



# Synthesis and spectroscopic studies of homo-binuclear, alkoxo bridged homo- and hetero-tetranuclear metal complexes of a bis-N<sub>2</sub>O<sub>4</sub> Schiff base ligand derived from ethanolamine and macroacyclic tetranaphthaldehyde

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## ABSTRACT

Three new homo-binuclear Ni(II), Cu(II), Zn(II) complexes (**2–4**), homo-tetranuclear Cu(II) complex (**5**), and hetero-tetranuclear Cu(II)–Ni(II) complex (**6**) of a macroacyclic potentially bis-hexadentate N<sub>2</sub>O<sub>4</sub> Schiff base have been synthesized. The imino-alcohol ligand, H<sub>4</sub>L was obtained by the condensation of ethanolamine with 2,2'-[2,3-bis(1-formyl-2-naphthyloxymethyl)-but-2-ene-1,4-diylidioxy]bis(naphthalene-1-carbaldehyde). The structures of both the Schiff base and its complexes have been proposed by elemental analyses, spectroscopic data i.e. IR, <sup>1</sup>H and <sup>13</sup>C NMR, UV–vis, electrospray ionisation mass spectra, molar conductivities and magnetic susceptibility measurements. The ligand has two similar compartments to bind first primary two metal ions, and acts bi- or tetra-negative, bis-tetradentate forming five membered chelate ring. However, secondary two metal ions (either Cu<sup>2+</sup> or Ni<sup>2+</sup>) are ligated with dianionic oxygen atoms of the alcohol groups and are linked to the 1,10-phenanthroline-nitrogen atoms in the tetranuclear complexes (**5** and **6**).

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## 1. Introduction

Schiff bases and the relevant transition metal complexes have great interest in coordination chemistry although this subject has been extensively studied [1]. These compounds exhibit biological activity as antiviral [2], antitumour [3], antibiotics [4], antifungal [5], antimicrobial [6] and anticancer [7] agents because of their specific structures and they have attracted much interest in recent years due to their significance in the development of new therapeutic agents [8]. In this aspect, 2-hydroxy-1-naphthaldehyde derivatives with amines have been extensively studied [9]. There are few reported Schiff base ligands derived from ethanolamine [10] and these ligands can form various kinds of polynuclear complex due to the property of terminal oxygens acting as good bridging groups. Accordingly, the design of such ligands is highly effective for establishing simple synthesis of new metal-assembled complexes. The variation of magnetic properties in these complexes was attributed to the diversity in the bonding modes of the bridging ligands and their orientation with respect to the paramagnetic centers. Designing these materials is becoming an interesting area in the field of material sciences.

The development of the field of bioinorganic chemistry has increased interest in Schiff base complexes since many of these di- and tetranuclear complexes may serve as models for biologically important species [11–13].

This work describes the synthesis and characterization of a novel macroacyclic Schiff base derived from ethanol amine and 2,2'-[2,3-bis(1-formyl-2-naphthyloxymethyl)-but-2-ene-1,4-diylidioxy]bis(naphthalene-1-carbaldehyde), its homo-binuclear Ni(II), Cu(II) and Zn(II) complexes, homo-tetranuclear Cu(II) and hetero-tetranuclear Cu(II)–Ni(II) complexes by elemental analysis, spectroscopic data, i.e. IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR, UV–vis, electrospray ionisation mass spectra, molar conductivities and magnetic susceptibility measurements. A detailed assignment of the spectra and the electrochemical behavior were proposed.

## 2. Experimental

### 2.1. Physical measurements

Melting points (m.p.) were determined on a Barnstead/Electrothermal 9100 apparatus in open capillary tubes. IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrophotometer as KBr pellets. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 200 and Varian Mercury 400 spectrometer using chloroform-d<sub>1</sub> solvent at Department of

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Chemistry, Karadeniz Technical University, Trabzon and Ataturk University, Erzurum, respectively. Chemical shifts ( $\delta$ ) are reported in part per million (ppm) relative to an internal standard of Me<sub>4</sub>Si. A Shimadzu 1601-PC UV/vis spectrophotometer was used to record the electronic spectra. Room temperature (296 K) solid state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance. MnCl<sub>2</sub>·6H<sub>2</sub>O was used as the standard. Elemental analyses were determined on a Costech 4010 CHNS instrument. Metal containings of the complexes were determined by Spectro Genesis Optical emission spectrometer with inductively coupled plasma excitation (ICP) and electrospray ionisation mass spectrometry (ESI-MS) was performed on a Micromass Quattro LC-MS/MS spectrometer at Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey. Solution electrical conductivities were measured at room temperature (r.t.) with approximately 10<sup>-3</sup> M DMF solutions, with a Hanna EC 215 conductivity meter by using 0.01 M KCl water solution as calibrant.

## 2.2. Materials

The perchlorate salts of Ni(II), Zn(II), and Cu(II), ethanol amine and 1,10-phenanthroline monohydrate were purchased from Merck, Germany. 2,2'-[2,3-bis(1-formyl-2-naphthylxymethyl)-but-2-ene-1,4-diylidioxo]bis(naphthalene-1-carbaldehyde) was synthesized according to the procedure [14]. Organic solvents were reagent grade chemicals.

