Spectroscopic, thermal, magnetic and electrochemical studies of Tetrakis-\(\mu-\)p-fluorobenzoatodicopper (II)

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Accepted 20 April, 2011

Tetrakis-\(\mu-\)p-fluorobenzoatodicopper (II) was synthesized and spectroscopically characterized to have a binuclear, paddle-wheel structure with axially ligated ethanol molecules but with unexpectedly high magnetic moment value of 1.91 B.M. The complex was found to be thermally stable up to 280°C, and underwent three stages of decomposition process. The differential scanning calorimetric (DSC) curve showed three small endotherms at 100, 150 and 190°C respectively, agreeable to the TG analysis data, indicating the initial weight loss due to solvated molecules and the starting of a major decomposition process. Cyclic voltammetry studies of the complex, in mixed-solvent system of methanol and ethanoic acid (20:1 v/v) showed three cathodic peaks at -0.22, -0.35 and -0.86 V, representing step-wise electron transfer process and a single broad anodic peak at +0.39 V. The high value of \(\Delta E\) ranging from 610 to 1250 mV indicated that the redox process was accompanied by extensive structural reorganization of the complex in the solution creating a different geometrical environment around central copper ion.

Key words: Copper (II) 4-fluorobenzoate, thermal stability, magnetic property, cyclic voltammetry.

INTRODUCTION

The chemistry of copper (II) carboxylates continues to attract a great deal of attention due to their unique and peculiar structural, magnetic, catalytic and electrochemical properties and also as potential models for a number of important biological system containing couple sites (Thirumavalavan et al., 2004; Halcrow and Christou, 1994; Jain et al., 2004; Chattopadhyay et al., 2007; Leita et al., 2004; Brooker, 2001; Suzuki et al., 2000; Bharati et al., 2007; Solomon et al., 1996). In addition, the versatility of copper (II) atom and carboxylates ligands in their coordination bonding has given rise to various mononuclear to polynuclear complexes with different physico-structural features (Melnik, 1981; Kato and Muto, 1988).

Among those classes of complexes, binuclear metal complexes are of considerable interest because they provide the opportunity to study the intramolecular binding, magnetic exchange interaction and multi electron redox reactions (Cains and Busch, 1986; Thompson et al., 1988). Apart from this, binuclear complexes normally results in the close proximity of the two central metal ions which at the moment is the sought-after feature for further study in biomimetic inorganic studies (Holm and Solomon, 2004) as well as in supramolecular chemistry and crystal engineering (Batten and Robson, 1988; Moler et al., 2001; Doulton and Zaworotko, 2001; Kim, 2002).

Copper (II) arylcarboxylates are generally dinuclear complexes with two close proximity copper (II) atoms. For example, Kawat et al. (1992) showed that copper (II) benzoate possess a very unique dinuclear complex with bidentate benzoate ligands giving rise to paddle-wheel structure (Figure 1), similar to copper (II) acetate, with Cu-Cu bond distance of 2.607(8) Å (Van Niekerk and Schoening, 1953). Such structure can lead to the development of supramolecular molecule and polymer-like compound with high potential in industrial application (Chen et al., 2001; Rosi et al., 1999; Li et al., 1999). As opposed to its counterpart, copper (II) acetate or other binuclear copper (II) alkylcarboxylates, the cage structure of copper (II) benzoate was found to be stronger and more stable due to the presence of high electron density at the bridging groups supplied by the phenyl rings, thus...
making stronger Cu – O coordinate bond.

Nevertheless, specifically for copper (II) arylicarboxylate, the existence of dinuclear structure depends predominantly on the stearic effect, namely bulky ortho-substituents. However, in the absence of stearic effect, the reduction of the charge on the copper ion is imperative. Higher ω electron density on the carboxylate oxygen atoms, which normally measured by the pKa of the parent acid, and adducts which lower the residual charge on the copper ions make the formation of dinuclear complexes favourable (Herring et al., 1971; Lewis et al., 1969). Hence the presence of substituent on the phenyl ring plays a major role in the overall physico-structural properties of the complex.

