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## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa



# The coupling of carbon dioxide and epoxides by phenanthroline derivatives containing different Cu(II) complexes as catalyst



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#### HIGHLIGHTS

- The two ligand and its mononuclear Cu(II) complexes have been synthesized.
- The Cu(II) complexes were synthesized for the coupling of carbon dioxide and epoxide.
- Dimethylamino pyridine (DMAP) was used as co-catalyst.
- A high selective conversion rate was obtained using catalyst and epichlorohydrine as the substrate.

#### G R A P H I C A L A B S T R A C T

A series of the mononuclear Cu(II) metal complexes containing the ligand Bdppz [(9a,13a-dihydro-4,5,9,14-tetraaza-benzo[b]triphenylene-11-yl)-phenyl-methanone] ( $L_1$ ) and Aqphen [(12,17-dihydro-naphthol[2,3-h]dipyrido[3,2-a:2',3'-c]-phenazine-12,17-dione)] ( $L_2$ ) were synthesized and used as catalyst for the coupling of carbondioxide and liquid epoxide which served as both reactant and solvent. The Cu(II) complexes were characterized by FT-IR, UV–Vis, elemental analysis, melting point, mass spectra, molar conductivity measurements and magnetic susceptibility techniques. The reaction of the Bdppz ( $L_1$ ) and Aqphen ( $L_2$ ) ligands in a 1:1, 1:2 or 1:3 mole ratio with CuCl<sub>2</sub>·2H<sub>2</sub>O afforded ionic Cu(II) complexes in the presence of Et<sub>3</sub>N. The catalytic results shown that the mononuclear complex [Cu( $L_2$ )Cl<sub>2</sub>] (**6**) has the best effective activities than the other mononuclear Cu(II) complexes for the formation of cyclic organic carbonates from carbon dioxide.



#### ARTICLE INFO

Article history: Received 19 November 2012 Received in revised form 24 April 2013 Accepted 29 April 2013 Available online 16 May 2013

*Keywords:* Cu(II) complexes Spectroscopy Mass spectra Carbon dioxide Cyclic carbonate

### ABSTRACT

A series of the mononuclear Cu(II) metal complexes containing the ligand Bdppz [(9a,13a-dihydro-4,5,9,14-tetraaza-benzo[b]triphenylene-11-yl)-phenyl-methanone] ( $L_1$ ) and Aqphen [(12,17-dihydro-naphthol[2,3-h]dipyrido[3,2-a:2',3'-c]-phenazine-12,17-dione)] ( $L_2$ ) were synthesized and used as catalyst for the coupling of carbon dioxide (CO<sub>2</sub>) and liquid epoxide which served as both reactant and solvent. Dimethylamino pyridine (DMAP) was used as co-catalyst. The yields 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. The mononuclear Cu(II) complexes of these ligands were synthesized by treating an ethanol solvent of the appropriate ligand with a different molar amount of CuCl<sub>2</sub>·2H<sub>2</sub>O. The Cu(II) complexes were characterized by FT-IR, UV–Vis, elemental analysis, melting point analysis, mass spectra, molar conductivity measurements and magnetic susceptibility techniques. The reaction of the Bdppz and Aqphen ligands in a 1:1, 1:2 or 1:3 mole ratio with CuCl<sub>2</sub>·2H<sub>2</sub>O afforded ionic Cu(II) complexes in the presence of Et<sub>3</sub>N.

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#### Introduction

Nitrogen-donor ligands play crucial biological roles in the binding of essential metal ions to proteins. Their synthetic analogs, which have an extensive general coordination chemistry (that includes different phenanthroline derivatives and ligands) in particular, have been the subject of numerous investigations on their possible applications not only in medicinal field but also in catalysis and materials science [1]. In the family of polypyridine ligands, different phenanthroline derivatives containing ligands are of special interest because of both its relatively easy synthesis with a wide range of additional functionalities and its ability to form highly stable complexes without necessarily occupying all the coordination sites of a metal [2]. However, the investigation on the derivatives of 1,10-phenanthroline has attracted much attention because they play important roles in synthesizing various metal complexes and coordination polymers with luminescent p-conjugated groups [3]. The [Cu(N-N)X<sub>2</sub>], [Cu(N-N)<sub>2</sub>X]X or [Cu(N-N)<sub>3</sub>]X<sub>2</sub> compounds may occur either in octahedral geometry, or in a tetrahedral geometry without space in inner sphere for X ligands, and also in a five-coordinate geometry with one X ligand in second coordination sphere. Furthermore, in dependence of steric demand of substituents of the phenanthroline rings. different coordination ability of the counter anions  $(NO_2, NO_2, Cl^- and ClO_4)$  towards copper (II) has been observed [4]. Like phenanthroline and bipyridine, phenanthroline derivates containing ligands can also provide two nitrogen atoms to act as bidentate chelating ligands in the reactions with transition-metal cations exhibiting as catalysts in transformation of carbon dioxide to cyclic carbonates.

