

# Synthesis and Characterization of Novel µ-Carbonato Tetranuclear Copper Complexes [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>] in Aprotic Media

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# Abstract

In this work, novel oxidative coupling complexes,  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  (n = 1 or 2, X = Cl or Br, Pip = piperidine), are synthesized from the reaction of well characterized Lewis base  $[(Pip)_{4n}Cu_4X_4O_2]$  with carbon dioxide as a Lewis acid in CH<sub>2</sub>Cl<sub>2</sub>. These carbonato-derivatives are isolated as stable solids. They are easily soluble in aprotic solvents as CH<sub>2</sub>Cl<sub>2</sub>or phNO<sub>2</sub>. Cryoscopic measurements support tetranuclear structure for all of them. Electronic spectra in the near infrared with high molecular absorptivity may be explained for tetranuclear cuban structure to fulfil 3 halo-ligands for each copper centre in  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$ . The EPR spectra for  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes are axial type of spectra ( $d_{x2-y2}$  G.S) suggesting elongated tetragonal distortion for all of them. Cyclic voltammograms for  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  are irreversible in character. These tetranuclear carbonato complexes show catalytical activity. They initiate the oxidation of 2,6-dimethylphenol (DMP) to 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (DPQ).

# **Keywords**

Complexes, Tetranuclear Cuban, Carbonato Bridge, Copper

# **1. Introduction**

There has been a great worldwide interest in the preparation and characterization of a large number of copper

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complexes using elemental oxygen to imitate the active sites of certain copper enzyme models [1]-[7]. Studies including the reactions of these models with dioxygen give good information for detecting the geometrical structure of the copper ion in protein [8]. Dioxygen is found to activate copper(I) complexes for synthesis of new oxidative coupling catalysts for phenols [9]-[11]. These catalysts show a great biological importance as they imitate the tyrosinase enzyme activity for phenol oxidation [9]-[11]. In these oxidation processes, copper(I) is oxidized to copper(II) and the molecular oxygen will be reduced to superoxo, peroxo, hydroxo or oxo species [12]-[16]. The oxo-type complexes are reported during the reaction of some tetranuclear Cu(I) complexes with  $O_2$  [13]-[16]. The 3-dimensional molecular geometry of tetranuclear [(Pip)CuI]<sub>4</sub> is elucidated using X-ray in previous work [17]. The molecular (core) structure of [(Pip)CuI]<sub>4</sub> is in fact, very closely identical to previous work for [LCuI]<sub>4</sub>; L = pyridine (Py) or N, N-diethylnicotinamide (DENC) [17] [18].

This work is designed to synthesize and characterize some novel  $\mu$ -carbonato complexes, [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub> (CO<sub>3</sub>)<sub>2</sub>] (where: n = 1 or 2, X = Cl or Br, Pip = piperidine) from the reaction of tetranuclear- $\mu$ -oxo [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>O<sub>2</sub>] complexes with CO<sub>2</sub>. In this work, both the basicity of oxo-centre and the non-linearity of Cu-O-Cu angle in [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>O<sub>2</sub>] allow the insertion of CO<sub>2</sub> to form the corresponding carbonato complexes.

# 2. Experimental

# 2.1. Reagents

Pip (Aldrich), was used after vacuum distillation, (pK<sub>b</sub> = 2.8). Gaseous CO<sub>2</sub>, was dried by passage through a 10 cm column of Drierite. PhNO<sub>2</sub>, was distilled from P<sub>2</sub>O<sub>5</sub>, and kept over 4 Å molecular sieves ( $K_f$  = 7.0°C/molal, d = 1.25). CH<sub>2</sub>Cl<sub>2</sub> was washed with concentrated sulphuric acid, dried over Na<sub>2</sub>CO<sub>3</sub>, refluxed over P<sub>2</sub>O<sub>5</sub>, then distilled and stored over anhydrous Na<sub>2</sub>CO<sub>3</sub>. DMP was purified by sublimation, (m.p. 46°C - 47°C). Dinitrogen gas was deoxygenated by passage through a column of Alfa-DE-Ox solid catalyst and dried by passage through a 60 cm column of dehydrated silica gel and 30 cm column of (Calcium chloride and molecular sieves). Copper(I) halides were prepared as described in literature (CuCl and CuBr) [19].