However, most work on binuclear copper (II) benzoate mainly focused on the magneto-structural relationship as well as solely on structural study (Schatzschneider et al., 2002; Lewandowski et al., 2005; Takamizawa et al., 2004). Cariati et al. (1983) reported on the synthesis of copper (II) 2,6-dihydroxybenzoate which was shown to have a polymeric structure in solid state. In addition, Lewis et al. (1969) had studied on the magnetic properties of a series of substituted aryl carboxylic acid complexes of copper (II) namely 2-methyl, 3-methyl, 2-chloro, 3-chloro, 4-chloro, 2-nitro, 3-nitro and 4-nitro. The study showed that all complexes prepared has a low value of magnetic moments (< 1.6 B.M) and thus were concluded to be having dimeric paddle-wheel structure (Lewis and Thompson, 1963). Apart from this, Erre et al. (1987) had also undertaken a study on the substituent effect on the thermal stability of the complex, focusing on the methoxy substituted benzoato ligands.

It is thus, a worthwhile endeavor to further explore other physico-structural studies of copper (II) benzoate with different substituent on the phenyl ring. Specifically for this study, we report a rather comprehensive physical study, namely magnetic, thermal and electrochemical behaviours of copper (II) benzoate with fluorine atom at the para position of the phenyl ring.

Figure 1. Dimeric and paddle-wheel structure of copper (II) benzoate.

MATERIALS AND METHODS

All chemicals and reagents were of analytical grade from commercial sources, and were used as received.

Synthesis

It is important to note that different structures of copper (II) arylicarboxylates have been reported, which seem to very much depend on the synthetic method (Fountain and Hatfield, 1965). In this paper, [Cu2(p-FC6H4COO)2]2CH3CH2OH was obtained by a metathesis reaction between copper (II) acetate and the p-fluorobenzoic acid in hot ethanol, as follows.

Copper (II) acetate monohydrate (0.02 mol) was added portion wise to the magnetically stirred hot ethanolic solution of p-fluorobenzoic acid (0.04 mol), and the mixture was further heated for an hour. The solid obtained was filtered off from the hot solution, washed several times with hot ethanol, and dried in an oven for an hour to give a blue powder (percent yield: 41%).

Physical measurements

The composition of the complex was established on the basis of the analysis of the content of metals, carbon, hydrogen and oxygen. Carbon, hydrogen and oxygen content were determined by elemental analysis using CHNS/O analyzer, Thermo Finnigam Flash EA 110. The copper content was determined by using spectrometric method using Perkin Elmer A Analyst 800 Flame Atomic Absorption Spectrometer with a slit width of 100 microns through the method of calibration curve. The IR spectrum was recorded over the range of 4000 to 400 cm$^{-1}$ using FTIR SPECTRUM RX 1 Perkin-Elmer spectrometer. The sample for the FTIR spectra measurements was prepared as potassium bromide (KBr) disc.

The UV-Visible spectrum was recorded on a Perkin-Elmer Lambda 35 UV-Visible Spectrophotometer using cm$^{-1}$ quartz cuvettes. The spectra were taken over the range of 1100 to 190 nm in mixed solvent system of methanol:ethanoic acid (20:1 v/v). The Molar absorptivity, $\varepsilon$, value was calculated on the basis of dimeric formula weight. The solid state UV-Vis spectra of the complex was also taken using Shimadzu UV-Vis-Nir Spectrophotometer. The Powder X-Ray Diffraction (PXRD) analysis was performed at room temperature by using Siemens D5000 X-Ray Diffractometer. The PXRD parameters are set in Table 1. The magnetic susceptibility measurement was performed at room temperature on a Sherwood Auto Magnetic Susceptibility Balance by the Gouy method using Hg[Co(SCN)3] as the calibrant. From the observed susceptibility, the magnetic moment, $\mu_{eff}$, is calculated using the following formula:

