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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<sub>2</sub>O<sub>2</sub> as the oxidant.

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# 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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# 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%) 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. <sup>1</sup>H NMR spectra were obtained on Brucker 400 NMR spectrometers in CDCl<sub>3</sub> 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 Ka 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 ligand1

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<sub>24</sub>H<sub>19</sub>NOS: C, 78.04; H, 5.14; N, 3.79. Found: C, 78.21; H, 5.29; N, 3.42%. IR (KBr, cm<sup>-1</sup>): 3435 ( $\nu$  O–H), 1613 and 1601  $\nu$ (C=N), 1324  $\nu$ (C–O), 751  $\nu$ (C–S). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.11 (CH<sub>2</sub>, 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<sub>48</sub>H<sub>36</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>: C, 58.29; H, 3.64; N, 5.66. Found: C, 58.35; H, 3.70; N, 5.60%. IR (KBr, cm<sup>-1</sup>): 1615 and 1597 v(C=N), 1383 v(O-C), 1295 v(N-O), 747 v(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<sup>-1</sup>): 1619 and 1601  $\nu$ (C=N), 1393  $\nu$ (O-C), 744  $\nu$ (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<sub>48</sub>H<sub>36</sub>CoN<sub>3</sub>O<sub>5</sub>S<sub>2</sub>: C, 67.14; H, 4.19; N, 4.89. Found: C, 67.35; H, 4.05; N, 4.67%. IR (KBr, cm<sup>-1</sup>): 1611 and 1597 v(C=N), 1385 v(O-C), 1336 v(N-O), 750 v(C-S). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.73 (CH<sub>2</sub>, d, 1H), 3.84 (CH2, 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*<sub>1/2</sub> [V]: 1.33.

#### 2.5. Procedure for catalytic oxidation of benzyl alcohol derivatives

To a solution of benzyl alcohol derivative (Eq. (4)) (5 mmol), in 10 mL acetonitrile catalyst  $[Cu_2(L)_2(NO_3)_2]$  (0.002 mmol), and 50% H<sub>2</sub>O<sub>2</sub> (5 mL) was added and the mixture was refluxed at 80 °C for 2 h. The mixture was then poured into water and the product was extracted with dichloromethane and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the product was purified by column chromatography. The product was characterized by IR and <sup>1</sup>H NMR spectra.

# 2.6. Crystallography

Single crystals of  $C_{48}H_{36}Cu_2N_4O_8S_2$  and  $C_{48}H_{36}N_2NiO_2S_2$  were grown by slow evaporation of methanol solutions at 298 K. Data were collected by  $\omega$ -scan technique on a Bruker Smart CCD diffractometer with Mo K $\alpha$  radiation monochromated by graphite crystal. Structure solution was done by direct method with SHELXS-97 program [39,40]. Full matrix least square refinements on  $F^2$  were performed using SHELXL-97 program [39,40]. All nonhydrogen atoms were refined anisotropically using reflections  $I > 2\sigma(I)$ . The C-bound hydrogen atoms were included in calculated positions and refined as riding atoms. Data collection parameters and relevant data crystal data are collected in Table 1.

# 3. Results and discussion

# 3.1. Synthesis

The Schiff base ligand HL **1** used in this work was synthesized by the condensation of 2-(benzylthio)aniline and 2-hydroxy-1naphthaldehyde in ethanol (Scheme 1). The preformed ligand HL upon reaction with copper(II) nitrate trihydrate, in methanol yielded the binuclear Cu(II) complex,  $[Cu_2(L)_2(NO_3)_2]$  **2**, where the ligand offers (O, N, S) coordination mode to each metal center. Whereas the reaction of nickel(II) nitrate hexahydrate and cobalt(III) nitrate hexahydrate separately with the ligand HL in 1:2 M ratio in MeOH afforded *bis* chelates of compositions  $[Ni(L)_2]$ , **3** and  $[Co(L)_2](NO_3)$ , **4** respectively (Scheme 1). The two deprotonated ligands coordinated to the metal centre (M = Ni<sup>II</sup>/Co<sup>III</sup>) in tridentate (O, N, S) manner offering octahedral geometry.

