

Thermal stability and electrochemical behaviour of Tetrakis- μ -benzoatodicopper(II)

Research Article

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Abstract: Copper(II) benzoate (CuB) was synthesized and structurally characterized to have a binuclear, paddle-wheel structure. The complex was found to be thermally stable up to 230°C, and underwent four stages of decomposition, loss of CO₂, C₆H₆, CH₃CH₂-OCH₂CH₃ and some aliphatic unsaturated organic materials. The DSC curve shows two endotherms at 80.0°C and 230.0°C respectively, indicating that the initial weight loss can be attributed to solvated molecules and the starting of the major decomposition process, (shown in the TG analysis). Cyclic voltammetry studies in a mixed-solvent system of methanol and ethanoic acid (20:1 v/v) show three cathodic peaks, at -0.13 V, -0.35 V and -0.74 V, representing a step-wise electron transfer process, and two overlapping anodic peaks at +0.31 V and +0.46 V. The high value of ΔE ranging from 400 mV to 1200 mV indicates that the redox process is accompanied by an extensive structural reorganization of the complex in the solution creating a different geometrical environment around the central copper ion.

Keywords: Copper(II) benzoate • Thermal analysis • Cyclic Voltammetry

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1. Introduction

Earlier research on copper(II) arylcarboxylates focused on their magneto-structural aspects in order to probe their unexpected magnetic behaviour and unique structural feature [1-6]. Most of these complexes adopted a paddle-wheel structure (shown in Fig. 1), as found for copper(II) acetate with a Cu...Cu distance of 2.607(8) Å [7]. This structure has been postulated to give rise to the existence of a strong electronic and magnetic communication between the two unpaired electrons on the Cu(II) ion and allows for ready delocalization of the electrons [8-9].

Copper(II) benzoate has also been shown to have a binuclear structure similar to copper(II) acetate and in addition to having a high value of -2 J of about 300 cm⁻¹, indicating a strong magnetic interaction in the compound. The structure of copper(II) benzoate has also been investigated to be very much dependent on the axial ligand as well as the substituent on the phenyl ring [10]. As opposed to copper(II) acetate or

other copper(II) alkylcarboxylates, the cage structure of copper(II) benzoate is deemed to be stronger and more stable due to the presence of high electron density at the bridging groups supplied by the phenyl rings. Thus, it has become a very good candidate for the development of metal organic framework (MOF) which have applications in many promising fields such as gas storage, catalysis and molecular recognition [11-13].

The current studies on copper(II) based compounds containing benzoate ligands are varied, either focusing on magneto-structural studies [14-16] or on complexes with different structural features [17-19]. To the best of our knowledge, no other physical and chemical studies, except on magnetic property have been done on copper(II) benzoate, having this structure. The primary focus of this paper is to investigate the thermal stability and electrochemical behaviour of the complex. These findings will help in understanding the properties of copper(II) benzoate. The thermal stability investigation will assist in the evaluation of the mechanism of complex decomposition as well as the stability of the cage

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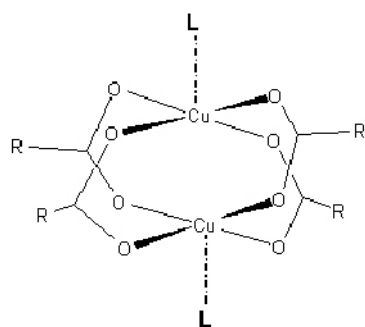


Figure 1. The paddle-wheel structure of copper(II) carboxylates

structure. The redox behaviour could shed some light on the electron flow in copper(II) benzoate which could give insight into the catalytic property of the compound. In addition, the findings of this study will become a reference point for further physico-structural studies on the derivatives of copper(II) benzoate.

2. Experimental Procedure

2.1 Materials and physical measurements

All chemicals and reagents were of analytical grade from commercial sources, and were used as received. The composition of the complex was established based on the analysis of the content of metals, carbon, hydrogen and oxygen. Carbon, hydrogen and oxygen content were determined by elemental analysis using a CHNS/O analyzer, Thermo Finnigan Flash EA 110. The copper content was determined using a spectrometric method with a Perkin Elmer AAnalyst 400 Flame Atomic Absorption Spectrometer with a slit width of 100 microns via the method of calibration curve.

