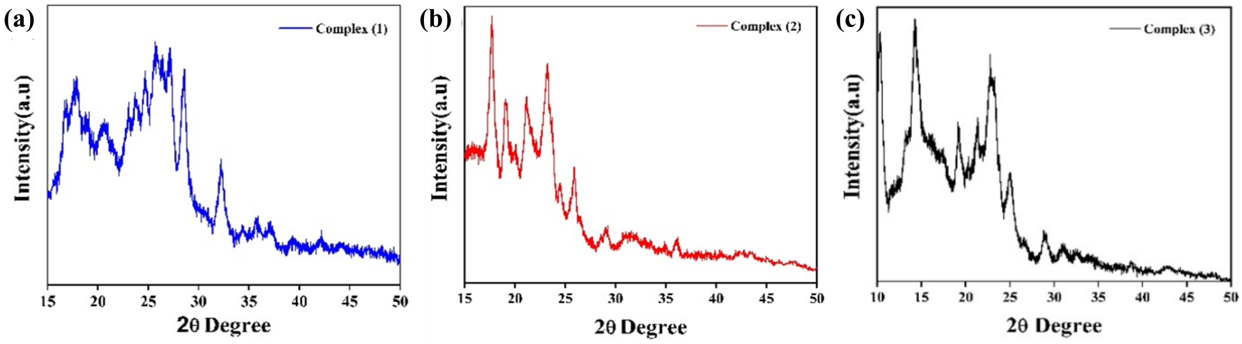

Figure 4. Powder X-ray diffraction of (a) complex-1, (b) complex-2, and (c) complex-3.

Table 5. Electronic absorption spectral properties of Ni(II) complexe-1 to complexe-3.

Ligand and complex	λ_{max}	
	Free	**Bound**
tptz	282	291
1,10-phenanthroline	267	271
2-Methyl Imidazole	243	251
Imidazole	210 to 220	253
Complex-1		271(LMCT, π-π*), 291(n- π*)
Complex-2		251, 295
Complex-3		253, 296

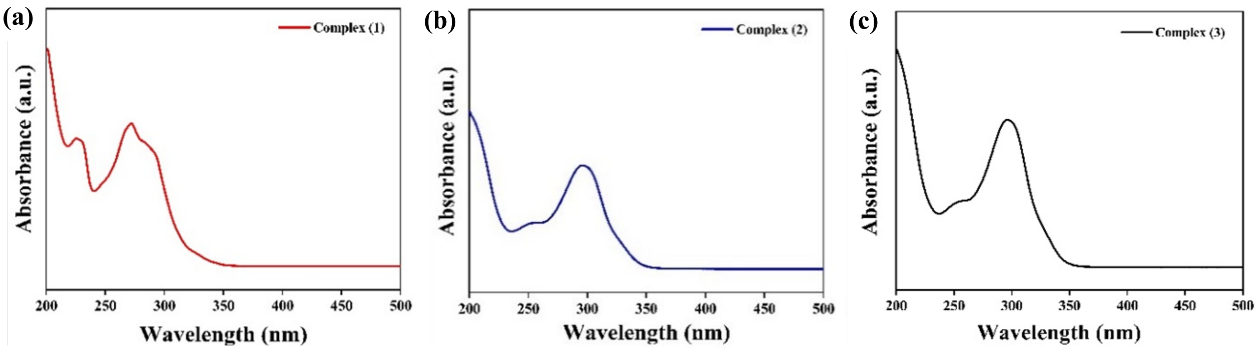

Figure 5. UV-Visible spectra of (a) complex-1, (b) complex-2, and (c) complex-3 .