### 3.2. Spectral characterization and solution structures

Ligand HL, **1**, and complexes **2–4** are soluble in dichloromethane furnishing yellow, green, light brown and brown solutions

| Table 1                           |
|-----------------------------------|
| Crystallographic data for 2 and 3 |

| Chemical formula                           | $C_{48}H_{36}Cu_2N_4O_8S_2$    | $C_{48}H_{36}N_2NiO_2S_2$      |
|--|--------------------------------|--------------------------------|
| Formula weight                             | 988.05                         | 795.62                         |
| Crystal system                             | monoclinic                     | triclinic                      |
| Space group                                | P21/n                          | P1                             |
| a (Å)                                      | 8.8425(3)                      | 11.1997(5)                     |
| b (Å)                                      | 12.0212(4)                     | 13.5316(6)                     |
| <i>c</i> (Å)                               | 19.8839(7)                     | 14.4342(5)                     |
| α (°)                                      | 90                             | 97.063(2)                      |
| β (°)                                      | 99.196(2)                      | 110.110(2)                     |
| γ (°)                                      | 90                             | 109.919(2)                     |
| $\lambda$ (Å)                              | 0.71073                        | 0.71073                        |
| $V(Å^3)$                                   | 2086.44(12)                    | 1858.46(14)                    |
| F(000)                                     | 1012                           | 828                            |
| Crystal size (mm)                          | $0.04 \times 0.18 \times 0.30$ | $0.02 \times 0.16 \times 0.44$ |
| Ζ  | 4                              | 2                              |
| T (K)                                      | 180                            | 180                            |
| $D_{\text{calc}} (\text{mg/m}^{-3})$       | 1.573                          | 1.422                          |
| $\mu ({\rm mm}^{-1})$                      | 1.183                          | 0.679                          |
| Theta min-max (°)                          | 2.4, 29.2                      | 2.1, 29.2                      |
| Reflections measured                       | 22350                          | 45861,                         |
| Unique reflections (Rint)                  | 5627 (0.042)                   | 10038 (0.049)                  |
| No. of reflections used $[I > 2\sigma(I)]$ | 4049                           | 7428                           |
| $R_1 \left[ I > 2\sigma(I) \right]$        | 0.0404                         | 0.0415                         |
| $wR_2$ (all data)                          | 0.1076                         | 0.1039                         |
| Goodness-of-fit (GOF)                      | 0.964                          | 1.057                          |
|  |                                |                                |



Scheme 1. Synthesis of ligand HL 1, and complexes 2-4.

respectively. The electronic spectral characteristics (230–800 nm) of the ligand and complexes in dichloromethane are shown in Fig. 1 and data are collected in Table 2. The electronic spectrum of the ligand in dichloromethane exhibits several structured bands in the range 230–470 nm owing to  $\pi$ – $\pi$ \* and n– $\pi$ \* transitions [29,30,41,42]. The electronic spectra of the ligand have also been studied in different organic solvents *viz*. acetonitrile, DMF, DMSO and methanol. The spectral data are collected in Table 3. The spectral data indicated that the higher energy absorption bands ( $\pi$ – $\pi$ \* and n– $\pi$ \*) within 250–330 nm suffers a very small shift and longer wavelength visible bands ( $\pi$ – $\pi$ \*) in the range 380–470 nm are more sensitive on the nature of the organic solvent.