The IR spectra were recorded over a range of 4000–400 cm^{-1} using FTIR SPECTRUM RX 1 Perkin-Elmer spectrometer. The samples for the FTIR spectra measurements were prepared as potassium bromide (KBr) discs.

The magnetic susceptibility measurement was performed at room temperature on a Sherwood Auto Magnetic Susceptibility Balance by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. From the observed susceptibility, the magnetic moment, μ_{eff} , in Bohr Magneton (B.M.) was calculated using the formula [20]: $\mu_{\text{eff}} = 2.839 [T(\chi_m^{\text{corr}} - N\alpha)]^{1/2}$ where T is the temperature in Kelvin, χ_m^{corr} is the molar susceptibility corrected for the diamagnetic susceptibility of the ligand using Pascal's constant [21] and $N\alpha$ is the temperature independent paramagnetism taken as 60×10^{-6} c.g.s e.m.u. [20].

The thermogravimetric-mass spectroscopic analysis (TGA-MS) was determined with a TA Instrument TGA Q500 connected to a MS Termostar™. A sample of 4.7 mg was placed in a cylindrical alumina crucible. The trace was recorded from 30°C to 1000°C with a heating rate of 20°C min^{-1} using nitrogen gas purging at the flow rate of 20 $\text{cm}^3 \text{min}^{-1}$. Differential scanning calorimetric analysis (DSC) was performed on a Rheometric Scientific DSC instrument. The sample (approximately 10 mg) was placed in a cylindrical alumina crucible and heated from 35°C to 300°C at the rate of 10°C min^{-1} under nitrogen gas purging at the flow rate of 10 $\text{cm}^3 \text{min}^{-1}$.

Cyclic voltammetric measurements were recorded using a Gamry Instrument Reference 600 potentiostat/galvanostat/ZRA. Using a three-electrode cell consisting of glassy carbon as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium tetrafluoroborate (TBATFB). The complex was dissolved in methanol-ethanoic acid (20:1 v/v). The working electrode was polished with aluminium oxide powder on chamois leather and the solution was degassed with nitrogen gas prior to analysis.

2.2 Synthesis of copper(II) benzoate

It is important to note that different structures of copper(II) benzoate (CuB) have been reported, which seem to very much depend on the synthesis method [5]. In this paper, CuB was obtained by a metathesis reaction between copper(II) acetate and benzoic acid in hot ethanol, as follows.

Benzoic acid (0.04 mol) was dissolved in ethanol (50 mL) and the solution was heated on a hot plate. Copper(II) acetate monohydrate (0.02 mol) was added dropwise to a magnetically stirred hot solution. 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. The resulting powder was blue. The yield was 36.6%. Anal. Calcd. for $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ (%): Cu, 18.1; C, 54.6; H, 4.5; O, 22.8. Found: Cu, 17.6; C, 54.1; H, 3.9; O, 24.4.

A beautiful, blue block of CuB crystals was grown from a reaction mixture of the complex with acetophenone and benzaldehyde by refluxing for 8 hours and leaving to cool slowly to room temperature. Single crystal X-ray analysis of the crystal revealed a paddle-wheel structure of a complex with benzoic acid at the axial positions, similar with that reported by Ohba *et al.* [22].

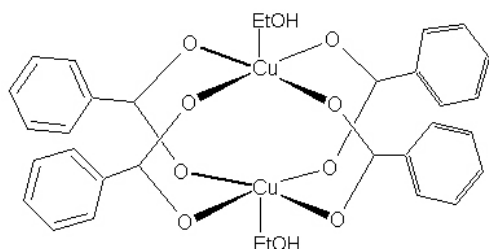


Figure 2. Dimeric and paddle-wheel structure of copper(II) benzoate with ethanol at the axial positions

