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# Synthesis, characterization and catalytic properties of dinuclear complexes of copper(II) and nickel(II): oxidation of cyclohexane, toluene and cyclopentane

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#### Abstract

Oxidation of saturated hydrocarbon by transition metal complexes is of great importance because this would give industrially valuable organic fine chemicals. Here, dinuclear copper(II) and dinuclear nickel(II) complexes with same N,O donor ligand have been used as catalyst for the oxidation of cyclohexane, toluene and cyclopentane using hydrogen peroxide as the oxidant to examine their catalyticactivityand effect of nature of metal center on catalysis.  $[Cu_2(L^1)_2(\mu_2 - \mu_2)_2(\mu_2 - \mu_2)_2$ Cl)Cl]·2.5H<sub>2</sub>O(1) and  $[Ni_2(L^1)_2(\mu_2-N_3)_2 (CH_3OH)_2]$ ·CH<sub>3</sub>OH(2) have been synthesized under mild conditions where  $HL^1$  is 1-((2-hydroxyethylimino)methyl)naphthalen-2-ol. These complexes have been characterized by elemental analysis, FT-IR, UV-Vis, mass spectroscopy, TGA-DTA and cyclic voltametric studies. Their structures have been confirmed by single crystal X-ray diffraction analysis. Some theoretical calculations have been performed to investigate spectral transitions. Copper(II) complex shows effective catalytic ability towards oxidation of the saturated hydrocarbons such as cyclohexane, toluene and cyclopentane in the presence of hydrogen peroxide when corresponding alcohols and ketones have been obtained as major products. However, complex 2 has been found to be inactive as catalyst for the oxidation. It is possible that Cu-hydroperoxo or Cu-peroxo species is formed during catalysis (as revealed from UV-vis spectral analysis) which could be the active species for the oxidation reaction.

Keywords: Homogenous catalysis; Saturated hydrocarbon; Oxidation; Copper; X-ray Structure.

#### **1. Introduction**

Activation of  $C_{sp3}$ -H bond is one of the most difficult tasks in chemistry. Natural gas and fuel are mainly saturated hydrocarbons. This bond in methane is inert and of high energy (104 kcal/mol) at ambient temperature, thus, the oxidation requires high temperature and pressure and/or acidic reaction media in addition to the presence of metal as catalyst [1]. Transformation of these compounds may give different valuable organic fine chemicals which are of great industrial importance. For example, methane can be converted to methanol with one functional group which could be converted to other compounds easily [2]. Modeling of metalloenzymes with particular catalytic activity is of great interest for the design and development of bioinspired catalysts. In connection with activation of C<sub>sp3</sub>-H bond, we could recall an enzyme, methane monooxogenase [3]. It exists in two forms; (a) particulate methane monooxogenase (pMMO) and (b) soluble methane monooxogenase (sMMO). Both of these forms are able to convert methane to methanol.sMMO contains two iron(III) centers in the active site. Active site of pMMO is not identified unambiguously by structural characterization of the enzyme. However, the existence of two Cu(II) centers in the active site of pMMO is of most acceptable belief [1a, 3]. Therefore, there are several copper(II) complexes including dinuclear copper(II) compounds which have used as catalyst for the activation of  $C_{sp3}$ -H bond [4]. Different hydrocarbons have utilized as the substrates such as methane, cyclohexane, cyclopentane. Oxidation of cyclohexane is useful because its oxidized products, mainly cyclohexanol and cyclohexanone, are of great industrial importance [5]. Cyclohexanol is, mainly, used as the raw material for the manufacture of adipic acid. Adipic acid is used for the preparation of nylon-6,6', soaps and detergents, pesticides, etc. Cyclohexanone is, mainly, utilized as a solvent in industries and activator in oxidation reactions. Pombeiro et al. have been working for long time on the development of different copper(II) complexes as active catalyst for such oxidation reactions [6]. Few other groups have also reported C-H activation reactions by Cu(II) complexes [7]. But, conversion of substrate to product is of comparatively low percentage because of high C-H bond energy. Although there is significant importance of copper(II) complexes as catalysts in various catalytic transformations [7i-7n], the field of alkane oxidation by copper complexes is less explored. It is to be noted that in addition to the original metal present in the metalloenzyme, some functional models with other transition metals have been designed and reported. For example, phenaxozinone synthase mimicking activity has been reported by complexes with

Mn(II), Co(III), etc.[8]. So other transition metal complexes can be designed for MMO activity to enable  $C_{sp3}$ -H bond activation. Thus, search for active catalyst for high conversion and better selectivity of a particular product continues. Effort should be given to design the catalyst which can mimic activity of naturally abundant enzymes.

In this respect, we report synthesis, characterization and catalytic properties of dinuclear  $[Cu_2(L^1)_2(\mu_2-Cl)Cl] \cdot 2.5H_2O(1)$ and  $[Ni_2(L^1)_2(\mu_2-N_3)_2]$ Cu(II) and Ni(II) complexes. (CH<sub>3</sub>OH)<sub>2</sub>]·CH<sub>3</sub>OH(**2**) where HL<sup>1</sup> is 1-((2-hydroxyethylimino)methyl)naphthalen-2-ol (Scheme 1). Some theoretical calculations have been performed to investigate spectral transitions of these complexes. Cu(II) complex has been prepared by the reaction between copper(II) chloride and HL<sup>1</sup> under mild conditions. It has been used as catalyst for oxidation of cyclohexane, toluene and cyclopentane using hydrogen peroxide as the oxidant. We wanted to check if replacement of copper by other metal, say nickel, in similar environment has any effect on catalytic activity. In other words, we wanted to use Ni for pMMO mimicking activity. Although Ni(II) complexes have been used as catalyst for different reactions including olefin epoxidation, C-C bond formation, etc.[9], attempt to use of nickel compounds in alkane oxidation is rare. Dinuclear Ni(II) complex has been synthesized with same ligand to provide similar chemical environment around the metal center.

#### 2. Experimental

#### 2.1. Materials and characterization

2-Hydroxy1-naphthaldehyde, 2-aminoethanol, copper(II) chloride dihydrate, nickel(II)nitrate hexahydrate, sodium azide and tetrabutylammonium perchlorate (TBAP) were purchased from Sigma Aldrich and used without further purification. Other reagents and solvents were obtained from commercial sources and used as received. NMR spectra of the compounds were recorded on a Bruker 500 MHz spectrometer. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 2400C elemental analyzer. FT-IR spectra were recorded on a Perkin Elmer spectrometer (Spectrum Two) with the samples by the use of attenuated total reflectance (ATR) technique. The UV-visible spectral measurements were recorded in Agilent 8453 diode array spectrophotometer. Analysis of reaction mixture of catalytic reactions was performed with a Shimadzu next generation high speed gas chromatography system (model: GC-2025 AF) equipped with a fused silica capillary column and

FID detector. All electrochemical measurements were performed using a personal computer (PC)-controlled PAR model 273A electrochemistry system. A GC working electrode, a platinum wire auxiliary electrode and Ag/AgCl saturated KCl reference electrode were employed in a standard three-electrode configuration. TBAP was used as supporting electrolyte in MeCN and was done under nitrogen atmosphere. TG-DTA analysis was carried out on Perkin-Elmer Pyris Diamond TG/DTA unit. All experiments were carried out at room temperature in air unless reported otherwise.

*CAUTION*: Organic perchlorates are potentially explosive. Only small amount of the perchlorate salt should be handled with care.

#### 2.2. Synthesis

#### 2.2.1. Synthesis of 1-((2-hydroxyethylimino)methyl)naphthalen-2-ol (HL<sup>1</sup>)

1-((2-Hydroxyethylimino)methyl)naphthalen-2-ol (HL<sup>1</sup>) has been synthesized following a published procedure with slight modification [10]. Typically, 2-aminoethanol (0.5 mmol, 0.030 mL) was added to a methanolic solution (10.0 mL) of 2-hydroxy1-napthaldehyde (0.5 mmol, 0.086 g) under stirring condition. The mixture was stirred for 30 min. Then the resulting solution was refluxed for 2 h. The color of the mixture turned yellow. It was then cooled to room temperature to obtain yellow color solid product. The product was collected by filtration and dried in air. Yield: 85% (0.091 g); C, H, N analysis: anal. calc. for C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub>: C, 72.54; H, 6.09; N, 6.51; found: C, 72.44; H, 5.98; N, 6.56%.<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  (ppm): 14.23 (s, 1H), 8.80 (s, 1H), 7.92 (d, J = 8.5Hz, 1H), 7.66 (d, J = 9.5 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.39 (1H, dd), 7.17 (dd, J = 6.0 Hz, 1H), 6.74 (d, J = 9.0 Hz, 1H), 4.11(t, J = 9.0 Hz, 2H), 3.71 (t, J = 4.0 Hz, 2H), 3.18 (s, 1H); <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  (ppm): 55.63, 62.08, 107.35, 119.29, 123.48, 126.10, 127.01, 129.02, 130.04, 135.45, 137.90, 160.69 and 177.62; FT-IR cm<sup>-1</sup>: 3152, 2918, 1635, 1539, 1358, 1072, 838, 744, 500; ESI-MS (*m*/z): [M + H]+ = 215.13.

