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# Synthesis, characterization, electrochemical properties and conversions of carbon dioxide to cyclic carbonates mononuclear and multinuclear oxime complexes using as catalyst

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#### 1. Introduction

#### ABSTRACT

Unsymmetrical dioxime ligand and its mono- and multinuclear metal complexes were synthesized and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra, FT-IR, UV–Vis, elemental analysis, melting point measurements, LC–MS spectroscopy, molar conductivity measurements and magnetic susceptibility and cyclic voltammetry techniques. We firstly prepared new unsymmetrical dioxime ligand (1) and its monnuclear [Ni(dioxime)<sub>2</sub>] complex (2). Then, the intramolecular  $O-H\cdots O$  bridges are replaced with Cu(II)(N–N) complex to synthesize multinuclear [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N–N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> oxime complexes (3–7) where N–N = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 3,3'-dicarboxy-2,2'-bipyridine (dcbpy), 4,5-diazafluoren-9-one (dafo) and 1,10-phenanthroline-5,6-dione (dione). The mononuclear complex [Ni(dioxime)<sub>2</sub>] (2) was used as a precursor for building multinuclear oxime complexes (3–7). In this paper, our goal is to study spectroscopic, electrochemical and catalytic properties of this new ligand and its metal complexes.

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The coupling reaction of carbon dioxide (CO<sub>2</sub>) with epoxides using different metal complexes as catalyst has intensively been studied in recent decades as one of the most promising processes for fixation of CO<sub>2</sub> [1–6]. The carbon dioxide fixation has received much attention in last decades, since carbon dioxide is the most inexpensive and infinite carbon resource [7,8]. A majority of these studies has involved the reaction of CO<sub>2</sub> with epoxides to generate polycarbonates and/or cyclic carbonates. Cyclic carbonates are being used industrially as polar aprotic solvent, substrate for small molecule synthesis, additive, anti-foam agent for antifreeze, and plasticizer [9,10]. For metal complex catalysts, salen-type metal complexes have been of significant interest in conjunction with Lewis base or organic salts as co-catalysts [11-13]. The most prominent advantages of these metal complexes are easy synthesis and excellent stability against moisture and air [14-18]. To the best of our knowledge, so far there is no literature report that uses mono- and multinuclear oxime metal complexes as a catalyst for coupling reaction of carbon dioxide (CO<sub>2</sub>) with epoxides. The dioxime ligands and their mono and multinuclear complexes have been studied for a long time as medicine [19–21], catalysis [22–24], electro optical sensors [25], liquid crystals [26], trace metal analysis [27] and hydrogen production from water as catalyst [28–30].

In the structure of multinuclear metal complexes, the Ni(II) ion is centered into the main oxime core by the coordination of the imino groups while the two Cu(II) ions are coordinated as dianionic oxygen donors of the oxime groups, and linked to the ligands such as 2,2'-bipyridine, 1,10-phenanthroline, 3,3'-dicarboxy-2,2'-bipyridine, 4,5-diazafluoren-9-one and 1,10-phenanthroline-5,6-dione. The development of new efficient catalysts that can be easily prepared, recovered and reused without losing their activities has received much attention from a practical and environmental point of view [31]. In this study, Unsymmetrical dioxime ligand and its mono- and multinuclear metal complexes were synthesized and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra, FT-IR, UV–Vis, elemental analysis, melting point measurements, LC-MS spectroscopy, molar conductivity measurements, magnetic susceptibility techniques and cyclic voltammetry techniques. The aim of this study is to investigate spectroscopic, electrochemical and catalytic properties of the new ligand and its metal complexes. The best of our knowledge, we have herein for the first time reported novel catalysts of mono- and multinuclear oxime metal complexes in conjunction



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with [bmim]PF<sub>6</sub> or other Lewis bases for the conversion of  $CO_2$  to cyclic carbonates.

# 2. Experimental

#### 2.1. Materials and measurements

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. <sup>1</sup>H NMR spectra were recorded on a Varian AS-400 MHz instrument at room temperature for catalytic measurements. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer for spectroscopic characterization. FT-IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR Spectrometer by KBr pellets in the wavenumber range of 4000–400 cm<sup>-1</sup>. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using Hg[Co(SCN)<sub>4</sub>] as a calibrant; diamagnetic corrections were calculated from Pascal's constants [32,33]. Electronic spectral studies were conducted on a Perkin-Elmer model Lambda 25 UV-Vis spectrophotometer in the wavelength range from 200 to 1100 nm. Melting points were measured in open capillary tubes with an Electrothermal 9100 melting point apparatus and were uncorrected. Molar conductivities  $(\Lambda_M)$  were recorded on an Inolab Terminal 740 WTW Series. Mass Spectra results were recorded on an Agilent LC/MSD LC-MS/MS spectrometer. Cyclic voltammetric (CV) measurements were carried out with an instrument (Princeton Applied Research Model 2263 potentiostat controlled by an external PC, using the computer program, Power CV) utilizing a three electrode configuration at 25 °C. A platinum wire served as the counter electrode. Ag/AgCl electrode was employed as the reference electrode. The working electrode was a platinum plate with an area of 0.2 cm<sup>2</sup>. The working electrode was polished with Al<sub>2</sub>O<sub>3</sub> prior to each experiment. Throughout the experiment, oxygen free nitrogen was bubbled through the solution for 10 min. Electrochemical grade tetrabutylammoniumperchlorate (TBAP)  $(0.1 \text{ mol } \text{dm}^{-3})$  was employed as the supporting electrode. Origin 7.5 graphing program was used to evaluate Power CV data, to draw voltammograms and analyze them. Catalytic tests were performed in a PARR 4843 50 mL stainless pressure reactor. 4,5-Diazafluoren-9-one (dafo) [34], 3,3'-dicarboxy-2,2'-bipyridine (dcbpy) [35] and 1,10-phenanthroline-5,6-dione [36] were prepared according to the literature procedures.