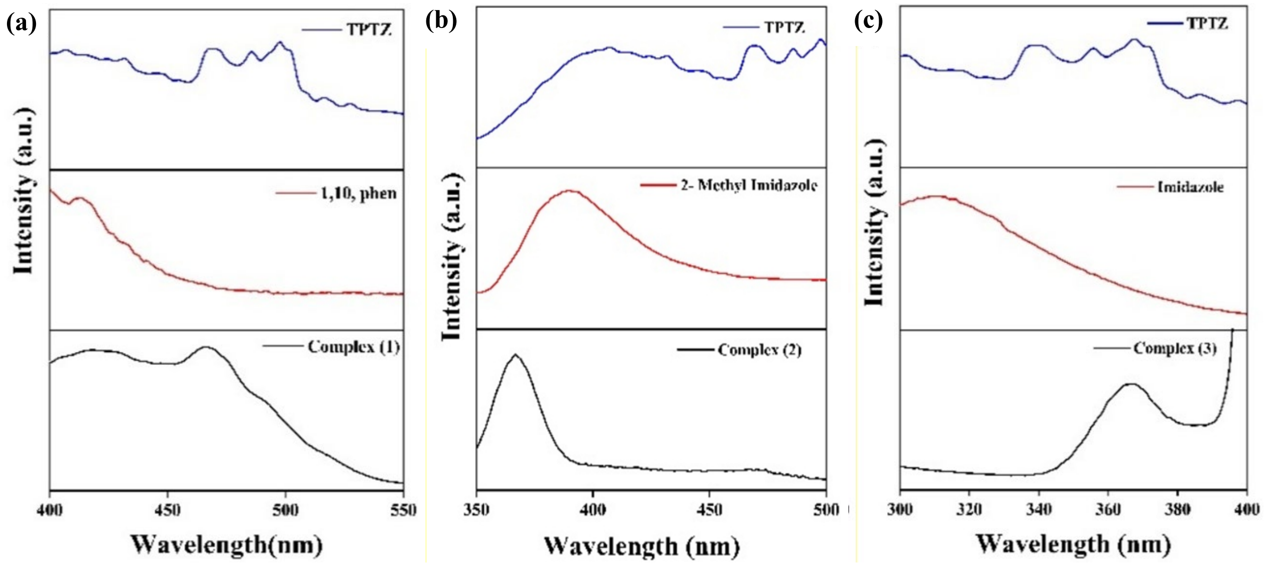

Figure 6. Photoluminescence spectra of (a) complex-1, (b) complex-2, and (c) complex-3.

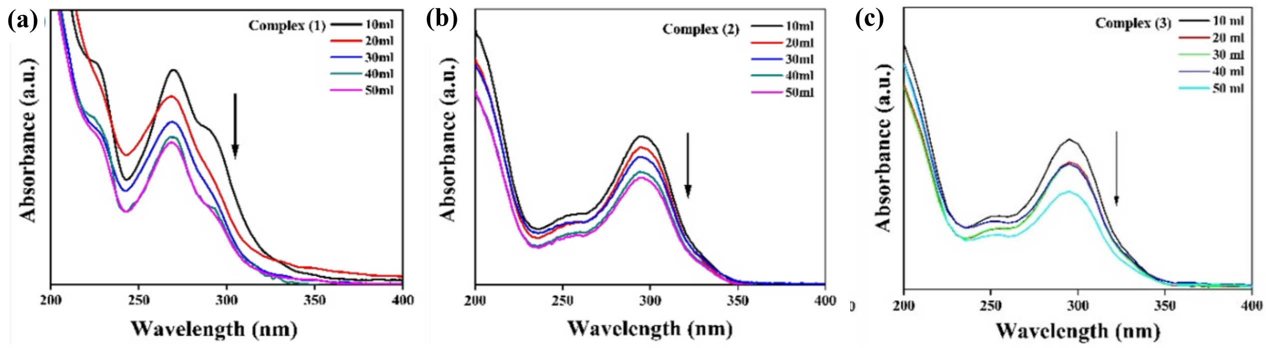

Figure 7. Electronic spectra of the Ni(II) complexes (10 μM) in the presence of 10 μL to 50 μL of CT-DNA (a) complex-1, (b) complex-2, and (c) complex-3.