#### 2.2.2. Synthesis of $[Cu_2(L^1)_2(\mu_2-Cl)Cl] \cdot 2.5H_2O(1)$

A methanolic solution (10.0 mL) of copper(II) chloride dihydrate (0.5 mmol, 0.067 g) was added to 5.0 mL methanolic solution of  $HL^1$  (0.5 mmol, 0.108 g). The mixture was stirred till it turned greenish. It was then refluxed for 1 h. Color of the solution became dark green. The mixture was finally cooled to room temperature and filtered to remove any precipitate or

suspended materials. The filtrate was kept at ambient temperature. Green crystals suitable for X-ray diffraction study were produced within few days. Yield 65%, 0.218 g; C, H, N analysis: anal. calc. for  $C_{26}H_{29}Cl_2Cu_2N_2O_{6.5}$ : C, 46.50; H, 4.35; N, 4.17; found: C, 46.44; H, 4.23; N, 4.32%.

#### 2.2.2. Synthesis of $[Ni_2(L^1)_2(N_3)_2(CH_3OH)_2] \cdot CH_3OH$ (2)

A methanolic solution (10.0 mL) of nickel(II) nitrate hexahydrate (0.5mmol, 0.091 g) was added to 5.0 mL methanolic solution of  $HL^1$  (0.5 mmol, 0.108 g)while the mixture was constantly stirred. It was stirred for 30 min. Then, sodium azide (0.5mmol, 0.034 g) in 2.0 mL of methanol/water was added dropwise to the resulting green solution. After addition of azide, the solution turned dark green. The solution was stirred for another 30 min before it was refluxed for 1 h. The mixture was finally cooled to room temperature and filtered to remove any precipitate or suspended materials. The filtrate was kept at ambient temperature. Green crystals suitable for X-ray diffraction analysis were produced within few days. Yield 70%, 0.253 g; C, H, N analysis: anal. calc. for C<sub>29</sub>H<sub>36</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>7</sub>: C, 47.97; H, 5.00; N, 15.43; found: C, 47.84; H, 4.92; N, 15.36%.

#### 2.3. X-ray data collection and structure determination

Details of the data collection and refinement parameters for complexes 1 and 2 are summarized in Table 1. The diffraction experiments were carried out on a Bruker APEX-II CCD diffractometer using graphite monochromated Mo  $K\alpha$  radiation at 298 K for both the complexes 1 and 2. Data were processed using the Bruker APEX2 and SAINT packages [11]. Absorption corrections based on multi-scans using the SADABS software [11] were applied to the intensity data. The structures were solved by direct methods using SHELXT [12] and refined with fullmatrix least-squares on  $F^2$  on all unique reflections using SHELXL-2014/7[13]. All the nonhydrogen atoms of the complexes were refined anisotropically. A few hydrogen atoms, which are highly acidic, are disordered due to thermal disturbances. These have been assigned to their best possible positions by chemical speculation.

#### 2.4. Computational details

The singlet ground state  $(S_0)$  geometry of ligand,  $HL^1$  and its copper and nickel complexes i.e. complexes 1 and 2 have been fully optimized by DFT method with B3LYP

(Becke's three-parameter hybrid functional and Lee–Yang–Parr's gradient corrected correlation functional) exchange correlation functional approach using the Gaussian 09 program [14]. The B3LYP functional has been adopted along with the 6-31G basis set for H, C, N, O atoms whereas the 6-311G (d,p) basis set was utilized for Cl atoms and LANL2DZ was adopted as the basis set for Cu and Ni atoms [15]. The nature of all the stationary points was confirmed by carrying out a normal mode analysis, where all vibrational frequencies were found to be positive. On the basis of the optimized ground state (S<sub>0</sub>) geometrical structures, the UV–vis absorption transition properties of the corresponding ligand and complexes **1** and **2** in methanol were computed by a time-dependent density functional theory (TDDFT) [16] approach associated with the conductor-like polarizable continuum model (CPCM) [17] using the same B3LYP level and the previous basis sets. Frontier Molecular Orbital (FMO) analysis has been done with gauss view software [18].

#### 2.5. Catalytic studies

Oxidation of cyclohexane, toluene and cyclopentane has been performed in a similar procedure in the presence of both the metal complexes as catalysts. Typically, Metal complex (0.03 mmol) was taken in 5.0 mL of acetonitrile in a two-neck round bottom flask which was fitted with a condenser. To this, 1.5 mmol of the substrate and varying amount of HNO<sub>3</sub> were added. Catalytic reaction started as soon as 3-10 mmol of hydrogen peroxide (30% in H<sub>2</sub>O) was added to it. The mixture was continuously stirred for 48 h at desired temperature under atmospheric pressure. Aliquots were collected at regular time intervals. The substrate and products from the reaction mixture were extracted with 2.0 mL diethyl ether. The product mixture was analyzed in gas chromatograph or GCMS before and after the treatment with triphenylphosphine (PPh<sub>3</sub>). The identification was done by either the comparison with known standards or GCMS.

#### 3. Results and Discussion

#### 3.1. Synthesis and ligand characterization

Synthesis of complexes 1 and 2 has been performed following route given in Scheme 1. First, HL<sup>1</sup> has been synthesized by one step Schiff-base condensation between 2-hydroxy-1napthaldehyde and 2-aminoethanol in 1:1 molar ratio in methanol. The ligand has been characterized by elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR spectra as well as by FT-IR and mass spectral analyses (Fig. s1-s4).<sup>1</sup>H NMR spectrum (Fig. s1) of the ligand shows a peak at 14.23 ppm indicating the presence of phenolic OH group. Presence of azomethine proton has been confirmed by the singlet peak at 8.80 ppm. Bands in the range of 4.19 to 3.66 ppm exhibit the presence of methylene protons while the peak at 3.18 ppm has been assigned to the presence of alcoholic proton. Signals for aromatic protons appear in the range of 7.92 to 6.72 ppm.  $^{13}C$ spectrum of the ligand corroborates well with the formation of the Schiff-base compound (Fig. s2). IR spectrum of the ligand shows most significant bands at 3152, 2918 and 1635 cm<sup>-1</sup> indicating the presence of phenolic OH, methylene and C=N moieties, respectively (Fig. s3). ESI mass spectrum of the compound shows m/z band at 215.13 confirming the formation of the Schiff-base ligand (Fig. s4) (calculated value 215.09). Reaction between  $HL^1$  and copper(II) chloride dihydrate gives 1. Complex 2 has been synthesized by the reaction between the ligand, nickel(II) nitrate hexahydrate and sodium azide where azide acts as a bridging ligand. HL<sup>1</sup> undergoes deprotonation in the reaction medium without any external deprotonating base.

#### 3.2. Crystal structures of 1 and 2

Complex 1 crystallizes from methanol in orthorhombic system with P212121 space group. A perspective view of the complex is given in Fig. 1. Selected bond lengths and bond angles are given in Table 2. Cu1 is tetracoordinated whereas Cu2 is in pentacoordination geometry. The two chloride ions from the copper(II) salt used for the complex formation, bind the Cu atoms differently as confirmed by the crystal structure. One chlorido is bridging while the other is terminal. Cu1 is in a distorted square planar environment bonded to O1, O2, N1 and Cl1. Cl1 is the bridging chlorine atom which links Cu1 and Cu2. There is deviation of donor-metal-donor bond angle from 90°. The O2-Cu1-N1 bond angle is 83°, O1-Cu1-N1 angle is 92°, Cl1-Cu1-O2 angle is 93° and Cl1-Cu1-O1 angle is 94°.The Cu1-Cl1 bond is slightly out of plane. This confirms the approximate square planar geometry around the Cu1 center. Cu2, on the other hand,

is bonded to O3, O4, N2, Cl1, Cl2. It is in distorted square pyramidal geometry as indicated by the value of the trigonal index,  $\tau$ . The trigonal index is calculated as the difference between the two largest donor-metal-donor angles divided by 60[19]. Its value is 1 for the ideal trigonal bipyramid and 0 for the square pyramid. Here the  $\tau$  value is calculated to be 0.25 which indicates its significantly distorted square pyramidal environment. O3, O4, N2 and Cl2 atoms form the basal plane of the square pyramid and C11 occupies the apical position. However, Cu center is out of the mean plane by 0.150 Å towards Cl1. There are 2.5 water molecules in the crystal structure. The solvent water molecules are disordered due to molecular vibrations. The H atoms in the alcoholic moiety and the water molecule have been assigned their best possible positions in spite of being disordered. The crystal has been refined as a merohedral twin. In packing structure, there are  $\pi$ - $\pi$  and CH- $\pi$  interactions (Fig. s5). The metal-metal distance is 3.485 Å. Metal-chlorine bond distances are long compared to other metal-donor distances as expected. Although Cu-Cl bond distances are long here (Table 2), similar long copper-chlorine distances are also reported [20].