In the current global climate, with high oil prices and increasing concern over global warming, and consumption petroleum resources, the development of renewable carbon sources is of the utmost importance. CO<sub>2</sub> is a particularly an attractive alternative feedstock as it is inexpensive, naturally abundant, and the byproduct of many industrial processes, including combustion [5]. The reactions of CO<sub>2</sub> with metal complexes have been extensively studied, revealing potential pathways for catalytic reactions [6-11]. A majority of these publications involve the reaction of CO<sub>2</sub> with epoxides to generate polycarbonates and-or cyclic carbonates. Cyclic carbonates are used industrially as polar aprotic solvents, substrates for small molecule synthesis, additives, antifoam agents for antifreeze, and plasticizers [12,13]. Due to such uses, a number of syntheses of cvclic carbonates have been described over the last 30 years. As observed in early studies, only a few metals are active for the coupling of epoxides and CO<sub>2</sub>, including Al. Cr. Co. Mg. Li. Zn. Cu. and Cd [6,14,15]. Studies have shown that large differences in catalytic efficiency result from the organic frameworks surrounding these metals. Accordingly, subsequent studies have largely focused on empirical modification of ligands to generate improved catalysts.

In this paper, we report synthesis, characterization, and spectroscopic properties of six new mononuclear Cu(II) complexes having Bdppz [(9a,13a-dihydro-4,5,9,14-tetraaza-benzo[b]triphen-ylene-11-yl)-phenyl-methanone] ( $L_1$ ) and Aqphen (12,17-dihydro-naphthol[2,3-h]dipyrido[3,2-a:2',3'-c]-phenazine-12,17-dione) ( $L_2$ ) ligands with 1:1, 1:2, and 1:3 molar ratios of metal and ligand (Scheme 1). We also report the catalytic activity of Bdppz and Aqphen Cu(II) metal complexes as catalyst in transformation of carbon dioxide to cyclic carbonates.

#### Experimental

#### Materials and measurements

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers (Aldrich or Merch). Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. For catalytic measurements, <sup>1</sup>H NMR spectra were recorded on a Varian AS-400 MHz instrument at room temperature for catalytic measurements. FT-IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR Spectrometer as 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  $(20 \circ C)$  using Hg[Co(SCN)<sub>4</sub>] as a calibrant; diamagnetic corrections were calculated from Pascal's constants [16,17]. 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 are uncorrected. Molar conductivities  $(\Lambda_M)$ were recorded on a Inolab Terminal 740 WTW Series. Mass Spectra results were recorded on a Micromass Ouatro LC/ULTIMA LC-MS/ MS spectrometer. Catalytic tests were performed in a PARR 4843 50 mL stainless pressure reactor. The ligands Bdppz [(9a,13a-dihydro-4,5,9,14-tetraaza-benzo[b]triphenylene-11-yl)-phenyl-methanone] (L<sub>1</sub>) and Aqphen (12,17-dihydronaphthol[2,3-h]dipyrido[3, 2-a:2',3'-c]-phenazine-12,17-dione) (L<sub>2</sub>) were synthesized following procedures with some modifications [10,18].

#### Synthesis of mononuclear Cu(II) complexes

The mononuclear Cu(II) complexes were synthesized according to the reported procedure with some modifications [19]. The syntheses of the complexes  $[Cu(L_n)_3]Cl_2$  (*n* = 1 or 2) were carried out by using three equivalents of the ligands Bdppz [(9a,13a-dihydro-4,5,9,14-tetraaza-benzo[b]triphenylene-11-yl)-phenyl-methanone] (L<sub>1</sub>) or Aqphen [(12,17-dihydronaphthol[2,3-h]dipyrido[3, 2-a:2',3'-c]-phenazine-12,17-dione)] (L<sub>2</sub>) in 70 mL of absolute ethanol to one equivalent of CuCl<sub>2</sub>·2H<sub>2</sub>O in 20 mL of absolute ethanol-water. In a glass flask, the ligand solution was added dropwise to the metal salt solution under Ar atmosphere with continuous stirring and to this mixture was added a few drops of Et<sub>3</sub>N while stirring. The stirred mixture was then heated to the reflux temperature for 4 h. The mixture then was allowed to cool down to room temperature and was stirred for 1 h additionally at room temperature. After 30 min a precipitate was formed. The solvent was evaporated slowly at room temperature and Cu(II) complexes were collected, then washed with cold ethanol-water and dried in air. The Cu(II) complexes  $[Cu(L_n)_2Cl]Cl$  (n = 1 or 2) and  $[Cu(L_n)Cl_2]$ (n = 1 or 2) were synthesized as described above for  $[Cu(L_n)_3]Cl_2$ (n = 1 or 2), with ligands:salt ratio of 2:1 and 1:1, respectively.