The complexes **2–4** in dichloromethane show relatively a weak absorption band near 640 nm due to ligand field transition (Fig. 1



**Fig. 1.** UV/Vis spectra of ligand HL  $(1.70 \times 10^{-4} \text{ M})$  (—), complex **2**  $(2.0 \times 10^{-4} \text{ M})$  (—), complex **3**  $(1.2 \times 10^{-4} \text{ M})$  (—) and complex **4**  $(1.4 \times 10^{-4} \text{ M})$  (—) in dichloromethane.

in set) in addition to several higher energy bands in the range 240–495 nm [29,30,41,42]. Electronic spectra of the complexes (**2–4**) in different organic solvents of different polarities have been studied at  $\sim 10^{-5}$  (M) concentration. The absorption maxima and extinction coefficients are presented in Table 3. The spectra of Cu(II) complex in different solvents are shown in Fig. 2 as representative. Other UV–Vis spectra are given as Supplementary Figs. S1–S3. In all the complexes the ligand field transition at  $\sim 640$  nm could not be observed in acetonitrile, DMF and DMSO except methanol

| Table 2 |          |      |     |           |         |    |
|---------|----------|------|-----|-----------|---------|----|
| UV-Vis  | spectral | data | (in | dichloron | nethane | ). |

| Compound        | $\lambda_{\rm max}/{\rm nm} \ (\epsilon/{\rm dm}^2 \ {\rm mol}^{-1})$ |
|-----------------|---|
|                 |   |
| Ligand <b>1</b> | 470 (2624); 390 (6562); 320 (5925); 236 (14482)                       |
| Complex 2       | 637 (300): 440 (8740): 340 (9415): 265 (26300): 240 (18760)           |
| Constant 2      | (22)(120)(120)(0271)(222)(10020)(272)(10020)(220)(2011))              |
| Complex 3       | 623(150); 470(9671); 335(10038); 276(19326); 250(26414)               |
| Complex 4       | 632 (500); 495 (4145); 350 (9965); 276 (22690); 238 (30916)           |
|                 |   |



Fig. 2. UV/Vis spectra of complex 2 (10<sup>-4</sup> M) in (–) acetonitrile, (––––) DMF, (–––––) DMSO and (–––––) methanol.

| Table 3 | 3 |
|---------|---|
|---------|---|

Electronic spectral data of 1-4 in different solvents at 25 °C.

| Compound | Acetonitrile                                |      | DMF  |                                | DMSO |                                | Methanol |                                 |
|----------|---|------|------|--------------------------------|------|--------------------------------|----------|---------------------------------|
|          | $\lambda/nm \ \epsilon_{max} 	imes 10^{-4}$ |      | λ/nm | $\epsilon_{max} 	imes 10^{-4}$ | λ/nm | $\epsilon_{max} 	imes 10^{-4}$ | λ/nm     | $\epsilon_{max} \times 10^{-4}$ |
| 1        | 254   | 1.0  | 260  | 1.2                            | 262  | 2.3                            | 259      | 4.7                             |
|          | 315   | 0.54 | 320  | 0.5                            | 320  | 0.6                            | 312      | 2.7                             |
|          | 388   | 0.55 | 393  | 0.6                            | 398  | 0.7                            | 442      | 1.7                             |
|          | 463   | 0.25 | 465  | 0.24                           | 467  | 0.3                            | 463      | 2.9                             |
| 2        | 264   | 1.2  | 277  | 1.5                            | 269  | 0.8                            | 263      | 2.3                             |
|          | 324   | 1.5  | 322  | 2.1                            | 326  | 1.5                            | 317      | 2.2                             |
|          | 434   | 1.9  | 428  | 3.9                            | 433  | 1.6                            | 339      | 2.3                             |
|          |   |      |      |                                |      |                                | 435      | 2.0                             |
|          |   |      |      |                                |      |                                | 450      | 2.1                             |
|          |   |      |      |                                |      |                                | 644      | 0.04                            |
| 3        | 254   | 1.0  | 263  | 0.6                            | 274  | 0.6                            | 275      | 3.2                             |
|          | 277   | 8.5  | 334  | 0.7                            | 335  | 0.3                            | 331      | 1.7                             |
|          | 328   | 4.0  | 470  | 0.2                            | 475  | 0.2                            | 469      | 1.6                             |
|          | 461   | 1.9  |      |                                |      |                                | 644      | 0.01                            |
| 4        | 255   | 3.3  | 269  | 5.7                            | 263  | 4.2                            | 275      | 4.1                             |
|          | 316   | 1.7  | 318  | 2.3                            | 318  | 2.1                            | 340      | 0.07                            |
|          | 385   | 1.5  | 399  | 1.5                            | 398  | 1.8                            | 463      | 1.3                             |
|          | 459   | 0.7  | 442  | 1.42                           | 468  | 1.0                            | 641      | 0.04                            |
|          |   |      | 467  | 1.45                           |      |                                |          |                                 |