Complex **2** crystallizes from methanol into a monoclinic system with P 21/n space group. A perspective view of the complex is given in Fig. 2. Selected bond lengths and bond angles are given in Table 2. The molecule consists of two nickel atoms, two deprotonated ligands, 1-((2-hydroxyethylimino)methyl)naphthalen-2-ol ( $HL^1$ ), two azido ligands and two coordinated methanol molecules. One methanol is present as solvent of crystallization. Each Ni atom is in similar coordination geometry i.e. in octahedral geometry. Ni1 is bonded with O4, N8 and O6 from the ligand, N1 and N4 from two different azido moieties and O5 from a methanol molecule. On the other hand, Ni2 is coordinated to O2, N7 and O3 atoms from the ligand, Ni and N4 from two different azido species and O1 from a methanol molecule. Two intramolecular hydrogen bonds are present in this molecule involving non-coordinated methanol (Fig. s6). Coordinated O3 atom is present in H-bonding with H-O moiety of methanol and second hydrogen bond is found involving O atom of methanol and H-O6 moiety of alcoholic group. All of the donor-Ni bond distances are in agreement with the reported values [21].

#### 3.3. IR spectral studies

FT-IR spectra of all of the complexes have been obtained with powder samples by ATR technique. Peaks at 1622 and 1617 cm<sup>-1</sup> in the IR spectra of Cu and Ni complex respectively,

confirm the presence of azomethine bond in both the complexes (Fig. s7). A sharp peak at 2054  $cm^{-1}$  indicates the presence of azido moiety in complex **2**. Both the complexes show broad band in the range of 3500-3400 cm<sup>-1</sup>. Broad peak in complex **1** is due to the presence of water molecule which is present as solvent of crystallization in complex **1** and that for complex **2** is probably due to the presence of methanol molecules in the Ni complex.

#### 3.4. UV-vis spectral studies

The electronic spectra of complexes **1** and **2** have been recorded in methanol at room temperature (Fig. s8,s9). For complex **1**, high intensity bands appear at 383 and 316 nm (molar extinction coefficient of 12100 and 13500 Lmol<sup>-1</sup>cm<sup>-1</sup>, respectively) which may occur due to ligand to metal charge transfer (PhO<sup>-</sup>  $\rightarrow$  Cu(II) and N(imino)  $\rightarrow$  Cu(II)) and intra ligand charge transfer respectively. The Cu complex shows broad bands at 646, 673 and 720 nm with low intensity. These spectral characteristics are in consistence with copper(II) complexes of distorted square pyramidal (SP) geometry. The observed bands originate from d<sub>xz</sub>,d<sub>yz</sub>  $\rightarrow$  d<sub>x</sub>2<sub>-y</sub>2 transitions [22]. They are accompanied by a low energy shoulder at 844 nm due to d<sub>xy</sub>, d<sub>x</sub>2<sub>-y</sub>2  $\rightarrow$  d<sub>z</sub>2 transitions. As the structure moves more towards TBP structure the low energy band along with high energy spin forbidden band becomes more pronounced. The characteristic bands observed here are results for distorted square pyramidal geometry.

UV spectrum of complex 2 shows high intensity bands at 312 and 395 nm with molar extinction coefficient of 9335 and 8261 Lmol<sup>-1</sup>cm<sup>-1</sup>, respectively. These bands are probably due to the intraligand charge transfer, and LMCT (PhO<sup>-</sup>  $\rightarrow$  Ni(II) and N(imino)  $\rightarrow$  Ni(II)), respectively.

Complex 2 also shows d-d transitions. The broad bands are obtained at 750 and 860 nm which probably indicate  $d_{xz}, d_{yz} \rightarrow d_z 2$  and  $d_{xy}, d_x 2_{-y} 2 \rightarrow d_z 2$  transitions [22].

#### 3.5. Geometry optimization and computational studies

Molecular structures of  $HL^1$  and its Cu, Ni complex have been optimized at their electronic ground state (S<sub>0</sub>) by means of DFT at B3LYP/(6-31G) level. For better understanding of the electronic transitions involved in absorption process, TD-DFT calculations have been carried out by the B3LYP/CPCM method in methanol by utilizing the ground state optimized geometries. We have computed the lowest 40 singlet–singlet transition and results of the TD calculations are

qualitatively very similar with the experimental results. The computed absorption energies along with their oscillator strengths, the main configurations, are summarized in Table 3. Fig. 3 displays the energy levels of different Frontier Molecular Orbital's of the ligand and complexes **1** and **2** associated with their HOMO-LUMO energy gap. Due to the presence of electronic correlation in the TD-DFT (B3LYP) method, it can yield more accurate electronic excitation energies. The UV spectra computed by TD-DFT calculations in methanol show the important peaks in the range 200–500 nm.

HL<sup>1</sup> shows lowest lying distinguishable singlet  $\rightarrow$  singlet absorption band at 418.14 nm (experimentally 415 nm, experimental absorption band in methanol are shown in Fig. s10) which is due to the contribution of HOMO-1 $\rightarrow$ LUMO+1, HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1 transitions, also a moderately intense peak at 400.12 nm (experimentally 400 nm) that corresponds to HOMO-1 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO + 1 transitions along with a shoulder at 311.24 nm (experimentally 306 nm) corresponding to HOMO-3 $\rightarrow$ LUMO+1, HOMO $\rightarrow$ LUMO+1, HOMO-1 $\rightarrow$ LUMO+2 and HOMO-1 $\rightarrow$ LUMO transitions.

Complex 1 shows an intense absorption peak at 384.21 nm (experimentally 383 nm) corresponding to HOMO-1 $\rightarrow$ LUMO+1, HOMO-3 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO transitions along with moderately intense absorption band at 317.88 nm (experimentally 316 nm) corresponding to HOMO-2 $\rightarrow$ LUMO+4, HOMO $\rightarrow$ LUMO+6 transitions (FIFURE4A). Besides the nickel dimer shows absorption peaks at 396.12 nm (experimentally 395 nm) due to the contribution of HOMO-3 $\rightarrow$ LUMO, HOMO-2 $\rightarrow$ LUMO, HOMO-1 $\rightarrow$ LUMO+1 transitions and peak at 314.40 nm (experimentally 312 nm) corresponding to HOMO-1 $\rightarrow$ LUMO+4, and HOMO $\rightarrow$ LUMO+1 transitions (Fig. 4B).

#### 3.6. Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been performed on powdered samples of complexes **1** and **2** from 35 to 800 °C (for complex **1**) and 35 to 750 °C (for complex **2**) to examine thermal stability of the complexes and fate of solvent of crystallization molecules.

In the TGA DTA plot of complex **1**, an initial loss of 2.6% is seen at temperature 50 °C which corresponds to an endothermic DTA peak. It depicts the loss of surface water probably (Fig. s11). The next visible loss at 190 °C is a weight loss of 6% which probably indicates the

loss of all the water molecules (calculated loss 6.7%) also depicted by an endothermic peak. A loss of almost 32% occurs at 280 °C which probably shows loss of one ligand moiety (calculated loss 32.2%). The next decomposition at 370 °C probably indicates loss of two Cl (observed ~10% vs calculated 10.6%). The final loss of 33% could be attributed to the loss of another ligand moiety after which a stable residue of CuO is obtained. All of the last three losses accompany a corresponding exothermic peak in the DTA curve.

In the TGA DTA plot of complex **2**, the initial loss of 13% at 86 °C can be attributed to the loss of 3 methanol molecules (bound and unbound (calculated loss 13.2%)) as confirmed by endothermic DT peak (Fig. s12). There are next two consecutive losses, each of 4%, which can be assigned to the loss of N<sub>2</sub> twice from the azide bridges. This loss occurs between 132 and 180 °C of temperature. The next loss of another 4% is the final decomposition of the nitrogens of the azide bridge and its evolution as another molecule of N<sub>2</sub> at and the process completes at 270 °C. The next loss of 40% probably confirms the loss of one part of the dinuclear complex which continues upto 400 °C. The residue as stable NiO is left behind. All show exothermic DT peaks other than the loss of solvent molecules at the starting temperatures.

#### 3.7. Cyclic voltametric studies

Electrochemical studies of complexes 1 and 2, and the ligand have been carried out in acetonitrile using TBAP as supporting electrolyte. A typical cyclic voltammogram (CV) has been obtained by using a glassy carbon electrode and an Ag/AgCl saturated KCl reference electrode. CV plots of the complexes are shown in Fig. 5.

The CV plot of the dinuclear complex, **1** has been obtained by scanning potential -2.0 to +1.5, wherein the electrochemical behavior of the complex is elucidated properly. The scan rate has been maintained at 50 mV s<sup>-1</sup>. The forward scan gives an anodic peak at 0.62 V and I<sub>pa</sub> 8 ×  $10^{-6}$  A and the cathodic counterpart in the reverse scan at E<sub>pc</sub> 0.48 V and I<sub>pc</sub> of 2.2 ×  $10^{-5}$  A. These peaks have been attributed to the redox couple Cu(II)-Cu(III) as the peaks clearly show a quasireversible one electron transfer process [23a-23d]. The similarity with literature values confirms the peaks. Of the copper centers, Cu2 is more competent to undergo oxidation to +3 state as it satisfies the 18-electron rule after the oxidation process. Comparison of the results of voltammetric peak current with those of the ferrocene–ferrocenium couple under the same

experimental conditions establishes that these responses involve one electron in each step. The electrochemical responses of the complex may be assigned as:

$$Cu^{II}; Cu^{II} - e \rightleftharpoons Cu^{III}; Cu^{II};$$

 $Cu^{III}; Cu^{II} - e \rightleftharpoons Cu^{III}; Cu^{III}$ 

The anodic peak at 1.2 V indicates an irreversible ligand oxidation which is characteristic of the oxidation of the Schiff base groups [24a-24c].