**For** [**Cu**(**L**<sub>1</sub>)<sub>3</sub>]**Cl**<sub>2</sub> (1) Color: Green; m.p: 205 °C; Yield (%): 58; Anal. Calc. for [ $C_{75}H_{42}N_{12}O_3Cl_2Cu$ ] (F.W: 1293.7 g/mol): C, 69.63; H, 3.27; N, 12.99. Found: C, 70.04; H, 3.15; N, 12.86%.  $A_M = 219 - \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,  $\mu_{\text{eff}} = 1.75$  [B.M]. FT-IR (KBr pellets,  $v_{\text{max}}/\text{cm}^{-1}$ ): 3058 v(Ar—CH), 1661 v(C=O), 1594 and 1578 v(C=N), 1493– 1447 v(C=C), 715 v(Cu—Cl), 488 v(Cu—N). UV–Vis ( $\lambda_{\text{max}}$ , nm, \* – = shoulder peak): 284, 366, 385, 532\* and 728 (in C<sub>2</sub>H<sub>5</sub>OH); 286, 369, 388, and 735\* (in CHCl<sub>3</sub>). MS (LSI, Scan ES<sup>+</sup>): *m/z* (%) 1294 (16) [M]<sup>+</sup>, 1097 (82), 1054 (100), 779 (26), 716 (53), 422 (18) and 141 (20).

**For** [**Cu**(**L**<sub>1</sub>)<sub>2</sub>**Cl**]**Cl** (2) Color: Green; m.p: >300 °C; Yield (%): 61; Anal. Calc. for [C<sub>50</sub>H<sub>28</sub>N<sub>8</sub>O<sub>2</sub>Cl<sub>2</sub>Cu] (F.W: 907.3 g/mol): C, 66.19; H, 3.11; N, 12.35. Found: C, 66.11; H, 3.08; N, 12.29%.  $A_M = 74 \Omega^{-1} - Cm^2 mol^{-1}$ ,  $\mu_{eff} = 1.81$  [B.M]. FT-IR (KBr pellets,  $v_{max}/Cm^{-1}$ ): 3060 v(Ar-CH), 1662 v(C=O), 1595 and 1578 v(C=N), 1494–1446 v(C=C), 716 v(Cu-Cl), 487 v(Cu-N). UV–Vis ( $\lambda_{max}$ , nm, \* = shoulder peak): 290, 354\*, 365, 384 (in C<sub>2</sub>H<sub>5</sub>OH); 288, 351\*, 368 and 386 (in CHCl<sub>3</sub>). MS (LSI, Scan ES<sup>+</sup>): m/z (%) 872 (82) [M–Cl+1]<sup>+</sup>, 870 (100), 835 (28), 484 (84), 372 (26) and 105 (63).

**For** [**Cu**(**L**<sub>1</sub>)**Cl**<sub>2</sub>] (**3**) Color: Dark green; m.p: >300 °C; Yield (%): 63; Anal. Calc. for [C<sub>25</sub>H<sub>14</sub>N<sub>4</sub>OCl<sub>2</sub>Cu] (F.W: 520.8 g/mol): C, 57.65;



Scheme 1. The structure of the proposed ligands and their Cu(II) complexes.

H, 2.71; N, 10.76. Found: C, 57.58; H, 2.78; N, 10.73  $\Lambda_M = 29 \Omega^{-1} - \text{cm}^2 \text{ mol}^{-1}$ ,  $\mu_{\text{eff}} = 1.74$  [B.M]. FT-IR (KBr pellets,  $v_{\text{max}}/\text{cm}^{-1}$ ): 3059 v(Ar-CH), 1660 v(C=O), 1594 and 1584 v(C=N), 1496–1446 v(C=C), 716 v(Cu-Cl), 482 v(Cu-N). UV–Vis ( $\lambda_{\text{max}}$ , nm, \* = shoulder peak): 239\*, 281, 382, 422 (in C<sub>2</sub>H<sub>5</sub>OH); 287, 334\*, 366, 385 and 431 (in CHCl<sub>3</sub>). MS (LSI, Scan ES<sup>+</sup>): m/z (%) 519 (10) [M–1]<sup>+</sup>, 484 (100), 453 (18), 237 (16), 228 (45) and 148 (19).

**For** [**Cu**(**L**<sub>2</sub>)<sub>3</sub>]**Cl**<sub>2</sub>·**H**<sub>2</sub>**O** (4) Color: Dark-Red; m.p: >300 °C; Yield (%): 66; Anal. Calc. for [C<sub>78</sub>H<sub>38</sub>N<sub>12</sub>O<sub>7</sub>Cl<sub>2</sub>Cu] (F.W: 1389.7 g/mol): C, 67.42; H, 2.76; N, 12.01. Found: C, 67.34; H, 2.68; N, 12.06%.  $\Lambda_M = 213 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}, \mu_{\text{eff}} = 1.80$  [B.M]. FT-IR (KBr pellets,  $\nu_{\text{max}}/ \ \text{cm}^{-1}$ ): 3383–3258 υ(H<sub>2</sub>O), 3067 υ(Ar–CH), 1671 υ(C=O), 1588 and 1537 υ(C=N), 1495–1478 υ(C=C), 719 υ(Cu–Cl), 476 υ(Cu–N). UV–Vis ( $\lambda_{\text{max}}$ , nm, \*= shoulder peak): 245\*, 269, 398 and 542\* (in C<sub>2</sub>H<sub>5</sub>OH); 260, 281, 398 and 503\* (in CHCl<sub>3</sub>). MS (LSI, Scan ES<sup>+</sup>): *m/z* (%) 1387 (8) [M]<sup>+</sup>, 1097 (82), 707 (20), 330 (23), 270 (35), 187 (33) and 135 (100).