because of dilute solution and low intensity of the band. A comparison of the spectral data of complexes (**2–4**) reveals that higher energy absorption bands in the range 250–330 nm ( $\pi$ – $\pi^*$  and n– $\pi^*$ ) shift marginally while the longer wavelength visible bands in the range 380–495 nm changes considerably with the solvent. This band may be assigned to metal to ligand charge transfer (MLCT) transitions, [43–47].

The azomethine v(HC=N) stretching frequency (1619 and 1602 cm<sup>-1</sup>) in the free ligand is shifted to lower frequency in the complex (1615 and 1597 cm<sup>-1</sup>) and the phenolic C–O band in the free ligand (1324 cm<sup>-1</sup>) has been shifted to higher frequency in all the complexes (1383–1393 cm<sup>-1</sup>) supporting the coordination through the azomethine v(HC=N) nitrogen and phenoxo oxygen atom respectively [48,49]. The v(O-H) in the ligand (3435 cm<sup>-1</sup>) was absent and the v(C-S) at 745 cm<sup>-1</sup> in the ligand appeared in the range 747–751 cm<sup>-1</sup> in all the complexes signifying the coordination of the thio-benzyl group [30,48,49]. A new band were observed for coordinated and uncoordinated nitrate ion at 1295 cm<sup>-1</sup> (for complex **2**) and 1336 cm<sup>-1</sup> (for complex **4**) respectively [29,50].

The compositions of ligand HL and complex [Co(L)<sub>2</sub>]NO<sub>3</sub> matched well with the C, H, N analytical data and <sup>1</sup>H NMR spectral data. In the <sup>1</sup>H NMR spectrum of the ligand, HL the phenolic –OH at 15.32 ppm appeared as a doublet due to intramolecular hydrogen bonding with imino nitrogen but this signal was disappeared in complex  $[Co(L)_2]NO_3$  indicating the dissociation of phenolic proton upon complexation. On the other hand a doublet band at 9.22 ppm for azomithine HC=N protons was observed due to significant coupling with hydrogen bonded proton on imine nitrogen which in the complex appeared as sharp singlet at 8.77 ppm supporting further the absence of phenolic proton upon complexation. A sharp singlet in the ligand at 4.11 ppm is assigned for benzylic protons CH<sub>2</sub> was appeared as two separate doublets in the complex at 3.75 and 3.83 ppm due to nonequivalent nature of two methylene protons. All the aromatic protons in the ligand appeared as five doublets at 8.07, 7.81, 7.72, 7.40 and 7.25 ppm for six protons, one triplet at 7.52 ppm for one proton and two multiplets in the range 7.11–7.20 ppm, and 7.29–7.36 ppm for eight protons. Whereas in the complex  $[Co(L)_2]NO_3$  the aromatic protons appeared as four doublets at 8.10, 7.46, 6.86 and 6.76 ppm for five protons, four triplets at 6.96, 7.13, 7.61 and 7.71 ppm for seven protons and one multiplet in the range 7.32–7.38 ppm for three protons.