In the scan of range 0.0 to -2.0 V, the cathodic peak at  $E_{pc}$  -0.78 V with  $I_{pc} 6 \times 10^{-6}$  A is seen as a broad peak which indicates two simultaneous reductions in this region. An irreversible Cu(II) to Cu(I) reduction occurs in this potential region. This is well supported by literature data [23b,25a-25b]. The ligand also undergoes an irreversible reduction at this potential as confirmed by the cyclic voltammogram of the isolated ligand as well. The peak in the isolated ligand is at -1.05 V, which has shifted to the new potential (shifted gradually to slightly higher potential values) due to coordination of the ligand to the Cu(II) center [25b-25c], may be assigned to the reduction of imine group [(-C=N-)/(-C=N-)<sup>-</sup>] [25a]. The cathodic peak at -1.5 V indicates a further reduction of Cu(I) to Cu(0). This is a one electron process as ascertained from literature values as well [23b]. The peak in the reverse scan is the anodic dissolution wave of deposited copper, for Cu(0)→Cu(I) which is indicated by along peak at -0.19 V [23b].

For the nickel complex, the quasireversible redox couple at  $E_{pc} 0.22$  V and  $I_{pc} 7 \times 10^{-7}$  A and  $E_{pa} 0.38$  V and  $I_{pa} 2 \times 10^{-6}$  A can be assigned to the Ni(II)/Ni(I) couple [25d-25f]. The scan rate has been kept at 100 mV s<sup>-1</sup>. The cathodic peak at -0.64 V indicates a ligand reduction which has also been observed in the free ligand at -1.05 V but shifted to higher potentials due to the binding to Ni(II) ion. The anodic peak at 1.05 V corresponds to a ligand oxidation as almost similarly observed in the Cu(II) complex.

The CV plot of the free ligand has been given in the supplementary information (Fig s16). It shows two cathodic peaks at -0.56 V and -1.05 V corresponding to the reductions on the ligand and an anodic peak at -0.57 V which corresponds to an oxidation. Scan rate has been maintained at 100 mV s<sup>-1</sup>.

#### 3.8. Catalysis studies

We have checked catalytic activity of both the complexes for oxidation of cyclohexane, toluene and cyclopentane. The oxidation of the substrates has been performed by  $H_2O_2$  as the

oxidant in a slightly acidic medium under ambient conditions. To set optimum conditions, we have varied amount of hydrogen peroxide (30% in H<sub>2</sub>O)as well as the acid (HNO<sub>3</sub>)keeping fixed amount of the metal complex (0.03 mmol) in 5.0 mL of acetonitrile. The ratio  $n(\text{HNO}_3)/n(\text{catalyst})$  has been varied in the range of 5 to 25. The  $n(\text{H}_2\text{O}_2)/n(\text{catalyst})$  has been varied from 100–500 with the best yield obtained at 500.

Results of oxidation are summarized in Table 4. The primary products of the oxidation of cyclohexane are cyclohexanol and cyclohexanone; toluene is oxidized mainly to benzyl alcohol and benzaldehyde, whereas oxidation of cyclopentane gives cyclopentanol and cyclopentanone as the major products. Cyclohexane oxidation gives a small amount of adipic acid (~9%) in addition to the major products when the ratio  $n(H_2O_2)/n(catalyst)$  is 250-300. At lesser ratio  $n(H_2O_2)/n(catalyst)$ , say 100, no adipic acid has been detected and at still higher ratio of 500 (which is the most optimized condition) the amount of adipic acid formed remains the same i.e. 9%. Benzoic acid has been obtained as a minor product from oxidation of toluene. Benzoic acid is generally obtained by aerial oxidation of benzaldehyde, hence this benzoic acid could have come from benzaldehyde which has been formed during the oxidation of toluene. Oxidation of cyclopentanol and cyclopentanol and cyclopentanol.

The yield has been optimized by varying the relative proportions of nitric acid and hydrogen peroxide with respect to the catalysts, temperature and varying the reaction time. It has been obvious from previous studies [6,7,26] that the presence of nitric acid has positive role in these catalytic reactions. Nitric acid has, mainly, two important roles: (i) it could increase the vacant coordination site at the metal center by the protonation of the ligand of these complexes and hence enhances oxidative properties of the catalyst; and (ii) decomposition of peroxide is retarded in the presence of nitric acid, the stability of peroxo intermediate is increased. However, it is difficult to determine the exact structure of the complex in solution. Copper center in dinuclear complex is in both tetra and penta-coordination. Thus, these metal centers would need nitric acid to increase the unsaturation at the metal center. The highest conversion has been ascertained at  $n(\text{HNO}_3)/n(\text{catalyst})$  ratio 20, while the yield decreases on further increasing the ratio. Hence, this ratio is maintained throughout for all the reaction sets.

The reaction mixture has been stirred for 48 h at room temperature (35°C) under atmospheric pressure. Different temperatures conditions have been applied to optimize the

highest yield. Reaction has been carried out at 40, 50, 60 and70°C. The best yield was obtained at 40°C. Upto 50°C, the reaction proceeds showing slight decrease in yield at 50°C which gradually declines upto 60°C. However, after 60°C, there is a drastic decrease in the yield of products as it has been confirmed by gas chromatographic analysis.

The catalysis has also been done at high pressure conditions which fail to yield the products. This indicates that normal pressure conditions are most desired condition for the reaction. The reaction has also been performed with TBHP as the oxidant under the similar experimental conditions but it shows lower yield, 5% in total. This can, probably, be due to its bulky structure which destabilizes the intermediate. Then, we have performed the same catalytic reaction under inert (argon) atmosphere to examine effect of the presence of oxygen. However, it has been found that this reaction shows almost equal yield when same catalytic reaction is carried out under normal experimental conditions. There is only a small decrease in amount of products formed under inert atmosphere which indicates only little participation of atmospheric oxygen in the oxidation process.

Instead of nitric acid, organic acid such as acetic acid has been employed in the reaction. The yield of product remains the same showing that organic acid is as effective in the role played by nitric acid. In order to find out the probable mechanisms, we have carried out the catalytic reaction of cyclohexane with the complex maintaining  $n(\text{HNO}_3)/n(\text{catalyst})$  ratio of 20 and  $n(\text{H}_2\text{O}_2)/n(\text{catalyst})$  ratio of 500 in the presence of TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl). The yield of the reaction is greatly suppressed in its presence. TEMPO is well known as a radical trap. This indirectly indicates that oxidation reactions occur mainly by mechanisms involving the formation of radicals.

Copper salts like  $Cu(NO_3)_2$ , under the same reaction conditions exhibit at much lower activity towards oxidation of all substrates under same experimental condition. It shows only about 6% conversion. So it is evident that the presence of N and O donor ligands is quite relevant.

To check the possibility of oxidation of all the substrates under acidic conditions, we have performed blank reactions for each of the substrates without any metal center. The amounts of nitric acid and hydrogen peroxide have been chosen at which concentration of these reagents maximum conversions of the substrates were achieved with the catalyst. Blank reactions have been carried out with substrate (1.5 mmol), hydrogen peroxide (15 mmol) and nitric acid (0.6

mmol) at 40 °C for 48 h. Conversion rate is very low (~3.7% for cyclohexane and toluene, and 4.5% for cyclopentane). This indicates that the conversion of the substrate to product is difficult reaction and accelerated by the presence of our copper complex.

The reaction is believed to proceed through the formation of alkyl hydroperoxide (ROOH) (e.g. cyclohexyl peroxideor benzyl peroxide) along with the alcohol (e.g. cyclohexanol, benzyl alcohol and cyclopentanol) and carbonyl compounds(such as cyclohexanone, benzaldehyde and cyclopentanone). The formation and quantification of these compounds have been carried out by following a method introduced by G. B. Shul'pin [27]. According to this procedure, the reaction mixture has been analyzed by GC before and after treating with excess PPh<sub>3</sub>. Treatment of the reaction mixture (alkyl hydroperoxide) by PPh<sub>3</sub> leads to the formation alcohol with subsequent formation of phosphane oxide (OPPh<sub>3</sub>). We have observed that after the reduction with PPh<sub>3</sub>, the alcohol peak in the GC analyses rises markedly for each of the substrate while the intensity of the>C=O compound's peak reduces. Alkyl hydroperoxides are, in many cases, the main primary products of alkane oxidation with hydrogen peroxide. The peroxides formed in the oxidation with H<sub>2</sub>O<sub>2</sub> can, sometimes, decompose in the injector of GC during the analysis with the formation of the corresponding alcohol and ketone. If we compare the yields of reaction before and after the treatment with triphenylphosphine, we can see that yield of alcohol increases tremendously after the treatment with PPh3 (representative case, Table 4). Before the treatment with PPh3, product of oxidation of cyclohexnae is almost solely cyclohexanone. This indicates that the saturated hydrocarbon oxidation may follow the Shul'pin pathway.