# 2.2. Synthesis of the ligand $(LH_2)$ (1)

The unsymmetrical ligand (LH<sub>2</sub>) was synthesized following the procedure with some modifications [37,38]. Sodium metal (0.8 g, 35 mmol) was dissolved in absolute ethanol (150 mL) at  $-5 \,^{\circ}\text{C}$  temperature. Followed by addition *n*-butyl nitrite (3.2 g, 31 mmol), the mixture was cooled to room temperature and kept at this temperature. To this solution, 4-ethyl acetophenone (0.4 g, 31 mmol) was added dropwise under N<sub>2</sub> atmosphere with continuous stirring during 1 h. The mixture was stirred for more than 2 h, and the temperature was raised to 20 °C. Then, the mixture was left to precipitate up to 2 days. The red-yellow precipitate was collected by vacuum filtration. The product was washed three times with diethyl ether. The collected product was dissolved in a little water, and precipitated by adding acetic acid dropwise. The yellow product was washed with water and recrystallized from EtOH/H<sub>2</sub>O (1:2). Then, hydroxylamine hydrochloride (1.1 g, 15 mmol) was dissolved in absolute ethanol (70 mL) at room temperature. To this solution, sodium acetate (2.2 g, 15 mmol) was added portionwise with continuous stirring

under Ar atmosphere. Followed by the addition of the yellow product (2.7 g, 15 mmol) synthesized in the first step to the solution. The stirred mixture was then heated to the reflux temperature for 4 h. The mixture was stirred for 1 h at room temperature and the precipitation formed after 30 min. The solvent was slowly evaporated at room temperature, and pale yellow crystals were obtained from EtOH/H<sub>2</sub>O (1:2). After filtration, the crystals were washed with EtOH and diethylether. Then, the crystals were dried under vacuum. Color: pale yellow, yield (%): 77, mp: 112 °C, Anal. Calc. for [C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>] (F.W: 192 g/ mol): C, 62.50; H, 6.25; N, 14.58. Found: C, 62.48; H, 6.28; N, 14.52%. FT-IR (KBr pellets, *v*<sub>max</sub>/cm<sup>-1</sup>): 3505–3102 *v*(O–H), 3025 v(Ar-CH), 2966-2871 v(Aliph-CH), 1609 v(C=N), 1461-1405 v(C=C), and 1285 v(N-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, TMS, 300 MHz,  $\delta$  ppm): 11.86 (d, 2H, OH, J = 8.7 Hz), 11.69 and 11.47 (s. 2H. OH) for cis/trans-isomer. 8.48 and 7.88 (s. 1H. HC=N) for cis/trans-isomer, 7.49 (d, 2H, J = 8.1 Hz, Ar-CH), 7.23 (d, 2H, J = 7.4 Hz, Ar–CH), 2.70–2.58 (q, 2H, CH<sub>3</sub>–CH<sub>2</sub>), 1.19 (t, 3H, J = 15 Hz; CH<sub>3</sub>–CH<sub>2</sub>), <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, TMS, 75 MHz,  $\delta$  ppm): C<sub>1</sub>(151.26 and 145.02), C<sub>2</sub>(153.48 and 148.46), C<sub>3</sub>(131.95), C<sub>4</sub>(129.48 and 127.74), C<sub>5</sub>(128.96 and 127.38), C<sub>6</sub>(141.28), C<sub>7</sub>(28.53 and 28.43), and C<sub>8</sub>(16.06 and 16.00). UV-Vis ( $\lambda_{max}$ , nm, \* = shoulder peak): 233 and (in CH<sub>3</sub>OH); 270 (in DMSO). LC-MS (Scan ES<sup>+</sup>): *m*/*z* (%) 192.2 (100) [M]<sup>+</sup>, 148.3 (45) [M-CH=N-OH]<sup>+</sup>, and 122.1 (5) [M-C<sub>8</sub>H<sub>9</sub>]<sup>+</sup>.

# 2.3. Synthesis of mononuclear $[Ni(dioxime)_2]$ (2) complex

A solution of ligand  $(LH_2)$  (3.0 g, 15.6 mmol) in absolute ethanol (50 mL) dissolved at room temperature and then NiCl<sub>2</sub>·6H<sub>2</sub>O (1.9 g, 7.8 mmol) dissolved in absolute ethanol (30 mL) was added by syringe and the solution turned red. Nitrogen was bubbled through the resulting red solution for 30 min. Then, a decrease in pH of the solution was observed. The pH of the solution was ca. 1.5-3.0 and was adjusted to 4.5-5.5 by the addition of 1% NaOH solution in EtOH. After refluxing the mixture for 5 h in a water bath, the precipitate was filtered off: washed with H<sub>2</sub>O and diethyl ether several times, and then dried in vacuo at 35 °C. Color: red, vield: (67%). mp = 286 °C. Anal. Calc. for  $C_{20}H_{22}N_4O_4Ni$  (MW: 441 g/mol): C, 54.46; H, 5.03; N, 12.70. Found: C, 54.52; H, 5.05; N, 12.68%.  $\Lambda_{\rm M}$  = 13  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $\mu_{\rm eff}$  = Dia, IR (KBr pellets,  $v_{\rm max}/{\rm cm}^{-1}$ ): 3558-3297 v(O-H···O) 3066 v(Ar-H), 2967-2865 v(Aliph-H), 1606 v(C=N), 1501-1417 v(C=C), 1275 v(N-O), and 514 v(Ni-N). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, TMS, 300 MHz,  $\delta$  ppm): 18.12 (s, 2H, O-*H*···O), 18.29 and 18.01 (s, 2H, O−*H*···O) for *cis/trans*-isomer, 8.20 and 8.14 (s, 2H, HC=N) for cis/trans-isomer, 8.03 and 8.01 (d, 4H, *J* = 3.3 Hz, Ar–CH), 7.35 and 7.32 (d, 4H, *J* = 3.0 Hz, Ar–CH) for *cis*/ *trans*-isomer, 2.69–2.61 (q, 4H, CH<sub>3</sub>–CH<sub>2</sub>), 1.20 (t, 3H, J = 15 Hz, CH<sub>3</sub>-CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, TMS, 75 MHz,  $\delta$  ppm) C<sub>1</sub>(147.30), C<sub>2</sub>(147.16 and 146.24), C<sub>3</sub>(129.31 and 129.16), C<sub>4</sub>(128.47), C<sub>5</sub>(126.24), C<sub>6</sub>(142.47 and 141.88), C<sub>7</sub>(28.62), and C<sub>8</sub>(15.71). UV-Vis ( $\lambda_{max}$ , nm, \* = shoulder peak): 242\*, 278, 382, and 402 (in CH<sub>3-</sub> OH); 297, 351, 409 and 522\* (in DMSO). LC–MS (Scan ES<sup>+</sup>): *m*/*z* (%) 441.3 (15) [M]<sup>+</sup>, 413.3 (100) [M-CH<sub>2</sub>CH<sub>3</sub>-H]<sup>+</sup>, 409.2 (55) [M-CH<sub>2</sub>- $(CH_3-3H)^+$  and 261.2 (20)  $[M-C_{16}H_{21}O_3]^+$ .