#### 2.2. Instrumentation

UV-vis spectrophotometer model 160A (Shimadzu) was used to record the electronic spectra of the investigated complexes. FT-IR spectra of the free ligands and their complexes were performed as KBr discs using Perkin Elmer System 2000 FT-IR spectrophotometer. Calibration of wave numbers was made with a polystyrene film. EPR spectra for the investigated copper complexes were measured using a Radiopan varian spectrometer at 100.0000 KHz at different G modulation amplitude with rectangular TE 102 cavity and 100 KHz modulation field Resonance conditions were found at 9.7 GHz (X-band) at room temperature. The field was calibrated with a powder of diphenylpicrylhydrazyl (DPPH; g = 2.0037) [20]. Cyclic voltammetery (CV) measurements were carried out using a bioanalytical system BAS-27 electrochemistry analyzer connected with BAS, X-Y recorder and in conjugation with a three electrodes cell fitted with a purged dinitrogen gas inlet and outlet. Three electrodes were a Beckman Pt working electrode at room temperature (5 mm diameter) and a Pt wire auxiliary electrode. All potentials of Cu-complexes  $(1.0 \times 10^{-3} \text{ M})$  were determined using Ag/Ag<sup>+</sup> as a reference electrode  $(1.0 \times 10^{-3} \text{ M AgNO}_3 \text{ in a } 0.1 \text{ M TBAP}$  (tetrabutylammonium perchlorate) in CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub> gas at room temperature [21]. Molecular weight determination was performed via freezing point depression of nitrobenzene solution containing a known amount of solute using Eutechnics precision temperature, model 4600 thermometer [22]. The elemental analyses for Cu and X (Cl, Br) were estimated using the same protocols reported before [23]. CHNS analysis was obtained using LECO CHNS-932 Elemental Analyzer.

## 2.3. Synthesis of Complexes

#### 2.3.1. Synthesis of [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>] (n = 1 or 2, X = Cl or Br)

A solution of Pip (2.5 mmole) in (30 ml)  $CH_2Cl_2$  was flushed with pure N<sub>2</sub> gas for 10 mins. The appropriate copper (I) halide (X = Cl orBr) (2.5 mmole) was then added under N2. The reaction mixture was stirred with a stream of N2.

# 2.3.2. Synthesis of $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$ (n = 1 or 2, X = Cl or Br) Complexes

[(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>] solution in a deoxygenated CH<sub>2</sub>Cl<sub>2</sub> was flushed with O<sub>2</sub> and CO<sub>2</sub> gases for about 10 min., then

the solvent was removed by vacuum rotary evaporator leaving a solid of the dicarbonato complex,  $[(Pip)_{4n}Cu_4 X_4(CO_3)_2]$ .

#### 2.4. Tests of Catalytic Activity

 $CH_2Cl_2$  Solutions of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes were added to various samples of 100 fold excess of DMP in  $CH_2Cl_2$ . O<sub>2</sub> was then streamed through each solution for 20 min. DPQ was characterized at 431 nm by comparison with an authentic sample.

### 3. Results and Discussion

### 3.1. Reaction of [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>] Complexes with O<sub>2</sub> and CO<sub>2</sub>

 $[(Pip)_{4n}Cu_4X_4]$  complexes are oxidized by stoichiometric amount of O<sub>2</sub> under N<sub>2</sub> condition to form  $[(Pip)_{4n}Cu_4X_4O_2]$ , Equation 1, followed by rapid reaction with CO<sub>2</sub> in accordance with Equation 2 under N<sub>2</sub> [24]-[28].

$$\left[ \left( \operatorname{Pip}_{4n} \operatorname{Cu}_{4} X_{4} \right] + \operatorname{O}_{2} \rightarrow \left[ \left( \operatorname{Pip}_{4n} \operatorname{Cu}_{4} X_{4} \operatorname{O}_{2} \right] \right]$$
<sup>(1)</sup>

$$\left[\left(\operatorname{Pip}\right)_{4n}\operatorname{Cu}_{4}X_{4}\operatorname{O}_{2}\right] + 2\operatorname{CO}_{2} \rightarrow \left[\left(\operatorname{Pip}\right)_{4n}\operatorname{Cu}_{4}X_{4}\left(\operatorname{CO}_{3}\right)_{2}\right]$$
(2)

In this reaction,  $CO_2$  acted as a Lewis acid for the accessible basic  $\mu$ -oxo copper(II) centers [24]-[28]. Solid [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>] products formed strong effervescence with dilute HCl to confirm the presence of carbonato moiety. The molar mass and analytical results for the prepared complexes are illustrated in **Table 1**. The molar mass determination confirmed that all [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>] complexes are stable tetranuclear species.

