Copper(II) and nickel(II) complexes with *N'*-[(*Z*)-phenyl(pyridin-2-yl)methylidene]acetohydrazide : Synthesis, Crystal Structures, DFT calculations and Antioxidant effects

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ABSTRACT

Two mononuclear copper(II) and nickel(II) complexes viz., $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1** and $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2** (where $\text{HL}/\text{L}^- = N'-[(Z)\text{-phenyl(pyridin-2-yl)methylidene]acetohydrazide}$) complexes were synthesized and characterized by routine physicochemical techniques. Both complexes were structurally characterized using single crystal X-ray diffraction studies and belonging to space group $P2_1/n$ for **1** and $P\bar{1}$ for **2** respectively. Complex **1** has hexacoordinated geometry with 1:2 metals to ligand ratio whereas complex **2** has pentacoordinated with two ligand and Schiff base and neocuproine donors sites. The room temperature EPR spectrum of **1** shows two $S = 1/2$ signals due to the elongated axial symmetry. Time dependent DFT calculations on the optimized structure of **1** and **2** in DMSO solvent allowed for the assignment of specific electronic transitions in the UV-Vis spectrum. The highest occupied molecular orbital (HOMO) was noted to consist of 55% Cu-d and 100% Ni-d character identified as the $d_{x^2-y^2}$ orbital. In addition, antioxidant activity showed that both complexes exhibited significant scavenging effect against super oxide anion from radicals.

Keywords: Cu(II) complex, Ni(II) complex, DFT calculations, EPR spectra Uv-visible spectra and Cyclic voltmmograms

1. Introduction

A Schiff base is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group is replaced by an imine or azomethine group. Schiff bases and their metal complexes play a key role in the coordination chemistry [1-3]. These ligands are well studied area of research in the coordination chemistry due to possessing good biological activities and capable of forming stable complexes with transition metal ions. The tridentate Schiff base (N_2O donors) could also be proposed easily and used to synthesized several copper(II) and nickel(II) complexes [4,5]. Complexes formed between metal(II) ions, Schiff bases and hetero aromatic nitrogen bases may be considered as a models for substrate metal(II) ion-enzyme interaction. Complexation causes in the biological properties of the Schiff base along with metal(II) ions. Antibacterial [6], antifungal [6, 7] anticancer [8], herbicidal [9] properties of such schiff base complexes are well documented.

The potential role played by copper(II) and nickel(II) ions, being present in a large number of metalloproteins [10-15], has inspired the design of new copper(II) and nickel(II) complexes with N_2O donor Schiff base as a models to provide a better understanding of biological systems. Copper is a bioessential element with relevant oxidation states +1 and +2. Copper serves as cofactor in many fundamental reactions mediated by copper enzymes [10, 11]. The catalytic processing pathways include copper ions which are mostly coordinated by amino acid residue and water [10, 11]. Nickel is an

important metal in the chemistry of life [12]. Nickel(II) is present in the active site of many proteins, among the most investigated metalloenzymes is urease and nickel hydrogenase [13,14]. These enzymatic nickels are usually taking different electronic structures in different enzymatic states and/or different chemical environments [15]. Keeping the above facts in mind and in continuation of our school's research work on transition metal complexes[16-18] with Schiff bases, herein we report Synthesis, characterization, spectroscopic and redox properties of two new copper(II) and nickel(II) complexes are described. The structures of these complexes in the solid state have been determined by X-ray analysis. Present ligand coordinates with metal(II) ions with keto or both by keto-enol forms. The keto-enol form of the ligands structure is depicted in Scheme 1. Antioxidant activity measurements for superoxide anion from radicals ($O_2^{\bullet -}$), Catalytic dismutation of superoxide ($O_2^{\bullet -}$) have also been carried out and discussed physiological pH. The super oxide anion ($O_2^{\bullet -}$) plays important roles in the pathogenesis of many cardiovascular diseases, including hypertension and others sclerosis. Low molecular weight compounds able to mimic the catalytic antioxidant activity of ($O_2^{\bullet -}$) have been recognized in terms of eliminating immunogenicity problems as associated with protein administration, low cost of goods, tissue permeability, potentials for oral delivery and potential for greater *in vivo* stability.

2. Experimental

2.1. Materials

Copper(II) nitrate trihydrate, nickel(II) perchlorate hexahydrate, acetylhydrazide and 2-benzoyl pyridine were purchased from Across Organics and all the other chemicals were of synthetic grade. The solvents were purchased from commercial sources.

2.2 .Physical Measurements

2.2.1. Elemental analysis

Elemental analyses of the complexes were performed on an Elementar Vario EL III Carlo Erba 1108 analyzer. FAB Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer/data system using xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature.

2.2.2. Spectroscopy

UV-Vis spectra were recorded at 25°C on a Shimadzu UV-Visible recording spectrophotometer UV-1601 in quartz cells. IR-spectra were recorded in KBr medium on a Perkin-Elmer 783 spectrophotometer. X-band epr spectra were recorded with a Varian E-line Century Series Spectrometer equipped with a dual cavity and operating at X-band (~ 9.4 GHz) with 100 kHz modulation frequency. TCNE was used as field marker. The Varian quartz tubes were used for measuring e.p.r. spectra of polycrystalline samples and frozen solutions.

2.2.3. Magnetic susceptibility

Magnetic susceptibility measurements were made on a Gouy balance using a mercury(II) tetrathiocynato cobaltate(II) as calibrating agent ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units).

2.2.4. Molar conductivity

The Molar conductivity of the freshly prepared 1×10^{-3} M DMSO solutions was measured on systronic conductivity TDS meter 308.