#### 2.4. Synthesis of the $[Ni(dioxime)_2Cu_2(N-N)_2](ClO_4)_2$ (3-7) complexes

All of multinuclear [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N–N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (N–N = 2, 2'-bipyridine (bpy), 1,10-phenanthroline (phen), 3,3'-dicarboxy-2,2'-bipyridine (dcbpy), 4,5-diazafluoren-9-one (dafo) and 1,10-phenanthroline-5,6-dione (dione)] complexes were synthesized according to the reported analogous procedure with some modifications. The mononuclear [Ni(dioxime)<sub>2</sub>] complex (0.4 g, 0.91 mmol) was added to Et<sub>3</sub>N (0.30 mmol) in absolute ethanol (70 ml) and the mixture was stirred for 2 h. A solution of Cu(ClO<sub>4</sub>)<sub>2</sub>.

 $\cdot$ 6H<sub>2</sub>O (0.69 g, 1.82 mmol) in absolute ethanol (20 ml) was added to the stirred ethanol mixture of [Ni(dioxime)<sub>2</sub>] (**2**) complex and Et<sub>3</sub>N. Then an ethanolic solution (15 mL) of the N–N ligand [2,2'-bipyridine (0.29 g, 1.82 mmol), 1,10-phenanthroline monohydrate (0.36 g, 1.82 mmol), 3,3'-dicarboxy-2,2'-bipyridine (0.44 g, 1.82 mmol), 4,5-diazafluoren-9-one (0.35 g, 1.82 mmol) or 1,10phenanthroline-5,6-dione (0.38 g, 1.82 mmol)] was added and stirred under reflux for 5 h. After boiling under reflux for 5 h, the mixture was left to precipitate up to 2 days. The solvent was slowly evaporated at room temperature, and the products were recrystallized from EtOH/H<sub>2</sub>O (1:2). Different color crystals obtained were filtered, washed with EtOH, MeOH and Et<sub>2</sub>O, and dried in air.

# 2.4.1. For $[Ni(dioxime)_2Cu_2(bpy)_2](ClO_4)_2$ (3)

Color: dark green; Yield (%): 65, m.p: 240 °C, *Anal.* Calc. for  $[C_{40-}H_{36}N_8O_{12}Cl_2Cu_2Ni]$  (F.W: 1077 g/mol): C, 44.59; H, 3.37; N, 10.40. Found: C, 44.54; H, 3.42; N, 10.43%.  $\Lambda_M = 146 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ ,  $\mu_{eff} = 1.41$  [B.M]. FT-IR (KBr pellets,  $v_{max}/cm^{-1}$ ): 3066 and 3055 v(Ar-H), 2964–2877 v(Aliph-H), 1602 and 1568 v(C=N), 1494–1445 v(C=C), 1270 v(N-O), 1089 and 626  $v(ClO_4)$ , 509 v(Ni-N), and 470 v(Cu-O). UV–Vis ( $\lambda_{max}$ , nm, \* = shoulder peak): 244, 298, 308, 382, 445\* and 646\* (in CH<sub>3</sub>OH); 265, 302, 312 and 465\*(in DMSO). LC–MS (Scan ES<sup>+</sup>): m/z (%) 1078.1 (16) [M+H]<sup>+</sup>, 1030.1 (30), 902.0 (100), 770.0 (14) and 708.2 (10).

# 2.4.2. For [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (4)

Color: green; Yield (%): 68, m.p: 236 °C, *Anal.* Calc. for  $[C_{44}H_{36}-N_8O_{12}Cl_2Cu_2Ni)]$  (F.W: 1125.5 g/mol): C, 46.96; H, 3.22; N, 9.96. Found: C, 46.88; H, 3.26; N, 9.92%.  $\Lambda_M = 116 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ ,  $\mu_{eff} = 1.56$  [B.M]. FT-IR (KBr pellets,  $\upsilon_{max}/\text{cm}^{-1}$ ): 3058  $\nu$ (Ar-H), 2961–2856  $\nu$ (Aliph-H), 1605 and 1558  $\nu$ (C=N), 1495–1428  $\nu$ (C=C), 1272  $\nu$ (N–O), 1088 and 626  $\nu$ (ClO<sub>4</sub>), 506  $\nu$ (Ni–N), and 471  $\nu$ (Cu–O). UV–Vis ( $\lambda_{max}$ , nm, \* = shoulder peak): 226, 269, 294, 453\* and 664\* (in CH<sub>3</sub>OH); 282, 302, 347, 469\* and 670\* (in DMSO). LC–MS (Scan ES<sup>+</sup>): m/z (%) 1125.3 (12) [M]<sup>+</sup>, 1032.1 (30), 902.0 (100), 770.0 (15) and 708.2 (10).

#### 2.4.3. For $[Ni(dioxime)_2Cu_2(dcbpy)_2](ClO_4)_2$ (5)

Color: pale green; Yield (%): 68, m.p: 236 °C, *Anal.* Calc. for [C<sub>44-</sub>H<sub>36</sub>N<sub>8</sub>O<sub>20</sub>Cl<sub>2</sub>Cu<sub>2</sub>Ni] (F.W: 1253.5 g/mol): C, 42.16; H, 2.90; N, 8.94. Found: C, 42.09; H, 2.86; N, 8.91%.  $\Lambda_{\rm M}$  = 138  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $\mu_{\rm eff}$  = 1.54 [B.M]. FT-IR (KBr pellets,  $v_{\rm max}/{\rm cm}^{-1}$ ): 3573–3100 v(COOH), 3079 and 3053 v(Ar–H), 2968–2869 v(Aliph–H), 1615 v(C=O) 1589 and 1570 v(C=N), 1461–1435 v(C=C), 1276 v(N–O), 1089 and 626 v(ClO<sub>4</sub>), 522 v(Ni–N), and 478 v(Cu–O). UV–Vis ( $\lambda_{\rm max}$ , nm, \* = shoulder peak): 238, 255, 298 and 471\* (in CH<sub>3</sub>OH); 264, 269, 281 and 368\* (in DMSO). LC–MS (Scan ES<sup>+</sup>): m/z (%) 1253.2 (14) [M]<sup>+</sup>, 1207.1 (8), 669.1 (100), 373.0 (28) and 102.2 (76).