Table 6. Antibacterial activity against *Bacillus subtilis.*

Sl no.	Zone of inhibition			
	Ligand [mm]	**Complex [mm]**	**Control [mm]**	**Standard [mm]**
1	45	12	0	26
2	7	12		
3	8	16		

Table 7. Antibacterial activity against *Escherichia coli.*

Sl no.	Zone of inhibition			
	Ligand [mm]	**Complex [mm]**	**Control [mm]**	**Standard [mm]**
1	42	10	0	32
2	0	12		
3	7	12		

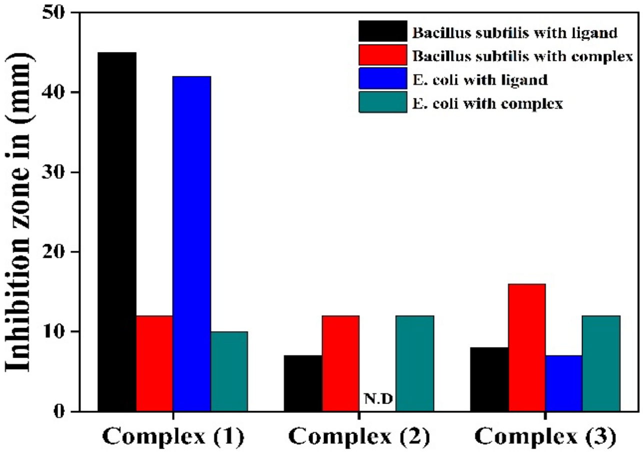

Figure 8. Antibacterial study of complex-1 to complex-3.

3.6 Antibacterial study

In the present study after complex formation, the synthesized ligands and their respective complexes are screened against two different bacterial strains namely *Bacillus subtilis* and *Escherichia coli*. The results of the antibacterial study showed that most of the ligands and their complexes are sensitive to the test organisms used as shown in Table 6-7. It was found that the complexes are more active towards the test bacterial strains compared to the ligands. It is quite interesting to note that the zone of inhibition increased in every case except complex-1 from uncoordinated state to complex state Figure 8. This may be due to the enhancement of stability and increase in the bioavailability of the complexes as compared to the ligands [53]. The decrease in the zone of inhibition for complex-1 (1,10-Phenanthroline) is due to its rigid, planar structure and strong π-π stacking interactions, which reduce its ability to enter bacterial membranes upon coordination, while complexation also diminishes its free ligand DNA intercalation ability, lowering antibacterial activity.

4. Conclusion

The synthesized Ni(II) complexes are characterized by micro analytical and various spectral studies. The observed spectral and DFT calculated data confirm the square planar environment around the Ni(II) ions in complex-1 and distorted tetrahedral in complex-2 and complex-3. The ligands coordinated to the metal ion in a tridentate manner with two pyridine N and triazine N donor sites. The powder X-ray diffraction pattern shows sharp crystalline peaks with micro-crystalline and homogeneous particle nature. DNA binding of Ni(II) complexes in solution has been investigated by UV-Visible spectroscopy. A moderate interaction has been found for the complexes with DNA. From the antibacterial activity studies, it has been found that these complexes are active against *Bacillus subtilis* and *Escherichia coli* and are more active than the free ligands owing to the lipophilic character of the complexes.

Acknowledgment

DS and RS are thankful to KIIT Central Research Facility, KIIT DU, Bhubaneswar, Odisha, for the characterization techniques.

Reference

[1] M. Ismael, A.-M. M. Abdel-Mawgoud, M. K. Rabia, and A. Abdou, "Synthesis, characterization, molecular modeling and preliminary biochemical evaluation of new copper (II) mixed-ligand complexes," *Journal of Molecular Structure*, vol. 1227, p. 129695, 2021.

[2] G. G. Mohamed, A. A. El-Sherif, M. A. S. S. E. A. El-Sawy, and Sh. M. Morgan, "Mixed-ligand complex formation of tenoxicam drug with some transition metal ions in presence of valine: Synthesis, characterization, molecular docking, potentiometric and evaluation of the humeral immune response of calves," *Journal of Molecular Liquids*, vol. 223, pp. 1311-1332, 2016.

[3] H. Xine, L. A. Rifai, M. Faize, F. Bentiss, S. Guesmi, A. Laachir, A. Smaili, K. Makroum, A. Sahibed-Dine, and T. Koussa, "Induced resistance in tomato plants against *Verticillium* wilt by the binuclear nickel coordination complex of the ligand 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole," *Journal of Agricultural and Food Chemistry*, vol. 64, no. 13, pp. 2661-2667, 2016.

[4] S. Shobana, P. Subramaniam, L. Mitu, J. Dharmaraja, and S. A. Narayan, "Synthesis, structural elucidation, biological, anti-

oxidant and nuclease activities of some 5-Fluorouracil–amino acid mixed ligand complexes," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 134, pp. 333-344, 2015.