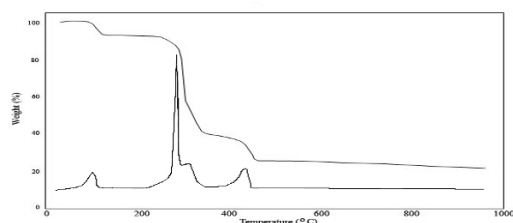
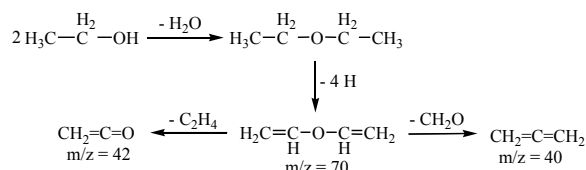


Figure 3. TG and DTA curves of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$



Scheme 1. Decomposition products of $\text{CH}_3\text{CH}_2-\text{OCH}_2\text{CH}_3$

3. Results and Discussion

3.1 Structural studies

The structural elucidation of the powdered complex was obtained based on the results of the elemental analysis to the calculated value. In addition, the presence of asymmetric (ν_{asym}) and symmetric (ν_{sym}) stretching bands at 1562 and 1408 cm^{-1} , respectively in IR spectrum as well as the Δ value ($\nu_{\text{asym}} - \nu_{\text{sym}}$) of 154 cm^{-1} agrees very well with the reported literature for a symmetrical bridging bidentate structure [23–24]. The room-temperature magnetic susceptibility measurement of the complex also gives a low value of magnetic moment of 1.49 B.M., which is very similar to the value reported for the same complex having a dimeric structure [25].

However, it is very important to note that the apical ligand of a powdered sample is different from the crystal structure, shown by the elemental analysis calculation, that still maintains a dimeric, paddle-wheel structure. The powdered sample of the complex is believed to have ethanol molecules at the apical positions, in agreement with some of the reported literature [26–28]. Therefore, the thermal analysis and cyclic voltammetric studies reported in this paper are based on a dimeric,

Table 1. The m/z values of the gaseous products of thermal decomposition of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4(\text{C}_2\text{H}_5\text{OH})_2$

Stage	m/z values
I	22, 42, 70
II	22, 38, 44, 70
III	22, 38, 44, 50, 52, 70, 78
IV	16, 22, 40, 44, 50, 52, 55, 57, 70, 78

paddle-wheel structure with ethanol molecules at the apical positions.

Hence, we believe that the powdered CuB complex prepared in this work has the structure shown in Fig. 2.

3.2 Thermal stability

The thermal stability and decomposition process of powdered CuB was studied by TGA-MS. The TGA scan is shown in Fig. 3 and the corresponding MS data is shown in Table 1. The scan shows four main decomposition steps. The initial weight loss of 7.4% occurs at about 81.7°C, and is assigned to the loss of $\text{CH}_3\text{CH}_2\text{OH}$ at the axial positions (expected 9.7%). The complex then decomposes at around 230.0°C, indicating the start of the Cu-O bond breaking, with a total weight loss of 68.3% (expected 68.8%).

The mass spectra of the complex are presented in Fig. 4 and the ion current plots are depicted in Fig. 5. The MS data indicates that the main gaseous product formed in all of the stages is CO_2 ($m/z = 22, 44$), formed from the decarboxylation of the $\text{C}_6\text{H}_5\text{COO}^-$ ligand. Also detected are decomposition products of $\text{CH}_3\text{CH}_2-\text{OCH}_2\text{CH}_3$, presumably formed from condensation of two $\text{CH}_3\text{CH}_2\text{OH}$ molecules (Scheme 1).

However, it is interesting to note that aromatic volatiles ($m/z > 70$) were also detected. This suggests that the aromatic ring cracks at higher temperatures to form an array of aliphatic conjugated organic volatiles with various m/z values 38, 50, 52, 55 and 57, respectively.

The amount of residue left above 500°C is 22.2%. Assuming that it is mainly CuO , as has been suggested for many copper(II) carboxylates [29–32], the estimated formula weight of CuB is 717 g mol^{-1} , which agrees fairly well with the calculated formula weight of the powdered compound, 703 g mol^{-1} , with ethanol as the apical ligands. Thus, in the absence of complete crystal data, the TG analysis could be another alternative technique used to support the proposed complex structure via the determination of the formula mass of metal complexes as well as the percentage of copper content, provided the identity of the residue is beyond a doubt.