# 2.4.4. For [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(dafo)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (6)

Color: dark green; Yield (%): 70, m.p: 220 °C, *Anal.* Calc. for [C<sub>42-</sub>H<sub>32</sub>N<sub>8</sub>O<sub>14</sub>Cl<sub>2</sub>Cu<sub>2</sub>Ni] (F.W: 1129.4 g/mol): C, 44.66; H, 2.86; N, 9.92. Found: C, 44.59; H, 2.83; N, 9.95%.  $\Lambda_{\rm M}$  = 127  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $\mu_{\rm eff}$  = 1.55 [B.M]. FT-IR (KBr pellets,  $v_{\rm max}/{\rm cm}^{-1}$ ): 3056 v(Ar–H), 2966–2872 v(Aliph–H), 1723 v(C=O) 1589 and 1561 v(C=N), 1471–1432 v(C=C), 1270 v(N–O), 1090 and 626 v(ClO<sub>4</sub>), 526 v(Ni–N), and 482 v(Cu–O). UV–Vis ( $\lambda_{\rm max}$ , nm, \* = shoulder peak): 241, 268, 303, and 316 (in CH<sub>3</sub>OH); 272, 281, 303, 317 and 710\* (in DMSO). LC–MS (Scan ES<sup>+</sup>): m/z (%) 1130.2 (16) [M+H]<sup>+</sup>, 764.5 (15), 684.0 (30), 303.2 (70) and 102.2 (100).

# 2.4.5. For [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(dione)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (7)

Color: dark green; Yield (%): 72, m.p: 285 °C, *Anal.* Calc. for [C<sub>44-</sub>H<sub>32</sub>N<sub>8</sub>O<sub>16</sub>Cl<sub>2</sub>Cu<sub>2</sub>Ni] (F.W: 1185.5 g/mol): C, 44.58; H, 2.72; N, 9.45. Found: C, 44.54; H, 2.69; N, 9.41%.  $\Lambda_{\rm M}$  = 130  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $\mu_{\rm eff}$  = 1.42 [B.M]. FT-IR (KBr pellets,  $\nu_{\rm max}$ /cm<sup>-1</sup>): 3078  $\nu$ (Ar–H), 2965–2873 v(Aliph–H), 1697 v(C=O) 1604 and 1577 v(C=N), 1456–1430 v(C=C), 1273 v(N–O), 1085 and 626 v(ClO<sub>4</sub>), 504 v(Ni–N), and 483 v(Cu–O). UV–Vis ( $\lambda_{max}$ , nm, \* = shoulder peak): 230, 241\*, 272, 298 and 412\* (in CH<sub>3</sub>OH); 278, 283, 296, and 421\* (in DMSO). LC–MS (Scan ES<sup>+</sup>): *m/z* (%) 1185.6 (18) [M]<sup>+</sup>, 744.1 (45), 566.2 (100), 372.9 (35) and 176.1 (20).

#### 2.5. General procedure for the cycloaddition of epoxides to $CO_2$

A 50 mL steel pressure reactor was charged with mononuclear [Ni(dioxime)<sub>2</sub>] complex or multinuclear [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub> (N–N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complexes  $(1.125 \times 10^{-5} \text{ mol})$ , epoxide  $(1.125 \times 10^{-2} \text{ mol})$ , and DMAP or other Lewis base  $(2.25 \times 10^{-5} \text{ mol})$ . The reaction vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to equilibrate. Carbon dioxide was charged into the autoclave with desired pressure then heated to the desired temperature. The pressure was kept constant during the reaction. The vessel was then cooled to 5–10 °C in an ice bath after the expiration of the desired time of reaction. The pressure was released, and the excess gases were vented. The conversions of epoxides to corresponding cyclic carbonates were determined by comparing the ratio of product to substrate in the <sup>1</sup>H NMR spectrum of an aliquot of the reaction mixture.

#### 3. Results and discussion

#### 3.1. Synthesis and spectral properties

The unsymmetrical ligand  $(LH_2)$  (1) was prepared in moderate yield by the procedure described in literature with some modifications [37,38] (Scheme 1). The mononuclear [Ni(dioxime)<sub>2</sub>] (2) complex (Scheme 2) was synthesized by treating NiCl<sub>2</sub>.6H<sub>2</sub>O with one/ two equivalents of the corresponding unsymmetrical ligand (1) in absolute ethanol at reflux temperature. For the multinuclear  $[Ni(dioxime)_2Cu_2(N-N)_2](ClO_4)_2$  (3-7) complexes, the mononuclear complex [Ni(dioxime)<sub>2</sub>] (2) was used as precursor and 2,2'bipvridine. 1.10-phenanthroline. 3.3'-dicarboxy-2.2'-bipvridine. 4,5-diazafluoren-9-one or 1,10-phenanthroline-5,6-dione were used as linked ligands. To confirm the identity of the pre-catalysts prepared in the present work, a variety of techniques including <sup>1</sup>H and <sup>13</sup>C spectra, FT-IR, UV-Vis, elemental analysis, melting point measurements, LC-MS spectroscopy, molar conductivity measurements, magnetic susceptibility techniques and cyclic voltammetry techniques were used for determination of the mononuclear and multinuclear oxime complexes. For mononuclear  $[Ni(dioxime)_2]$ (2) complex, the Ni(II) ion is tetra coordinated and has a square planar arrangement with four  $Ni \leftarrow N$  bonds. In the multinuclear complexes (3-7), the Ni(II) ion is coordinated to the imino nitrogen atoms of the oxime core and the two Cu(II) ions are coordinated to oxygen donors of oxime groups and the N-N ligand (2,2'-bipyridine, 1,10-phenanthroline, 3,3'-dicarboxy-2,2'-bipyridine, 4,5diazafluoren-9-one or 1,10-phenanthroline-5,6-dione). We have attempted to prepare single crystals of ligand (LH<sub>2</sub>) (1) and monoand multinuclear metal complexes (2-7) in different solvents and techniques, but we could not prepare convenient single crystals of ligand and its metal complexes. However, the spectroscopic and analytical results supported the proposed structures for these complexes.

