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Synthesis, crystal structure, spectral properties and catalytic activity of binuclear copper(II), mononuclear nickel(II) and cobalt(III) complexes containing Schiff base ligand

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ABSTRACT

Newly designed tridentate ligand, HL **1** derived from 2-(benzylthio)aniline and 2-hydroxy-1-naphthaldehyde, upon reaction with Cu(II), Ni(II) and Co(III) nitrate separately in methanol yielded binuclear Cu(II) complex, $[Cu_2(L)_2(NO_3)_2]$ **2**, and mononuclear $[Ni(L)_2]$ **3** and $[Co(L)_2](NO_3)$ **4** which were characterized by spectral data and authenticated by single crystal X-ray diffraction of **2** and **3**. The diffraction analysis revealed that the ligand binds to metals in (O, N, S) fashion. Single crystal X-ray diffraction studies confirmed that the $[Cu_2(L)_2(NO_3)_2]$ complex consist of centrosymmetric binuclear entities containing square-pyramidal copper(II) ions bridged through the phenoxo oxygen atoms. The emission and redox properties of both the ligand and corresponding complexes were examined. The redox property of the complexes has been qualitatively explained by single point DFT calculations. The catalytic activities of Cu(II) complex $[Cu_2(L)_2(NO_3)_2]$ towards oxidation of benzyl alcohol derivatives to carbonyl compounds was tested using H_2O_2 as the oxidant.

1. Introduction

Research have been continuing in the area of coordination chemistry of transition metal complexes of Schiff base ligands and have gained importance due to the interesting applications in development of new materials, asymmetric catalysis, biological applications like DNA cleavage, antibacterial, antiviral and antifungal activities [1–14]. Chiral complexes of Schiff bases were used as catalyst for the asymmetric organic transformations such as olefin polymerization/enantioselective epoxidation and asymmetric hetero-Diels Alder reactions [15–21]. The binuclear copper complexes have received attention due to their interesting magnetic properties, luminescence behavior [22,23]. Such binuclear Cu complexes having oxidase activity have been considered as the synthetic analogues of Cu containing natural oxidases [22–24]. Metal complexes incorporating tridentate (O, N, S) Schiff base ligand containing phenolic OH, azomethine group and thioether sulfur donors (StructureA) have exhibited catalytic activity towards C–C coupling, polymerization and biological activity *viz* antibacterial, DNA cleavage [25–31]. Recently, we reported the coordination chemistry and properties of transition metal complexes incorporating 2-((2(alkylthio)phenylimino)methyl)phenol, (**A**) [29,30]. Thereafter we contemplated to design and synthesize the similar type of ligands replacing the phenol fragment by naphthol in the ligand backbone as shown in **1**. Incorporation of naphthyl group in the ligand backbone might be useful to obtain emission properties of ligands and metal complexes.

Herein, we describe the synthesis of newly designed tridentate ligand, HL **1** and its binuclear Cu(II) complex, $[Cu_2(L)_2(NO_3)_2]$ **2**, and mononuclear $[Ni(L)_2]$ **3** and $[Co(L)_2](NO_3)$ **4**. The ligand and complexes **2**–**4** have been characterized by the spectroscopic data. The crystal structures of the complexes **2** and **3** have been determined to confirm the molecular structure. The fluorescence behaviour and redox properties of the ligand and complexes were examined. Plausible descriptions of electronic spectra and redox orbitals have been ascribed on the basis of single point DFT calculations. The catalytic oxidation of benzyl alcohol derivatives to corresponding carbonyl compounds have been investigated for complex **2** using H_2O_2 as oxidant.

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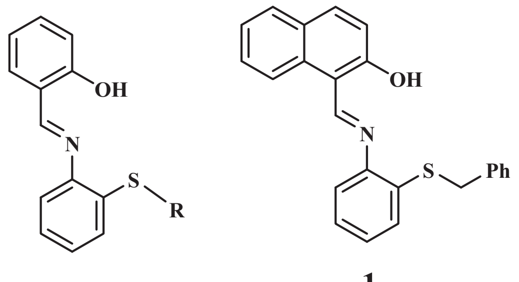

A **1**

Structure. A and **1**.

2. Experimental

2.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by general procedure [32]. Copper nitrate trihydrate (99%), nickel nitrate hexahydrate (99%), cobalt(III) nitrate hexahydrate (99%), benzyl alcohol (99%) were purchased from Emark, India. 4-Iodobenzyl alcohol (98%), 3-methoxybenzyl alcohol (98%), 4-nitrobenzyl alcohol (99%) were purchased from Spectrochem, India. 2-Hydroxy-1-naphthaldehyde (98%), 2-aminothiophenol (99%), 4-chlorobenzyl alcohol (99%) and 4-methylbenzyl alcohol (98%) were purchased from Aldrich. 2-(Benzylthio)aniline was prepared following reported procedure [33]. Ferrocene (98%) was bought from Emark, India.

2.2. Physical measurements

Microanalysis (C, H, N) was performed using Perkin-Elmer 2400 C, H, N, S/O series II elemental analyzer. IR spectra were recorded on Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on Shimadzu UV-1800 PC spectrophotometer. ^{1}H NMR spectra were obtained on Brucker 400 NMR spectrometers in $CDCl_3$ using TMS as the internal standard. Emission spectra were recorded with Perkin Elmer LS-55 Luminescence Spectrometer. X-ray crystallography data were collected by ω-scan technique on a Bruker Smart CCD diffractometer with Mo Kα radiation monochromated by graphite crystal. Electrochemical measurements were made under dinitrogen atmosphere using a CH instruments model 600D potentiostat. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. Ferrocene reference was checked at the beginning and the end of the experiment. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

2.3. DFT calculations

Using the X-ray coordinates of the $[Cu_2(L)_2(NO_3)_2]$ **2**, and mononuclear $[Ni(L)_2]$ **3** complexes, ground state electronic structure calculations have been carried out using DFT methods with the ORCA 2.7 program [34]. Becke's hybrid function with the Lee–Yang–Parr (LYP) correlation function was used throughout the study [35,36]. The valence-only SV (P) SV/J basis set and B3LYP/G functional were used [34,35]. All energy calculations were performed using the self-consistent field "tight" option of the ORCA 2.7 program to ensure sufficiently well converged values for the state energies [34,37,38].