**For** [**Cu**(**L**<sub>2</sub>)<sub>2</sub>**Cl**]**Cl** (**5**) Color: Dark brown; m.p: >300 °C; Yield (%): 63; Anal. Calc. for [C<sub>52</sub>H<sub>24</sub>N<sub>8</sub>O<sub>4</sub>Cl<sub>2</sub>Cu] (F.W: 959.3 g/mol): C, 65.11; H, 2.52; N, 11.68. Found: C, 65.08; H, 2.46; N, 11.54%.  $\Lambda_M = 72 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}, \ \mu_{\text{eff}} = 1.79$  [B.M]. FT-IR (KBr pellets,  $\nu_{\text{max}}/$  cm<sup>-1</sup>): 3064  $\nu$ (Ar–CH), 1670  $\nu$ (C=O), 1587 and 1538  $\nu$ (C=N), 1495–1441  $\nu$ (C=C), 719  $\nu$ (Cu–Cl) and 465  $\nu$ (Cu–N). UV–Vis ( $\lambda_{\text{max}}$ , nm, \* = shoulder peak): 246, 268, 387\* and 537\* (in C<sub>2</sub>H<sub>5</sub>OH); 287,

353\*, 368 and 387 (in CHCl<sub>3</sub>). MS (LSI, Scan ES<sup>+</sup>): *m/z* (%) 924 (16) [M–Cl+1]<sup>+</sup>, 872 (23), 835 (28), 387 (100), 263 (14) and 104 (16).

**For** [**Cu**(**L**<sub>2</sub>)**Cl**<sub>2</sub>] (**6**) Color: Dark brown; m.p: >300 °C; Yield (%): 63; Anal. Calc. for [ $C_{26}H_{12}N_4O_2Cl_2Cu$ ] (F.W: 546.8 g/mol): C, 57.11; H, 2.21; N, 10.25. Found: C, 57.17; H, 2.18; N, 10.19  $\Lambda_M = 32 \ \Omega^{-1} \ cm^2 \ mol^{-1}, \ \mu_{eff} = 1.85$  [B.M]. FT-IR (KBr pellets,  $\nu_{max}/$ cm<sup>-1</sup>): 3067  $\nu$ (Ar—CH), 1671  $\nu$ (C=O), 1588 and 1537  $\nu$ (C=N), 1495–1467  $\nu$ (C=C), 720  $\nu$ (Cu—Cl), 478  $\nu$ (Cu—N). UV–Vis ( $\Lambda_{max}$ , nm, \* = shoulder peak): 243, 275, 474\* (in C<sub>2</sub>H<sub>5</sub>OH); 248, 287, 334, 366, 385 and 429\* (in CHCl<sub>3</sub>). MS (LSI, Scan ES<sup>+</sup>): m/z (%) 547 (8) [M+1]<sup>+</sup>, 418 (16), 387 (100), 263 (14) and 104 (12).

#### General procedure for the cycloaddition of epoxides to CO<sub>2</sub>

A 50 mL stainless pressure reactor was charged with Cu(II)  $(1.125 \times 10^{-5} \text{ mol})$ , epoxide  $(1.125 \times 10^{-2} \text{ mol})$ , and DMAP  $(2.25 \times 10^{-5} \text{ mol})$ . The reaction vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to equilibrate and CO<sub>2</sub> 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 yields 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.

#### **Results and discussion**

#### Synthesis and spectral properties

The ligands  $(L_1)$  and  $(L_2)$  were prepared in moderate yields by refluxing the 1,10-phenantroline-5,6-dione with 3,4-diaminobenzophenone or 1,2-diamino antraquinone (one equivalent ratio) in absolute ethanol (Scheme 1), following procedures with some modifications [10,18]. The mononuclear Cu(II) complexes (Scheme 1) were synthesized by treating CuCl<sub>2</sub>·2H<sub>2</sub>O with one, two or three equivalents of the corresponding ligands in absolute ethanol-water at reflux temperature. To confirm the identity of the pre-catalysts prepared in the present work, a variety of techniques including FT-IR, UV-Vis, elemental analysis, melting point, mass spectra, molar conductivity measurements and magnetic susceptibility techniques determination for the  $[Cu(L_n)_3]Cl_2$ ,  $[Cu(L_n)_2Cl]Cl$  or  $[Cu(L_n)Cl_2]$  (in here n = 1 or 2) complexes have been utilized. The metal to ligand ratios in the mononuclear Cu(II) complexes were found to be 1:1, 1:2 or 1:3 (Scheme 1). It is reported, for complexes number (1) and (4), that copper is hexacoordinated and has an octahedral arrangement with six Cu-N bonds. In addition to the copper coordinated cation, there are two chloride ions [20,21]. In (2) and (5), copper is pentacoordinated and presents trigonal bipyramidal geometry [20,22], while in complexes (3) and (6) copper is probably tetracoordinated with a ligand  $(L_1 \text{ or } L_2)$ , and two chlorines in a plane [20,23]. The mononuclear Cu(II) complexes are paramagnetic, thus their NMR spectra could not be obtained. The other results are presented in the 'Experimental' section.