### 3.2. Infrared Spectra

In the FTIR spectrum of the free Pip ligand, a peak appeared at 3445 cm<sup>-1</sup> assigned as  $v_{NH}$  which was shifted to 3281 cm<sup>-1</sup> in the spectra of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  indicating the coordination of Cu-centres to piperidyl nitrogen, **Figure 1**. For n = 2 complexes, these bands were broad or splitted which may be attributed to the fact that each Cu centre is surrounded by two Pip ligands, in which the hydrogen of one Pip ligand is free, while the other hydrogen in pip ligand is hydrogen bonded with basic centre existing in carbonato complexes as described before in similar reported cases for the oxo  $[(Pip)_{4n}Cu_4X_4O_2]$  complexes [24]-[28]. The spectrum of Pip showed also two bands at 1652 cm<sup>-1</sup> and 1542 cm<sup>-1</sup> due to  $\delta_{NH}$ , which became overlapped, broad and shifted to 1610 cm<sup>-1</sup> on complexation, **Figure 1** [24]-[28]. The carbonato bridge has characteristic vibrational bands,  $v_3$  at 1600 - 1500 cm<sup>-1</sup> and at 1490 - 1350 cm<sup>-1</sup>,  $v_2$  (900 - 800) cm<sup>-1</sup> and  $v_4$  (750 - 700) cm<sup>-1</sup> [26] [27]. The increase in the intensity of  $v_3$  band at 1450 cm<sup>-1</sup>, for the [(Pip)\_4Cu\_4Cl\_4(CO\_3)\_2], **Figure 1** confirmed the fact that the CO<sub>3</sub><sup>2-</sup> bridge is tridentate to fulfil the 6-coordinated Cu(II) centres, (**Scheme 1(a)**). While in the [(Pip)\_8Cu\_4Cl\_4(CO\_3)\_2], the CO<sub>3</sub><sup>2-</sup> bridge switches to bidentate ligand (**Scheme 1(b)**). From (900 - 800) cm<sup>-1</sup>, the carbonato bridge has  $v_2$  while Pip has three bands; 805, 830 and a very strong one at 863 cm<sup>-1</sup>. Therefore, the strong band at 863 cm<sup>-1</sup> will be moved to 877 cm<sup>-1</sup> for [(Pip)\_4Cu\_4Cl\_4(CO\_3)\_2] and its intensity at the same wave number, 877 cm<sup>-1</sup>, becomes weak by adding one extra Pip per each Cu(II) centre as in [(Pip)\_8Cu\_4Cl\_4(CO\_3)\_2], **Figure 1**, supporting the

| Complex                     |        |       | Molar mass |        |        |               |
|-----------------------------|--------|-------|------------|--------|--------|---------------|
|                             | С      | Н     | Ν          | Cu     | Х      | Ma            |
| $[(Pip)_4Cu_4Cl_4(CO_3)_2]$ | 29.8   | 5.3   | 6.2        | 29.2   | 17.4   | $890 \pm 20$  |
|                             | (30.8) | (5.1) | (6.4)      | (29.7) | (16.6) | (856)         |
| $[(Pip)_4Cu_4Br_4(CO_3)_2]$ | 24.2   | 4.4   | 5.4        | 24.9   | 30.3   | $1128 \pm 20$ |
|                             | (25.5) | (4.3) | (5.4)      | (24.6) | (30.9) | (1033)        |
| $[(Pip)_8Cu_4Cl_4(CO_3)_2]$ | 39.0   | 6.6   | 9.2        | 21.1   | 12.2   | $1190 \pm 20$ |
|                             | (42.1) | (7.3) | (9.4)      | (21.2) | (11.9) | (1197)        |
| $[(Pip)_8Cu_4Br_4(CO_3)_2]$ | 34.0   | 6.1   | 7.8        | 18.4   | 23.0   | $1390 \pm 20$ |
|                             | (36.7) | (6.4) | (8.2)      | (18.5) | (23.3) | (1375)        |

**Table 1.** Analytical and cryoscopic data for  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$ ; n = 1 or 2 and X = Cl or Br.



**Figure 1.** KBr disk or plates I.R. spectra for (a) Piperidine, (b)  $[(Pip)_4Cu_4Cl_4(CO_3)_2]$  and (c)  $[(Pip)_8Cu_4Cl_4(CO_3)_2]$ .



Scheme 1. Proposed molecular core structures for  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$ .

change of carbonato bridge from structure **<u>b</u>** as in (Scheme 1) [24]-[28].