# 3.2.1. *X*-ray structure of **2**

The dimeric molecule **2** assembles on a crystallographically imposed center of inversion forming a bridged dinuclear structure with each copper being five-coordinate in distorted square pyramidal arrangement. In the square pyramid, the basal plane is completed by the coordination of phenolato oxygen atom, imine nitrogen, thioether sulfur from tridentate ligand, acting as a uninegative (O, N, S) donor and oxygen atom of coordinated nitrate ion. A bridging oxygen atom from the second ligand unit occupies the apical position. The structure of **2** is shown in Fig. 3 along with the atom labels. Hydrogen atoms are omitted for the clarity. Selected bond distances and angles are collected in Table 4.

In the complex the Cu···Cu distance between two bridging copper ions through phenoxo oxygen atoms in Cu<sub>2</sub>O<sub>2</sub> core is ~3.19 Å [51,52]. The Cu–O(1) (basal) bond lengths is 1.9363(15) Å while the bond length observed for Cu–O(1\_a) (bridge) is 2.3559(16) Å [52]. The bond distances Cu–S(1) (thioether) and Cu–N(1) (imine nitrogen) in the basal plane are 2.3692(7) and 1.9291(18) Å, respectively [30,49]. The angles in Cu<sub>2</sub>O<sub>2</sub> core are O(1\_a)–Cu–O(1), 86.54(6); Cu–O(1)–Cu(\_a), 93.46(6). Probably due to Jahn–Teller distortion of square pyramidal copper(II) the observed bond distances and bond are near or far from expected values [50,51].



Fig. 3. Molecular structure of [Cu<sub>2</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>], 2 with atom numbering scheme. Hydrogen atoms are omitted for clarity.

| Table 4  |  |
|--|--|
| Selected bond distances (Å) and angles (°) for compound <b>2</b> . |  |

| Distances  |            |            |            |
|------------|------------|------------|------------|
| Cu-S1      | 2.3692(7)  | S1-C17     | 1.773(2)   |
| Cu-01      | 1.9363(15) | S1-C18     | 1.844(3)   |
| Cu-02      | 1.9608(17) | 01-C1      | 1.317(3)   |
| Cu-03      | 2.731(2)   | 02-N2      | 1.273(3)   |
| Cu-N1      | 1.9291(18) | 03-N2      | 1.227(3)   |
| Cu-01_a    | 2.3559(16) | N1-C11     | 1.304(3)   |
| 04-N2      | 1.232(3)   | N1-C12     | 1.407(3)   |
| Angles     |            |            |            |
| S1-Cu-O1   | 174.26(5)  | S1-Cu-O2   | 94.30(5)   |
| S1-Cu-O1_a | 94.01(4)   | S1-Cu-N1   | 84.85(6)   |
| 01-Cu-02   | 91.43(7)   | 01-Cu-N1   | 89.43(7)   |
| C17-S1-C18 | 102.45(11) | Cu-01-C1   | 122.60(13) |
| Cu-S1-C17  | 92.91(9)   | C11-N1-C12 | 120.45(19) |
| 01-Cu-01_a | 86.54(6)   | 02-Cu-N1   | 179.07(7)  |
| 01_a-Cu-02 | 88.04(6)   | 01_a-Cu-N1 | 91.66(6)   |
| Cu-O1-Cu_a | 93.46(6)   | Cu_a-01-C1 | 121.22(12) |



Fig. 4. Molecular structure of  $[Ni(L)_2]$ , 3 with atom numbering scheme. Hydrogen atoms are omitted for clarity.