The FT-IR spectra of the mono- and multinuclear oxime complexes (2-7) were compared with those of the free ligand (1) in order to determine the coordination sites that could be involved in chelation. There are some guide peaks in the spectrum of the ligand, which are of significant help for achieving this goal. The position and/or the intensities of these peaks are expected to be changed upon chelation. Coordination of the unsymmetrical oxime



**Scheme 1.** The structure of the proposed ligand (LH<sub>2</sub>) (1).



Scheme 2. The structure of the proposed  $[Ni(dioxime)_2]$  (2) and  $[Ni(dioxime)_2Cu_2(N-N)_2](CIO_4)_2$  (3-7) complexes.

ligand (1) to the Ni(II) ion through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the v(C=N) absorption frequency. The remarkably strong and sharp bands located at 1609 cm<sup>-1</sup>, between 1606–1589 and 1577–1558 cm<sup>-1</sup>, were assigned to the v(C=N) stretching vibrations of the azomethine of the oxime ligand (1), the mono- and multinuclear complexes (2-7), respectively. Some shifts to a lower wavenumbers were clearly observed by the formation of the mono- and multinuclear complexes. Hence, these shifts suggested the participation of the azomethine group of this ligand in binding to the Ni(II) ion [39,40]. In the FT-IR spectrum of the ligand and mononuclear  $[Ni(dioxime)_2]$  (1) complex, the stretching vibrations of the intramolecular hydrogen bonds  $v(O-H \cdots O)$  were observed between 3558-3102 cm<sup>-1</sup>, whereas in the FT-IR spectra of multinuclear metal complexes (3-7), these bonds were not observed as a result of disappearing the H-bonds  $v(O-H \cdots O)$  of mononuclear nickel complex where the copper ions encapsulated to form multinuclear metal complexes, namely  $Cu_2(bpy)_2$ ,  $Cu_2(phen)_2$ ,  $Cu_2($  $dcbpy)_2$ ,  $Cu_2(dafo)_2$  or  $Cu_2(dione)_2$  [40–42]. However, the disappearance of v(O-H) stretching bands of free ligand together with the existence of H-bridge  $v(O-H\cdots O)$  between 3558– 3297 cm<sup>-1</sup> and the shift of -C=N and -N-O stretches in the FT-IR spectra of the mononuclear metal complexes provided support for MN<sub>4</sub>-type coordinations in the metal complexes (**2**–**7**) [43]. The FT-IR spectra showed a strong peak at 1615 cm<sup>-1</sup> for complex (**5**), 1723 cm<sup>-1</sup> for complex (**6**), and 1697 cm<sup>-1</sup> for complex (**7**), due to carbonyl or carboxylic acid group. Perchlorate salts showed strong antisymmetric stretching band observed between 1089– 1085 cm<sup>-1</sup>, an indication of uncoordinated perchlorate anions [44]. The coordination mode of the ligand (**1**) was further supported by new frequencies occurring in the range 526–504 cm<sup>-1</sup>



Fig. 1. <sup>1</sup>H NMR spectrum of ligand (LH<sub>2</sub>) (1).



due to  $v(Ni \leftarrow N)$  stretching vibrations and 483–470 cm<sup>-1</sup> due to v(Cu-O) stretching vibrations that were not observed in the infrared spectra of the ligand.

Electronic spectra of free ligand and mono- and multinuclear metal complexes (1–7) have been recorded on the 200–1100 nm range in CH<sub>3</sub>OH and DMSO solvents, and their corresponding data were given in the experimental part. The position of absorption bands was strongly influenced by the structure of the compounds and the electronic and steric nature of the N–N ligand (2,2'-bipyr-idine, 1,10-phenanthroline, 3,3'-dicarboxy-2,2'-bipyridine, 4,5-diazafluoren-9-one or 1,10-phenanthroline-5,6-dione) substituted on the conjugated system of multinuclear metal complexes. The reflectance UV–Vis spectra of the complexes (1–7) have contained absorption bands in the 226–471 (in CH<sub>3</sub>OH) and 264–465 (in DMSO) nm region which are attributable to ligand-to-Ni(II) metal or the linked ligands to the Cu(II) metal CT transition and the

electronic  $\pi \to \pi^*$  or  $n \to \pi^*$  transitions of the organic ligand. Additionally, the new broad bands with the lowest energies and in lower intensities between 646–664 (in CH<sub>3</sub>OH) and 522–710 (in DMSO) nm are attributed to d–d transitions for mononuclear [Ni(dioxime)<sub>2</sub>] (**2**), and multinuclear [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N–N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3**–**7**) complexes. These modifications in shifts and intensities for the absorption bands supported coordination of the ligand to the Ni(II) and Cu(II) ion in the proposed compounds.

<sup>1</sup>H and <sup>13</sup>C NMR chemical data for the ligand  $(LH_2)$  (1) and mononuclear  $[Ni(dioxime)_2]$  (2) complex in DMSO-d<sub>6</sub> were reported in the experimental section and Figs. 1-3. The chemical shifts were observed as one doublet (11.86 ppm, 2H) or two singlet (11.69 and 11.47 ppm, 1H each) as a double resonance for the deuterium exchangeable protons of the C=N-OH groups of oxime in the <sup>1</sup>H NMR spectra of unsymmetrical free ligand (1) (Fig. 1). The existence of intramolecular deuterium exchangeable H-bridge  $(O-H \cdots O)$  protons was characterized by a new different singlet signals at low field, (18.29 and 18.01 ppm, 1H each) or (18.12 ppm, 2H) as a double resonance (Fig. 3). The <sup>1</sup>H NMR resonances with expected integrated intensities were observed as two doublet peaks at 8.48 and 7.88 ppm corresponding to the HC=N as a double resonance, 7.49 and 7.23 ppm as doublet, corresponding to the Ar-CH, 2.70–2.58 ppm as quartet, corresponding to the  $CH_3$ – $CH_2$ , and 1.19 ppm as triplet, corresponding to the  $CH_3$ - $CH_2$ , respectively for free ligand. In the <sup>1</sup>H NMR spectrum of  $[Ni(dioxime)_2]$  (2) complex, these resonances were observed at 8.20 and 8.14 ppm as doublet, corresponding to the HC=N as a double resonance, 8.03 and 8.01 ppm with 7.35 and 7.32 ppm as doublet, corresponding to the Ar-CH as a double resonance, 2.69–2.61 ppm as quartet, corresponding to the CH<sub>3</sub>-CH<sub>2</sub>, and 1.20 ppm as triplet, corresponding to the  $CH_3$ - $CH_2$ , respectively. The azomethine group has shifted to the different field region indicating coordination of -C=N to the nickel ion. The other chemical shift values of  $[Ni(dioxime)_2]$ (2) complex are extremely close to that of ligand (1) protons.

