

STRUCTURAL ELUCIDATION OF [Cu₂(*p*-H₂NC₆H₄COO)₃(CH₃(CH₂)₁₄COO)(H₂O)(NH₃)

Ahmad Nazeer Che Mat^{1*}, Mohamad Isa Mohamadin²

¹Faculty of Applied Sciences, Universiti Teknologi MARA, Perak Branch Tapah Campus, 35400 Tapah Road, Perak, Malaysia

²Faculty of Applied Sciences, Universiti Teknologi MARA, 94300 Kota Samarahan, Sarawak, Malaysia

*nazeer@uitm.edu.my

Abstract: A novel copper (II) mixed carboxylates namely bis(*p*-aminobenzoato)bis(hexadecanoato)dicopper(II), [Cu₂(*p*-H₂NC₆H₄COO)₃(CH₃(CH₂)₁₄COO)(H₂O)(NH₃)], from one-pot self-assembly of the corresponding ions was designed to function as a low-temperature and thermally-stable metallomesogen applications. The as-prepared copper (II) complex was characterized by means of elemental analyses, FTIR and UV-Vis spectroscopy for the determination of its elemental compositions, chemical bonding, and electronic transition, respectively. FTIR analysis indicate the presence of all expected functional group with Δ_{COO} value were 106 cm⁻¹ and 194 cm⁻¹, suggesting the binding mode of carboxylate ligands at Copper(II) centre are chelating and bridging (monoatomic, syn-anti), respectively. **Complex 1** exhibit square pyramidal geometry around Copper(II) as indicated by UV-Vis spectroscopy in solid state condition. Meanwhile, dissolution of **Complex 1** in DMSO:CH₃COOH lead to the structural reorganization into producing symmetrical mononuclear complex (D_{2h} symmetry) and an unsymmetrical mononuclear complex (C₁ symmetry).

Keywords: Copper(II) mixed-carboxylates; One-pot synthesis; Binuclear; Square pyramidal

INTRODUCTION

Metal contained liquid crystal or so-called metallomesogens have been introduced for a couple of years by Giroud-Godquin and Maitlis (Giroud-Godquin and Maitlis 1991). It involved first-row transition metals that combined the advantage of anisotropy and fluidity of liquid crystals with valuable characteristics for example the presence of polarizable d-electrons, tunable geometry and colour, thermal stability, electronic conductivity, magnetic and redox properties. This makes metalloomesogens suitable for various applications (Rajendiran, Yoganandham et al. 2021). The objective of the present research work is to synthesis copper(II) based carboxylate complex as thermally-stable and low-temperature metallomesogens by adopting two strategies in designing the desired materials. The first strategy is to induce self-assembly through the formation of hydrogen bonds by replacing at least one of the alkanoates with an aroate carrying an -OH or -NH₂ functional group. The second strategy is to lower the melting temperature by lowering the molecular symmetry and by using ligands with long or non-linear alkyl chains (Paschke, Balkow et al. 2002). The research concept is based on copper(II) homocarboxylates, [Cu₂(μ -RCOO)₄], where R is a long linear or branched hydrocarbon chain. Examples are [Cu₂(μ -CH₃(CH₂)₁₄COO)₄] and [Cu₂(μ -(CH₃(CH₂)₆)₂CHCOO)₄], with melting temperature of 112 °C and lower than -20 °C, respectively; the linear chain complex was found to exhibit a columnar discotic mesophase (D_{ho}).

METHODOLOGY

In brief, Cu(CH₃COO)₂.3H₂O (1.5865 g; 7.95 mmol) was added to 100 ml of hot ethanolic solution of *p*-H₂NC₆H₄COOH (1.1078 g; 8.08 mmol) and CH₃(CH₂)₁₄COOH (2.0196 g; 7.88 mmol). The green solution formed was cooled and an excess NH₃ (30%) was added dropwise, forming a purple solution. The solution was magnetically stirred at room temperature overnight, and the excess NH₃ removed by gentle heating.

FINDINGS

The results of the elemental analyses (52.23% C, 5.11% H, 6.48% N) are in good agreement with the values calculated for Cu₂C₃₇H₅₄N₄O₉ (FW = 825.1 g mol⁻¹; 53.8% C, 6.54% H and 6.78% N). Based on FTIR Spectrum, the presence of the expected functional groups based on the proposed structural formula namely -NH₂ at about 3200-3067 cm⁻¹, CH₂ at 2900 cm⁻¹ (asymmetrical stretching) and ~2850 cm⁻¹ (symmetrical stretching). The Δ_{COO} value obtained from FTIR is 106 cm⁻¹ and 194 cm⁻¹, suggesting the binding mode of carboxylate ligands are chelating and bridging (monoatomic, syn-anti), respectively, therefore **Complex 1** can be inferred as a binuclear complex. Additionally, the UV-Vis analysis was conducted in two different conditions namely in solid state and solution by dissolving **Complex 1** in DMSO:CH₃COOH. The solid state UV-Vis spectrum of **Complex 1** (**Figure 2a**) shows two broad d-d bands at 624 nm (Band I) and 442 nm (Band II), with absorbance ratio of about 1:1 indicating the square pyramidal geometry at Cu(II). Meanwhile, the spectrum of the **Complex 1** which was dissolved in DMSO-CH₃COOH (**Figure 2(b)**) shows a broad d-d peak at 713 nm ($\epsilon = 388 \text{ M}^{-1}\text{cm}^{-1}$) for Band I and a weak shoulder at about 400 nm ($\epsilon = 291 \text{ M}^{-1}\text{cm}^{-1}$) for Band II. This indicates that the geometry at Cu(II) of

Complex 1 remained unchanged in the current solvents. Based on the results discussed above, the proposed structural formula of **Complex 1** is shown in **Figure 2 (a)**.