| Table 5                 |                                 |      |
|-------------------------|---------------------------------|------|
| Selected bond distances | (Å) and angles (°) for compound | i 3. |

| Distances |            |            |            |
|-----------|------------|------------|------------|
| Ni-S1     | 2.4416(7)  | S1-C17     | 1.774(2)   |
| Ni-S2     | 2.5309(6)  | S1-C18     | 1.833(2)   |
| Ni-01     | 1.9916(17) | S2-C41     | 1.777(2)   |
| Ni-02     | 2.0006(15) | S2-C42     | 1.830(2)   |
| Ni-N1     | 2.0162(15) | N2-C36     | 1.418(3)   |
| Ni-N2     | 2.0243(17) | N2-C35     | 1.300(3)   |
| 01-C1     | 1.288(3)   | 02-C25     | 1.289(2)   |
| N1-C11    | 1.308(3)   | N1-C12     | 1.419(3)   |
| Angles    |            |            |            |
| S1-Ni-S2  | 91.04(2)   | S1-Ni-N2   | 91.17(6)   |
| S1-Ni-O1  | 172.58(4)  | S2-Ni-01   | 84.39(5)   |
| S1-Ni-O2  | 92.49(5)   | S2-Ni-02   | 167.14(4)  |
| S1-Ni-N1  | 83.77(6)   | S2-Ni-N1   | 96.22(5)   |
| 01-Ni-N1  | 90.91(7)   | 01-Ni-02   | 93.25(7)   |
| N1-Ni-N2  | 173.28(8)  | Ni-S1-C17  | 95.31(8)   |
| Ni-S1-C18 | 107.46(8)  | C17-S1-C18 | 100.16(10) |
| 01-Ni-N2  | 93.72(7)   | 02-Ni-N1   | 96.45(6)   |
| 02-Ni-N2  | 88.16(6)   | S2-Ni-N2   | 79.40(5)   |
|           |            |            |            |



**Fig. 5.** Emission spectra of  $(8.39 \times 10^{-4} \text{ M})$  solution of ligand HL (–), complex 2 (\_\_\_\_\_), complex 3 (\_\_\_\_\_) and complex 4 (\_\_\_\_\_) in acetonitrile-chloroform mixed solvent(v/v, 1:1) at 390 nm.

#### 3.2.2. X-ray structure of 3

A perspective view of the molecule has been shown in Fig. 4 and selected bond distances and angles are collected in Table 5. The geometry about nickel is distorted octahedral, where the ligand (HL) dissociating one phenolic proton binds meridionally in mono anionic (L<sup>-</sup>) tridentate (O, N, S) fashion forming the *bis* chelate. The Ni(II) center is coordinated by two phenoxo oxygens [O(1) and O(2)], two imine nitrogens [N(1) and N(2)], and two thoiether sulfur [S(1) and S(2)]. The relative orientations within the pairs of phenoxo oxygen, imine nitrogen, and thioether sulfur are *cis*, *trans* and *cis* respectively.

The averages of Ni–N(imine) and Ni–O(phenoxo) bond distances (2.01 and 2.0 Å, respectively) are within the normal range [29,31]. The Ni–S2(thioether) length is longer (2.53 Å) than that of other Ni–S1(thioether) (2.44 Å) bond. The azomethine bond distances (N(1)–C(11) and N(2)–C(35) ~1.30 Å) and the bite angles around Ni(II) are (O(1)–Ni–N(1), 90.91(7); N(1)–Ni–S(1), 83.77(6); O(2)–Ni–N(2), 88.16(6) and N(2)–Ni–S(2), 79.40(5) Å) in the normal range [29,31].

# 3.3. Fluorescence

The  $\pi$ -conjugated naphthyl chromophore containing ligand, HL  $(8.93 \times 10^{-4} \text{ M})$  upon excitation at 390 nm exhibited emission maxima at 499 nm in acetonitrile-chloroform (v/v, 1:1) mixed solvent solution. In comparison,  $8.93 \times 10^{-4}$  M solution of Cu(II) complex,  $[Cu_2(L)_2(NO_3)_2]$  **2** and Co(III) complex,  $[Co(L)_2](NO_3)]$  **4** in acetonitrile-chloroform (v/v, 1:1) mixed solvent exhibited marked quenching of emission at 487 and 527 nm, respectively compared to ligand HL. On the other hand, the Ni-complex, [Ni(L)<sub>2</sub>] **3** showed a reverse change with respect to the Cu- and Co-complexes. Upon excitation of the Ni-complex (8.93  $\times$  10<sup>-4</sup> M) at 390 nm in acetonitrile-chloroform (v/v, 1:1) solvent an increase in emission at 505 nm is observed although the increment is not too large compared to the ligand. To our opinion, the increase in emission of Ni(II) complex can be attributed to chelation-enhanced fluorescence (CHEF) [53,54]. On contrary, under identical condition the decrease in emission for Cu(II) and Co(III) complexes can be ascribed as "heavy atom effect" [55,56]. The "heavy atom effect" causes the quenching through two well-defined mechanisms either naphthyl→metal energy transfer (ET) or metal→naphthyl electron transfer (et) [53,54] (Fig. 5).