**Caution!** Perchlorates and perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

### 2.3. Synthesis of 2-{[2-(4-{1-[(2-hydroxy-ethylimino)-methyl]-naphthalen-2-yloxy)-2,3-bis-{1-[(2-hydroxy-ethylimino)-methyl]-naphthalen-2-yloxymethyl}-but-2-enyloxy)-naphthalen-1-ylmethylene]-amino}-ethanol, H<sub>4</sub>L, (**1**) (yield 65%, color: white, m.p.: 179 °C)

An ethanolic suspension (100 mL) of 2,2'-[2,3-bis(1-formyl-2-naphthylxymethyl)-but-2-ene-1,4-diylidioxo]bis(naphthalene-1-carbaldehyde) (1.0 g, 1.31 mmol) was mixed with ethanol amine (0.32 cm<sup>3</sup>, 5.24 mmol). The resulting mixture was stirred at r.t. for 10 days then refluxed 6 h. Reaction was monitored by IR. White crystalline solid Schiff base ligand was filtered then washed with cold ethanol and diethyl ether several times, dried over P<sub>2</sub>O<sub>5</sub> in vacuo. Analytical and physical data; C<sub>58</sub>H<sub>56</sub>N<sub>4</sub>O<sub>8</sub>; C, 74.18; H, 6.18; N, 5.98. Calculated C, 74.34; H, 6.02; N, 5.98. UV-vis (DMF)  $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 362 (3005); 330 (3147); 309 (3148); 297 (2996). IR (cm<sup>-1</sup>): 3435  $\nu$ (OH); 1618, 1598  $\nu$ (C=C); 1644  $\nu$ (C=N); 1235, 1219  $\nu$ (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.610 (bs, 4H, -OH), 3.411, 3.423, 3.435 (t, 8H, -CH<sub>2</sub>-N=C), 3.659, 3.673, 3.685 (t, 8H, -CH<sub>2</sub>-OH), 5.109 (s, 8H, -OCH<sub>2</sub>-), 7.266, 7.289 (d, 4H, Ar<sub>(C4)</sub>-H), 7.369, 7.389, 7.408 (t, 4H, Ar<sub>(C8)</sub>-H), 7.495, 7.516, 7.537 (t, 4H, Ar<sub>(C9)</sub>-H), 7.538, 7.758 (d, 4H, Ar<sub>(C7)</sub>-H), 7.812, 7.835 (d, 4H, Ar<sub>(C5)</sub>-H), 8.862, 8.884 (d, 4H, Ar<sub>(C10)</sub>-H), 8.782 (s, 4H, -HC=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 62.224 C<sub>14</sub>; 64.813 C<sub>15</sub>; 67.135 C<sub>2</sub>; 114.300 C<sub>12</sub>; 124.828 C<sub>4</sub>; 125.564 C<sub>8,9</sub>; 128.365 C<sub>6</sub>; 128.411 C<sub>7</sub>; 129.815 C<sub>9</sub>; 132.145 C<sub>5</sub>; 132.790 C<sub>1</sub>; 156.517 C<sub>3</sub>; 160.600 C<sub>13</sub>. MS(ESI-*m/z*): 937 (32.35%) [M]<sup>+</sup>.

## 2.4. Synthesis of homo-binuclear complexes (**2-4**)

Complexes **3** and **4** were synthesized following the same procedure adopted for complex **2** using Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1185 g, 0.32 mmol) and Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1192 g, 0.32 mmol), respectively instead of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

### 2.4.1. Preparation of [Ni<sub>2</sub>(H<sub>2</sub>L)](ClO<sub>4</sub>)<sub>2</sub>, (**2**) (yield 92%, color: light green, dec.: 239 °C)

The Schiff base (0.15 g, 0.16 mmol) was dissolved in CHCl<sub>3</sub> (30 cm<sup>3</sup>) and pH of the solution was measured. A solution of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1170 g, 0.32 mmol) in 10 cm<sup>3</sup> EtOH was added to the hot solution (60 °C) of Schiff base. The resulting mixture was boiled under reflux for 6 h. The mixture was stirred for overnight at r.t. and a decrease in the pH of the mixture was observed. The solid products were collected by filtration, washed with water, ethyl alcohol, diethyl ether, respectively and dried over silica gel in vacuo. Analytical and physical data; C<sub>58</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>16</sub>; C, 54.98; H, 4.24; N, 4.37; Ni, 9.27. Calculated C, 55.67; H, 4.35; N, 4.48; Ni, 9.38. UV-vis (DMF)  $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 375 (1819); 362 (2337); 351 (2312); 326 (2479); 298 (2340). IR (cm<sup>-1</sup>): 3429  $\nu$ (OH); 1622, 1587  $\nu$ (C=C); 1649  $\nu$ (C=N); 1239 (C-O); 1141, 1107, 1092, 625  $\nu$ (ClO<sub>4</sub>)<sup>-</sup>. Molar conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) 177.  $\mu_{\text{eff}}$  B.M. (298 K): 2.08 (for per metal ion); MS(ESI-*m/z*): 1052 (9.85%) [M-2ClO<sub>4</sub>]<sup>+</sup>.