The IR spectra of the mononuclear Cu(II) complexes (1-6) were carried out in the range 4000–400 cm<sup>-1</sup>. The FT-IR spectra of the Cu(II) complexes (1-6) are compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. There are some guide peaks in the spectra of the ligands, which are of good help for achieving this goal. The position and/or the intensities of these peaks are expected to be changed

upon chelation. Coordination of the hindered ligands  $(L_1)$  and  $(L_2)$  to the Cu(II) metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the v(C=N) absorption frequency. The very strong and sharp bands located at 1595–1578 and 1588–1537  $\text{cm}^{-1}$  are assigned to the v(C=N) stretching vibrations of the azomethine of the mononuclear Cu(II) complexes. These FT-IR spectra are located different wavenumber for free ligands. So, these shifts to different wavenumbers suggest the participation of the azomethine group of these ligands in binding to the Cu(II) ion [24]. A strong peak observed at range 1671-1660 cm<sup>-1</sup> in the mononuclear Cu(II) complexes has been assigned to v(C=0) stretching vibrations. The coordination mode of the ligands  $(L_1)$  and  $(L_2)$  are further supported by new frequencies occurring in the range 488–465 cm<sup>-1</sup> due to  $\upsilon(Cu \leftarrow N)$  stretching vibrations that are not observed in the infrared spectra of the ligands [25,26]. Also, the coordination mode of the ligands  $(L_1)$  and  $(L_2)$  are further supported by new frequencies occurring in the range 720–715 cm<sup>-1</sup> due to v(Cu-Cl)stretching vibrations that are not observed in the infrared spectra of the ligands. These remain almost unchanged in the spectra of complexes, indicating that chlorines in a plane and absence in coordination. These values are in good agreement with those for mononuclear Cu(II) complexes (1-6).

Electronic spectra of mononuclear Cu(II) complexes (1-6) have been recorded in the 200–1100 nm range in C<sub>2</sub>H<sub>5</sub>OH and CHCl<sub>3</sub> solvents and their corresponding data are given in experimental part. The electronic spectra of mononuclear Cu(II) complexes (1-6) recorded in C<sub>2</sub>H<sub>5</sub>OH and CHCl<sub>3</sub> solutions showed an intense energy charge-transfer absorption band in the UV-Vis region (in 'Experimental' section). The position of this band was strongly influenced by the structure of the compounds, such as by the length of the  $\pi$ -conjugated bridge, by the electronic nature of the ligands, and also by the number of the phenanthroline moieties substituted on the conjugated system of ligand [27]. The reflectance UV-Vis spectra of the complexes (1-6) contain bands in the 239-474 nm region which are attributable to ligand-to-Cu(II) metal CT transition and the electronic transitions of the organic ligands, as expected from the higher aromaticity of the ligands which eases delocalization of electron density. However, the absorption shift

#### Table 1

Synthesis of styrene carbonate from styrene oxide and CO<sub>2</sub> catalyzed by Cu(II) complexes (1-6).

	+ CO <sub>2</sub>	0.1 % cat., 0.2 % DMAP 2 h, 100 °C, 1.5 MPa		
Entries	Catalysts	Yield <sup>a</sup>	TON <sup>b</sup>	$TOF^{c}$ $(h^{-1})$
1.	$[Cu(L_1)_3]Cl_2(1)$	64	640	320
2.	$[Cu(L_1)_2Cl]Cl(2)$	53	530	265
3.	$[Cu(L_1)Cl_2]$ (3)	32	320	160
4.	$[Cu(L_2)_3]Cl_2(4)$	72	720	360
5.	$[Cu(L_2)_2Cl]Cl(5)$	39	390	195
6.	$[Cu(L_2)Cl_2]$ (6)	75	750	375
7.	_	5 <sup>d</sup>	50	25
8.	$[Cu(L_2)Cl_2]$ (6)	16 <sup>e</sup>	160	80
9.	$[Cu(L_2)_3]Cl_2$ ( <b>4</b> )	14 <sup>e</sup>	140	70

Catalyst (1.125  $\times$  10<sup>-5</sup> mol), DMAP (2.25  $\times$  10<sup>-5</sup> mol), epoxide (1.125  $\times$  10<sup>-2</sup> mol), CO<sub>2</sub> (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.

<sup>c</sup> The rate is expressed in terms of the turnover frequency (TOF (mol of product (mol of catalyst h)<sup>-1</sup>) = turnovers/h.

<sup>d</sup> Only DMAP used as catalyst.

<sup>e</sup> Only catalyst used (without DMAP).

#### Table 2

Coupling of  $CO_2$  and various epoxides catalyzed by complex  $[Cu(L_2)Cl_2]$  (6).