[5] S. Shobana, P. Subramaniam, J. Dharmaraja, and S. A. Narayan, "Stability and structural studies on Ni(II)-5-fluorouracil mixed ligand complex systems," *Journal of Solution Chemistry*, vol. 45, no. 3, pp. 334-358, 2016.

[6] T. Begum, K. Crouse, M. I. M. Tahir, A. R. Cowley, and M. Ali, "Synthesis, characterization and bioactivity of mixed-ligand Cu(II) complexes containing Schiff bases derived from S-benzyldithiocarbazate and saccharinate ligand and the X-ray crystal structure of the copper-saccharinate complex containing S-benzyl-β-N-(acetylpyrid-2-yl)methylenedithiocarbazate," *Polyhedron*, vol. 26, no. 6, pp. 1159-1165, 2007.

[7] B. Annaraj, C. Balakrishnan, and M. A. Neelakantan, "Synthesis, structure information, DNA/BSA binding affinity and *in vitro* cytotoxic studies of mixed ligand copper(II) complexes containing a phenylalanine derivative and diimine co-ligands," *Journal of Photochemistry and Photobiology B: Biology*, vol. 160, pp. 278-291, 2016.

[8] Q.-X. Wang, K. Jiao, F.-Q. Liu, X.-L. Yuan, and W. Sun, "Spectroscopic, viscositic and electrochemical studies of DNA interaction with a novel mixed-ligand complex of nickel (II) that incorporates 1-methylimidazole and thiocyanate groups," *Journal of Biochemical and Biophysical Methods*, vol. 70, no. 3, pp. 427-433, 2007.

[9] T. Yoshida, T. Suzuki, K. Kanamori, and S. Kaizaki, "Synthesis, magnetic properties, and electronic spectra of octahedral mixed-ligand (*β*-diketonato) nickel(II) complexes with a chelated nitronyl nitroxide radical," *Inorganic Chemistry*, vol. 38, no. 6, pp. 1059-1068, 1999.

[10] J. Y. Lu, M. A. Lawandy, J. Li, T. Yuen, and C. L. Lin, "A new type of two-dimensional metal coordination systems: Hydrothermal synthesis and properties of the first oxalate−bpy mixed-ligand framework [M(ox)(bpy)] (M = Fe(II), Co(II), Ni(II), Zn(II); ox = $C_2O_4^{2-}$; bpy = 4,4'-bipyridine) ," *Inorganic Chemistry*, vol. 38, no. 11, pp. 2695-2704, 1999.

[11] Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, E. Tas, and A. Cukurovali, "Solid state electrical conductivity properties of copper complexes of novel oxime compounds containing oxolane ring," *Materials Letters*, vol. 57, no. 24-25, pp. 3755-3760, 2003.

[12] S. G. Thangavelu, S. J. A. Pope, C. L. Cahill, "Synthetic, structural, and luminescence study of uranyl coordination polymers containing chelating terpyridine and trispyridyltriazine ligands," *CrystEngComm*, vol. 17, no. 31, pp. 6236-6247, 2015.

[13] Z. Li, F. Gao, Z. Xiao, G. Ao, X. Wu, Y. Fang, Z. Nie, T-H. Wei, J. Yang, Y. Wang, X. Zhang, J. Zuo, and Y. Song, "Synthesis and third-order nonlinear optical properties of a sandwich-type mixed (phthalocyaninato)(schiff-base) triple-decker complexes," *Dyes and Pigments*, vol. 119, pp. 70-74, 2015.

[14] O. Tamer, D. Avci, and Y. Atalay, "Synthesis, X-ray structure, spectroscopic characterization and nonlinear optical properties of nickel (II) complex with picolinate: A combined experimental and theoretical study," *Journal of Molecular Structure*, vol. 1098, pp. 12-20, 2015.

[15] M. Muthuppalani, A. Al Otaibi, S. Balasubramaniyan, S. Manikandan, P. Manimaran, G. Mathubala, A. Manikandan, T. Kamal, A. Khan, H. M. Marwani, K. A. Alamry, and A. M. Asiri, "An in-vitro anti-inflammatory and anti-microbial essential on Ni(II), Cd(II) mixed ligand complexes by using 2,4-dinitrophenyl hydrazine and dimethylglyoxime." *Journal of King Saud University-Science,* vol 34, no. 5, p. 102114, 2022.