#### 3.3. Electronic Spectra

The electronic spectral data of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes are presented in **Table 2** and **Figure 2**. A splitted peak within (740 - 840) nm range for the studied complexes are observed indicating the presence of at least 3 halo ligands per each Cu(II) centre which indicates a tetranuclear cuban core structured complexes (**Scheme 1**) [24]-[28]. It is noticed that the values of  $\varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>) of the splitted peak in case of bromo-complexes are 1.7 times greater than those of the chloro-complexes for similar n. To maintain the coordination number 6 for Cu(II), the only possible change is the conversion of carbonato bridging ligand from tridentate as in structure **a** to bidentate as in structure **b** (**Scheme 1**). A previous work showed a similar spectral behavior for the comparable complexes, of which the electronic spectra were attributed to LMCT between a minimum of 3 halo ligands and a Cu(II) site [24]-[31].

## 3.4. EPR Spectra

The solid state EPR spectra of [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>], Figure 3 and Table 2 show axial spectra with  $g_{\parallel} > g_{\perp} > 2.04$ , confirming the  $d_{x2-y2}$  ground state for elongated tetragonal octahedral geometry [32] [33].





| Table 2. | EPR and   | electronic | spectral | data for | $[(Pip)_{4n}C$ | $Cu_4X_4(CO_3)$ | $_{3})_{2}]; n =$ | $1 \text{ or } 2, \lambda$ | $\mathbf{K} = \mathbf{C}\mathbf{I}$ | or Br, i | in CH | $_2Cl_2$ at |
|----------|-----------|------------|----------|----------|----------------|-----------------|-------------------|----------------------------|-------------------------------------|----------|-------|-------------|
| room tem | perature. |            |          |          |                |                 |                   |                            |                                     |          |       |             |

| Complex                     |                 | E     | Electronic spectra |         |  |
|-----------------------------|-----------------|-------|--------------------|---------|--|
|                             | A <sub>ll</sub> | g∥    | $g_{\perp}$        | <g></g> | $\lambda$ max., nm ( $\varepsilon$ , M <sup>-1</sup> ·cm <sup>-1</sup> ) |
| $[(Pip)_4Cu_4Cl_4(CO_3)_2]$ | 166.00          | 2.379 | 2.065              | 2.172   | 740 (680), 840 (675)   |
| $[(Pip)_8Cu_4Cl_4(CO_3)_2]$ | 102.13          | 2.390 | 2.075              | 2.180   | 740 (590), 840 (560)   |
| $[(Pip)_4Cu_4Br_4(CO_3)_2]$ | 162.16          | 2.440 | 2.077              | 2.198   | 740 (1130), 840 (1080)   |
| $[(Pip)_8Cu_4Br_4(CO_3)_2]$ | 53.00           | 2.387 | 2.090              | 2.187   | 740 (1000), 840 (950)  |



#### **3.5. Redox Chemistry**

The CV measurements, **Table 3** and **Figure 4** for  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes are conducted in CH<sub>2</sub>Cl<sub>2</sub> made of 0.1 M TBAP using a Pt-working electrode with non-aqueous reference electrode (Ag/Ag<sup>+</sup>, 1.0 × 10<sup>-3</sup> M AgNO<sub>3</sub> in 0.1 M TBAP in CH<sub>2</sub>Cl<sub>2</sub>) and Pt-wire auxiliary electrode. The electrode potentials are measured against Ag/Ag<sup>+</sup> as a reference electrode. The Ferrocene (Fc) internal standard was used against Ag/Ag<sup>+</sup> under similar experimental conditions to correlate the electrode potentials to NHE. The formal electrode potential of a reversible one-electron standard Fc/Fc<sup>+</sup> against NHE is 0.4 volt [34] [35]. The CV of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes are irreversible in character and show two cathodic peaks as in **Table 3**. The above systems are quite similar to  $[(Pip)_{4n}Cu_4X_4O_2]$  cyclic voltammograms in which the electrolysis at -1.3 volt, indicated four electrons to reduce four copper(II) [34] [35]. In  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$ , the reduction occurs in two steps separated by about 0.35 volt, due to the morphology of the tetranuclear cuban structure on the electrode surface.