Reaction conditions:  $[Cu(L_2)Cl_2]$  (6)  $(1.125 \times 10^{-5} \text{ mol})$ , DMAP  $(2.25 \times 10^{-5} \text{ mol})$ , epoxide  $(1.125 \times 10^{-2} \text{ mol})$ , CO<sub>2</sub> (1.5 MPa), 100 °C, 2 h.

and intensity change in the spectra of the mononuclear Cu(II) complexes most likely originated from the metallation, increased the conjugation and delocalization of the whole electronic system and resulted in the energy change of the  $\pi \to \pi^*$  and  $n \to \pi^*$ transitions of the conjugated chromophore [28,29]. The new broad bands of the lowest energies and in lower intensities at between 503 and 735 are assignable to d-d transitions  $(dxy \rightarrow dx^2 - v^2)$  or  $dz^2 \rightarrow dx^2 - y^2$ ), seems to be little influenced by the different substitutions on the ligands, suggesting that the coordination geometry at the metal ion could be probably a distorted octahedron for complexes (1) and (4) and five-coordinate geometry for complex (5) in C<sub>2</sub>H<sub>5</sub>OH or CHCl<sub>3</sub> solvents. These modifications in shifts and intensity for the absorption bands support that coordination of the ligands to the central Cu(II) ion occurred. Whereas, these absorption band (d-d transitions) could not be observed in the UV-Vis spectra for complexes (2), (3) and (6), due to forbidden transition rules. The energy of the band assigned to d-d transitions provides a rough estimate of the ligand field strength, since one of the electronic transitions comprised in the band envelope is  $dx^2-y^2 \rightarrow dxy$  and the energy associated with this transition is 10Dq-C [30].

Magnetic susceptibility measurements provide sufficient data to characterize the structure of the metal complexes. Magnetic moments measurements of compounds were carried out at room temperature. The room temperature effective magnetic moments ( $\mu_{eff}$ ) of all the complexes were measured on samples after necessary diamagnetic corrections were done using Pascal's table. The observed effective magnetic moments: 1.75 µB (**1**), 1.81 µB (**2**), 1.74 µB (**3**), 1.80 µB (**4**), 1.79 µB (**5**) and 1.85 µB (**6**) are comparable to the expected spin-only value (1.73 µB) for one unpaired electron and confirm the formal +2 oxidation state of the copper centers. It is obvious that the mononuclear Cu(II) complexes do not possess anti-ferromagnetic properties at room temperature [9,30].

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 more 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 [31]. With a view to studying the electrolytic nature of the mononuclear Cu(II) complexes, their molar conductivities were measured in DMF ( $10^{-3}$  M). The molar conductivity ( $\Lambda_M$ ) values of the mononuclear Cu(II) complexes (3) and (6) are in the range of 29–32  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> at room temperature [32,33], indicating their almost non-electrolytic nature. The results indicate that these Cu(II) complexes are poor in molar conductivity due to the nonfree ions in Cu(II) complexes (3) and (6). The molar conductivities  $(\Lambda_M)$  values of these Cu(II) complexes (2) and (5) are in the range of  $72-74 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at room temperature, indicating 1:1 electrolytes or presence of two ionic species in solution, whereas the complexes (1) and (4) are in the range of 213–219  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> at room temperature, indicating 1:2 electrolytes or existence of three ionic species in solution [34,35].

The results of mass spectra of the mononuclear Cu(II) complexes are taken as evidence for the formation of the proposed structures. The values of molecular weights by mass spectrometer are presented in the 'Experimental' section. The spectrums show the molecular ion peak at m/z = 1294 [M]<sup>+</sup> for (1), 872 [M–Cl+1]<sup>+</sup> for (2), 519 [M–1]<sup>+</sup> for (3), 1387 [M]<sup>+</sup> for (4), 924 [M–Cl+1]<sup>+</sup> for (5), and 547 [M+1]<sup>+</sup> for (6) which are consistent with the suggested structure as well as the theoretical molecular weight. The spectra show some prominent peaks corresponding to the various fragments of the Cu(II) complexes. The appearance of many peaks is due to the presence of isotopic atoms in the compounds. However, the mass spectrum of the complexes (2) and (5) does not display a peak refers to molecular ion peak. This may reflecting the sudden fragmentation during the evaporation process. We think a cleavage happened to an organic part surrounds the Cu(II) metal ion.

#### Catalytic properties

The coupling of carbon dioxide and epoxides catalyzed by mononuclear Cu(II) complexes (Scheme 1) was investigated under different reaction conditions. The results were shown in Tables 1 and 2. Lewis base and Lewis acid work together to open the epoxy ring and then CO<sub>2</sub> react with this intermediate to give the corresponding cyclic carbonate via a recyclization step. In our previous study [10],  $[Ru(L_1)_3](PF_6)_2$  complex has been synthesized and used as catalyst at the identical conditions (1.6 MPa, 2 h, 0.02 mol% DMAP, 0.01 mol% cat, 100 °C). When compared  $[Cu(L_1)_3]Cl_2$  and  $[Ru(L_1)_3](PF_6)_2$  complexes, the yield of SC were almostly the same, yields were 64 and 62.7 respectively.