[16] F. Islam, Md. A. Hossain, N. M. Shah, H. T. Barua, Md. A. Kabir, M. J. Khan, and R. Mullick, "Synthesis, characterization, and antimicrobial activity studies of Ni(II) complex with pyridine as a ligand," *Journal of Chemistry*, vol. 2015, no. 1, p. 525239, 2015.

[17] C. J. Dhanaraj, and J. Johnson, "Quinoxaline based bio-active mixed ligand transition metal complexes: Synthesis, characterization, electrochemical, antimicrobial, DNA binding, cleavage, antioxidant and molecular docking studies," *Journal of Photochemistry and Photobiology B: Biology*, vol. 151, pp. 100-109, 2015.

[18] F. X. Campos, M. R. S. Soares, A. J. Terezo, and A. B. Siqueira, "Synthesis, characterization, and antioxidant evaluation of solid-state mefenamates of some bivalent metals," *Journal of Thermal Analysis and Calorimetry*, vol. 115, no. 1, pp. 167-176, 2014.

[19] T. M. Hunter, I. W. McNae, D. P. Simpson, A. M. Smith, S. Moggach, F. White, M. D. Walkinshaw, S. Parsons, and P. J. Sadler, "Configurations of nickel-cyclam antiviral complexes and protein recognition," *Chemistry - A European Journal*, vol. 13, no. 1, pp. 40-50, 2007.

[20] M. H. Soliman, G. G. Mohamed, and A. M. M. Hindy, "Biological activity, spectral and thermal characterization of mixed ligand complexes of enrofloxacin and glycine: in vitro antibacterial and antifungal activity studies," *Monatshefte für Chemie - Chemical Monthly*, vol. 146, no. 2, pp. 259-273, 2015.

[21] A. Kareem, Laxmi, M. Arshad, S. A. A. Nami, and N. Nishat, "Herbo-mineral based Schiff base ligand and its metal complexes: Synthesis, characterization, catalytic potential and biological applications," *Journal of Photochemistry and Photobiology B: Biology*, vol. 160, pp. 163-171, 2016.

[22] G. Psomas and D. P. Kessissoglou, "Quinolones and non-steroidal anti-inflammatory drugs interacting with copper(II), nickel(II), cobalt(II) and zinc(II): Structural features, biological evaluation and perspectives," *Dalton Transactions*, vol. 42, no. 18, pp. 6252-6276, 2013.

[23] M. Monti, V. Ciccone, A. Pacini, R. Roggeri, E. Monzani, L. Casella, and L. Morbidelli, "Anti-hypertensive property of a nickel-piperazine/NO donor in spontaneously hypertensive rats," *Pharmacological Research*, vol. 107, pp. 352-359, 2016.

[24] W. J. Hoekstra, T. Y. Hargrove, Z. Wawrzak, D. G. J. Batista, C. F. da Silva, A. S. G. Nefertiti, G. Rachakonda, R. J. Schotzinger, F. Villalta, M. de. Nazare C. Soeiro, and G. I. Lepesheva, "Clinical candidate VT-1161's antiparasitic effect *In Vitro*, activity in a murine model of chagas disease, and structural characterization in complex with the target enzyme CYP51 from *Trypanosoma cruzi*," *Antimicrobial Agents and Chemotherapy*, vol. 60, no. 5, pp. AAC-02287, 2016.

[25] M. M. Abd-Elzaher, A. A. Labib, H. A. Mousa, S. A. Moustafa, M. M. Ali, and A. A. El-Rashedy, "Synthesis, anticancer activity and molecular docking study of Schiff base complexes containing thiazole moiety," *Beni-Suef University Journal of Basic and Applied Sciences*, vol. 5, no. 1, pp. 85-96, 2016.

[26] C. Zhao, X. Chen, D. Zang, X. Lan, S. Liao, C. Yang, P. Zhang, J. Wu, X. Li, N. Liu, Y. Liao, H. Huang, X. Shi, L. Jiang, X. Liu, Z. He, Q. P. Dou, X. Wang, and J. Liu, "A novel nickel complex works as a proteasomal deubiquitinase inhibitor for cancer therapy," *Oncogene*, vol. 35, no. 45, pp. 5916-5927, 2016.