The DSC curve (Fig. 6) shows a small endothermic peak with an onset temperature of around 80.0°C, and

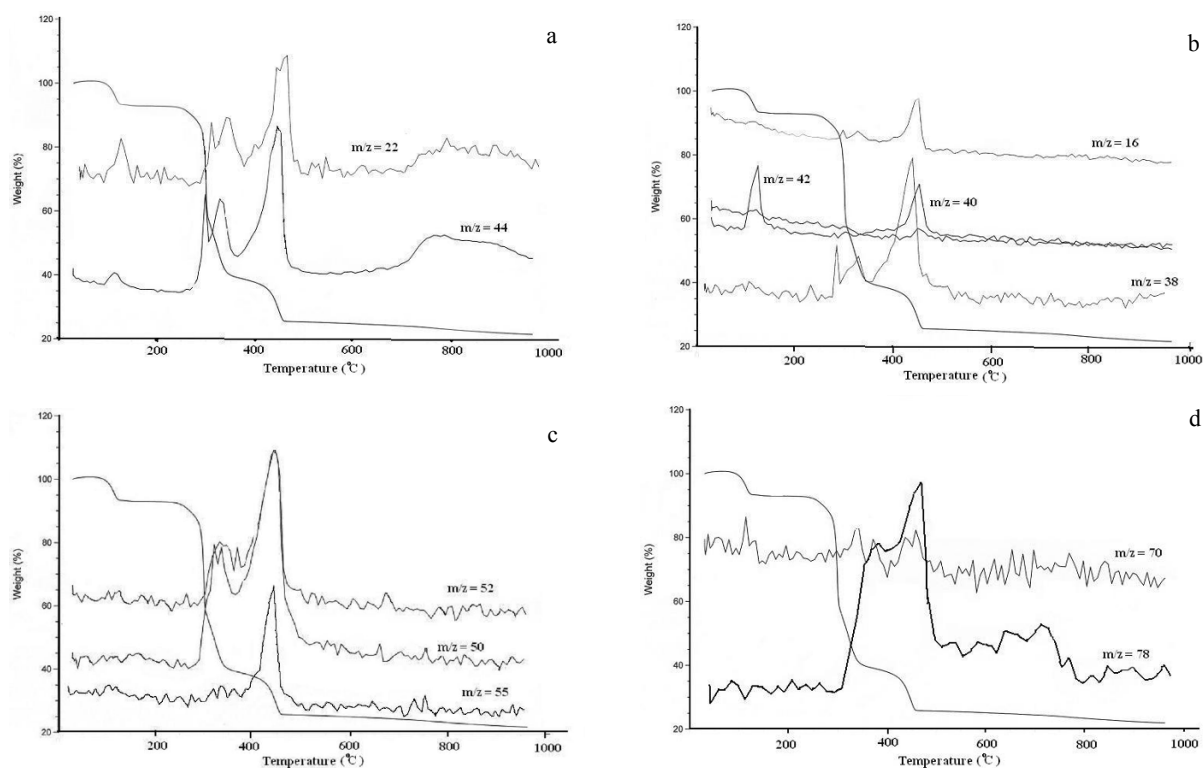


Figure 4. TG Curve of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ and ion current detected by MS for a - $m/z = 22, 44$; b - $m/z = 16, 38, 40, 42$; c - $m/z = 50, 52, 55$; d - $m/z = 70, 78$

can be assigned to the loss of ethanol molecules as indicated by the TGA results. Another endotherm at an onset of a temperature around 230°C agrees fairly well with the TGA result, indicating the starting temperature of a major decomposition process.

3.3 Electrochemical properties

The cyclic voltammetric (CV) studies of CuB solution in methanol-ethanoic acid (20:1 v/v), measured from +1.5 V to -1.0 V with a scan rate of 150 mV s^{-1} , is shown in Fig. 7. This figure shows three reduction peaks at -0.13, -0.35 and -0.74 V and two overlapping anodic peaks at +0.31 and +0.46 V.