2.2.5. Electrochemistry

Cyclic voltammetry was carried out with a BAS-100 Epsilon electrochemical analyzer having an electrochemical cell with a three-electrode system. Ag/AgCl was used as a reference electrode, glassy carbon as working electrode and platinum wire as an auxiliary electrode. 0.5 M Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte and DMSO as solvent. All measurements were carried out at room temperature under a nitrogen atmosphere.

2.2.6. Crystal structure determination

Crystals suitable for single crystal X-ray analysis for all the complexes were grown from the slow evaporation of the reaction mixtures at room temperature. Single crystals suitable for single crystal X-ray of **1** and **2** were mounted on a glass fiber and used for data collection. Crystal data were collected on Bruker APEX-II diffractometer using graphite monochromatized $M_o K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal orientation, cell refinement and intensity measurements were made using the program CAD-4PC performing ψ -scan measurements. The structures were solved by direct method using the program SHELXS-97 [19] and refined by full-matrix least-square techniques against F^2 using SHELXL-97 [20]. All hydrogen atoms were modelled with idealised geometry; this is not the case for the proton attached to N3B in **1**. The location of this hydrogen atom was picked from a peak in the Fourier difference map.

2.2.7. Antioxidant assay

The *in-vitro* antioxidant assay superoxide anion free radical scavenging activity was measured using alkaline DMSO as a source of superoxide radical ($O_2^{\bullet -}$) and nitro blue tetrazolium chloride (NBT) as $O_2^{\bullet -}$ scavenger [21-23]. In general, 400 μ l sample to be assayed was added to a solution containing 2.1 ml of 0.2 M potassium phosphate buffer (pH 8.6) and 1 ml of 56 μ M of alkaline DMSO solution was added while string. The absorbance was then monitored at 540 nm against a sample prepared under similar condition except NaOH was absent in DMSO. The 50% of activity (IC_{50}) was calculated using the percentage activity results. The percentage activity was calculated using the formula $[(A_0 - A_c) \times 100]$ (A_0 and A_c are the absorbance in the presence and absence of the test complex respectively).

2.2.8. Computational Details

The input files for the copper(II) and nickel(II) complexes were prepared with Gauss View 5.0.9 [24]. All calculation were made using the GAUSSIAN09 package

program [25] by the DFT/B3LYP method. LANL2DZ and 6-31G (d,p) are the standard basic sets. 6-31G (d,p) is a popular polarized basis set which adds p functions to hydrogen atoms in addition to the d functions on heavy atoms, while LANL2DZ is a basis set for post-third-row atoms. In the computational model, the anion was ignored and the cationic complex was taken into account. The electronic spectrum was predicted by calculating the excitation energy between states. Electronic spectra calculations of the complexes were made using the time dependent density functional theory (TD-DFT)/B3LYP method with the LANL2DZ basis set in the gas phase [26]. Vertical electronic excitations based on B3LYP optimized geometries were computed using the time dependent density functional theory (TDDFT) formalism [27–29] in DMSO using a conductor-like polarizable continuum model (CPCM) [30–32].

3. Synthesis

3.1 Synthesis of the ligand (HL)

The Schiff base was synthesized by the reacting acetylhydrazide (0.741 g, 10.0 mmol) and 2-benzoylpyridine (1.832 g, 10.0 mmol) in ethanol [33]. The resulting solution was refluxed for 4 h. The resulting light green solution was cooled to room temperature (RT) and filtered. The solid was dried over fused CaCl_2 desiccator. The product was recrystallized in yield from hot ethanol. Yield: 2.426 g, (53%). *Anal. Calcd.* For $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$: C, 70.28; H, 5.48; N, 17.56%. Found: C, 70.02; H, 5.26; N, 18.05%.

3.2. Synthesis of metal complexes $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1**

The ligand (HL) (0.239 g, 1.0 mmol) was dissolved in 10 mL of methanol. After stirring for 10 min, a batch of $\text{CuNO}_3 \cdot 3\text{H}_2\text{O}$ (0.242 g, 1.0 mmol) was added drop wise, the color of solution changed to green. After 1 h stirring. The reaction mixture was further stirred for 3 h. After 3 h stirring, reaction mixture was filtered off and allowed to stand at room temperature for a few days. Dark green block shape crystals suitable for X-ray analysis appear by slow evaporation of a green solution of complex 1. The complex so isolated was dried over a fused CaCl_2 in a desiccator. Yield: 0.265 g, (45%). *Anal. Calcd.* for $\text{C}_{28}\text{H}_{27}\text{CuN}_7\text{O}_6$: C, 62.45; H, 4.70; N, 15.60 %. Found: C, 62.15; H, 4.66; N, 15.53 %.

3.3. $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2**

Complex **2** was synthesized following the same procedure as **1**; only a batch of neocuproine (0.217 g, 1.0 mmol) was added drop wise. The reaction mixture was further stirred for 3 h. After 3 h stirring, reaction mixture was filtered off and dried over fused desiccator at room temperature. Light brown niddle shape crystals suitable for single crystal X-ray analysis appear by slow evaporation of a solution of complex 2 in methanol after 3 days at room temperature. Yield: 0.381 mg, (68%). *Anal. Calcd.* for $\text{C}_{29}\text{H}_{28}\text{ClN}_5\text{NiO}_6$: C, 65.10; H, 5.23; N, 14.65%. Found: C, 64.90; H, 5.03; N, 14.55%.

4. Results and discussion

4.1. Synthesis

Condensation of 2-benzoylpyridine and acetylhydrazide in a 1:1 molar ratio yields Schiff base (Scheme 2) which further react with copper nitrate trihydrate and nickel perchlorate hexahydrate to yield the corresponding copper(II) and nickel(II) complexes **1** and **2** respectively (Scheme 3). The ligand and its complexes were identified by microanalysis and FAB⁺ mass spectrometry. The complexes are stable to O₂ and moisture. Complexes show the molar conductivity (λ_m) 125 for **1** and 135 for **2** ohm cm⁻² mol⁻¹ in DMSO solution corresponding to 1: 1 electrolyte [34].