The hydroxyl radical HO<sup>•</sup> could be formed as a result of metal-assisted decomposition of hydrogen peroxide. The hydroxyl radical abstracts H from the substrate (RH) to form R·[26a]. The formation of ROOH may be occurred by the reaction between a metal-peroxo intermediate, e.g. bearing a Cu(II)–OOH type moiety and the organoradical R<sup>•</sup>, to form ROOH [28]. The formation of Cu–peroxo species has been determined by UV-vis spectra. The metal-assisted homolytic cleavage of alkyl hydroperoxide generates alkoxyl (RO<sup>•</sup>, upon O–O bond rupture) and alkylperoxyl (ROO<sup>•</sup>, upon O–H bond breakage) radicals which can form an alcohol (ROH) upon H-abstraction from the alkane (RH) by RO<sup>•</sup> or both ROH and the>C=O upon decomposition of ROO<sup>•</sup> [29].

ESI-mass spectrum of complex 1 in methanol shows the presence of both mononuclear and dinuclear species (Fig. s13). Peak at 641.09 indicates the presence of dinuclear species and

may be attributed to the presence of  $[Cu_2(L^1)_2(\mu_2-Cl)(H_2O)(CH_3OH)]$ . It shows additional m/z peak at 277.05 which is assigned to  $[Cu(L^1)]^+$ . This indicates that dinuclear species also exists in solution. UV-vis spectra for the complexes have been recorded in methanol at room temperature as discussed earlier. To further observe the effect of hydrogen peroxide, we have recorded the UV-vis spectra of the complexes in the presence of hydrogen peroxide (Fig. s14 and s15). It has been observed that an intense peak at 400 nm, with a shoulder in the range of 410–420 nm, appears for complex 1. This may be attributed to the existence of Cu–hydroperoxo or Cu–peroxo species [30] However, there is no observable change in the UV-vis spectrum of complex 2 when it is recorded in the presence of hydrogen peroxide (Fig. s15).

Complex **2** has also been checked for its catalytic property in oxidizing the substrates. But the Ni catalyst shows very poor conversion i.e. about 7% total yield for cyclohexane, 5% for toluene and 4% for cyclopentane. This could be attributed to the coordinatively saturated nature of the each Ni center in complex **2** with coordination number 6. The UV vis data of the complex in the presence of H<sub>2</sub>O<sub>2</sub>couldnot confirm the presence of Ni-hydroperoxo or peroxo species like Cu– hydroperoxo or Cu–peroxo in case of complex **1**. Also electrochemical studies of the complex indicate no formation of higher oxidation state species in the said voltage range whereas Cu(III) species has been detected in the said voltage range indicating more vulnerability character of complex **1**. Thus replacement of Cu by Ni in the complex actually stops the catalytic ability of the material.

Conversion of saturated hydrocarbons is one of the most difficult reactions in organic chemistry. Results from past decade [6,7] and recent past [31] indicate that our catalyst is very good in this respect.Recent report on catalysis with copper(II) complexes of vinylphosphonic acid and 1,10-phenanthroline shows that only ~32% products are formed where main product is corresponding carboxylic acid [31a]. Formation of cyclohexanol and cyclohexanone is extremely low. Copper(II) complexes of functionalized 2,2':6',2''-terpyridines and 2,6-di(thiazol-2-yl)pyridine could be used as catalyst for cyclohexane oxidation in the presence of hydrogen peroxide and highest conversion achieved is ~23% [31b]. Three copper(II) complexes of pyromellitic acid and different aminoalcohols can catalyze cyclohexane oxidation and highest conversion is ~33% [31c]. Conversion for cyclopentane is also difficult as revealed from the small yield with Cu(II) complexes [31d].

#### 4. Conclusions

We have been able to synthesize and characterize two dinuclear transition metal complexes with a Schiff-base ligand. One of them is copper containing complex, complex 1 and another with nickel, complex 2. Complex 1 has been found to be active catalyst for the oxidation of cyclohexane, toluene and cyclopentane in the presence of hydrogen peroxide as the terminal oxidant. Corresponding alcohol and aldehyde have been produced as the major products. Conversion of the substrates is quite high in comparison to the results published by other groups in recent time. However, complex 2 is not able to convert these substrates under similar conditions. UV-vis spectral analysis shows that complex 1 could generate Cu-peroxo or Cuhydroperoxo species in the presence of hydrogen peroxide whereas formation of such type of species with nickel complex is not evident from the UV-vis spectral studies.CV of complex 1 shows that two Cu(II) centers could be converted to Cu(III) center with transfer of one electron in each of two steps. Formation of higher oxidation state species of Ni is not indicated from its electrochemical studies. These analyses support that formation of Cu-peroxo as active species for the catalytic conversions. Possible mechanism indicates the involvement of Cu(III) species. Probably other metals also need higher oxidation states for this catalysis. As generation of Cu(III) center is feasible, not the higher oxidation state for nickel center evident from electrochemical studies under normal condition, the dinuclear copper complex can catalyze the oxidation of saturated hydrocarbons mimicking the activity of particulate methane monooxygenase while dinuclear nickel complex cannot.

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#### Appendix A. Supplementary data

CCDC 1848336-1848337 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at xxxxxx.

#### References

- (a) Sazinsky M.H., Lippard S.J. (2015) Methane Monooxygenase: Functionalizing Methane at Iron and Copper. In: Kroneck P., Sosa Torres M. (eds) Sustaining Life on Planet Earth: Metalloenzymes Mastering Dioxygen and Other Chewy Gases. Metal Ions in Life Sciences, vol 15. Springer, Cham; (b) A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879; (c) A.A. Fokin, P.R. Schreiner, Chem. Rev. 102 (2002) 1551; (d) A. Sen, Acc. Chem. Res. 31 (1998) 550; (e) R.A. Periana, O. Mironov, D. Taube, G. Bhalla , C.J. Jones, Science 301 (2003) 814.
- (a) L. Que Jr., W. B. Tolman, Nature 455 (2008) 333; (b) J. C. Nesheim, J. D. Lipscomb, Biochemistry 35 (1996) 10240; (c) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329.
- 3 (a) A. S. Hakemian, A. C. Rosenzweig, Annu. Rev. Biochem. 76 (2007) 223; (b) M. O. Ross, A. C. Rosenzweig, J. Biol. Inorg. Chem. 22 (2017) 307; (c) S. Sirajuddin, A. C. Rosenzweig, Biochemistry 54 (2015) 2283; (d) C. E. Tinberg, S. J. Lippard, Acc. Chem. Res. 44 (2011) 280.
- (a) A. M. Kirillov, M.V. Kirillova, A.J.L. Pombeiro, Coord. Chem. Rev. 256 (2012) 2741;
  (b) M. M. Vinogradov, Y. N. Kozlov, A. N. Bilyachenko, D. S. Nesterov, L. S. Shul'pina, Y. V. Zubavichus, A. J. L. Pombeiro, M. M. Levitsky, A. I. Yalymov, G. B. Shul'pin, New J. Chem. 39 (2015) 187; (c) C.-C. Liu, D. Janmanchi, D.-R. Wen, J.-N. Oung, C.-Y. Mou, S. S.-F. Yu, S. I. Chan, ACS Sustainable Chem. Eng. 6 (2018) 5431.
- 5 A. E. Shilov, G. B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, Dordrecht, The Netherlands (2000).
- (a) A. M. Kirillov, M. N. Kopylovich, M. V. Kirillova, M. Haukka, M. F. C. G. da Silva,
  A. J. L. Pombeiro, Angew. Chem. 117 (2005) 4419; (b) Y. Y. Karabach, A. M. Kirillov,
  M. Haukka, M. N. Kopylovich , A.J.L. Pombeiro, J. Inorg. Biochem.102 (2008) 1190; (c)
  M. V. Kirillova, Y. N. Kozlov, L. S. Shul'pina, O. Y. Lyakin, A. M. Kirillov, E. P. Talsi,
  A. J.L. Pombeiro, G. B. Shul'pin, J. Catal. 268 (2009) 26; (d) K. R. Gruenwald, A. M.
  Kirillov, M. Haukka, J. Sanchizand A.J. L. Pombeiro, Dalton Trans. (2009) 2109; (e) M.
  Sutradhar, E. C.B.A. Alegria, T. R. Barman, F. Scorcelletti, M. F. C. G. da Silva, A. J.L.
  Pombeiro, Mol. Catal. 439 (2017) 224; (f) E. A. Buvaylo, V. N. Kokozay, O. Yu.

Vassilyeva, B. W. Skelton, O. V. Nesterova, A. J.L. Pombeiro, Inorg. Chem. Commun.78 (2017) 85.