## 3.6. Test of Catalytic Activity

 $CH_2Cl_2$  solutions of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes were added to various samples of a 100-fold excess of DMP in  $CH_2Cl_2$ .  $O_2$  was then streamed through each solution for 20 min. The DPQ which was characterized at



Potential, volt vs. Ag/Ag+

Figure 4. Cyclic voltammetry of  $1.0 \times 10^{-3}$  M of (a) [(Pip)<sub>4</sub>Cu<sub>4</sub>Cl<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>], (b) [(Pip)<sub>8</sub>Cu<sub>4</sub>Cl<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>], (c) [(Pip)<sub>4</sub>Cu<sub>4</sub>Br<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>], (d) [(Pip)<sub>8</sub>Cu<sub>4</sub>Br<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>] in (e) 0.1 M TBAP in CH<sub>2</sub>Cl<sub>2</sub> solvent at Pt working electrode at room temperature, and scan rate 100 mV/s.

**Table 3.** Cyclic voltammetric data for  $1.0 \times 10^{-3}$  M [(Pip)<sub>4n</sub>Cu<sub>4</sub>X<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>]; n = 1 or 2 and X = Cl or Br, at scan rate 100 mV/sec in 0.1 M TBAP in CH<sub>2</sub>Cl<sub>2</sub> and at room temperature.

| Complex   | Cathodic p | beaks, Volt | A 1' 1 37.1/       |  |
|---|------------|-------------|--------------------|--|
| Complex   | $E_{c_1}$  | $E_{c_2}$   | Anodic peaks, voit |  |
| Ferrocene*  | -0.25      |             | -0.05              |  |
| $[(Pip)_4Cu_4Cl_4(CO_3)_2]$   | -0.67      | -1.06       |                    |  |
| $[(Pip)_8Cu_4Cl_4(CO_3)_2]$   | -0.70      | -1.13       |                    |  |
| $[(Pip)_4Cu_4Br_4(CO_3)_2]$   | -0.85      | -1.16       |                    |  |
| $[(\operatorname{Pip})_8\operatorname{Cu}_4\operatorname{Br}_4(\operatorname{CO}_3)_2]$ | -0.81      | -1.13       |                    |  |

\*0.4 volt is the formal electrode potential of a reversible one-electron standard couple (Fc/Fc+) versus NHE [21].

431 nm by making comparison with an authentic sample ( $\varepsilon = (5.05 \pm 0.01) \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ) [36] was the only product in all reactions, Scheme 2.

After 3 days, the yield of (DPQ) formed was in the range of  $(55\% \pm 5\%)$ , the same yield was also observed for  $[(Pip)_4Cu_4Cl_4O_2]$  [24].

### 4. Conclusion

According the characterization data, novel complexes of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  can be used as oxidative coupling initiators for oxidation of DMP to DPQ, Scheme 2. It is worth to mention that the formation of  $[(Pip)_{4n}Cu_4X_4(CO_3)_2]$  complexes can be explained on the basis that the angle of Cu-O-Cu in  $[(Pip)_{4n}Cu_4X_4O_2]$  is



Scheme 2. Catalytical cycle for homogenous oxidative coupling of phenols by copper catalyst.

acute to a degree suitable to let oxo centre basic enough for catalytic activity and to permit  $CO_2$  insertion to produce the carbonato complexes. Cryoscopic measurements support tetranuclear structure for all of them.