4.2. Infra red spectra

The IR spectra of complex **1** and **2** several bands appear in the region 405-3500 cm⁻¹. The (C=N) band of the Schiff base is found to be shifted to lower energies in the spectra of complex **1**, indicating the coordination via the azomethine nitrogen. This is confirmed by the bands in the range 440-464 cm⁻¹, which have been assigned to the (Cu-N) band [35]. The increase in frequency of this band in the spectra of both complexes is due to the increase band strength, again confirming the coordination via the azomethine nitrogen. In all the complexes a strong band is observed in the region 466-480 cm⁻¹, which is consistent with the (Cu-N) of pyridine ring [36]. The presence of a strong, sharp band at ~1650 cm⁻¹ that can be attributed to a (C=O) vibration. This is probably due to the oxygen atom of the carbonyl group [37]. However, some new bands with medium to weak intensities appear in the region 405-415 cm⁻¹ in the complexes under study, which are tentatively assigned to (M-O)/ (M-N) modes [38].

Based on the above spectral evidences, it is confirmed that the ligand is coordinated to the metal center as a tridentate mode, coordinating via the azomethine nitrogen, pyridyl nitrogen and carbonyl / enolic oxygen. In complex **1** and **2** these bands are sensitive to the coordination and shifted to higher frequencies in the complexes with respect to the free ligands [39]. The presence of uncoordinated water, nitrate and perchlorate in the complexes **1** and **2** is indicated by a broad band in the region 3500-3200 cm⁻¹ [40] and two weaker bands in the region 400-750 cm⁻¹ and 720 cm⁻¹ due to (OH) rocking and wagging mode of vibration, respectively [41,42]. The $\nu(\text{ClO}_4)$ band in complex **2** is found at 1103 cm⁻¹ [43]. The absence of $\nu(\text{NH})$ and $\nu(\text{C=O})$ band confirming that complexation occurs through enolic oxygen [44].

4.3. Single crystal X-ray crystallography structural characterization of the complexes

X-ray measurements of both copper(II) and nickel(II) complexes were made at 100 K using suitable crystal for data collection. The molecular structure of complex **1** and **2** shown in Figure 1 and 2. Crystallographic data and molecular structure refinement

important inter atomic parameters are given Table 1. The relevant bond angles and bond lengths are presented in Tables 2 and 3.

[Cu(HL)(L)]NO₃·2H₂O 1 Single-crystal X-ray analysis of complex **1** crystallized in the monoclinic space group **P2₁/c** with four molecules in the unit cell. The complex exhibits a distorted octahedral geometry with the basal plane occupied by NNO ligand for metal center. The ligand HL is deprotonated mono negative ligand NNO tridentate, coordinating *via* its ketonic or enolic oxygen azomethine nitrogen and pyridine nitrogen giving a distorted octahedral geometry around copper center. Ligand molecule can be deprotonated in the presence of metal ion and form complex with metal in neutral media. Protonated ligand can also undergo similar reaction with metals. Complex **1** contains one nitrate ion and two water as non coordinated (**Fig. 1**). One interesting feature of this complex is that one of the N-H proton of one ligand is **deprotonated** which allows the charge on the complex to be balanced. The apical position is occupied by 2-benzoyl pyridine nitrogen atoms, carbonyl oxygen atom completing the coordination sphere. In complex **1** C-N bond length N(3 A)-C(13 A) 1.338(2) is double bond character and N(3B)-C(13B) 1.373(2) Å single bond character. These factors are confirm coordination through the enolate form by deprotonation after enolization of the ligand and one of the N-H proton of one ligand is **deprotonated** coordination through the ketonic form of the ligand. The distortion of the molecule is indicated by the decreased value of the *trans* angles, N(2A)-Cu(1)-N(1B) = 173.01(5)°, O(1A)-Cu(1)-N(1A) = 159.13(5)° and O(1B)-Cu(1)-N(1B) = 145.10(5)° for complex **1**. Bond distances around the metal are Cu-N(2A) = 1.9414(14) Å, Cu-O(1A) = 1.9801(13) Å, Cu-N(1A) = 2.0434(14) Å, Cu-N(2B) = 2.0687(14) Å, Cu-N(1B) = 2.2559(15) Å, Cu-O(1B) = 2.4329(13) Å, for complex **1**. Individual bond distances and angles within the coordination polyhedron compare well with those found in other octahedral complexes of copper(II) involving N donors reported in literature [16]. The *cisoid* and *transoid* angles reflect the degree of distortion from ideal octahedral geometry. Thus the coordination polyhedron around the copper atom may be best described as a distorted octahedron. From the packing view of this complex, it is clear that four molecules of the complex are arranged in the unit cell. **In the crystal structure 1, the hydrogen bonds are well pronounced and they are formed by involving coordinated azo groups as well as co-crystallized nitrate and water molecules (Fig. 3 and Table 4). The hydrogen atom of HL belonging to azo group is involved in the hydrogen binding, i.e. N-H---N with N atom of azo group of L⁻ of the neighbouring molecule (catemeric azo-azo hydrogen bonding). Other hydrogen atom of co-crystallized water molecule is involved in hydrogen bonding with carbonyl group of L⁻. Similarly, O atom of nitrate anion also involved in H-bonding with hydrogen atom of pyridinic group of L⁻.**