The presence of three reduction peaks during cathodic process might suggest the existence of multiple species in the solution, possibly as a result of a complex partial dissociation into mononuclear units [26]. The monomeric Cu(II) complex is much easier to reduce compared to the dimer and therefore it occurs at a less negative potential. As one of the Cu(II) ion in the dimer is being reduced, some of the structural distortion of the dimer starts to occur, preventing the reduction of the second Cu(II) ion in the mixed-valence species at a much lower potential. As a result, three distinct reduction peaks can be observed. The broad and overlapping oxidation peak observed on the other hand

can be inferred to be due to the multiple close charge transfer oxidation process with nearly similar potential, which hinders the observation of separate current peaks for each anodic process [33].

It is worth noting that the appearance of only a single anodic peak has deterred the study of the redox process for each of the species, thus limiting the determination of $E_{1/2}$ and ΔE for each reduction-oxidation couple. However, the level of reversibility of the process can be investigated generally by determining the range of peak separations (ΔE), the ratios of anodic to cathodic peak currents (I_{pa}/I_{pc}) and the potential dependency on the scan rate, v . The CV within the potential window can be investigated by varying the sweeping rate and the resulting voltammogram is shown in Fig. 8. From this plot, it is obvious that the peak current varies with the scan rate, ΔE ranges from about 400 mV to 1200 mV for all scan rates, suggesting an extensive structural reorganization upon reduction. The potential of the reduction and oxidation peaks also seem to be independent of the scan rate. This would indicate that the process is a quasireversible redox reaction. In addition, the ratio of I_{pc}/I_{pa} is also less than unity, hence supporting the conclusion as well as indicating that the electron transfer reaction is followed by a chemical reaction [34-36]. Additionally, as shown in Fig. 9, the

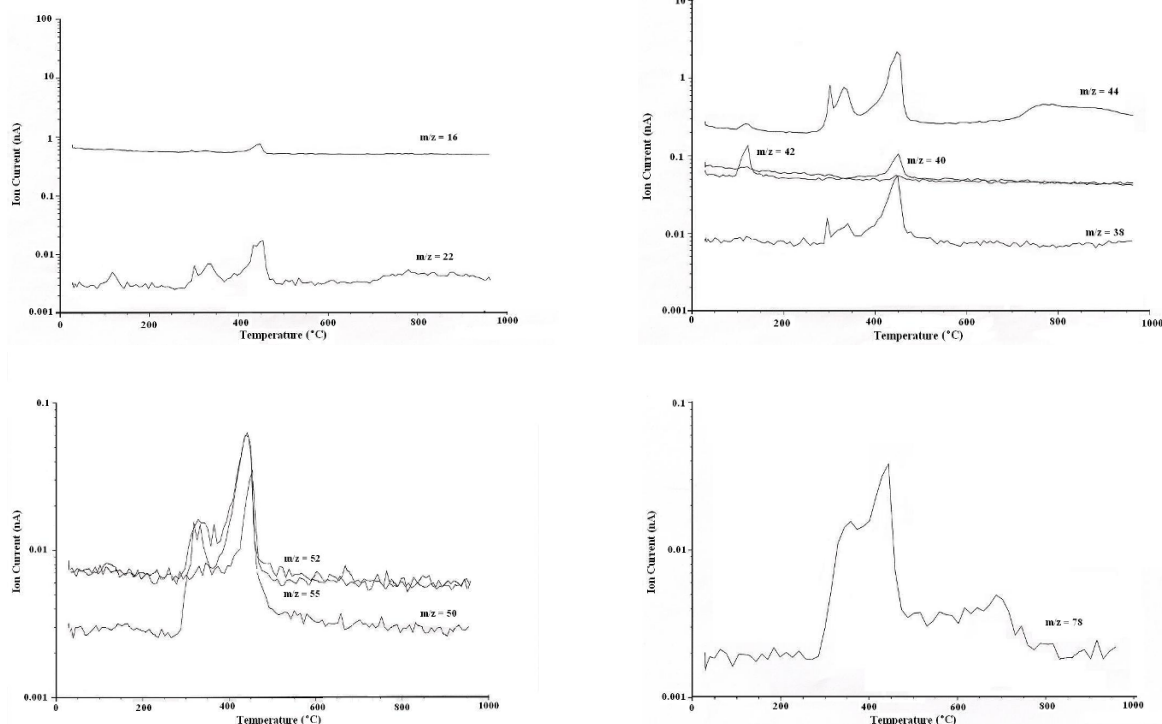


Figure 5. Ion current vs. temperature for $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ (sample mass 4.80 mg, heating rate $20^\circ\text{C min}^{-1}$)