### 2.4.2. Preparation of [Cu<sub>2</sub>(H<sub>2</sub>L)](ClO<sub>4</sub>)<sub>2</sub>, (**3**) (yield 89%, color: green, dec.: 190 °C)

Analytical and physical data; C<sub>58</sub>H<sub>54</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>16</sub>; C, 55.0; H, 4.14; N, 4.56; Cu, 9.83. Calculated C, 55.24; H, 4.32; N, 4.44; Cu, 10.08. UV-vis (DMF)  $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 662 (101); 399 (2657); 362 (3100); 326 (3385); 296 (3197). IR (cm<sup>-1</sup>): 3422  $\nu$ (OH); 1623, 1590  $\nu$ (C=C); 1644  $\nu$ (C=N); 1237(C-O); 1144, 1110, 1090, 626  $\nu$ (ClO<sub>4</sub>)<sup>-</sup>. Molar conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) 169.  $\mu_{\text{eff}}$  B.M. (298 K): 1.44 (for per metal ion); MS(ESI-*m/z*): 1262 (18.15%) [M+1]<sup>+</sup>.

### 2.4.3. Preparation of [Zn<sub>2</sub>(L)], (**4**) (yield 71%, color: white, dec.: 230 °C)

Analytical and physical data; C<sub>58</sub>H<sub>52</sub>N<sub>4</sub>O<sub>8</sub>Zn<sub>2</sub>; C, 65.34; H, 4.68; N, 4.96; Zn, 12.32. Calculated C, 65.48; H, 4.93; N, 5.27; Zn, 12.29. UV-vis (DMF)  $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 386 (2143); 362 (2447); 322 (2623); 281 (2409). IR (cm<sup>-1</sup>): 1619, 1590  $\nu$ (C=C); 1672  $\nu$ (C=N); 1235  $\nu$ (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 5.398 (s, 8H, -OCH<sub>2</sub>-), 7.376, 7.408, 7.446 (t, 4H, Ar<sub>(C8)</sub>-H), 7.524, 7.561, 7.598 (t, 4H, Ar<sub>(C9)</sub>-H), 7.683, 7.730 (d, 4H, Ar<sub>(C4)</sub>-H), 7.856, 7.896 (d, 4H, Ar<sub>(C7)</sub>-H), 8.190, 8.235 (d, 4H, Ar<sub>(C5)</sub>-H), 8.930, 8.972 (d, 4H, Ar<sub>(C10)</sub>-H), 10.628 (s, 4H, -HC=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 55.89 C<sub>15</sub>; 55.99 C<sub>14</sub>; 66.62 C<sub>2</sub>; 114.87 C<sub>12</sub>; 115.56 C<sub>4</sub>; 123.94 C<sub>10</sub>; 128.27 C<sub>8</sub>; 128.48 C<sub>7</sub>; 129.61 C<sub>6</sub>; 130.53 C<sub>9</sub>; 135.40 C<sub>5</sub>; 137.64 C<sub>1</sub>; 162.94 C<sub>3</sub>; 190.83 C<sub>13</sub>. Molar conductivity ( $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) 0.8.  $\mu_{\text{eff}}$  B.M. (298 K): diamagnetic; MS(ESI-*m/z*): 1101.12 (9.18%) [M+K]<sup>+</sup>.

## 2.5. Synthesis of homo- and hetero-tetranuclear complexes (**5, 6**)

Complex **6** was synthesized following the same procedure adopted for complex **5** using Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (183 mg, 0.5 mmol) instead of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and 1.0 mmol 1,10-phenanthroline monohydrate instead of 0.5 mmol.

### 2.5.1. Synthesis of [Cu<sub>4</sub>(L)phen<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub>, (**5**) (yield 30%, color: turquoise, dec.: 266 °C)

Solid NaOEt (34 mg, 0.5 mmol) was added to the hot solution of [Cu<sub>2</sub>(H<sub>2</sub>L)](ClO<sub>4</sub>)<sub>2</sub>, (**3**) (315 mg, 0.25 mmol) in EtOH (20 cm<sup>3</sup>) and the solution was refluxed for 2 h. Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (185 mg, 0.5 mmol) in EtOH (10 cm<sup>3</sup>) was added to the reaction solution and the mixture was stirred for 30 min and then a solution of 1,10-phenanthroline monohydrate (100 mg; 0.5 mmol) in EtOH (10 cm<sup>3</sup>) was added. The mixture was stirred for 6 h under reflux and the mixture stirred for overnight at r.t. and the resulting precipitate was filtered off, washed successively with water, ethyl alcohol and diethyl ether, respectively and dried over silica gel in vacuo. Analytical and physical data; C<sub>82</sub>H<sub>68</sub>Cl<sub>4</sub>Cu<sub>4</sub>N<sub>8</sub>O<sub>24</sub>; C, 50.14;

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