More detailed information about the structure of free ligand (1) and its mononuclear  $[Ni(dioxime)_2]$  (2) complex was provided by the <sup>13</sup>C NMR spectrum (Fig. 2 and experimental section). In the <sup>13</sup>C NMR spectrum, the carbon resonances of oxime groups were observed at 151.26 and 145.02 ppm with 153.48 and 148.46 ppm as a double resonance for free ligand and 147.30 and 146.80 ppm



Fig. 3. <sup>1</sup>H NMR spectrum of [Ni(dioxime)<sub>2</sub>] (2) complex.



with 147.16 and 146.24 ppm as a double resonance for [Ni(diox $ime_{2}$  (2) complex. However, the other some carbon resonances have a double resonance both for free ligand (1) and its mononuclear  $[Ni(dioxime)_2]$  (2) complex. Consequently, both in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of free ligand (1) and its mononuclear [Ni(dioxime)<sub>2</sub>] (**2**) complex, some proton and carbon resonances have a double resonance indicating that free ligand (1) and its mononuclear [Ni(dioxime)<sub>2</sub>] (**2**) complex have *cis*–*trans* isomerism [43,45]. In this work, the *cis*-isomer refers to the two hydroxy groups sitting on the same side to each other in both ligand (1) and mononuclear  $[Ni(dioxime)_2]$  (2) complex, whereas hydroxy groups sit on opposite sides to each other at trans-isomer. The formation of both isomers has been reflected by NMR spectra as the difference in intensities of proton and carbon signals, corresponding to both isomers. There was a significant difference between the intensities of the two peaks, hence one of the isomers was formed in higher intensities than the other one. The isomer ratio was found



to be 70% *cis*-isomer and 30% *trans*-isomer from the <sup>1</sup>H NMR and <sup>13</sup>C NMR data. Since multinuclear [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N-N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> oxime complexes have paramagnetic properties, their NMR spectra could not be obtained.

Magnetic susceptibility measurements provided sufficient data to characterize the structure of the metal complexes. Magnetic moment measurements of compounds were carried out at room temperature. The effective magnetic moments ( $\mu_{eff}$ ) of all the complexes were measured on samples at room temperature, thereafter necessary diamagnetic corrections were done using Pascal's table. The results showed that the mononuclear  $[Ni(dioxime)_2]$ (2) complex was diamagnetic, indicating the low-spin (S = 0)square planar d<sup>8</sup>-systems, whereas magnetic moments of the multinuclear Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N-N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3**-**7**) complexes were found between 1.56–1.41 B.M. The observed effective magnetic moments were comparable to the expected spin-only value  $(1.73 \mu B)$  for one unpaired electron and confirmed the formal +2 oxidation state of the copper centers. However, it is obvious that the multinuclear oxime complexes (3-7) possess antiferromagnetic properties at room temperature by strong intramolecular



Fig. 6. The LC-MS spectra of [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (3) complex.



Fig. 7. Cyclic voltammograms of the ligand (1) and  $[Ni(dioxime)_2]$  (2) complex in DMSO/0.1 M TBAP at 0.1 V  $s^{-1}$  scan rate.

antiferromagnetic spin exchange interaction as reported previously for the intramolecular  $O-H\cdots O$  bridges replaced Cu(II) containing metal complexes with oximate bridge ligands [40,46].

The conductivity measurements have frequently been used in structural elucidation of metal chelates within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution (in case of presence of anions outside the coordination sphere), the higher will be its molar conductivity and vice versa. The molar conductivity values indicate that the anions may be present outside the coordination sphere or inside or absent [47]. With a view to studying the electrolytic nature of the mononuclear [Ni(dioxime)<sub>2</sub>] (2) complex and multinuclear Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N-N)2](ClO<sub>4</sub>)2 (**3–7**) complexes, their molar conductivities were measured in DMF ( $10^{-3}$  M). The molar conductivity ( $\Lambda_{M}$ ) values of the mononuclear [Ni(dioxime)<sub>2</sub>] (**2**) complex is found  $13 \Omega^{-1} \text{ cm}^2$  mol<sup>-1</sup> at room temperature, indicating its almost non-electrolytic nature. The result indicates that this complex (2) is poor in molar conductivity due to the non-free ions in complex (2), whereas multinuclear Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N-N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3-7**) complexes are in the range of 146–116  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> at room temperature, indicating 1:2 electrolytes or existence of three ionic species in solution [48]. The higher values of multinuclear Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N- $N_{2}$  (ClO<sub>4</sub>)<sub>2</sub> (**3**-**7**) complexes than the mononuclear [Ni(dioxime)<sub>2</sub>] (2) complex, indicated the presence of ClO<sub>4</sub> ions as counter ion. The ligand (1) is soluble in common organic solvents such as THF,  $C_2H_5OH$ ,  $CH_2Cl_2$ , and DMSO Multinuclear Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>



**Fig. 8.** Cyclic voltammograms of the  $[Ni(dioxime)_2Cu_2(dafo)_2](ClO_4)_2$  (6) complex on Pt electrode and GC electrode in DMSO/0.1 M TBAP at 0.1 V s<sup>-1</sup> scan rate.