[Ni(L)(Neocup)]ClO₄·MeOH 2 complex **2** crystallized in the triclinic space group **P 1̄** with two molecules in the unit cell. X-ray data showed one molecule of Schiff base (enol form) was N₂O donor and other N₂ donor sets of neocuproine for coordination to the nickel atom. The coordination environment around the nickel(II) ion is a slightly distorted square pyramidal N₄O geometry (**Fig. 2**). The Addison parameter tau (τ) is defined as (β-α)/60° [where β = the first largest angle and α = the second largest angle in the coordination sphere] and its value varies from 0 (in regular square-based pyramidal geometry) to 1 (in regular trigonal bipyramidal geometry) [45] for the pent coordinated nickel(II) ions in **2** is 0.072, thus indicating that the geometry is slightly distorted square pyramidal with N(1) and N(5) at the axial positions, forming a trans N(2)-Ni-

N(5)(162.74) (6)°. The bond distances Ni-N (1.93 – 2.20 Å) are typical for complexes of high-spin Ni(II) with nitrogen donor atoms [46]. From the packing view of this complex, it is clear that two molecules of the complex are arranged in the unit cell. The crystal packing diagram (Fig. 4) reveals a three dimension chain structure through a hydrogen bonding network. In complex **2**, the nature of bifurcated (or three centered) hydrogen bondings (Fig. 4) have been investigated along with normal hydrogen bondings. Bifurcated hydrogen bondings are intermolecular in a nature. The hydrogen atom of the co-crystallized methanol molecule forms bifurcated hydrogen bonding with two oxygen atoms of perchlorate anion. Additionally, H atom of pyridinic group of L⁻ participates in a discrete weak hydrogen bonding interaction with O atom of perchlorate anion.

4.5. Electronic spectra and TDDFT Calculations

Electronic spectra for the complexes **1** and **2** were recorded in 100% DMSO (3×10^{-3} M). Electronic spectra are shown in Fig. 5. The electronic spectral data for the complexes in DMSO are in good agreement with their geometries. The absorption spectra of complex **1** exhibited a broad absorption band at 14700 cm^{-1} assignable to ${}^2T_{2g} \rightarrow {}^2E_g$ transition indicating octahedral geometry [47]. The $T_{2g} - E_g$ separation in regular octahedral Cu(II) complex varies viz. $\sim 13000 \text{ cm}^{-1}$ for CuO_6 , $\sim 14000 \text{ cm}^{-1}$ CuN_4O_2 and $\sim 18000 \text{ cm}^{-1}$ CuN_6 . However, the mixed system Ni(II) does show three d-d bands (Table 6) may be observed in distorted square pyramids whose effective symmetry is no higher than C_s . These data suggests the same square pyramidal geometry for the $\text{Ni}^{\text{II}}\text{N}_4\text{O}$ chromophore in the polycrystalline state and in the solution. Absorption data (d-d bands) for similar complexes are reported [48-52]. These absorption properties in combination with the magnetic moments are consistent with the solid-state structural characterization of complexes **1** and **2**.

The calculated vertical excitation energies oscillator strength and tentative nature of the transition obtained at the TD-DFT level have been presented in Tables 5 and 6. The complex **1** shows a well resolved experimentally absorption band at 680 nm originates mainly in the HOMO/HOMO-1,-2,-3 $\rightarrow$ LUMO of beta spin state transition and can be interpreted as intra-ligand charge transfer ($\pi \rightarrow \pi^*$) according to the orbital characters beta HOMO (20%) and LUMO (40%) are contributed by carbon atoms. The theoretically obtained these bands at 1200 nm (0.7988 eV and $f = 0.0027$), 752 nm (1.7327 eV and $f = 0.0001$), 715 nm (1.7327 eV and $f = 0.0000$) and 699 nm (1.7727 eV and $f = 0.0002$). These excitation states are contributed to HOMO-3 $\rightarrow$ LUMO (57%), HOMO-2 $\rightarrow$ LUMO (89%), HOMO $\rightarrow$ LUMO (66%), HOMO-1 $\rightarrow$ LUMO (36%) and HOMO-1 $\rightarrow$ LUMO+1 (36%) respectively. The absorption bands observed by experimentally at 391 nm originates at HOMO/HOMO-1/HOMO-3 to LUMO of beta spin state transitions. These are theoretically two excitation composition 1.8416 eV (673 nm and $f = 0.0002$) and 2.0447 eV (606 nm and $f = 0.0004$) and shown in Fig. 6. These bands can be assigned to d-d/LMCT/ILCT transitions. The complex **2** shows experimentally absorption band at 985 nm originates mainly in the HOMO $\rightarrow$ LUMO of

beta spin state transition and can be interpreted as intra-ligand charge transfer ($\pi \rightarrow \pi^*$) according to the orbital character. The theoretically obtained these bands at 859 nm (1.4430 eV and $f = 0.0025$), these excitation states are contributed to HOMO $\rightarrow$ LUMO/LUMO+2. The absorption bands observed by experimentally at 454 nm originates at HOMO/HOMO-1 to LUMO/LUMO+2 of beta spin state transitions and shown in Fig. 7. These bands can be assigned to d-d/LMCT/ILCT transitions. The TD-DFT calculations exhibits good quantitative agreement with the spectral position of the absorption bands of Cu(II) and Ni(II) complex.

4.6. Magnetic measurements

The magnetic susceptibility measurements in the solid state represent that the complexes were paramagnetic at room temperature. The observed magnetic moment of complex **1** is quite close to the values expected for other copper(II) complexes. Magnetic moment values (μ_{eff}) lies within the range normally found for other magnetically coupled copper(II) complexes having pseudodipolar interactions [52]. This magnetic moment values is suggestive of distorted octahedral nature of the complex [54]. The observed magnetic moments (2.79 B.M.) of complex **2** is comparable with spin only value of 2.83 B.M. for nickel(II) ion. A little less than the spin only value of absorbed magnetic moment also shows that the square pyramidal environment of nickel(II) ion involve high spin species [55]. These results reveal that the electronic configurations derived from structural analysis are in good agreements. These copper(II) and nickel(II) complexes are paramagnetic, with respect to one ($S = \frac{1}{2}$) and two ($S = 1$) electrons respectively [56,57].