Fig. 6. CV of ligand HL (-), complex 2 (\_\_\_\_\_), 3 (\_\_\_\_\_) and 4 (\_\_\_\_\_) in dichloromethane vs. SCE at 50 mV/s scan rate.

# 3.4. Electrochemistry

The electrochemical behavior of ligand HL and complexes  $[Cu_2(L)_2(NO_3)_2]$  **2**,  $[Ni(L)_2]$  **3** and  $[Co(L)_2](NO_3)$  **4**, were investigated in dichloromethane solvent (0.1 M TBAP) by cyclic voltammetry with a variable scan rate of 50, 75, 100 and 150 mV s<sup>-1</sup> vs. SCE. The full scan cyclic voltammogram of ligand HL and complexes  $[Cu_2(L)_2(NO_3)_2]$  **2**,  $[Ni(L)_2]$  **3** and  $[Co(L)_2](NO_3)$  **4**, with scan rate 50 mV s<sup>-1</sup> vs. SCE is shown as representative one. The other spectra are given in Supplementary Figs. S10–S13. The cyclic voltammograms of complexes **2–4** do not undergo significant variation upon several scan rate measurements and exhibited one

electron quasi-reversible oxidative responses with the  $E_{1/2}$  at 1.36, 0.89 and 1.33 V, respectively versus SCE [57,58]. The oxidation has been assigned according to the couple of Eqs. (1)–(3). The cyclic voltammogram of ligand HL and complexes **2–4** are shown in Fig. 6.

$$[\operatorname{Cu}(\mathrm{L})(\mathrm{NO}_3)] = [\operatorname{Cu}(\mathrm{L})(\mathrm{NO}_3)]^+$$
(1)

$$[Ni(L)_2] = [Ni(L)_2]^+$$
(2)

$$[\operatorname{Co}(L)_2]^+ = [\operatorname{Co}(L)_2]^{2+}$$
(3)



Fig. 7. Surface plot of  $[Cu_2(L)_2(NO_3)_2]$  2, and  $[Ni(L)_2]$  3.

#### Table 6

Oxidation of alcohols catalyzed by [Cu<sub>2</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] in acetonitrile solvent<sup>a</sup>.

| Entry  |                      | H <sub>2</sub> O <sub>2</sub> (50%) (mL) | Time (h) | Yield (%) |
|--------|----------------------|--|----------|-----------|
| ОН     | CHO                  | 5  | 2        | 90        |
| ОН     | СНО                  | 5  | 2        | 85        |
| О2N    | O <sub>2</sub> N CHO | 5  | 2        | 88        |
| МеО ОН | MeO                  | 5  | 2        | 80        |
| СІ     | СНО                  | 5  | 2        | 83        |
| Н3С ОН | H <sub>3</sub> C CHO | 5  | 2        | 80        |

<sup>a</sup> Reaction conditions: catalyst (0.002 mmol), substrate (5 mmol), temperature (80 °C).