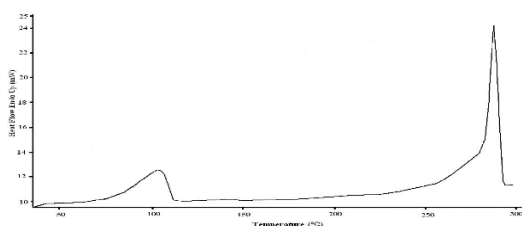


Figure 6. DSC of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$

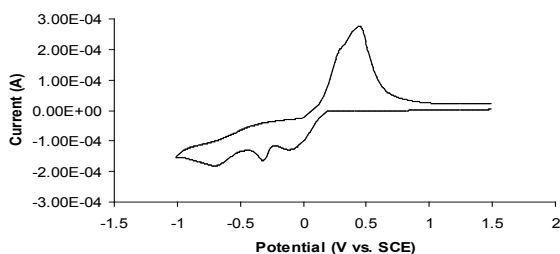


Figure 7. Cyclic voltammogram of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ at scan rate 150 mV s^{-1}

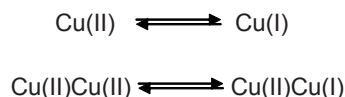
dependence of the currents at difference scan rates on the square roots of the scan rates is linear. Allowing us to draw the conclusion that the redox process of the complex is controlled by diffusion [37].

An attempt has been made to investigate any redox coupling by reducing the potential window and switching potential from +0.5 V to -0.2 V. As shown in Fig. 10, a

single anodic and cathodic peak is observed. The CV shows the shift of the anodic peak approaching zero with a significant increase of current having i_{pc}/i_{pa} near unity and ΔE of around 171 mV. Therefore again supporting the conclusion that the redox process is believed to be quasireversible and again diffusion controlled.

Initially, it was very tempting to assign those peaks to redox couple of the monomer species of copper(II) complex. However, when the scanning rate is subsequently lowered, as shown by Fig. 11, at $v = 150 \text{ mV s}^{-1}$, one reduction peak and two oxidation peaks were observed at -0.1 V, +0.05 V and +0.18 V respectively, with $\Delta E = 150 \text{ mV} - 280 \text{ mV}$ indicating a quasireversible process. Thus, the single reduction peak observed might represent a one-step, concurrent reduction of a monomer, Cu(II) to Cu(I) and also a dimer, Cu(II)Cu(II) to Cu(II)Cu(I) accompanying with structural reorganization.

During the reverse sweep, two oxidation waves were observed representing the back formation of Cu(II) and Cu(II)Cu(II) as indicated below.



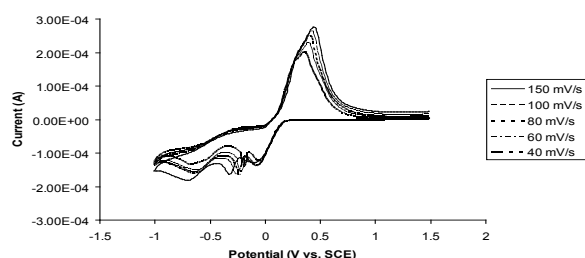


Figure 8. Cyclic voltammogram of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ as a function of the scan rate.

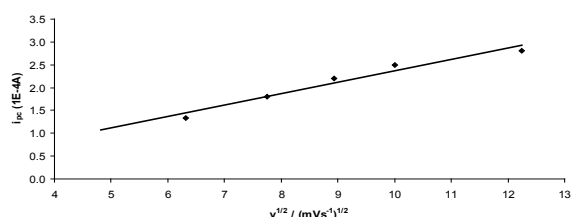


Figure 9. Dependence of the currents on the square root of the scan rates.