- 7 (a) A. A. Alshaheri, M. I. M. Tahir, M. B. A. Rahman, T. B.S.A. Ravoof, T. A. Saleh, Chem. Eng. J. 327 (2017) 423; (b) I. Garcia-Bosch, M. A. Siegler, Angew. Chem. 128 (2016) 13065; (c) A. N. Bilyachenko, A. N. Kulakova, M. M. Levitsky, A. A. Petrov, A. A. Korlyukov, L. S. Shul'pina, V. N. Khrustalev, P. V. Dorovatovskii, A. V. Vologzhanina, U. S. Tsareva, I. E. Golub, E. S. Gulyaeva, E. S. Shubina, G. B. Shul'pin, Inorg. Chem. 56 (2017)4093; (d) N. Bilyachenko, V. N. Khrustalev, Y. A. V. Zubavichus, L.S. Shul'pina, A.N. Kulakova, X. Bantreil, F. Lamaty, M. M. Levitsky, E. I. Gutsul, E. S. Shubina, G. B. Shul'pin, Inorg. Chem. 57 (2018) 528; (e) A. N. Bilyachenko, M. M. Levitsky, A. A. Korlyukov, V. N. Khrustalev, Y. V. Zubavichus, L. S. Shubina, A. V. Vologzhanina, G. B. Shul'pin, Eur. J. Inorg. S.Shul'pina, E. Chem. (2018) 2505; (f) P. Roy, K. Dhara, M. Manassero, P. Banerjee, Eur. J. Inorg. Chem. (2008) 4404; (g) S. Thakurta, P. Roy, R. J. Butcher, M. S. E. Fallah, J. Tercero, E. Garribba, S. Mitra, Eur. J. Inorg. Chem. (2009) 4385; (h) S. Thakurta, P. Roy, G. Rosair, C. J. Gómez-García, E. Garribba, S. Mitra, Polyhedron 28 (2009) 695; (i) K. C. Gupta, A. K. Sutar, Coord. Chem. Rev. 252 (2008) 1420; (j) K. C. Gupta, A. K. Sutar, C.-C. Lin, Coord. Chem. Rev. 253 (2009) 1926; (k) A. Bhattacharjee, S. Halder, K. Ghosh, C. Rizzoli, P. Roy, New J. Chem. 41 (2017) 5696; (1) S. Halder, S. Dey, C. Rizzoli, P. Roy, Polyhedron 60 (2014) 85; (m) M. Nandi, P. Roy, H. Uyama, A. Bhaumik, Dalton Trans. 40 (2011) 12510; (n) P. Roy, M. Nandi, M. Manassero, M. Riccó, M. Mazzani, A. Bhaumik, P. Banerjee, Dalton Trans. (2009) 9543.
- 8 (a) A. Panja, Polyhedron 79 (2014) 258; (b) A. Panja, M. Shyamal, A. Saha, T. KantiMandal, Dalton Trans. 43 (2014) 5443; (c) A. Panja, Dalton Trans. 43 (2014) 7760; (d) K. Ghosh, K. Harms, S. Chattopadhyay, Polyhedron 123 (2017) 162; (e) S. K. Dey, A. Mukherjee, Coord. Chem. Rev. 310 (2016) 80.
- (a) C. Kordulis, K. Bourikas, M. Gousi, E. Kordouli, A. Lycourghiotis, Appl. Catal. B 181 (2016) 156; (b) S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, Acc. Chem. Res. 48 (2015) 1995; (c) X. Lu, B. Xiao, Z. Zhang, T. Gong, W. Su, J. Yi, Y. Fu, L. Liu, Nature Commun. 7 (2016) 11129; (d) J. Chakraborty, M. Nandi, H. Mayer-Figge, W. S Sheldrick, L. Sorace, A. Bhaumik, P. Banerjee, Eur. J. Inorg. Chem. (2007) 5005;

- (a) H.-Y. Lin, P.-Y. Cheng, C.-F. Wan, A.-T. Wu, Analyst 137 (2012) 4415; (b) Yu. M. Chumakov, V. L Tsapkov, P. A. Petrenko, L. G. Popovski, Yu. A. Simonov, G. Bocelli, B. Ya. Antosyak, A. O. Paraschivescu, A. P. Gulea, Russian J. Coord. Chem. 35 (2009) 504; (c) K. K. Rajak, S. Mondal, S. P. Rath, Polyhedron 19 (2000)931.
- 11 Bruker, APEX2, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, (2008).
- 12 G. M. Sheldrick, Acta Cryst. A71 (2015) 3.
- 13 G. M. Sheldrick, Acta Cryst. C71 (2015) 3.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski , D. J. Fox, GAUSSIAN 09, Revision D.01, Gaussian Inc., Wallingford, CT, (2009).
- 15 A. D. Becke, J. Chem. Phys. 98 (1993) 5648.
- 16 P. J. Hay, W. R. Wadt, J. Chem. Phys. 82 (1985) 299.
- 17 S. Miertus, E. Scrocco, J. Tomasi, Chem. Phys. 55 (1981) 117.
- 18 V. Barone, M. Cossi, J. Tomasi, J. Comput. Chem. 19 (1998) 404.
- 19 A. W. Addison, T. N. Rao, J. Reedijk, J. Vanrijn, G. C. Verschoor, J. Chem. Soc. Dalton Trans. (1984) 1349.
- (a) R. L. Forman, A. J. Gale, C. P. Landee, M. M. Turnbull, J. L. Wikaira, Polyhedron 89 (2015) 76; (b) A. Jaffe, Y. Lin, W. L. Mao and H. I. Karunadasa, J. Am. Chem. Soc. 137 (2015) 1673; (c) M. Julve, A. Gleizes, L. M. Chamoreau, E. Ruiz, M. Verdaguer, Eur. J. Inorg. Chem. (2018) 509; (d) F. F. Awwadi, M. M. Turnbull, M. I. Alwahsh, S. F. Haddad, New J. Chem. 42 (2018) 10642.

- (a) S. Halder, J. Mondal, J. Ortega-Castro, A. Frontera, P. Roy, Dalton Trans. 46 (2017) 1943; (b) P. Ghorai, A. Chakraborty, A. Panja, T. K. Mondal, A. Saha, RSC Adv. 6 (2016) 36020; (c) S. Roy, A. Bhattacharyya, S. Purkait, A. Bauzá, A. Frontera, S. Chattopadhyay, Dalton Trans. 45 (2016) 15048.
- (a) Comprehensive Coordination Chemistry, ed. B. J. Hathaway, G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon Press, Oxford, England 5 (1987); (b) F. A. Mautner, C. N. Landry, A. A. Gallo, S. S. Massoud, J. Mol. Struct. 837 (2007) 72; (c) F. A. Mautner, J. H. Albering, R. Vicente, F. R. Louka, A. Gallo, S. S. Massoud, Inorg. Chim. Acta 365 (2011) 290; (d) S. S. Massoud, L. L. Quan, K. Gatterer, J. H. Albering, R. C. Fischer, F. A. Mautner, F. A. Mautner, Polyhedron 31 (2012) 601.
- (a) Z. Wu, Z. Zhang, L. Liu, Electrochim. Acta 42(1997) 2719; (b) E. Chiyindiko, J. Conradie, J. Electroanal. Chem. 837(2019) 76; (c) E. Franco, E. López-Torres, M. A. Mendiola, M. T. Sevilla, Polyhedron 19(2000) 441; (d) J. P. Naskar, B. Guhathakurta, L. Lu, M. Zhu, Polyhedron 43 (2012) 89;
- (a) J. Losada, I. del Peso, L. Beyer, Inorg. Chim. Acta 321 (2001) 107; (b) F. Bedioui, E. Labbe, S. Gutierrez-Granados, J. Devynck, J. Electroanal. Chem. 301 (1991) 267; (c) J. Losada, I. del Peso, L. Beyer, J. Electroanal. Chem. 447 (1998) 147.
- (a) G. Saha, K. K. Sarkar, T. K. Mondal, C. Sinha, Inorg. Chim. Acta 387(2012) 240; (b)
  M. Sarigul, S. E. Kariper, P. Deveci, H. Atabey, D. Karakas, M. Kurtoglu, J. Mol. Struc 1149 (2017) 520; (c) K. Ouari, S. Bendia, J. Weiss, C. Bailly, Spectrochim. Acta A 135 (2015) 624; (d) G. B. Bagihalli, P. G. Avaji, S. A. Patil, P. S. Badami, Eur. J. Med Chem 43 (2008) 2639; (e) A.H. Kianfar, L. Keramat, M. Dostani, M. Shamsipur, M. Roushani, F. Nikpour, Spectrochim. Acta Part A 77 (2010) 424; (f) A. Anthonysamy, S. Balasubramanian, Inorg. Chem. Comm. 8 (2005) 908–911
- 26 (a) T. F. S. Silva, G. S. Mishra, M. F. G. da Silva, R.Wanke, L. M. D. R. S. Martins , A. J.
  L. Pombeiro, Dalton Trans. (2009) 9207; (b) M. Nandi, P. Roy, Indian J. Chem. 52A (2013) 1263.
- (a) G. B. Shul'pin, J. Mol. Catal. A189 (2002) 39; (b) G. B. Shul'pin, Y. N. Kozlov, L. S. Shul'pina, A. R. Kudinov, D. Mandell, Inorg. Chem. 48 (2009) 10480; (c) G. B. Shul'pina, Y. N. Kozlov, L. S. Shul'pina, P. V. Petrovskiy, Appl. Organometal. Chem. 24 (2010), 464.