$$
\mu_{eff} = 2.824 \left[ T (\chi_m^{corr} \cdot N_{a})^{1/2} \right] B.M.
$$

Where $\chi_m^{corr}$ is the molar magnetic susceptibility per mole of metal ion corrected for diamagnetic contribution from the constituent atoms estimated from Pascal’s constant (Gordon and John, 2008), $N_a$ is the temperature independent paramagnetism, taken as 60 x 10$^{-6}$ c.g.s e.m.u (Fountain and Hatfield, 1965) and T is the temperature in Kelvin. The thermal stability and decomposition process were investigated by Perkin-Elmer Thermogravimetric Analyzer TGA 6. The sample (4.7 mg) was placed in a cylindrical alumina crucible. The trace was recorded from 30 to 900°C at the heating rate of 20°C min$^{-1}$ with nitrogen gas purging at the flow rate of 20 cm$^3$ min$^{-1}$. Differential scanning calorimetric analysis (DSC) was performed on a Rheometric Scientific DSC instrument. The sample (about 10 mg) was placed in a cylindrical alumina crucible.
and heated from 35 to 300°C at the rate of 10°C min\(^{-1}\) under nitrogen gas purging at the flow rate of 10 cm\(^3\) min\(^{-1}\).

Cyclic voltammetric measurements were recorded using Gamry Instrument Reference 600 potentiostat/galvanostat/ZRA. The measurements were carried out using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated calomel electrode (SCE) was the reference electrode, and platinum wire was used as the counter electrode. The working electrode was polished with aluminium oxide powder on chamois leather and the solution was degassed with nitrogen gas prior to analysis.

### RESULTS AND DISCUSSION

**Synthesis and structural elucidation**

\[\text{[Cu}_2(p\text{-FC}_6\text{H}_4\text{COO})_4]_{2}\text{CH}_3\text{CH}_2\text{OH} \]

was obtained as pale blue powder by a metathesis reaction between \(\text{[Cu}_2(p\text{-FC}_6\text{H}_4\text{COO})_4] \) and \(p\text{-FC}_6\text{H}_4\text{COOH} \) in a mole ratio of 1:2. Since monocrystal of the complex has not been hitherto obtained, the structural features of the complex was elucidated based on elemental and spectroscopic studies as well as comparison to the already existed copper (II) arylicarboxylates physico-structural information (Herring et al., 1971; Lewis et al., 1969). The result of elemental analysis of \(\text{[Cu}_2(p\text{-FC}_6\text{H}_4\text{COO})_4]_{2}\text{CH}_3\text{CH}_2\text{OH} \) (Table 2) showed a good agreement between the found and calculated values. The result was clearly indicative to a binuclear, paddle-wheel complex having the suggested molecular formula, \(\text{[Cu}_2(p\text{-FC}_6\text{H}_4\text{COO})_4]_{2}\text{CH}_3\text{CH}_2\text{OH} \), with ethanol molecules at the apical position.

The powder X-ray diffraction (PXRD) spectrum of the complex shown in Figure 2, indicated that the \(\text{[Cu}_2(p\text{-FC}_6\text{H}_4\text{COO})_4]_{2}\text{CH}_3\text{CH}_2\text{OH} \) was polycrystalline, with some very prominent peaks at certain scattering angles.

By using the Bragg's Law (Smith, 1990) the spacing between the diffracting planes, \(d\), for 5 prominent peaks were determined (Table 3). The particle size of the complex was found to be 10.907 Å which was calculated by using Scherrer equation (Patterson, 1939):

\[
D = \frac{k\lambda}{\beta_{1/2} \cos \theta}
\]

Where \(D\) is the particle size; \(\lambda\) is the wavelength used; \(\theta\) is the Bragg angle, \(k\) is a Scherrer constant whose value is approximately 0.99; \(\beta_{1/2}\) is the full width half maximum (FWHM) of the Bragg peak.