 $(N-N)_2](ClO_4)_2$  (**3–7**) complexes are more soluble than  $[Ni(diox-ime)_2]$  (**2**) complex, due to the presence of  $Cu_2(bpy)_2$ ,  $Cu_2(phen)_2$ ,  $Cu_2(dcbpy)_2$ ,  $Cu_2(dafo)_2$  or  $Cu_2(dione)_2$  bridged groups in the oxime moieties. Although the mononuclear  $[Ni(dioxime)_2]$  (**2**) complex is soluble in DMSO, DMF and slightly soluble in  $CH_2Cl_2$ ,  $CHCl_3$  All complexes are stable in the solvents reported in this study at room temperature.

LC–MS was used to obtain the molecular masses of the ligand (1) and its mono- and multinuclear (2–7) oxime complexes. The LC–MS spectra of the ligand (1) and their mono- and multinuclear (2–7) oxime complexes were taken as evidence for the formation of the proposed structures (Figs. 4–6). The values of molecular weights supplied by mass spectrometer are presented in the experimental section. Mass spectrometric analysis of the resulting solution revealed that a peak at m/z = 192.2 (100%) for ligand (1), 441.3 (15%) for complex (2), 1078.1 (16%) for complex (3), 1125.3 (12%) for complex (4), 1253.2 (14%) for complex (5), 1130.2 (16%) for complex (6) and 1185.6 (%18) for complex (7), respectively that could be assigned to the [M]<sup>+</sup> or [M+H]<sup>+</sup> molecular ion fragment, supported the proposed structure of the ligand (1) and its mono- and multinuclear (2–7) oxime complexes.

# 3.2. Electrochemical properties

The electrochemical properties of the metal complexes were investigated using cyclic voltammetric techniques in DMSO

#### Table 1

Synthesis of styrene carbonate from styrene oxide and  $CO_2$  catalyzed by complexes (2–7).



Entry	Catalyst	Additive	Yield <sup>a</sup>	TOF <sup>b</sup>
1	2	DMAP	55	275
2	3	DMAP	8	40
3	4	DMAP	5	25
4	5	DMAP	2	10
5	6	DMAP	10	50
6	7	DMAP	12	60
7	-	DMAP	5	25
8	2	-	trace	-
9	2	[bmim]I	64	320
10	-	[bmim]I	14	70
11	2	[bmim]PF <sub>6</sub>	91	455
12	-	[bmim]PF <sub>6</sub>	52	260
13	2	NBu <sub>4</sub> Br	69	345
14	-	NBu <sub>4</sub> Br	25	125
15	3	[bmim]I	15	75
16	4	[bmim]I	13	65
17	5	[bmim]I	5	25
18	6	[bmim]I	17	85
19	7	[bmim]I	20	100
20	3	[bmim]PF <sub>6</sub>	46	230
21	4	[bmim]PF <sub>6</sub>	43	215
22	5	[bmim]PF <sub>6</sub>	22	110
23	6	[bmim]PF <sub>6</sub>	50	250
24	7	[bmim]PF <sub>6</sub>	55	275
25	3	NBu <sub>4</sub> Br	27	135
26	4	NBu <sub>4</sub> Br	22	110
27	5	NBu <sub>4</sub> Br	10	50
28	6	NBu <sub>4</sub> Br	28	140
29	7	NBu <sub>4</sub> Br	31	155

Catalyst (1.125  $\times$   $10^{-5}$  mol), DMAP (2.25  $\times$   $10^{-5}$  mol), styrene oxide (1.125  $\times$   $10^{-2}$  mol), CO\_2 (1.5 Mpa), 2 h.

<sup>a</sup> Yield of epoxides to corresponding cyclic carbonates was determined by comparing the ratio of product to substrate in the <sup>1</sup>H NMR spectrum of an aliquot of the reaction mixture.

<sup>b</sup> Moles of cyclic carbonate produced per mole of catalyst.

containing 0.1 M TBAP. The data obtained in this work are listed in Table 3. Fig. 7 represents the cyclic voltammetry of the ligand (1) and  $[Ni(dioxime)_2]$  (2) complex. As seen from Fig. 7, the ligand has one cathodic peak in Ag/AgCl electrode system. The cathodic peak potential of this reduction process was observed at  $E_{pc}$  = -0,825 V. The cathodic peak corresponding to the ligand was also seen in [Ni(dioxime)<sub>2</sub>] (2) complex, but it negatively shifted and appeared at  $E_{1/2} = -0,864$  V. The ligand (1) has an irreversible reduction-oxidation process because of the high value for the anodic-to-cathodic peak separation and the smaller anodic-to-cathodic peak current ratio. Second reduction peak could be assigned to the Ni<sup>2+</sup>/Ni<sup>+</sup> species [49]. All the complexes (except [Ni(diox- $\operatorname{ime}_{2}(2)$  complex) gave the reduction and oxidation couple within the positive potential window, which were attributed to the  $Cu^{2+}/Cu^{+}$  and  $Cu^{2+}/Cu^{3+}$  processes [50,51]. These redox couples have irreversible character with high peak separation values and lower anodic-to-cathodic peak current ratios (Table 3). Fig. 8 showed cyclic voltammograms of the [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(dafo)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> (6) complex on Pt and GC electrodes in DMSO/0.1 M TBAP at 0.1 V s<sup>-1</sup> scan rate where the complex clearly exhibited a reversible reduction process based on the ligand. Although the ligand reduction processes were seen in all of the complexes but only dafo

#### Table 2

Coupling of  $CO_2$  and various epoxides catalyzed by complex (2).



Reaction conditions: 2 ( $1.125 \times 10^{-5}$  mol), [bmim]PF<sub>6</sub> ( $2.25 \times 10^{-5}$  mol), epoxide ( $1.125 \times 10^{-2}$  mol), CO<sub>2</sub> (1.5 Mpa), 100 °C, 2 h.