4.7. Electron paramagnetic resonance spectra

EPR spectra of the Cu(II) complex were recorded at room temperature in polycrystalline sample and liquid nitrogen temperature in DMSO solution (Fig. 8). The complex shows two $S = \frac{1}{2}$ EPR signals at RT due to the elongated axial symmetry, with $g_{\parallel(z)} = 2.2071$ and $g_{\perp(x,y)} = 2.073$. A half-field transition ($\Delta M_s = 2$, $g = 4.2975$ and inset Fig. 8) is observed at 1560 G and therefore presence of pseudodipolar (intermolecular) interactions is suggested in polycrystalline state. The half-field signal is not appeared in frozen solution spectrum as pseudodipolar interaction is lost in solution [58]. There are three well resolved peaks in the low field region corresponding to $g_{\parallel}$ and $g_{\perp}$. The trend $g_{\parallel}$ (2.2848) $>$ $g_{\perp}$ (2.0731) $>$ g_e (2.0023) observed for the complex suggests that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the copper ion [59, 60]. The fact that the unpaired electron lies predominately in the $d_{x^2-y^2}$ orbital is also supported by the value of the exchange coupling parameter G . If $G > 4$, the exchange interaction is negligible and if $G < 4$, indicates exchange interaction [60-62]. The value of the exchange-coupling parameter G in solution is ~ 4.00 , suggesting exchange interactions in this complex at LNT [62]. The value of G for copper complex is 2.90, indicating exchange interactions in polycrystalline state at room temperature.

4.8. Cyclic Voltammetry

The redox behavior of the present copper(II) and nickel(II) complexes was studied by cyclic voltammetry (CV) in degassed DMSO solution. The redox properties of complex **1** and **2** have been studied by cyclic voltammetry under nitrogen atmosphere in DMSO solution $3.0 \times 10^{-3} \text{ mol L}^{-1}$ in the potential range +4.0 to -7.0V versus the Ag/AgCl reference electrode. Voltammograms consist of defined one cathodic peak potential (E_{pc}) and one anodic peak potential (E_{pa}). The CV of complexes shown in Fig. 9 corresponding data is presented in Table 7. The complex **1** shows one reduction peak corresponding to Cu(II)–Cu(I). Inspection of Figure indicates that the reduction wave and its oxidation counterpart are related to the Ni(II)/Ni(I) redox couple. The electrochemical reduction of these complexes is diffusion controlled as evidenced by I_{pa}/I_{pc} value. The value of I_{pa}/I_{pc} [63] is less than unity also showing that the electron transfer reaction is followed by a chemical reaction (EC mechanism) [64]. The potentials of the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox couples for the present complexes are significantly less negative than those obtained previously for the nickel(II) complexes with non macrocyclic N- or N,O-donor ligands ($E_{1/2} < -1.5 \text{ V}$) [65-69]. Pyridine nitrogen donors are softer than aliphatic amines because of π -acceptor properties of an aromatic pyridine ring, allowing for better stabilization of the low oxidation state of Ni(I). Additionally, the ligands with long pendant arms are expected to form thermodynamically weaker complexes with Ni(II) than their short-armed analogues [70,71] resulting in less negative reduction potentials for the Ni(II)/Ni(I) couple.

4.9. Electronic structure and DFT calculations

B3LYP-6-31G (d,p) level of calculation of the molecules have been carried out to understand the electronic structure of complexes. The structural agreement has been verified on the comparing the bond distances and angles between the DFT optimized and X-ray determined structures of complexes **1** and **2** (Table 2 and 3). The optimized structures of complexes **1** and **2** are shown in Fig. 10. According to Table 2 and 3, the optimized bond lengths and angles are slightly larger than the experimental ones since the theoretical calculation were performed on an isolated molecule in gas phase. Whereas, the experimental results were obtained in solid state [72, 73]. Counter plots of selected molecular orbital's of complexes **1** and **2** are shown in Fig. 6 and 7, respectively. The energy and compositions of some selected molecular orbitals of complex **1** and **2** are presented in Table 8 and 9. The HOMO energy level of **1**, -5.3120 eV and -3.3623 eV for **2** while the LUMO energy level of **1**, -5.2987 and -4.5354 eV for **2**. The HOMO–LUMO energy gap (ΔE) are -0.0133 eV, -1.1731 eV in **1** and **2** respectively. The energy gap between HOMO and LUMO characterizes the molecular chemical stability. The less value of HOMO–LUMO (descriptor ΔE) means that molecule is more active [74]. According to the ΔE values, the biological activity of mentioned complexes should be:

$$\mathbf{1} > \mathbf{2}$$

The low energy unoccupied molecular orbital's are constructed on coordinated ligand for **1** and **2**. For complex **1**, the HOMO orbital has 0% π (L) along with greater

contribution 55% of $d\pi$ (Cu) orbital's (Table 8). The HOMO to HOMO-2 have 45-90% $\pi(L)$ character, while HOMO-3 to HOMO-7 have mixed $\pi(L)$ and $d\pi(Cu)$ feature. Similarly for complex **2**, the HOMO has 0% $\pi(L)$ and 100% $d\pi(Ni)$ orbital (Table 9). Above HOMO (HOMO-1 to HOMO-3) have 100% $\pi(L)$ features. After HOMO-3 mixed % of $\pi(L)$ remains. **Fig. 11** represents the spin density of the unpaired spin distributed coordinated atoms along with major contribution on the metal centre.