Structural studies through IR spectroscopic analysis were based on the following factors: (a) the position of the bands of the characteristic vibrations of the dissociated carboxylate group \(v_{\text{asym}}\ (\text{COO}^-)\) and \(v_{\text{sym}}\ (\text{COO}^-)\); (b) the value of the split of these bands \(\Delta v = v_{\text{asym}} - v_{\text{sym}}\) and (c) the direction of the shifts in relation to carboxylate group bound by an ionic bond. In the spectrum of the \(\text{Cu}_2(p\text{-FC}_6\text{H}_4\text{COO})_4]_{2}\text{CH}_3\text{CH}_2\text{OH} \), the asymmetric and symmetric stretching bands were observed at 1427 and 1549 cm\(^{-1}\) respectively and originated from the band at about 1680 cm\(^{-1}\) from the RCOOH group, presented in the spectrum of acid. The presence of these asymmetric and symmetric vibrations of \(\text{COO}^-\) group in the spectrum of the compound was a good indication of formation of coordination complex. The complex under study seemed to give a relatively high vibration frequency for the two bands, consistent to a much stronger resonance effect of the fluoro substituents, which increased the strength of the bond between C and O. The smaller \(\Delta v\) of 122 cm\(^{-1}\) for the complex also in agreement with greater vibration modes due to the substituent factor. The low value of

<table>
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<tr>
<td>Step size</td>
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</tr>
<tr>
<td>Applied voltage</td>
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</tr>
<tr>
<td>Current</td>
<td>40 mA</td>
</tr>
<tr>
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<td>2</td>
</tr>
<tr>
<td>Source</td>
<td>CuK (\alpha) line</td>
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<tr>
<td>X-ray wavelength</td>
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<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>O</th>
<th>Cu</th>
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<tbody>
<tr>
<td>Calcd.</td>
<td>Found</td>
<td>Calcd.</td>
<td>Found</td>
</tr>
<tr>
<td>49.1</td>
<td>48.9</td>
<td>3.6</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Coper(II) 4-fluorobenzoate

![Figure 2](image)

**Figure 2.** Relationship between I/\(I_0\) and \(2\theta\) for Cu\(_2(\mu-p-FC_6H_4COO)\_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}\).

**Table 3.** PXRD Data for Cu\(_2(\mu-p-\text{FC}_6\text{H}_4\text{COO})\_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}\).

<table>
<thead>
<tr>
<th>(2\theta)</th>
<th>(d) (Å)</th>
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<tr>
<td>5.6</td>
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<tr>
<td>11.2</td>
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<tr>
<td>28.4</td>
<td>3.140</td>
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<tr>
<td>16.85</td>
<td>5.257</td>
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<tr>
<td>15.95</td>
<td>5.552</td>
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\(\Delta\nu\) for the complex with respect to their sodium salt (\(\Delta\nu = 133\)) might indicate the presence of bidentate symmetric bridging –COO groups in this complex (Deacon and Philips, 1980; Manhas and Trikha, 1982). The presence of strong and broad peak at about 3500 cm\(^{-1}\) suggests the presence of –OH group which could be postulated to come from ethanol molecule which occupies the axial position of the complex.

The occurrence of absorption peak at around 715 nm in solid state electronic spectrum represented a d-d transition of the Cu (II) centers with a square pyramidal geometry (Meier et al., 1985). Due to the low solubility of the complex in many organic solvents, a UV-Vis solution study was also undertaken in mixed solvent system of MeOH/AcOH acid (20:1 v/v). The spectrum in this solution gave rise to two typical absorption peaks, normally known as band I and Band II, at 697 nm and 380 nm respectively. The presence of band I was rather at the same position as that in solid state, indicative of a similar geometrical environment around Cu (II) in either state. In addition, the occurrence of band II at about 380 nm as a shoulder peak strongly suggested that the studied complex existed as dimeric structure in the studied solvent (Tabbi et al., 1997). It is also worth noting that the large molar absorptivity, \(\varepsilon\) value around 430 L mol\(^{-1}\) cm\(^{-1}\) for the complex was believed to be due to a greater resonance effect of the fluoro group which in turn strengthen the metal to ligand bond. In addition, such result as well is an indicative of a more distorted, less symmetrical geometry of the complex in such solvent.