- (a) T. F. S. Silva, E. C. B. Alegria, L. R. Martins, A. J. L. Pombeiro, Adv. Synth. Catal. 350 (2008) 706; (b) M. Costas, M. P. Mehn, M. P. Jensen, L. Que Jr., Chem. Rev. 104 (2004) 939; (c) M. Costas, K. Chen, L. Que Jr., Coord. Chem. Rev. 200–202 (2000) 517; (d) T. Hogan, A. Sen, J. Am. Chem. Soc. 119 (1997) 2642.
- (a) G.B. Shul'pin in Transition Metals for Organic Synthesis (ed.:M. Beller, C. Bolm), 2nd edn, vol. 2, Wiley-VCH, New York(2004) 215; (b) G. B. Shul'pin, H. Stoeckli-Evans, D. Mandelli, Y. N. Kozlov, A. T. Vallina, C. B. Woitiski, R. S. Jimenez, W. A. Carvalho, J. Mol. Catal. A219 (2004) 255.
- 30 (a) J. Reim, R. Werner, W. Haase, B. Krebs, Chem. Eur. J. 4 (1998) 289; (b) P. Roy, K. Dhara, M. Manassero, P. Banerjee, Inorg. Chem. Commun. 11 (2008) 265; (c) S. Halder, S. Dey, C. Rizzoli, P. Roy, Polyhedron 78 (2014) 85.
- (a) E. Armakola, R. M. P. Colodrero, M. Bazaga-García, I. R. Salcedo, D. Choquesillo-Lazarte, A. Cabeza, M. V. Kirillova, A. M. Kirillov, K. D. Demadis, Inorg. Chem. 57 (2018) 10656; (b) K. Czerwińska, B. Machura, S. Kula, S. Krompiec, K. Erfurt, C. Roma-Rodrigues, A. R. Fernandes, L. S. Shul'pina, N. S. Ikonnikove, G. B. Shul'pin, Dalton Trans. 46 (2017) 9591; (c) T. A. Fernandes, C. I. M. Santos, V. André, J. Kłak, M. V. Kirillova, A. M. Kirillov, Inorg. Chem. 2016, 55, 125; (d) S. S. P. Dias, M. V. Kirillova, V. André, J. Kłak, A. M. Kirillov, Inorg. Chem. 54 (2015) 5204.

Complex	1	2
Formula	$C_{26}H_{26}Cl_2Cu_2N_2O_6$	C <sub>29</sub> H <sub>36</sub> N <sub>8</sub> Ni <sub>2</sub> O <sub>7</sub>
Formula weight	660.47	726.08
<i>T</i> (K)	298 K	298 K
Crystal color	Dark green	Green
Crystal system	orthorhombic	Monoclinic
Space group	P212121	P 21/n
<i>a</i> (Å)	13.5722(7)	16.7002(5)
<i>b</i> (Å)	11.8931(6)	7.4796(2)
<i>c</i> (Å)	17.3627(8)	25.7434(7)
α (°)	90.00	90.00
β (°)	90.000(3)	100.802(2)
γ (°)	90.00	90.00
$V(\text{\AA}^3)$	2802.6(2)	3158.65(15)
Ζ	4	4
Crystal dimensions (mm)	0.5  imes 0.2  imes 0.15	0.4 imes~0.2 imes~0.1
<i>F</i> (0 0 0)	1344	1512
$D_{\rm c}~({\rm g~cm^{-3}})$	1.565	1.527
$\lambda$ (Mo Ka) (Å)	0.71073	0.71073
$\theta$ Range (°)	1.90- 24.99	1.601 - 27.220
Reflection collected/	33619,4936 ,4098	51406, 7017, 5070
unique/observed		
Absorption correction	multi-scan	multi-scan
R <sub>int</sub>	0.0735	0.0342
Final $R_1$ index $[I > 2\sigma(I)]$	0.0479	0.0504
Final $wR_2$ index (all reflections)	0.1391	0.1450
Goodness-of-fit	1.150	1.033

#### Table 1 Crystal data, data collection and structure refinement of complexes

Complex 1			
Cu1–O2	1.997(6)	Cu2–O3	1.885(6)
Cu1– N1	1.911(8)	Cu2–N2	1.918(7)
Cu1–O1	1.906(6)	Cu2–O4	2.022(6)
Cu1–Cl1	2.250(3)	Cu2–Cl2	2.280(3)
		Cu2–Cl1	2.724(3)
O2–Cu1–N1	83.0(3)	N2-Cu2-O4	82.5(3)
O2–Cu1–O1	170.1(3)	O3–Cu2–Cl2	96.7(2)
N1-Cu1-O1	91.7(3)	N2-Cu2-Cl2	156.8(2)
O2–Cu1–Cl1	93.0(2)	O4–Cu2–Cl2	89.9(2)
N1–Cu1–Cl1	163.0(2)	O3-Cu2-Cl1	89.9(2)
O1–Cu1–Cl1	94.45(19)	N2-Cu2-Cl1	107.1(2)
O3–Cu2–N2	92.7(3)	O4Cu2Cl1	85.88(19)
O3–Cu2–O4	172.4(3)	Cl2–Cu2–Cl1	94.03(9)
	0		
Complex 2			
Ni1- N8	1.969(3)	Ni2- N7	1.968(3)
Ni1- O6	1.977(2)	Ni2- O2	1.990(2)
Ni1- N1	2.035(3)	Ni2- N4	2.038(3)
Ni1- N4	2.133(3)	Ni2- N1	2.144(3)
Ni1- O4	2.155(2)	Ni2- O3	2.162(3)
Ni1- O5	2.170(3)	Ni2- O1	2.164(3)
N8- Ni1- O6	91.24(10)	N7- Ni2- O2	89.62(11)
N8- Ni1- N1	169.95(12)	N7- Ni2- N4	171.16(13)
O6- Ni1- N1	97.73(11)	O2- Ni2- N4	94.28(11)
N8- Ni1-N4	95.65(12)	N7- Ni2- N1	92.80(12)
06- Ni1- N4	92.44(12)	O2- Ni2- N1	91.65(12)
N1- Ni1-N4	79.55(16)	N4- Ni2-N1	79.18(12)

Table 2 Selected bond lengths (Å) and bond angles (°) of complexes 1 and 2

O6- Ni1- O4 173.12(9 N1- Ni1- O4 89.08(1 N4- Ni1- O4 87.84(1 N8- Ni1- O5 91.09(1 O6- Ni1- O5 92.49(1 N1- Ni1- O5 93.03(12 N4- Ni1- O5 171.56( O4- Ni1- O5 88.08(1	<pre>(9) 11) 11) 11) 11) 12) (11) 11)</pre>	02- N4- N1- N7- 02- N4- N1- 03-	- Ni2- O3 - Ni2- O3 - Ni2- O3 - Ni2- O1 - Ni2- O1 - Ni2- O1 - Ni2- O1 - Ni2- O1	5	171.06(12 94.66(12 90.28(12 96.10(13 93.62(12 91.58(13 169.69(12) 85.88(13)	10) 2) 2) 3) 2) 3) 12) 3)
N1- Ni1- O4 89.08(1	11)	N4-	- Ni2- O3	5	94.66(12	2)
N4- Ni1- O4 87.84(1	11)	N1-	- Ni2- O3		90.28(12	2)
N8- Ni1- O5 91.09(1	11)	N7-	- Ni2- O1		96.10(13	3)
O6- Ni1- O5 92.49(1	11)	O2-	- Ni2- O1		93.62(12	2)
N1- Ni1- O5 93.03(12	12)	N4-	- Ni2- O1		91.58(13	3)
N4- Ni1- O5 171.56(	(11)	N1-	- Ni2- O1		169.69(12)	12)
O4- Ni1- O5 88.08(1	11)	O3-	- Ni2- O1		85.88(13)	3)
N4- Ni1- O4 87.84(1	11)	N1-	- Ni2- O3	5	90.28(12	2)
N8- Ni1- O5 91.09(1	11)	N7-	- Ni2- O1		96.10(13	3)
O6- Ni1- O5 92.49(1	11)	O2-	- Ni2- O1		93.62(12	2)
N1- Ni1- O5 93.03(12	12)	N4-	- Ni2- O1		91.58(13	3)
N4- Ni1- O5 171.56(	(11)	N1-	- Ni2- O1		169.69(12	12)
O4- Ni1- O5 88.08(1	11)	O3-	- Ni2- O1		85.88(13	3)
N8- Ni1- O5 91.09(1	11)	N7-	- Ni2- O1	5	96.10(13	3)
O6- Ni1- O5 92.49(1	11)	O2-	- Ni2- O1		93.62(12	2)
N1- Ni1- O5 93.03(1)	12)	N4-	- Ni2- O1		91.58(13	3)
N4- Ni1- O5 171.56(	(11)	N1-	- Ni2- O1		169.69(1	12)
O4- Ni1- O5 88.08(1	11)	O3-	- Ni2- O1		85.88(13	3)
O6- Ni1- O5 92.49(1	11)	02-	- Ni2- O1	5	93.62(12	2)
N1- Ni1- O5 93.03(1)	12)	N4-	- Ni2- O1		91.58(13	3)
N4- Ni1- O5 171.56(	(11)	N1-	- Ni2- O1		169.69(1	12)
O4- Ni1- O5 88.08(1	11)	03-	- Ni2- O1		85.88(13	3)
N1- Ni1- O5 93.03(1:	12)	N4-	• Ni2- O1	5	91.58(1)	3)
N4- Ni1- O5 171.56(	(11)	N1-	• Ni2- O1		169.69(1	12)
O4- Ni1- O5 88.08(1	11)	O3-	• Ni2- O1		85.88(1)	3)
N4- Ni1- O5 171.56( O4- Ni1- O5 88.08(1	(11)	N1- O3-	- Ni2- O1 - Ni2- O1	5	169.69(1 85.88(13	12) 3)
04- Ni1- O5 88.08(1	11)	03-	- Ni2- O1	5	85.88(12	3)
			~	5	2	