#### **References**

- [1] Karlin, K.D. and Tyklar, Z. (1993) Bioinorganic Chemistry of Copper. Chapman and Hall, New York.
- [2] Sorell, T.N. (1989) Tetrahedron. Synthetic Models for Binuclear Copper Proteins, 45, 3.
- [3] Segoviano-Garfias, J.N.J., Mendoza-Díaz, G. and Moreno-Esparza, R. (2014) A Comparative Study of the Speciation in Methanol Solution and Activity in the Oxidative Coupling of 2,6-Di-tert-butylphenol Presented by the Complexes: Cop-per(II)-N,N'-di-tert-butylethylenediamine-halogen and Some Copper(II)-diamine-halogen Complexes. *Inorganica Chimica Acta*, **411**, 148-157. http://dx.doi.org/10.1016/j.ica.2013.12.009
- [4] Liu, Q. and Wu, H.G. (2013) Carboxylic-Supported Copper Complexes as Catalyst for the Green Oxidative Coupling of 2,6-Dimethylphenol: Synthesis, Characterization and Structure. *Comptes Rendus Chimie*, 16, 451-461. http://dx.doi.org/10.1016/j.crci.2012.11.011
- [5] Meghdadi, S., Amirnasr, M., Mirhashemi, A. and Amiri, A. (2015) Synthesis, Characterization and X-Ray Crystal Structure of Copper(I) Complexes of the 2-(2-Quinolyl) Benzothiazole Ligand. *Electrochemical and Antibacterial Studies*, *Polyhedron*, **97**, 234-239. <u>http://dx.doi.org/10.1016/j.poly.2015.05.026</u>
- [6] Peterson, R.L., Kim, S. and Karlin, K.D. (2013) Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, from Comprehensive Inorganic Chemistry II. Vol. 3, 2nd Edition, 149-177.
- [7] Lee, J.Y. and Karlin, K.D. (2015) Elaboration of Copper-Oxygen Mediated C-H Activation Chemistry in Consideration of Future Fuel and Feedstock Generation. *Current Opinion in Chemical Biology*, 25, 184-193. http://dx.doi.org/10.1016/j.cbpa.2015.02.014
- [8] Magnus, K.A., Ton-that, H. and Carpenter, J.E. (1993) Bioinorganic Chemistry of Copper. In: Karlin, K.D. and Tyklar, Z., Eds., Chapman and Hall, New York, 143.
- [9] Gamez, P., Simons, C., Steensma, R., Driessen, W.L., Ghalla, G. and Reedijk, J. (2001) A Spectacular Increase in the Polymerisation Rate of 2,6-Dimethylphenol Induced by Acetonitrile. *European Polymer Journal*, 37, 1293. http://dx.doi.org/10.1016/S0014-3057(00)00259-7
- [10] Gamez, P., Von Harras, J., Roubeau, O., Driessen, W.L. and Reedijk, J. (2001) Synthesis and Catalytic Activities of Copper(II) Complexes Derived from a Tridentate Pyrazole-Containing Ligand. X-Ray Crystal Structure of [Cu2(μdpzhp-O, N,N')2][Cu(MeOH)Cl3]2. *Inorganica Chimica Acta*, **324**, 27. http://dx.doi.org/10.1016/S0020-1693(01)00498-4
- [11] Reedijk, J. and Bouwman, E. (1999) Bioinorganic Catalysis. Second Edition, Marcel Dekker, New York. <u>http://dx.doi.org/10.1201/9780203908457</u>
- [12] Davies, G. and El-Sayed, M.A. (1985) Some Aspects of Aprotic Copper(I)-Dioxygen Systems. Comments on Inorganic Chemistry, 4, 151-162. <u>http://dx.doi.org/10.1080/02603598508072257</u>
- [13] Churchill, M.R., Davies, G., El-Sayed, M.A., Fournier, J.A., Hutchinson, J.P. and Zubieta, J.A. (1984) Crystal and Molecular Structure of bis(μ-bromo)bis(N,N,N',N'-tetraethylethylenediamine)dicopper(I) and the Kinetics of Its Oxidation by Dioxygen in Nitrobenzene. *Inorganic Chemistry*, 23, 783-787. <u>http://dx.doi.org/10.1021/ic00174a029</u>
- [14] Davies, G., El-Sayed, M.A. and Fasano, R.E. (1983) A Spectrophotometric Study of the Reactions of the Phenolic Oxidative 1 Coupling Initiator py<sub>4</sub>Cu<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub> and of py<sub>4</sub>Cu<sub>4</sub>Cl<sub>6</sub>O with Pyridine. *Inorganica Chimica Acta*, **71**, 95-99. http://dx.doi.org/10.1016/S0020-1693(00)83644-0
- [15] El-Sayed, M.A., Ismail, K.Z., El-Zayat, T.A. and Davies, G. (1994) Unusually Stable Peroxocopper Complexes. Stoichiometry, Products and Kinetics of Oxidation of the Dimeric Copper(I) Complex [LCuBr]<sub>2</sub> (L=N,N'-diethylethylenediamine) by Dioxygen in Methylene Chloride from -51 to 30 °C. *Inorganica Chimica Acta*, **217**, 109-119. http://dx.doi.org/10.1016/0020-1693(93)03755-Y
- [16] El-Sayed, M.A., El-Toukhy, A. and Davies, G. (1985) Stoichiometry and Kinetics of Oxidation of Dimeric bis(μ-halo)bis((diamine)Copper(I)) Complexes L<sub>2</sub>Cu<sub>2</sub>X<sub>2</sub> by Dioxygen in Aprotic Solvents. *Inorganic Chemistry*, 24, 3387-3390. <u>http://dx.doi.org/10.1021/ic00215a018</u>