**Magnetic property**

The corrected molar magnetic susceptibility, \(\chi_m^{corr}\) and mass magnetic susceptibility, \(\chi_s\) of Cu\(_2(\mu-p-\text{FC}_6\text{H}_4\text{COO})\_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}\) were determined to be 0.297 x 10\(^{-5}\) cm\(^3\) g\(^{-1}\) and 1.610 x 10\(^{-3}\) cm\(^3\) mol\(^{-1}\) respectively, while the room temperature magnetic moment was calculated as 1.91 B.M. This magnetic moment value was rather too high if compared to the magnetic moment of copper (II) benzoate, 1.4 B.M (Kato et al., 1964). Such a high magnetic moment value indicated the absence of electronic interaction within the complex, which probably lead to a non-dimeric structure of the complex. However, such anomaly could be practically explained in term of the substituent effect of the fluorine atom. While the dimeric structure of the complex remain in tact, the presence of fluoro group at the phenyl ring exerted a strong resonance effect which resulted in pushing the electron density more to the central copper atom, thus disallowed any electronic interaction through the ligands. It is important to note that the coupling interaction between the unpaired electrons in dimeric paddle-wheel structural system has been shown to occur through super exchange pathway rather than through direct interaction between the two central copper atoms (Eugene et al.,
Thermal property

The decomposition process and thermal stability of Cu$_2$(μ- p-FC$_6$H$_4$COO)$_4$.2CH$_3$CH$_2$OH were studied via TGA and DSC analysis. The thermogram of the complex is shown in Figure 3, showing a multi-step decomposition process. The initial weight loss seemed to occur in a very close temperature range, constituted of three small steps approximately at the temperature of 100, 150 and 190°C respectively. The overall weight loss for this step was about 10% (expected 11.5%) representing the loss of solvated molecules as well as the apical ligands.

The major decomposition process started to occur at around 280°C with total weight loss of about 21% and immediately after that, the last decomposition process took place at about 305°C with highest drop of weight loss around 43%. These final two decomposition steps depicted the starting of bond breaking process especially between Cu and O bond as well as indicating the ligand decarboxylation process and formation of volatile products. The experimental combined weight loss of carboxylate ligands (64%) during this step was in excellent agreement with the calculated values based on its chemical formula (62.1%). The amount of residue left above 500°C is 26%. Assuming that the final residue left at the end of the process is mainly CuF$_2$ (Drew et al., 2007), the formula weight of the complex is estimated to be 780 g mol$^{-1}$.

Electrochemical property

The electrochemical studies on the complex is a very novel effort as by far, to the best of our knowledge, no reported works has been done on copper (II)
arylcarnoxylate having a dimeric structure. Further study on the electrochemical behaviour is indeed a worthwhile endeavor especially to ascertain and clarify the role of oxidation states in catalytic processes involving Cu(II) compounds (Endicott and Taube, 1965; Felhendler et al., 1980) and also to further understand the electrochemical properties of copper (II) complexes, the dominated role of copper in catalyzing biologically important reaction namely oxidation and oxygenation reaction using copper containing enzymes (Torelli et al., 2000; Sosa et al., 2005). Thus in this study, the electrochemical properties of the complex is studied by cyclic voltammetry. The cyclic voltammogram of Cu$_2$(µ-p-FC$_6$H$_4$COO)$_4$.2CH$_3$CH$_2$OH recorded in mixed solvent system of MeOH/AcOH (20:1 v/v) is given in Figure 5.

The cyclic voltammogram of the studied complex showed three reduction peaks at -0.22, -0.35 and -0.86 V during forward sweeping and a single broad anodic peak at +0.39 V during reversal. The partial dissociation of the dimer species of the complex in this solvent cannot be ruled out, indicative by the presence of three separate reduction peaks in the voltammogram. The reduction peak at the least negative value, -0.22 V was possibly due to the reduction of the monomer species, as it was relatively much easier to reduce if compare to the dimer. As one of the Cu (II) ion in the dimer was being reduced,
some structural distortion of the dimer was expected to take place simultaneously, thus preventing the reduction of the second Cu (II) ion in the mixed-valence species at a much lower potential. Hence, three distinct reduction peaks could be observed. The single broad oxidation peak observed on the other hand could be inferred to be due to multiple close charge transfer oxidation process with nearly similar potential, which hindered the observation of separate current peaks for each anodic process (Kogerler et al., 1998).