[27] U. M. Rafi, D. Mahendiran, A. K. Haleel, R. P. Nankar, M. Doble, and A. K. Rahiman, "New pyridazine-based binuclear nickel(II), copper(II) and zinc(II) complexes as prospective anticancer agents," *New Journal of Chemistry*, vol. 40, no. 3, pp. 2451-2465, 2016.

[28] P. Byers, G. Y. S. Chan, M. G. B. Drew, M. J. Hudson, and C. Madic, "Concomitant binding of a nickel(II) cation and a nitrate anion by the ligand 2,4,6-tri-2-pyridyl-1,3,5-triazine (TPTZ): The crystal structure of $[Ni(HTPTZ)(H_2O)_3]^{3+}\cdot 3NO_3^{-}\cdot H_2O$," *Polyhedron*, vol. 15, no. 17, pp. 2845-2849, 1996.

[29] A. Kamiyama, T. Noguchi, T. Kajiwara, and T. Ito, "A graphite-like complex with large cavities constructed with the complex ligand $[Ni^{II}(bpca)_2]$," *Angewandte Chemie International Edition*, vol. 39, no. 17, pp. 3130-3132, 2000.

[30] A. Burkhardt, and W. Plass, "Modeling the coordination chemistry of chitosan: Synthesis and characterization of a nickel(II) complex with a 2-aminoglucose Schiff-base ligand," *Inorganic Chemistry Communications*, vol. 11, no. 3, pp. 303-306, 2008.

[31] C. R. De Silva, J. Wang, M. D. Carducci, S. A. Rajapakshe, and Z. Zheng, "Synthesis, structural characterization and luminescence studies of a novel europium(III) complex $[Eu(DBM)_3(TPTZ)]$ (DBM: dibenzoylmethanate; TPTZ: 2,4,6-tri(2-pyridyl)-1,3,5-triazine)," *Inorganica Chimica Acta*, vol. 357, no. 3, pp. 630-634, 2004.

[32] W. H. Al-Assy, A. M. H. El-Askalany, and M. M. Mostafa, "Structural comparative studies on new Mn^{II}, Cr^{III} and Ru^{III} complexes derived from 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (TPTZ)," *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, vol. 116, pp. 401-407, 2013.

[33] M. Maghami, F. Farzaneh, J. Simpson, and M. Azarkish, "Synthesis, crystal structure and characterization a new ionic complex $MoO_2Cl_3(MeOH)\cdot H_3tptz\cdot Cl_2$ (tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine) as epoxidation catalyst," *Inorganica Chimica Acta*, vol. 445, pp. 28-36, 2016.

[34] M. M. Najafpour, M. Holynska, A. N. Shamkhali, M. Amini, S. H. Kazemi, S. Zaynalpoor, R. Mohamadi, M. Bagherzaden, and T. Lis, "New mononuclear manganese(II) complexes with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*) – selective catalyst in UHP oxidation of sulfides," *Polyhedron*, vol. 34, no. 1, pp. 202-209, 2012.

[35] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *Journal of Chemical Physics*, vol. 98, no. 7, pp. 5648-5652, 1993.

[36] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B*, vol. 37, no. 2, pp. 785-789, 1988.

[37] V. A. Rassolov, J. A. Pople, M. A. Ratner, and T. L. Windus, "6-31G* basis set for atoms K through Zn," *Journal of Chemical Physics*, vol. 109, no. 4, pp. 1223-1229, 1998.

[38] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[39] K. Abdi, H. Hadadzadeh, M. Salimi, J. Simpson, and A. D. Khalaji, "A mononuclear copper(II) complex based on the polypyridyl ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz), $[Cu(tptz)_2]^{2+}$: X-ray crystal structure, DNA binding and *in vitro* cell cytotoxicity," *Polyhedron*, vol. 44, no. 1, pp. 101-112, 2012.

[40] I. Ucar, O. Z. Yesilel, A. Bulut, H. Olmez, and O. Buyukgungor, "Tris(1,10-phenanthroline)nickel(II) squarate octahydrate," *Acta Crystallographica Section C-crystal Structure Communications*, vol. 61, no. 8, pp. m947-m949, 2005.