4.10. Antioxidant assay

The superoxide anion free radical scavenging assay was on the reduction of NBT to MF^+ kinetically at 560 nm [75]. These complexes exhibit significant catalytic activity toward the scavenging of superoxide anion radicals. The 50% activity of the NBT reduction defined as IC_{50} were estimated for complexes **1** and **2**. The observed IC_{50} values of the present complexes summarized in **Table 10** reveal that their antioxidant activity in the range of the SOD mimics represented in literature [76-80]. The IC_{50} value of complex **2** (104 μ mol) is greater than **1** (62 μ mol). The SOD activity **1** is greater than **2** the same trend of biological activity is also verified from DFT calculations. The catalytic rate constant (k_{McCF}) was also evaluated of these complexes. The kinetic catalytic constant k_{McCF} was obtained by the equation $k_{McCF} = k_{NBT} \times [NBT] / IC_{50}$, where $k_{NBT} = 5.94 \times 10^{-4} (\text{molL}^{-1})^{-1} \text{s}^{-1}$ is the second order rate constant for NBT [81] of **1** and **2** are $5.36 \times 10^{-4} (\text{molL}^{-1})^{-1} \text{s}^{-1}$ and $3.19 \times 10^{-4} (\text{molL}^{-1})^{-1} \text{s}^{-1}$ respectively [82-84]. The value of the catalytic constant for $O_2^{\bullet -}$ dispropotionation clearly indicates that these complexes can be used as superoxide scavengers. Comparison of k_{McCF} of both complexes reveal that complex **1** is better suited to react with superoxide anion free radicals.

5. Conclusion

Using tridentate Schiff base two new complexes **1** and **2** were synthesized and characterized using various physico-chemical techniques. The electronic and spectral features of the complexes have been discussed by DFT and TD-DFT calculations. Time dependent DFT calculations on the optimized structure of **1** and **2** in DMSO solvent allowed for the assignment of specific electronic transitions in the UV-Vis spectrum. The highest occupied molecular orbital (HOMO) was noted to consist of 55% Cu-d and 100% Ni-d character identified as the $d_{x^2-y^2}$ orbital. The EPR spectrum of complex **1** ($S=1/2$) showed a signal which in characteristic of mononuclear copper(II) complexes. Single crystal structure of complex **1** showed octahedral geometry whereas, complex **2** showed distorted square pyramidal geometry. In addition, the complexes also exhibit good antioxidant SOD activity and SOD activity of complex **1** is better than that of **2**.

Acknowledgements

The Head CDRI, Central Drug Research Institute, Lucknow is thankfully acknowledged for providing analytical and spectral facilities. The authors also wish to acknowledge the assistance of Dr. Matthias Zeller in the collection of diffraction data and NSF Grant CHE 0087210, Ohio Board of Regents Grant CAP-491 and by Youngstown State University for funds to purchase the X-ray diffractometer.

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Scheme 1: *N'*-[(*Z*)-phenyl(pyridin-2-yl)methylidene]acetohydrazide (HL/ L).

Acethydrazide

2-benzoylpyridine

Scheme2: Synthesis of ligand

Scheme 3. Synthetic route of complexes **1** and **2**.

Fig. 1. ORTEP Structure of Complex $[\text{Cu}(\text{HL})(\text{L})]^+$ (**1**).

Fig.2. ORTEP Structure of $[\text{Ni}(\text{HL})(\text{Neocup})]^+$ (**2**).

Fig. 3. Unit cell diagram of Complex $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1**.

Fig. 4. Unit cell diagram of Complex $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2**.

Fig. 5. UV-Vis spectra of Complexes for $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1** and $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2** in DMSO at RT $3 \times 10^{-3}\text{M}$.

Fig. 6. HOMO-LUMO molecular orbital energy level diagram for $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1**.

Fig. 7. HOMO-LUMO molecular orbital energy level diagram for $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2**.

RT

LNT

Fig. 8. EPR spectrum of Complex $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1** in polycrystalline state (RT) and in DMSO solution at liquid nitrogen temperature (LNT).

1

2

Fig. 9. Cyclic voltammograms of complexes in different scan rate 100, 200 and 300 mV s^{-1} for $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O} **1** and $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH} **2**.$$

1

2

Fig. 10. Optimized structures of $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1** and $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2**.

1

2

Fig. 11. Spin density plots of [Cu(HL)(L)]NO₃·2H₂O **1** and [Ni(L)(Neocup)]ClO₄·MeOH **2**.

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

Compounds	1	2
Empirical formula	C ₂₈ H ₂₇ Cu N ₇ O ₆	C ₂₉ H ₂₈ Cl N ₅ Ni O ₆
Formula weight	621.10	636.72
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
Unit cell dimensions (Å) (°)		
A	9.1941(11)	8.4345(14)
b	16.831(2)	10.8382(18)
c	17.855(2)	16.785(3)
α	90	71.411(2)
β	99.705(2)	79.620(2)
γ	90	76.304(2)
V Å ³	2723.6(6)	1403.9(4)
Z	4	2
Density (calculated) Mg/m ³	1.515	1.506
Absorption coefficient	0.859 mm ⁻¹	0.839
F(000)	1284	660
Crystal size mm ³	0.550 x 0.540 x 0.480	0.550 x 0.330 x 0.290
θ range for data collection	2.348 to 32.205°	2.020 to 32.095°
Index ranges	-13 ≤ <i>h</i> ≤ 7, -23 ≤ <i>k</i> ≤ 22, -18 ≤ <i>l</i> ≤ 25	-12 ≤ <i>h</i> ≤ 12, -15 ≤ <i>k</i> ≤ 16, -23 ≤ <i>l</i> ≤ 23
Reflections collected	16579	23056
Independent reflections	8059 [R(int) = 0.0211]	8892 [R(int) = 0.0205]
Completeness to θ = 25.500°	98.9 %	99.4 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7464 and 0.6048	0.7463 and 0.6041
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	8059 / 18 / 401	8892 / 0 / 384
Goodness-of-fit on F ²	1.041	1.036
Final R indices [I > 2σ(I)]	R1 = 0.0397, wR2 = 0.1002	R1 = 0.0393, wR2 = 0.1057
R indices (all data)	R1 = 0.0466, wR2 = 0.1037	R1 = 0.0439, wR2 = 0.1083
Extinction coefficient	n/a	n/a
Largest diff. peak and hole. Å ⁻³	1.246 and -0.787	1.397 and -0.932

Table 2. Selected theoretical and experimental structural parameters [$\text{\AA}$] and angles [$^\circ$] of complex **1**.