- [17] Shramm, V. (1978) Crystal and Molecular Structure of Tetrameric Copper(I) Iodide-Piperidine, a Complex with a Tetra-Hedral Tetrakis[Copper(I) Iodide] Core. *Inorganic Chemistry*, **17**, 714-718. <u>http://dx.doi.org/10.1021/ic50181a043</u>
- [18] (a) Raston, C.L. and White, A.H. (1976) Crystal Structure of the Copper(I) Iodide-Pyridine (1/1) Tetramer. *Journal of the Chemical Society, Dalton Transactions*, No. 21, 2153-2156.
  (b) Churchill, M.R., Davies, G., El-Sayed, M.A., Hutchinson, J.P. and Rupich, M.W. (1982) Synthesis, Structure and Properties of the Tetranuclear Complexes [(DENC)CuX]4 (DENC = N,N-diethylnicotinamide; X = Cl, Br, I) and the Kinetics of Oxidation of the Chloride and Bromide by Dioxygen in Aprotic Solvents. *Inorganic Chemistry*, 21, 995-1001. http://dx.doi.org/10.1021/ic00133a025
- [19] Keller, R.N., Wycoff, H.D. and Marchi, L.E. (1946) Copper(I) Chloride. In: Fernelius, W.C., Ed., *Inorganic Syntheses*, Vol. 2, John Wiley & Sons, Inc., Hoboken, 1-4. <u>http://dx.doi.org/10.1002/9780470132333.ch1</u>
- [20] Wertz, J.E. and Bolfon, J.R. (1972) Electron Spin Resonance. McGraw-Hill, New York.
- [21] Gange, R.R., Koval, C.A. and Lisensky, G.C. (1980) Ferrocene as an Internal Standard for Electrochemical Measurements. *Inorganic Chemistry*, 19, 2854-2855. <u>http://dx.doi.org/10.1021/ic50211a080</u>
- [22] Davies, G., El-Sayed, M.A. and Henary, M. (1987) Stoichiometry and Kinetics of Low-Temperature Oxidation of di-μ-chlorobis(N,N,N',N'-tetraethylethylenediamine)dicopper by Dioxygen in Methylene Chloride and Properties of the Peroxocopper Products. *Inorganic Chemistry*, **26**, 3266-3273. <u>http://dx.doi.org/10.1021/ic00267a011</u>
- [23] (a) Schwarzenbach, G. (1957) Complexometric Titration. Methuem Co., London.
  (b) Kalthoff, M., Sandell, E.B., Meehan, E.J. and Bruckenstien, S. (Eds.) (1969) Quantitative Chemical Analysis. Macmillan, New York, 812.
- [24] El-Sayed, M.A., AbdelSalam, A.H., El-Zayat, T.A., El-Dissouky, A. and Isamil, K.Z. (2004) Homogeneous Oxidative Coupling Catalysts: Stoichiometry and Characterization of the First Stable Oxotetranuclear Solids [(Pip)<sub>n</sub>CuX]<sub>4</sub>O<sub>2</sub> (n = 1 or 2, Pip = piperidine, X = Cl, Br, I). *Inorganica Chimica Acta*, **357**, 4057-4064. http://dx.doi.org/10.1016/j.ica.2003.06.021
- [25] El-Sayed, M.A., Abdel Salam, A.H., Abo-El-Dahab, H.A., Refaat, H.M. and El-Dissouky, A. (2009) Homogeneous Oxidative Coupling Catalysts: Stoichiometry and Product Characterization of the Oxidation of Copper(I) Complexes [(Pyr)<sub>n</sub>CuX]4 (n = 1 or 2, Pyr = pyrrolidine, X = Cl, Br or I) by Dioxygen in Aprotic Media. *Journal of Coordination Chemistry*, **62**, 1015-1024. <u>http://dx.doi.org/10.1080/00958970802353652</u>
- [26] Churchill, M.R., Davies, G., El-Sayed, M.A., El-Shazly, M.F., Hutchinson, J.P. and Rupich, M.W. (1980) Synthesis, Physical Properties and Structural Characterization of μ-carbonato-dicopper(II) Complexes. 2. Products of Oxidation of Cu(I) by Dioxygen in Aprotic Media Containing Carbon Dioxide and Alkylated Diamine Ligands and the Crystal Structure of Paramagnetic (Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NEt<sub>2</sub>)<sub>2</sub>Cu<sub>2</sub>Cl<sub>2</sub> (asym-μ-CO<sub>3</sub>). *Inorganic Chemistry*, **19**, 201-208. http://dx.doi.org/10.1021/ic50203a041