The presence of only single anodic peak has to certain extent hindered the study of redox process for each species individually, thus limiting the possible determination of \( E_{1/2} \) and \( \Delta E \) for each distinct reduction-oxidation couple. However, the level of reversibility of the process can be investigated generally by determining the range of peak separations (\( \Delta E \)) and the ratios of anodic to cathodic peak currents (\( I_{pa}/I_{pc} \)) as well as potential dependency on the scan rate, \( V \). Thus, the cyclic voltammogram within the potential window was further investigated by varying the sweeping rate and the voltammogram is shown in Figure 6. From this plot, it was obvious that the peak current varied with the scan rate and \( \Delta E \) range from about 610 to 1250 mV for all scan rates, suggesting an extensive structural reorganization upon reduction. The potential of the reduction and oxidation peaks also seemed to be independent of the scan rate. Thus, this would indicate that the process was a quasireversible redox reaction. In addition, the ratio of \( I_{pc}/I_{pa} \) was also less than unity, hence supporting the conclusion made above as well as indicating that the electron transfer reaction was followed by a chemical reaction (Nicholson and Shain, 1964; Raman et al., 2004; Patel et al., 2008). Additionally, as shown in Figure 7, the dependence of the currents at different scan rates on the square roots of the scan rates was linear. Thus, the redox
process of the complex was diffusion controlled (Zhou et al., 2007).

An attempt has been made to investigate any redox couple by reducing the potential window and switching potential from +1.0 V to -0.5 V. As depicted in Figure 8, a single anodic and two cathodic peaks were expectedly observed. The voltammogram showed a rather similar plot as Figure 5 but with a slight shift of the anodic peak to a more negative potential.

The two cathodic peaks were now could be confidently assigned to the reduction of the monomer and the dimer respectively. The appearance of only single anodic peak again strongly suggested multiple oxidation process at similar potential of the species. In addition, the sweeping process at different scan rates, depicted in Figure 9, also showed similar behaviour of the species with current ratio \( i_{pc}/i_{pa} \) near unity and \( \Delta E \) of about 400 to 500 mV. Thus the redox process was believed to be quasireversible and again diffusion controlled.

The reduction of \( \text{Cu}(\text{II}) \) complex in this mixed solvent system seemed to occur in a stepwise process. However, the oxidation process seemed to occur concurrently, possibly due to structural reorganization of the complex with some possible interference from couple chemical reactions which took place simultaneously in the system. Besides, the \( \text{Cu} (\text{I}) \) species in the solution were all being oxidized at almost the same potential also indicating a less hindrance to a formation of higher valent species as copper (II) ion is a much more stable species. Thus, the possible electrochemical mechanism for the \( \text{Cu}(\mu-p-\text{FC}_{6}H_{4}\text{COO})_{4}.2\text{CH}_{3}\text{CH}_{2}\text{OH} \) complex in this solvent mixture is proposed as follows:

\[
\text{Cu}(\text{II}) + e^{-} \underset{-0.22V}{\xrightarrow{+0.39V}} \text{Cu}(\text{I})
\]

**Figure 8.** Cyclic voltammogram of \( \text{Cu}(\mu-p-\text{FC}_{6}H_{4}\text{COO})_{4}.2\text{CH}_{3}\text{CH}_{2}\text{OH} \) within potential window of +1.0 V to -0.5 V and scan rate of 100 mV s\(^{-1}\).

**Figure 9.** The cyclic voltammogram of \( \text{Cu}(\mu-p-\text{FC}_{6}H_{4}\text{COO})_{4}.2\text{CH}_{3}\text{CH}_{2}\text{OH} \) within potential window of +1.0 V to -0.5 V and scan rates : 100, 80 and 60 mV s\(^{-1}\).
The physico-structural investigation described in this study demonstrated that 

\[
Cu(II)Cu(II) + e^{-} \rightarrow Cu(I)Cu(I)
\]

Cu(I)Cu(II) + e^{-} \rightarrow Cu(I)Cu(I)

The electron-inductive nature of the substituent at the para positions of the benzene rings exert an apparent effect on the complex structurally, hence affecting the overall physical properties of the complex. The resonance effect is very dominant in fluoro substituted complex, which is very stable, and therefore it is harder to be reduced.

**Acknowledgement**

This work was supported by a PPP grant PS191/2008A from the University Malaya, Kuala Lumpur, Malaysia.

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