**Table 3** Main calculated UV-Vis transition for  $HL^1$ , complexes 1 and 2 with vertical excitation energies ( $E_{cal}$ ), oscillator strengths ( $f_{cal}$ ) of the lowest few excited singlets obtained from TDDFT/B3LYP/CPCM method in methanol.

Compound	Excitation	Electronic	excitation	Osc.	CI	Key transitions
	(eV)	transition	(nm)	strength		
		State		(f)		0-
	2.904	S <sub>0-</sub> S <sub>1</sub>	418.14	0.0423	0.1965	(08%)HOMO-1 →LUMO+1
			<u> </u>	<u> </u>	0.6204	(77%)HOMO→LUMO
					0.1274	(03%)HOMO →LUMO+1
$HL^1$	2.991	S <sub>0</sub> -S <sub>2</sub>	400.12	0.0252	0.5570	(62%)HOMO-1→LUMO
				V	0.1192	(02%)HOMO-1→LUMO+1
			6		0.2872	(16%)HOMO→LUMO+1
	3.983	S <sub>0-</sub> S <sub>5</sub>	311.24	0.6564	0.1188	(03%)HOMO-3→LUMO+1
			Ŧ		0.4700	(44%)HOMO-1→LUMO
	0				0.1195	(43%)HOMO-1→LUMO+2
					0.4220	(35%)HOMO→LUMO+1
	3.070	$S_{0-}S_{1}$	390.05	0.0642	0.6714	(89%)HOMO→LUMO
Y			I	I	0.2031	(08%)HOMO-2→LUMO
					0.1180	(02%)HOMO→LUMO+1
	3.227	S <sub>0-</sub> S <sub>2</sub>	384.21	0.1501	0.6418	(82%)HOMO-1→LUMO+1
			l	l	0.1114	(02%)HOMO-3→LUMO

					0.1834	(06%)HOMO→LUMO
Complex 1	3.254	S <sub>0-</sub> S <sub>4</sub>	380.93	0.0402	0.2215	(10%)HOMO-2→LUMO
					0.1046	(02%)HOMO-9→LUMO
					0.5468	(60%)HOMO→LUMO+1
	3.900	S <sub>0-</sub> S <sub>8</sub>	317.88	0.2581	0.1483	(04%)HOMO-2→LUMO+3
		<u> </u>	<u> </u>	<u> </u>	0.6705	(90%)HOMO→LUMO+1
	3.956	S <sub>0-</sub> S <sub>9</sub>	313.40	0.0304	0.6101	(74%)HOMO-4→LUMO+3
		<u> </u>	<u> </u>		0.2635	(14%)HOMO-4→LUMO+5
				5	0.1190	(03%)HOMO-4→LUMO+8
	3.083	S <sub>0-</sub> S <sub>1</sub>	400.01	0.0104	0.2156	(10%)HOMO-2→LUMO
					0.1169	(02%)HOMO-2→LUMO+1
					0.6153	(74%)HOMO→LUMO
	3.120	S <sub>0-</sub> S <sub>2</sub>	396.12	0.1033	0.1788	(06%)HOMO-2→LUMO
		I	1	I	0.3422	(23%)HOMO-3→LUMO
Complex 2					0.4418	(39%)HOMO-1→LUMO+1
	3.961	S <sub>0-</sub> S <sub>5</sub>	314.40	0.0309	0.2967	(17%)HOMO-1→LUMO+4
		I	1	I	0.5512	(61%)HOMO→LUMO+1
	3.986	S <sub>0-</sub> S <sub>6</sub>	311.21	0.0571	0.2806	(15%)HOMO-3→LUMO+2
		1	1	1	0.1165	(02%)HOMO-3→LUMO+1

Cyclohexane							
$n(H_2O_2)/n(catalyst)$	Time	Yield <sup>t</sup>	'(%)	Total <sup>c</sup>	Selectivity <sup>d</sup> of	TON <sup>e</sup>	
	(h)	Cyclohexanone	Cyclohexanol		cyclohexanol (%)		
100	8	3.2	5.8	9	64.4	4.5	
	48	6.4	9.1	15.5	58.7	7.75	
250	8	7.6	14.1	21.7	65	10.8	
	48	9.3	21.4	30.7	69.7	15.3	
500	8	11.1	19.3	30.4	63.4	15.2	
	48	18.4	29.8	48.2	62	24.1	
	48 <sup>f</sup>	47	0.5	47.5	0.01	23.5	
<u>Toluene</u>							
$n(H_2O_2)/n(catalyst)$	Time (h)	Yield	<sup>b</sup> (%)	Total <sup>c</sup>	Selectivity <sup>d</sup> of	TON <sup>e</sup>	
		Benzyl	Benzaldehyde		benzyl alcohol		
		alcohol			(%)		
100	8	7.4	4.8	12.2	60.6	6	
	48	11.1	7.2	18.3	60.6	9	
250	8	11.8	9.3	21.1	56	10.55	
	48	19.4	14.4	33.8	57.4	16.9	
500	8	19.1	13.8	32.9	58	16.45	
	48	23.8	15.9	39.7	60	19.8	
Cyclopentane							
$n(H_2O_2)/n(catalyst)$	Time (h)	Yield	<sup>b</sup> (%)	Total <sup>c</sup>	Selectivity <sup>d</sup> of	TON <sup>e</sup>	
		Cyclopentanone	Cyclopentanol		Cyclopentanol		
0					(%)		
100	8	5.2	5.8	11	52.7	5.5	
	48	9.2	11.4	20.6	55.3	10.3	
250	8	8.5	10.9	19.4	56.1	9.8	
	48	13.6	14.9	28.5	52.2	14.25	
500	8	14.5	17.2	31.7	54.2	15.85	
	48	16.7	19.1	35.8	53.3	17.9	

### **Table 4** Oxidation<sup>a</sup> of cyclohexane, toluene and cyclopentane

<sup>a</sup>Solvent: acetonitrile; <sup>b,d</sup>Yield and selectivity calculated after treatment with PPh<sub>3</sub>; <sup>c</sup>Acohol + ketone; <sup>e</sup>TON (turn over number) = moles of product/mole of catalyst; <sup>f</sup>before treatment with PPh<sub>3</sub>.

#### Figure legends

Scheme 1 Synthesis of complexes 1 and 2.

**Fig. 1** A perspective view of complex **1** with partial atom numbering scheme. Hydrogen atoms and solvent molecules are omitted for the clarity.

Fig. 2 A perspective view of complex 2 with partial atom numbering scheme. Hydrogen atoms are omitted for the clarity.

Fig. 3 Frontier MOs along with their HOMO-LUMO energy gap of HL<sup>1</sup>, complexes 1 and 2

Fig. 4 Frontier molecular orbitals involved in the UV-vis absorption of complexes 1 (A) and 2 (B).

Fig. 5 Cyclic voltammograms of complexes 1 (A) and 2 (B).

















#### Highlights

 $[Cu_2(L^1)_2(\mu_2-Cl)Cl]\cdot 2.5H_2O$  and  $[Ni_2(L^1)_2(\mu_2-N_3)_2 (CH_3OH)_2]\cdot CH_3OH$  prepared and • characterized [HL<sup>1</sup> is 1-((2-hydroxyethylimino)methyl)naphthalen-2-ol]

• They were characterized by elemental analysis, FT-IR, UV-Vis, mass spectroscopy, TGA-DTA, cyclic voltametric studies and single crystal X-ray diffraction analysis.

• Copper(II) complex showed catalytic ability for oxidation of cyclohexane, toluene and cyclopentane

• Nickel(II) complex acted as inactive in the same catalysis

**Graphical Abstract** 



Dinuclear complexes of Cu(II) and Ni(II) with 1-((2-hydroxyethylimino)methyl)naphthalen-2-ol have been synthesized, charcaterized and explored as catalyst for the oxidation of cyclohexane, toluene and cyclopentane using hydrogen peroxide as the oxidant. Copper(II) complex has been found to be active catalyst for oxidation of these hydrocarbons whereas nickel(II) complex is not.