- [27] El-Sayed, M.A., Abdel-Salam, A.H., Abo-El-Dahab, H.A. and Refaat, H.M. (2012) Homogeneous Oxidative Coupling Catalysts: Reactivity of  $[(Pyr)_nCuX]_4O_2$  with Carbon Dioxide to Generate New Active Initiators  $[(Pyr)_nCuX]_4(CO_3)_2$  (n = 1 or 2, X = Cl, Br or I, Pyr = Pyrrolidine). *Journal of Chemistry and Chemical Engineering*, **6**, 74-83.
- [28] El-Sayed, M.A., Abo-El-Dahab, H.A., Abdel Salam, A.H. and Refaat, H.M. (2013) Homogeneous Oxidative Coupling Catalysts: Kinetics of the Oxidation of Copper(I) Complexes [(Pyr)<sub>n</sub>CuX]<sub>4</sub> (n = l or 2, Pyr = pyr-rolidine, X = Cl, Br or I) by Dioxygen in Aprotic Media. *Asian Journal of Chemistry*, **25**, 3353.
- [29] Davies, G., El-Sayed, M.A., El-Toukhy, A., Henary, M. and Martin, C.A. (1986) Distinguishable Sites in Tetranuclear Oxocopper(II) Complexes (py)<sub>3</sub>Cu<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub> and (DENC)<sub>3</sub>Cu<sub>3</sub>M(H<sub>2</sub>O)Cl<sub>4</sub>O<sub>2</sub> (M = Co, Ni, Cu, Zn). *Inorganic Chemistry*, 25, 4479-4487. <u>http://dx.doi.org/10.1021/ic00245a007</u>
- [30] Davies, G., EL-Shazly, M.F., Rupich, M.W., Churchill, M.R. and Rotella, F.J. (1978) Synthesis, X-Ray Crystal Structure, and Properties of a Tetranuclear Complex Formed by Oxidation of Copper(I) Chloride with Molecular Dioxygen in *N*-methylpyrrolidin-2-one. Isolation of a Catalyst for the Oxidative Coupling of Phenols by Dioxygen. *Journal of the Chemical Society, Chemical Communications*, No. 23, 1045-1046. <u>http://dx.doi.org/10.1039/c39780001045</u>
- [31] Churchill, M.R. and Rotella, F.J. (1979) Crystal Structure and Molecular Configuration of a Tetranuclear Copper(II) Complex Active as a Catalyst in the Oxidative Coupling of Phenols by Dioxygen: Cu<sub>4</sub>OCl<sub>6</sub> (nmp)<sub>3</sub>(OH<sub>2</sub>···nmp) (nmp = N-methyl-2-pyrrolidinone). *Inorganic Chemistry*, **18**, 853-860. <u>http://dx.doi.org/10.1021/ic50193a063</u>
- [32] Hathawy, B.J. and Billiny, D.E. (1970) The Electronic Properties and Stereochemistry of Mono-Nuclear Complexes of the Copper(II) Ion. *Coordination Chemistry Reviews*, 5, 143-207. <u>http://dx.doi.org/10.1016/S0010-8545(00)80135-6</u>
- [33] Hathawy, B.J. (1972) The Correlation of the Electronic Properties and Stereochemistry of Mononuclear {CuN<sub>4-6</sub>} Chromophores. *Journal of the Chemical Society, Dalton Transactions*, No. 12, 1196-1199. <u>http://dx.doi.org/10.1039/dt9720001196</u>
- [34] Kissinger, P.T. and Heineman, W.R. (1983) Cyclic Voltammetry. Journal of Chemical Education, 60, 702. http://dx.doi.org/10.1021/ed060p702

- [35] Gagne, R.R., Allison, J.L. and Lisensky, G.C. (1978) Unusual Structural and Reactivity Types for Copper: Structure of a Macrocyclic Ligand Complex Apparently Containing Copper(I) in a Distorted Square-Planar Coordination Geometry. *Inorganic Chemistry*, **17**, 3563-3571. <u>http://dx.doi.org/10.1021/ic50190a046</u>
- [36] El-Sayed, M.A., Abu Raqabah, A., Davies, G. and EL-Toukhy, A. (1989) Kinetic Roof That the Tetranuclear Oxocopper(II) Complex (py)<sub>3</sub>Cu<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub> Initiates and Catalyzes the Oxidative Coupling of 2,6-methylphenol by Dioxygen in Nitrobenzene. *Inorganic Chemistry*, 28, 1909-1914. <u>http://dx.doi.org/10.1021/ic00309a028</u>