Parameters	Single crystal XRD Data	Theoretical data	Parameters	Single crystal XRD Data	Theoretical data
Bond length					
Cu-N(2A)	1.9414(14)	2.0989	Cu-O(1A)	1.9801	2.1799
Cu-N(2B)	2.0687(14)	2.1597	Cu-N(1A)	2.0434	2.1397
Cu-N(1B)	2.2559(15)	2.3458	Cu-O(1B)	2.4329	2.5298
Bond angle					
N(2A)-Cu-O(1A)	79.06(5)	84.04	O(1A)-Cu-N(1A)	159.13(5)	164.87
N(2A)-Cu-N(1A)	80.10(5)	85.08	O(1A)-Cu-N(2B)	94.42(5)	96.92
N(2A)-Cu-N(2B)	173.01(5)	176.09	N(1A)-Cu-N(2B)	106.45(5)	107.95
N(2A)-Cu-O(1B)	112.15(5)	114.98	N(1A)-Cu-N(1B)	94.69(5)	96.29
N(2A)-Cu-N(1B)	102.33(5)	103.89	N(2B)-Cu-O(1B)	71.31(5)	73.93
O(1A)-Cu-N(1B)	90.71(6)	94.99	O(1A)-Cu-O(1B)	100.72(5)	103.86
N(2B)-Cu-N(1B)	75.03(5)	76.97	N(1B)-Cu-O(1B)	145.10(5)	146.18
N(1A)-Cu-O(1B)	86.22(5)	87.89			

Table 3. Selected theoretical and experimental structural parameters [$\text{\AA}$] and angles [$^\circ$] of complex **2**.

Parameters	Single cystal XRD Data	Theoretical data	Parameters	Single cystal XRD Data	Theoretical data
Bond length					
Ni-N(2)	1.9332(14)	2.1987	Ni-N(4)	2.2016(14)	2.3987
Ni-O(1)	1.9735(12)	2.2685	Ni-N(5)	2.0162(13)	2.1180
Ni-N(1)	2.0276(14)	2.1865			
Bond angle					
N(2)-Ni-O(1)	79.25(5)	80.97	O(1)-Ni-N(5)	96.80(5)	98.83
N(2)-Ni-N(5)	162.74(6)	167.84	N(2)-Ni-N(1)	80.29(6)	81.79
O(1)-Ni-N(4)	90.75(5)	92.82	N(5)-Ni-N(1)	100.70(6)	104.75
O(1)-Ni-N(1)	158.38(5)	163.40	N(2)-Ni-N(4)	117.13(6)	118.93
N(1)-Ni-N(4)	104.79(5)	107.70	N(5)-Ni-N(4)	79.49(5)	84.89

Table 4. Hydrogen bonding parameters in complex **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1A)-H(1AA)...O(2)#1	0.95	2.41	3.293(2)	154.5
C(2A)-H(2AA)...O(1)#1	0.95	2.61	3.242(2)	124.3
N(3B)-H(3B)...N(3A)#2	0.81(2)	2.55(2)	3.324(2)	161(2)
C(1B)-H(1BA)...O(3)	0.95	2.63	3.232(2)	121.4
C(2B)-H(2BA)...O(3)	0.95	2.57	3.189(3)	122.9
C(14B)-H(14E)...N(3A)#2	0.98	2.65	3.563(2)	154.8
O(1WA)-H(1W2)...N(1)	0.80(2)	2.47(5)	3.219(6)	156(11)
O(1WA)-H(1W2)...O(1)	0.80(2)	2.27(10)	2.823(7)	126(11)
O(1WA)-H(1W2)...O(3)	0.80(2)	2.05(3)	2.847(6)	173(12)
O(1WB)-H(1W4)...O(1A)#3	0.79(2)	2.61(2)	3.396(5)	174(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y-1/2,-z+1/2   #2 -x+1/2,y-1/2,-z+1/2

#3 -x+1,-y+1,-z+1

Table 5 .TD-DFT calculated excitations approximate assignments for Complex **1**.

Eexcitation (eV)	Wavelength (nm)	Oscillator strength (f)	Major Contribution	Exp. Wave length (nm)
0.7988	1200	0.0027	BHOMO-3 → BLUMO (57%) BHOMO-2 → BLUMO (89%)	-
1.6475	752	0.0001	BHOMO-1 → BLUMO (74%) BHOMO → BLUMO(66%)	-
1.7327	715	0.0000	BHOMO-1 → BLUMO (36%)	-
1.7727	699	0.0002	BHOMO-1 → BLUMO+1 (36%) BHOMO → BLUMO (47%)	680
1.8416	673	0.0002	BHOMO-1 → BLUMO (62%) BHOMO → BLUMO(81%)	-
2.0447	606	0.0004	BHOMO -3→ BLUMO (46%) BHOMO → BLUMO (48%)	391

Table 6. TD-DFT calculated excitations approximate assignments for complex **2**.