It should be noted that all of the mononuclear Cu(II) complexes are air-stable and robust. The yields 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. It can be seen that the catalyst of  $[Cu(L_2)Cl_2]$  (6) have better effective than the other mononuclear Cu(II) complexes in the formation of cyclic organic carbonates from carbon dioxide (Fig. 1). A very high selective conversion rate was obtained using this catalyst  $[Cu(L_2)Cl_2]$  (6) and epichlorohydrine as the substrate. In general, differences in the ligand substitution pattern in the phenanthroline derivatives containing mononuclear Cu(II) complexes do not have a great effect on the catalytic activity. This suggests that the overall coordination sphere in these phenanthroline derivatives containing catalyst precursors is favorable for the efficient coupling reaction and the nature and size of ligand substituents in the series have a minor influence on the course of the reaction [36].



Fig. 1. Conversion of styrene oxide as a function of (a) time, (b) pressure and (c) temperature with  $[Cu(L_2)Cl_2]$  (6) as catalyst.

The catalysts  $[Cu(L_2)_3]Cl_2(4)$  and  $[Cu(L_2)Cl_2](6)$  show low activity without additive (DMAP). The catalytic run blank without Cu(II) catalyst to ascertain the activity of DMAP alone under the given conditions was done and found to be 5% SC conversion. Similarly, when metal catalysts  $[Cu(L_2)_3]Cl_2(4)$  and  $[Cu(L_2)Cl_2](6)$  used alone, SC conversion were 14% and 16% respectively (Table 1). As a conclusion, it can be said that both a metal catalyst and a co-catalyst must be used together. Similar results have been reported elsewhere [37–40].

It can be seen from Table 2 that the electron withdrawing groups at the 2-position of the epoxide activate the substrate, while electron donating substituents deactivated the epoxide. Epichlorohydrine was found to be the most reactive epoxide, while 1,2-epoxy butane exhibited the lowest activity of the epoxides surveyed. The reaction time was shown to have an influence on the catalytic activity of transformation of SO to its related cyclic carbonate using  $[Cu(L_2)Cl_2]$  (6) as catalyst. The influence of time on the yield of styrene carbonate (SC) was investigated at CO<sub>2</sub> pressures of 1.5 MPa and 100 °C. The yield increased with increasing the catalytic reaction time (Fig. 1a).

The CO<sub>2</sub> pressure has also an important effect on the yield of SC. Between 0.5 and 2.5 MPa CO<sub>2</sub> pressure, SC yield was proportional to the pressure. In the higher pressures than 2.5 MPa, it was found that there was an inverse proportion between pressure and SC yield (Fig. 1b). The effect of temperature has also been investigated. While the reaction did not occur at 50 °C, the SC yield has increased suddenly at the region of 75–125 °C. However, at higher temperatures than 125 °C, SC yield has decreased rapidly (Fig. 1c).

#### Conclusion

A series of the mononuclear Cu(II) metal complexes containing the ligand Bdppz [(9a,13a-dihydro-4,5,9,14-tetraaza-benzo[b] triphenylene-11-yl)-phenyl-methanone] ( $L_1$ ) and Aqphen [(12,17dihydronaphthol[2,3-h]dipyrido[3,2-a:2',3'-c]-phenazine-12,17dione)] ( $L_2$ ) as catalyst were synthesized for the coupling of carbon dioxide and liquid epoxide which served as both reactant and solvent. Besides the classical methods such as FT-IR, UV-Vis, elemental analysis, melting point, mass spectra, and molar conductivity measurements for structural determination in addition to magnetic susceptibility techniques were also employed for structural characterization. The results agree with the expected structure. The reaction of the Bdppz ( $L_1$ ) and Aqphen( $L_2$ ) ligands in a 1:1, 1:2 or 1:3 mole ratio with CuCl<sub>2</sub>·2H<sub>2</sub>O afforded ionic Cu(II) complexes in the presence of Et<sub>3</sub>N. The catalytic results shown that the mononuclear complex [Cu(L<sub>2</sub>)Cl<sub>2</sub>] (**6**) has better effective activities than the other mononuclear Cu(II) complexes in the formation of cyclic organic carbonates from carbon dioxide.

#### Acknowledgements

This research was supported by the Technological and Scientific Research Council of Turkey TUBITAK (*TBAG Project No:111T944 and 110T655*) and the Research Fund of Harran University (*HUBAK Projects No: 1042, Sanliurfa, Turkey*). We would like to thank Prof. Dr. H. KANTEKIN from the Karadeniz Technical University Trabzon/Turkey for recording the mass spectra.