[41] R. Zibaseresht, and R. M. Hartshorn, "The nickel(II)/2,4,6-Tris (2-pyridyl)-1,3,5-triazine system: Synthesis and crystallographic characterization of a series of complexes," *Australian Journal of Chemistry*, vol. 58, no. 5, pp. 345-353, 2005.

[42] H. Hadadzadeh, M. Maghami, J. Simpson, K. Abdi, A. D. Khalaji, and K. Abdi, "Nickel(II) polypyridyl complexes of 2,4,6-Tris(2-pyridyl)-1,3,5-triazine," *Journal of Chemical Crystallography*, vol. 42, no. 6, pp. 656-667, 2012.

[43] M. S. S. Babu, B. U. Rao, V. Krishna, S. Mustafa, and G. N. Rao, "Synthesis, characterization and DNA cleavage studies of isomeric pyridyl-tetrazole ligands and their Ni(II) and Zn(II) complexes," *Journal of Saudi Chemical Society*, vol. 21, no. 3, pp. 291-299, 2017.

[44] M. M. Najafpour, M. Holynska, M. Amini, S. H. Kazemi, T. Lis, and M. Bagherzadeh, "Two new silver(I) complexes with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*): Preparation, characterization, crystal structure and alcohol oxidation activity in the presence of oxone," *Polyhedron*, vol. 29, no. 14, pp. 2837-2843, 2010.

[45] L. Wang, L. Zhang, and J. Zhang, "Improved ORR activity of non-noble metal electrocatalysts by increasing ligand and metal ratio in synthetic complex precursors," *Electrochimica Acta*, vol. 56, no. 16, pp. 5488-5492, 2011.

[46] P. Kavitha, and K. L. Reddy, "Pd(II) complexes bearing chromone based Schiff bases: Synthesis, characterisation and biological activity studies," *Arabian Journal of Chemistry*, vol. 9, no. 5, pp. 640-648, 2016.

[47] A. Panda, K. K. Das, K. R. Kaja, M. Belal, and B. K. Panigrahi, "Single electrode mode triboelectric nanogenerator for recognition of animal sounds," *Journal of Metals, Materials and Minerals*, vol. 34, no. 4, p. e2170, 2024.

[48] S. J. Azahari, M. H. Abdel Rhman, and M. M. Mostafa, "Spectroscopic, analytical and DFT calculation studies of two novel Al^{3+} complexes derived from 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (TPTZ)," *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, vol. 132, pp. 165-173, 2014.

[49] Z. Onal, H. Zengin, and M. Sonmez, "Synthesis, characterization, and photoluminescence properties of Cu(II), Co(II), Ni(II), and Zn(II) complexes of N-aminopyrimidine-2-thione," *Turkish Journal of Chemistry*, vol. 35, no. 6, pp. 905-914, 2011.

[50] A-L. Wang, D. Zhou, Y-N. Chen, J-J. Li, H-X. Zhang, Y-L. Zhao, and H-B. Chu, "Crystal structure and photo-luminescence of europium, terbium and samarium compounds with halogen-benzoate and 2,4,6-tri(2-pyridyl)-s-triazine," *Journal of Luminescence*, vol. 177, pp. 22-30, 2016.

[51] S. P. Parua, P. Mondal, P. Pattanayak, and S. Chattopadhyay, "Synthesis, structure and photoluminescence properties of functionalized azoimine ligands and their nickel complexes," *Polyhedron*, vol. 89, pp. 142-148, 2015.

[52] H. A. Shahid, S. Jahangir, S. Yousuf, M. Hanif, and S. K. Sherwani, Synthesis, crystal structure, structural characterization and *in vitro* antimicrobial activities of 1-methyl-4-nitro-1*H*-imidazole," *Arabian Journal of Chemistry*, vol. 9, no. 5, pp. S668-S675, 2016.

[53] P. Subbaraj, A. Ramu, N. Raman, and J. Dharmaraja, "Synthesis, characterization, DNA interaction and pharmacological studies of substituted benzophenone derived Schiff base metal(II) complexes," *Journal of Saudi Chemical Society*,vol. 19, no. 2, pp. 207-216, 2015.