Excitation (eV)	Wavelength (nm)	Oscillator strength (f)	Major Contribution	Exp. Wave length (nm)
1.3863	894	0.0139	β HOMO $\rightarrow$ β LUMO (46%) β HOMO $\rightarrow$ β LUMO +2(37%)	965
1.4430	859	0.0025	β HOMO $\rightarrow$ β LUMO (58%) β HOMO $\rightarrow$ β LUMO +2(59%)	865
1.5389	805	0.0011	β HOMO-1 $\rightarrow$ β LUMO (70%) β HOMO $\rightarrow$ β LUMO+2 (61%)	600

Table 7. Cyclic voltammetric data for **1** and **2** 3×10^{-3} M mmolL⁻¹ solution of the copper(II) complexes in DMSO containing 0.1molL⁻¹ TBAP as supporting electrolytes.

Scan rate (mVs ⁻¹)	E_{pc} (V)	I_{pc} (μ A)	E_{pa} (V)	I_{pa} (μ A)	ΔE_p (V)	$E^{\bullet}$ (V)
1						
100	-0.139	1.157	0.258	1.670	0.397	0.059
200	-0.168	1.200	0.268	1.099	0.436	0.050
300	-0.185	1.251	0.287	0.728	0.472	0.051
2						
100	-0.255	1.350	0.243	0.590	0.498	0.006
200	-0.263	1.480	0.268	0.390	0.511	0.002
300	-0.272	1.520	0.284	0.205	0.556	0.006

$\Delta E_p = E_{pa} - E_{pc}$; $E^{\bullet} = (E_{pa} + E_{pc})/2$

Table 8. Energy and composition of some selected Molecular Orbitals (β spin) of complex **1**.

S. No.	Orbital	Energy (eV)	% Composition	
			Metal (%)	Ligand (%)
1.	HOMO-7	-7.0079	22	78
2.	HOMO-6	-6.9145	2	98
3.	HOMO-5	-6.6582	0	100
4.	HOMO-4	-6.4288	1	99
5.	HOMO-3	-6.0062	15	85
6.	HOMO-2	-5.8636	10	90
7.	HOMO-1	-5.5833	30	70
8.	HOMO	-5.3120	55	45
9.	LUMO	-5.2987	20	80
10.	LUMO+1	-2.4172	32	68
11.	LUMO+2	-2.2294	2	98
12.	LUMO+3	-1.9911	1	99
13.	LUMO+4	-1.2898	0	100
14.	LUMO+5	-1.0980	0	100
15.	LUMO+6	-0.6930	0	100
16.	LUMO+7	-0.5635	0	100

Table 9. Energy and composition of some selected Molecular Orbitals (β spin) of complex **2**.

S. No.	Orbital	Energy (eV)	% Composition	
			Metal (%)	Ligand (%)
1.	HOMO-7	-6.4897	45	55
2.	HOMO-6	-6.2285	25	75
3.	HOMO-5	-6.1901	0	100
4.	HOMO-4	-5.9937	100	0
5.	HOMO-3	-5.4913	0	100
6.	HOMO-2	-5.0200	0	100
7.	HOMO-1	-4.4731	0	100
8.	HOMO	-3.3623	100	0
9.	LUMO	-4.5354	100	0
10.	LUMO+1	-2.3538	0	100
11.	LUMO+2	-2.1704	0	100
12.	LUMO+3	-1.3570	0	100
13.	LUMO+4	-0.9135	0	100
14.	LUMO+5	-0.5499	0	100
15.	LUMO+6	-0.3499	0	100
16.	LUMO+7	-0.0557	45	55

Table 10. Antioxidant SOD activity of some copper(II) and nickel(II) complexes.

S.No.	Complex	IC ₅₀ ($\mu\text{mol dm}^{-3}$)	SOD activity (μmol^{-1})	k _{McCF} ($\text{mol L}^{-1}\text{s}^{-1}$) $\times 10^4$	Reference
1	Vc	852	1.17	0.39	76
2	[Ni(BH) ₃]NO ₃ ·ClO ₄ ·H ₂ O	74	13.51	4.49	77
3	[Ni(BH) ₂ (NO ₃) ₂]	105	9.52	3.16	77
4	[Ni(BH) (Tren)](ClO ₄) ₂	108	9.25	3.08	77
5	[Cu(L)(bipy)]	62	16.12	5.36	78
6	[Cu(glygly)]·3H ₂ O	132	7.57	2.52	79
7	[Cu(phen)2(H ₂ O)](ClO ₄) ₂	26	38.46	12.79	80
8	[Cu(bipy)2(NO ₃)]ClO ₄	33	30.30	10.08	80
9	[Cu(HL)(L)] NO ₃ ·2H ₂ O	62	16.12	5.36	Present work
10	[Ni(L)(Neocup)](ClO ₄ ·MeOH	104	9.61	3.19	Present work

k_{McCF} where calculated by $k_{\text{McCF}} = k_{\text{NBT}} \times [\text{NBT}]/\text{IC}_{50}$, k_{NBT} (pH; 7.8) = $5.94 \times 10^4 (\text{mol L}^{-1})^{-1}\text{s}^{-1}$ [82]

Graphical abstract pictogram

Graphical Abstract

Two new copper(II) and nickel(II) complexes viz., $[\text{Cu}(\text{HL})(\text{L})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1** and $[\text{Ni}(\text{L})(\text{Neocup})]\text{ClO}_4 \cdot \text{MeOH}$ **2** (where $\text{HL}/\text{L}^- = N'-[(Z)\text{-phenyl(pyridin-2-yl)methylidene]acetohydrazide}$) complexes were synthesized and characterized. Both complexes were structurally characterized using single crystal X-ray diffraction studies and belonging to space group $\text{P2}_1/\text{n}$ for **1** and $\text{P}\bar{1}$ for **2** respectively. Further, complexes catalyzed the dismutation of superoxide ($\text{O}_2^{\bullet -}$) at biological pH.