#### References

- [1] S. Brooker, J.A. Kitchen, J. Chem. Soc. Dalton (2009) 7331-7340.
- [2] M. Walesa-Chorab, A.R. Stefankiewicz, A. Gorczynski, Polyhedron 30 (2011) 233-240.
- [3] F. Xu, B. Hu, T. Tao, W. Huang, Struct. Chem. 22 (2011) 123-133.
- [4] B. Machura, J.G. Malecki, A. Switlicka, I. Nawrot, R. Kruszynski, Polyhedron 30 (2011) 864–872.
- [5] M.R. Kember, A.J.P. White, C.K. Williams, Inorg. Chem. 48 (2009) 9535-9542.
- [6] G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6618-6639.
- [7] D.J. Darensbourg, M. Ulusoy, O. Karronnirun, R.R. Poland, J.H. Reibenspies, B. Cetinkaya, Macromolecules 42 (2009) 6992–6998.
- [8] D.H. Gibson, Chem. Rev. 96 (1996) 2063-2095.
- [9] A. Kilic, M. Durgun, M. Ulusoy, E. Tas, J. Chem. Res. 11 (2011) 622-626.
- [10] A. Kilic, M. Ulusoy, M. Durgun, Z. Tasci, I. Yilmaz, B. Cetinkaya, E. Tas, Appl. Organomet. Chem. 24 (2010) 446–453.
- [11] M. Ulusoy, A. Kilic, M. Durgun, Z. Tasci, B. Cetinkaya, J. Organomet. Chem. 696 (2011) 1372–1379.

- [12] G. Shaikh, Chem. Rev. 96 (1996) 951-976.
- [13] J.H. Clements, Ind. Eng. Chem. Res. 42 (2003) 663-676.
- [14] S. Inoue, ChemTech 6 (1976) 588–594.
- [15] W. Kuran, Prog. Polym. Sci. 23 (1998) 919-992.
- [16] A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London, 1968. pp. 4.
- [17] I. Yilmaz, S. Ilhan, H. Temel, A. Kilic, J. Incl. Phenom. Macrocycl. Chem. 63 (2009) 163–169.
- [18] R. Lopez, B. Loeb, T. Boussie, T.J. Meyer, Tetrahedron Lett. 37 (1996) 5437– 5440.
- [19] F.P. Canhota, G.C. Salomao, N.M.F. Carvalho, O.A.C. Antunes, Catal. Commun. 9 (2008) 182–185.
- [20] C. Detoni, N.M.F. Carvalho, Rodrigo O.M.A. de Souza, Donato A.G. Aranda, O.A.C. Antunes, Catal. Lett. 129 (2009) 79–84.
- [21] F.F. Jian, J.H. Lin, S.S. Zhang, Chin. J. Chem. 19 (2001) 772-777.
- [22] G. Murphy, C. O'Sullivan, B. Murphy, B. Hathaway, Inorg. Chem. 37 (1998) 240-248.
- [23] G.H. Faye, Can. J. Chem. 44 (1966) 2165-2171.
- [24] N. Gokhale, S. Padhye, D. Rathbone, D. Billington, P. Lowe, C. Schwalbe, C. Newton, Inorg. Chem. Commun. 4 (2001) 26–29.
- [25] S. Shit, J. Chakraborty, B. Samanta, A.M.Z. Slawin, V. Gramlich, S. Mitra, Struct. Chem. 20 (2009) 633–642.
- [26] M. Ulusoy, O. Sahin, A. Kilic, O. Buyukgungor, Catal. Lett. 141 (2011) 717-725.
  [27] R.M.F. Batista, S.P.G. Costa, M. Belsley, C. Lodeiro, M. Manuela, M. Raposo, Tetrahedron 64 (2008) 9230-9238.
- [28] Z. Chen, Y. Wu, D. Gu, F. Gan, Spectrochim. Acta A 68 (2007) 918–926.
- [29] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.I. Abou-Dobara, H.A. Seyam, Spectrochim. Acta A 104 (2013) 213–221.
- [30] G. Maki, J. Chem. Phys. 28 (1958) 651-662.
- [31] M.S. Refat, J. Mol. Struct. 742 (2007) 24-37.
- [32] R.L. Dutta, Inorganic Chemistry Part II, second ed., The New Book Stall, Calcutta, 1981, p. 386.
- [33] A. Kilic, E. Tas, I. Yilmaz, J. Chem. Sci. 121 (1) (2009) 43-56.
- [34] S. Ilhan, H. Temel, I. Yilmaz, A. Kilic, Trans. Metal. Chem. 32 (2007) 344–349.
- [35] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81-122.
- [36] A. Sibaouih, P. Ryan, K.V. Axenov, M.R. Sundberg, M. Leskel, T. Repo, J. Mol. Catal. A: Chem. 312 (2009) 87–91.
- [37] A. Sibaouih, P. Ryan, M. Leskel, B. Rieger, T. Repo, Appl. Catal. A 365 (2009) 194–198.
- [38] K. Mori, Y. Mitani, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, Chem. Commun. (2005) 3331–3333.
- [39] F. Li, C. Xia, L. Xu, W. Sun, G. Chen, Chem. Commun. (2003) 2042-2043.
- [40] R.L. Paddock, S.T. Nguyen, J. Am. Chem. Soc. 123 (2001) 11498-11499.