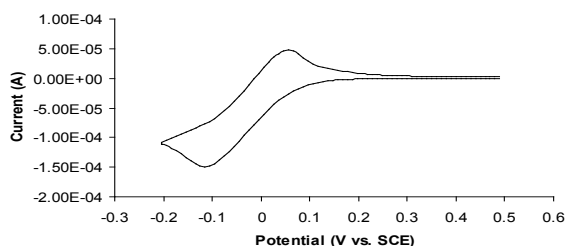


Figure 10. Cyclic voltammogram of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ at smaller potential window and scan rate 200 mV s^{-1}

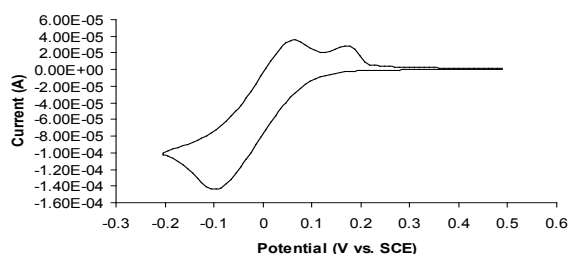


Figure 11. Cyclic voltammogram of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ at smaller potential window and scan rate 150 mV s^{-1}

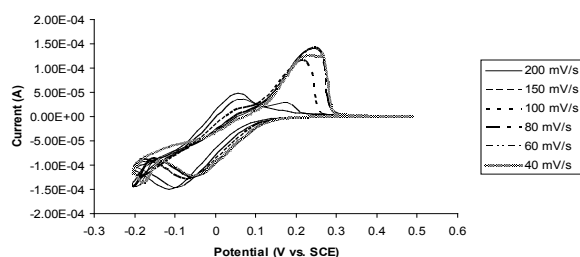
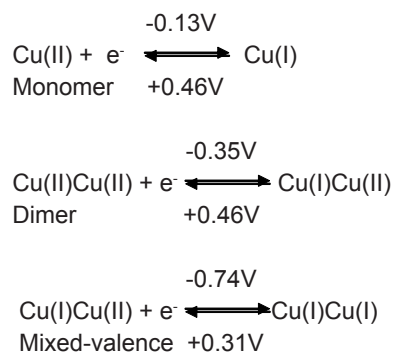


Figure 12. Cyclic voltammogram of $\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ at smaller potential window as a function of scan rate.

Upon a further lowering of the scan rate as shown in Fig. 12, a new anodic peak appears at an increased positive potential with a higher I_{pa} value, giving rise to two distinct anodic peaks. Ultimately, the initial anodic peak at a potential of +0.05 V disappears and the new anodic peak at 0.25 V emerges. The complete disappearing of the initial anodic peak takes place at a scan rate below 80 mV s^{-1} . The CV also shows that the potential of both anodic and cathodic peaks seem to shift to a more positive value upon a lowering of the scan rate. As the scan rates became slower, the material appears to have enough time to undergo structural reorganisation after initial reduction and as a result the two Cu(I) (after reduction) environments are almost similar, and thus reoxidise at almost the same potentials.

The reduction of the complex in this mixed solvent system seems to occur in a stepwise process. However, the oxidation process seems to occur concurrently, possibly due to a structural reorganization of the complex with some possible interference from the coupled chemical reactions which occur simultaneously in the system. Additional, the Cu(I) species in the solution are all being oxidized at almost the same potential also indicating a reduced hindrance to the formation of higher valent species as copper(II) ion is a much more stable species.

Thus, the possible redox reactions mechanism for the CuB complex in this solvent mixture are proposed as follows:



4. Conclusions

Copper(II) benzoate has been successfully synthesised with in a facile method and the complex seemed to maintain the paddle-wheel structure. The thermal and electrochemical studies indicate that the complex is a thermally stable electroactive material which has a possible application in catalysis. An extension of this work involving the catalytic property of this complex as well as physico-structural studies of derivatives of copper(II) benzoate are currently being explored.

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