Table 3	
Voltammetric data for	complexes in (2-7) DMSO-TBAP.
	2

MetalComplexes	$L/L^{-}$	Ni <sup>2+</sup> /Ni <sup>+</sup>	Cu <sup>2+</sup> /Cu <sup>+</sup>	Cu <sup>2+</sup> /Cu <sup>3+</sup>
	$E_{1/2} (V)^{a}$	$E_{\rm pc}\left({\sf V}\right)$	$E_{\rm pa}\left({\sf V}\right)$	$E_{\rm pa}\left({\rm V}\right)$
(2)	-0.941	-1.302	-	_
(3)	-1.246	-	-0.005	0.321
( <b>4</b> ) <sup>b</sup>	-1.161	-	0.010	0.806
(5)	-0.928	-	0.217	0.490
(6)	-0.956	-	0,040	0.522
(7)	-0.928	-	-0.128	0.569

 $E_{1/2}^{a} = (E_{\rm pc} + E_{\rm pa})/2.$ 

<sup>b</sup> GC electrode.

complex showed reversibility at a scan rate of 100 mV s<sup>-1</sup>.  $\Delta E_p$  values of [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(dafo)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**6**) increased with the scan rate but remained in the range of reversible systems. In addition differently on the other complexes, glassy carbon (GC) electrode measurements showed better results than Pt electrode. Pt electrode showed only reversible character of the ligand based reduction. Cu<sup>2+</sup>/Cu<sup>+</sup> and Cu<sup>2+</sup>/Cu<sup>3+</sup> couples were not clearly seen. However, the glassy carbon electrode showed the reduction and oxidation of all species.

# 3.3. Catalytic properties

Catalytic efficiencies of metal complexes for the cycloaddition reaction of CO<sub>2</sub> were experimented (Tables 1 and 2). Catalytic experiments were carried out at optimized conditions, which were determined at our previous studies [4–6]. It was obvious that whereas, monometallic Ni(dioxime)<sub>2</sub> complex (2) gave moderate conversion (55%) bimetallic complexes (3–7) did not work well for this catalytic reaction when DMAP was chosen as a Lewis base (Table 1). While the catalytic efficiency is expected to increase in the presence of bimetallic complexes in accordance with the

literature [52,53], a lower catalytic efficiency was exhibited by our bimetalic complexes (**3–7**). This unexpected result was also seen at Zn-cluster compounds of Kleij and Co-workers [54]. They suggested that reactivity of the outer Zn ions was determined by the axial substrate binding ability, steric factors, and flexibility of the bridging fragment in the salen ligand. By the way, in this study the lower catalytic efficiencies of bimetalic complexes may be due to the insolubilities of them in the epoxide (styrene oxide). It was observed that before and after the catalytic reaction, bimetallic complexes (**3–7**) were in a solid form in the reaction vessel while the complex **2** was soluble.

Instead of DMAP, other organic additives [tetrabutylammonium bromide (NBu<sub>4</sub>Br), butylmethylimidazolium iodide (bmiml) or butylmethylimidazolium hexafluorophosphate (bmimPF<sub>6</sub>)] were used with the complex **2**. Conversion of styrene carbonate was found increasing by the order of DMAP < [bmim]I < NBu<sub>4</sub>-Br < [bmim]PF<sub>6</sub>. This order did not change with the other complexes (Table 1, entries 15–29). Without any additive, Ni(dioxime)<sub>2</sub> complex (**2**) did not work at all (entry 8). It was remarkable that [bmim]PF<sub>6</sub> was efficient alone in the ratio of 0.1 mol%. Ni(dioxime)<sub>2</sub>/[bmim]PF<sub>6</sub> catalytic system which was examined to survey the applicability of other terminal epoxides (Table 2). Among the epoxides surveyed, the epichlorohydrin was the most reactive epoxide, and the reaction finished perfectly in 2 h with a 99% conversion.

For the coupling mechanism of epoxides, Lu and Darensbourg have recently published detailed studies [55,56]. While nucleophilic attack was estimated to be less hindered carbon atom of a terminal epoxide up to this time, in their study, they pointed out that mechanism for SO is different from the PO. Due to enhanced electrophilic nature of methine, nucleophilic attack occurs at the methine  $C_{\alpha}$ –O bond.

# 4. Conclusion

In this study, the unsymmetrical dioxime ligand (1), its the mononuclear complex  $[Ni(dioxime)_2]$  (2) and the multinuclear metal complexes  $[Ni(dioxime)_2Cu_2(N-N)_2](ClO_4)_2$  (3-7) were synthesized and characterized by a variety of spectroscopic techniques. The intramolecular O-H···O bridges on the mononuclear complex [Ni(dioxime)<sub>2</sub>] (2) were replaced with Cu(II)(N–N) complex to synthesize the multinuclear complexes [Ni(dioxime)<sub>2</sub>Cu<sub>2</sub>(N-N)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3**–**7**). The spectroscopic, electrochemical and catalytic properties of the complexes were compared with those of well-established O-H···O analogues in a detail. To best of our knowledge, we herein for the first time reported novel catalysts of mono- and multinuclear oxime metal complexes in conjunction with  $[bmim]PF_6$  for the conversion of CO<sub>2</sub> to cyclic carbonates. Among the epoxides surveyed, the epichlorohydrin was the most reactive epoxide, and the reaction finished perfectly in 2 h with a 99% conversion. The free ligand (1) and its mononuclear [Ni(diox $ime_{2}$  (2) complex have a double resonance at their <sup>1</sup>H and <sup>13</sup>C NMR spectrum, which indicate that the free ligand (1) and its the mononuclear [Ni(dioxime)<sub>2</sub>] (**2**) complex have *cis*-*trans* isomerism. All the complexes (except  $[Ni(dioxime)_2]$  (2) complex) gave the reduction and oxidation couple within the positive potential window, which were attributed to the  $Cu^{2+}/Cu^{+}$  and  $Cu^{2+}/Cu^{3+}$ processes. Additionally, the measurements carried out by glassy carbon (GC) working electrode showed better results than those by Pt working electrode. The nature of the ligands around the metal has dramatically been found to affect the energy conversion process. Particularly, the introduction of electronic effects via electron-donor substituents on 2,2'-bipyridine, 1,10-phenanthroline, 3,3'-dicarboxy-2,2'-bipyridine, 4,5-diazafluoren-9-one and 1,10phenanthroline-5,6-dione ligands have notably improved the absorption in the visible region for efficient sunlight collection [57–59]. The disappearance of H-bonding (O–H···O) in the  $[Ni(dioxime)_2Cu_2(N-N)_2](ClO_4)_2$  metal complexes showed that the Cu(II)-capped groups attached to the main oxime core. Also, these complexes have enabled us a systematically probe the phenomenon of proton-coupled electron transfer that occurs when oxime ligand is coordinated to a redox active metal center [60].

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