To gain further insight into the electron transfer processes the nature of the frontier orbitals (HOMO; Fig. 6a and LUMO; Fig. 6b) was assessed theoretically employing single point DFT calculations using the crystallographic coordinates of  $[Cu_2(L)_2(NO_3)_2]$  **2**, and  $[Ni(L)_2]$  **3**, no optimization was carried out. From the orbital diagrams it appears that the HOMO of **2** and **3** are metal orbital while the LUMO of **2** and **3** are metal–ligand mixed centered. The metal centered oxidative response is consistent with the nature of HOMO (Figs. 6a and 7).

# 3.5. Oxidation of benzyl alcohols

Metal catalysed oxidation of various organic substrates to their corresponding oxidized products is important in organic chemistry because of academic and industrial relevance [59–64]. Copper catalysed oxidation of alcohol, alkene, alkane etc. have drawn much attention in current chemical research [59–64]. Consistent with the other studies [59–64] in the present work the  $[Cu_2(L)_2(NO_3)_2]$  complexes were capable of oxidizing benzyl alcohol and its derivatives into corresponding aldehydes in good yield. The oxidation reactions were carried out at atmospheric pressure with H<sub>2</sub>O<sub>2</sub> (50%) and catalytic amount of  $[Cu_2(L)_2(NO_3)_2]$  in acetonitrile solvent (Table 6 and Eq. (4)). In order to find out the optimized condition for the oxidation process, benzyl alcohol oxidation was studied in different reaction condition. In presence of 4 mol% catalyst, H<sub>2</sub>O<sub>2</sub> as oxidant and 10 ml acetonitrile at 80°C for 2 h the best yield of benzaldehyde (90%) was obtained after the oxidation of benzylalcohol. At the end of reaction we could not isolate the unreacted benzvlalcohol. At room temperature the vield of the reaction was very low (10%). A blank reaction was also performed in absence of catalyst which also gives very low yield of oxidation product. The oxidation reaction was also carried out in presence of Cu(CH<sub>3</sub>COO)<sub>2</sub>. H<sub>2</sub>O, the yield of the benzaldehyde was 30%. However at the end of the reaction the green coloured catalyst was changed to brown. The results of other oxidation reactions are given in Table 6.



 $R = H, I, OMe, NO_2, Cl, CH_3$ 

# 4. Conclusion

In conclusion, the newly designed ligand HL and its corresponding complexes of Cu(II), Ni(II) and Co(III) have been prepared with a  $\pi$ -conjugated naphthyl moiety in the ligand framework. Single crystal X-ray diffraction studies on [Cu<sub>2</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] confirmed that this complex consisted of centrosymmetric binuclear entities containing square-pyramidal copper(II) ions bridged through the phenoxo oxygen atoms whereas [Ni(L)<sub>2</sub>] complex is distorted octahedral where ligand form bis chelate. The redox property and emission behaviour of the ligand and complexes were studied. Luminescence properties of the ligand and its corresponding metal (M = Cu(II)/ Ni(II)/Co(III)) complexes are discussed considering 'Chelation Enhanced Fluorescence' and 'heavy atom effect'. The activity of the binuclear Cu(II) complex as catalyst toward the oxidation of benzyl alcohol derivatives to corresponding benzaldehydes were tested in presence of H<sub>2</sub>O<sub>2</sub> as oxidant under atmospheric condition.

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# Appendix A. Supplementary material

CCDC 968205 and 968206 contain the supplementary crystallographic data for compounds C<sub>48</sub>H<sub>36</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub> **2** and C<sub>48</sub>H<sub>36</sub>N<sub>2</sub>NiO<sub>2</sub> S<sub>2</sub> **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data\_request/cif. Figs. S1–S3 shows the UV-Vis spectra of compounds **1**, **3** and **4**, Figs. S4–S7 show the IR spectra, Figs. S8–S9 <sup>1</sup>H NMR spectra of the ligand HL and complex C<sub>48</sub>H<sub>36</sub>N<sub>3</sub>CoO<sub>5</sub>S<sub>2</sub> **4** and Figs. S10–S13 show the CV plot of compounds **1–4** respectively. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.04.021.

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