2.4. Syntheses

2.4.1. Synthesis of ligand**1**

To a (30 mL) ethanol solution of 2-hydroxy-1-naphthaldehyde (1.01 g, 5.86 mmol) was slowly added a (20 mL) ethanol solution of 2-(benzylthio)aniline (1.26 g, 5.86 mmol). After complete addition, the reaction mixture was stirred at room temperature for 6 h and allowed to stand for 2 h at room temperature. The product was separated as yellow precipitation that was collected by filtration and used for further reactions. The filtrate on standing for an additional 24 h provides a little crop of product and the combined yield was 90%. *Anal.* Calc. for $C_{24}H_{19}NOS$: C, 78.04; H, 5.14; N, 3.79. Found: C, 78.21; H, 5.29; N, 3.42%. IR (KBr, cm^{-1}): 3435 (ν O–H), 1613 and 1601 ν(C=N), 1324 ν(C–O), 751 ν(C–S). ^{1}H NMR (400 MHz, $CDCl_3$): 4.11 (CH_2, s, 2H), 7.11–7.20 (ArH, m, 5H), 7.25 (ArH, d, 2H), 7.29–7.36 (ArH, m, 3H), 7.40 (ArH, d, 1H), 7.52 (ArH, t, 1H), 7.72 (ArH, d, 1H), 7.81 (ArH, d, 1H), 8.07 (ArH, d, 1H), 9.21 (CH=N, d, 1H), 15.31 (Ar–OH, s, 1H).

2.4.2. Synthesis of complex **2**

A solution of copper(II) nitrate trihydrate (0.1 g, 0.413 mmol) in methanol (15 mL) a solution of ligand HL (0.153 g, 0.413 mmol) in methanol (10 mL) was added under constant stirring. The colour of the solution changes immediately to olive green which gradually turned into green as the stirring was continued for 6 h at room temperature. The resulting green solution was then filtered and allowed to stand. After slow evaporation of the solvent at room temperature, green colored X-ray quality crystals were obtained. Yield: 80%. *Anal.* Calc. for $C_{48}H_{36}Cu_2N_4O_8S_2$: C, 58.29; H, 3.64; N, 5.66. Found: C, 58.35; H, 3.70; N, 5.60%. IR (KBr, cm^{-1}): 1615 and 1597 ν(C=N), 1383 ν(O–C), 1295 ν(N–O), 747 ν(C–S). $E_{1/2}$ [V]: 1.36.

2.4.3. Synthesis of complex **3**

A solution of nickel(II) nitrate hexahydrate (0.100 g, 0.343 mmol) in methanol (15 mL) a solution of ligand HL (0.254 g, 0.687 mmol) in methanol (10 mL) was added under stirring. The solution changes its colour from yellow to brown increasingly upon addition of ligand into the methanolic solution of metal substrate under the stirring and it was continued for 8 h at room temperature. The resulting brown solution was then filtered and allowed to stand. After slow evaporation of the solvent at room temperature, dark coloured X-ray quality crystals were obtained. Yield: 65%. *Anal.* Calc. for $C_{48}H_{36}NiN_2O_2S_2$: C, 72.39; H, 4.52; N, 3.51. Found: C, 72.23; H, 4.68; N, 3.25%. IR (KBr, cm^{-1}): 1619 and 1601 ν(C=N), 1393 ν(O–C), 744 ν(C–S). $E_{1/2}$ [V]: 0.89.

2.4.4. Synthesis of complex **4**

A methanol (10 mL) solution of cobalt(III) nitrate hexahydrate (0.1 g, 0.344 mmol) was added to the solution of ligand HL (0.255 g, 0.688 mmol) in methanol (10 mL) under stirring at hot condition (60 °C). The colour of the solution was changed immediately to brown and it was continued for 5 h. The resulting brown solution was then filtered and allowed to stand at room temperature. After slow evaporation of the solvent at 25 °C, the dark coloured crystal was obtained, washed with cold methanol, and dried in vacuum. Yield: 85%. *Anal.* Calc. for $C_{48}H_{36}CoN_3O_5S_2$: C, 67.14; H, 4.19; N, 4.89. Found: C, 67.35; H, 4.05; N, 4.67%. IR (KBr, cm^{-1}): 1611 and 1597 ν(C=N), 1385 ν(O–C), 1336 ν(N–O), 750 ν(C–S). ^{1}H NMR (400 MHz, $CDCl_3$): 3.73 (CH_2, d, 1H), 3.84 (CH_2, d, 1H), 6.76 (ArH, d, 1H), 6.86 (ArH, d, 2H), 6.96 (ArH, t, 2H), 7.13 (ArH, t, 1H), 7.32–7.38 (ArH, m, 3H), 7.46 (ArH, d, 1H), 7.61 (ArH, t, 2H), 7.71 (ArH, t, 2H), 8.10 (ArH, d, 1H), 8.77 (CH=N, s, 1H). $E_{1/2}$ [V]: 1.33.