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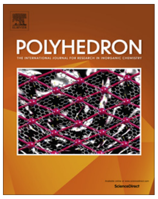

Copper(II) and nickel(II) complexes with N′-[(Z)-phenyl(pyridin-2-yl) methylidene]acetohydrazide: Synthesis, crystal structures, DFT calculations and antioxidant effects

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Two mononuclear copper(II) and nickel(II) complexes viz., $[Cu(HL)(L)]NO_3\cdot 2H_2O$ **1** and $[Ni(L)(Neocup)]ClO_4\cdot MeOH$ **2** (where HL/L^- = N'-[(Z)-phenyl(pyridin-2-yl)methylidene]acetohydrazide) complexes were synthesized and characterized by routine physiochemical 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.

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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

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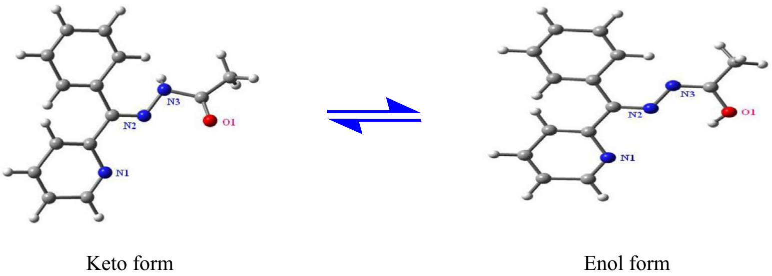

Scheme 1. *N′*-[(*Z*)-phenyl(pyridin-2-yl)methylidene]acetohydrazide (HL/L).

measurements for superoxide anion from radicals ($O_2^{\cdot-}$), Catalytic dismutation of superoxide ($O_2^{\cdot-}$) have also been carried out and discussed physiological pH. The super oxide anion ($O_2^{\cdot-}$) 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 ($O_2^{\cdot-}$) 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–Vis 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) tetrathiocyanato 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 Tetrabutylammoniun 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 Mo Kα radiation (λ = 0.71073 Å). 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 modeled with idealized 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 ($O_2^{\cdot-}$) and nitro blue tetrazolium chloride (NBT) as $O_2^{\cdot-}$ scavenger [21–23]. In general, 400 μl 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 μM 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

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