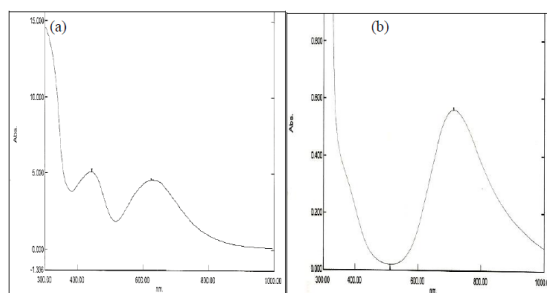


Figure 1. UV-Vis spectrum of **Complex 1** in (a) solid state; (b) solution.

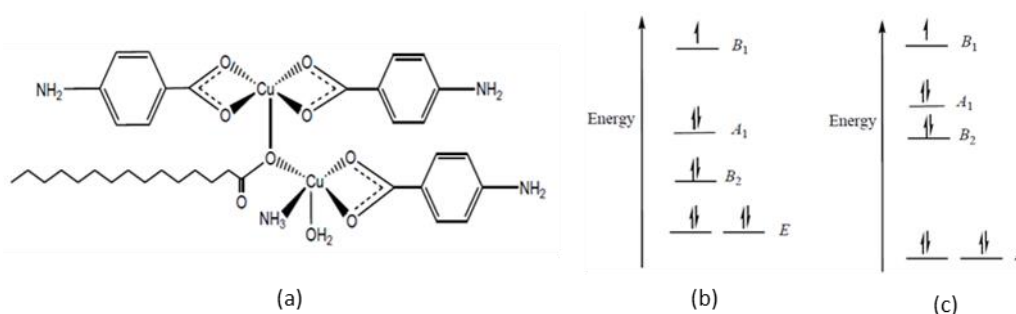


Figure 2. (a) Proposed **Complex 1** structure; Electronic transitions of **Complex 1** in (a) solid state; (c) solution.

The proposed structure (**Figure 2 (a)**) is consistent with the chemical formula $\text{Cu}_2\text{C}_{37}\text{H}_{54}\text{N}_4\text{O}_9$ (FW = 825.1 g mol⁻¹) as suggested by the elemental analyses, syn-anti monodentate bridging $\text{CH}_3(\text{CH}_2)_{14}\text{COO}$ and chelating *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{COO}$ based on FTIR, and square pyramidal geometry at Cu(II) as suggested from UV-vis (local symmetries for the two Cu(II) are C_{2v} and C_1). In the solid state condition (**Figure 2 (b)**), the electronic transitions are assigned based on the C_{4v} point group, as follows: $\text{B}_2 \rightarrow \text{B}_1$ (Band I; 624 nm) and $\text{E} \rightarrow \text{B}_1$ (Band II; 442 nm). Meanwhile, the $\text{A}_1 \rightarrow \text{B}_1$ transition appears as a shoulder at the low energy end of Band I. Additionally, shifting to lower energy for Band I and to higher energy for Band II can be observed when **Complex 1** was dissolved in DMSO- CH_3COOH (**Figure 2 (c)**). In the solution, reaction of the ligand NH_3 with CH_3COOH temporarily frees one of the equatorial positions. As a result, rearrangement in terms of binding mode of monoatomic $\text{CH}_3(\text{CH}_2)_{14}\text{COO}$ takes place from initially syn, anti-bridged the two Cu(II) to chelate one Cu(II), forming two mononuclear complexes with DMSO molecules coordinated at the axial positions elongated octahedral Cu(II) centres. The effect of the above reaction is to produce a highly symmetrical mononuclear complex (D_{2h} symmetry) and a highly unsymmetrical mononuclear complex (C_1 symmetry). The electronic transition corresponding to Band I decreased in energy under octahedral geometry. The d_{xy} (B_2), and d_{xz} , d_{yz} (E) are the two d-orbitals of Cu(II) that are most strongly affected by the distortion. The energy of the d_{xy} orbital is expected to decrease (increase in stability) as the ligands move away from it, while the energy of the (d_{xz} , d_{yz}) orbitals are expected to increase (decrease in stability) as the ligands move nearer to it. Thus, the assignments are: $\text{E} \rightarrow \text{B}_1$ (Band I; 713 nm) and $\text{B}_2 \rightarrow \text{B}_1$ (Band II; ~400 nm). The geometry of both Cu(II) centres are distorted out of the x,y plane towards the z-axis. The effects are to increase the energy of the xy orbital (B_2) and decrease the energy of the x^2-y^2 orbital.

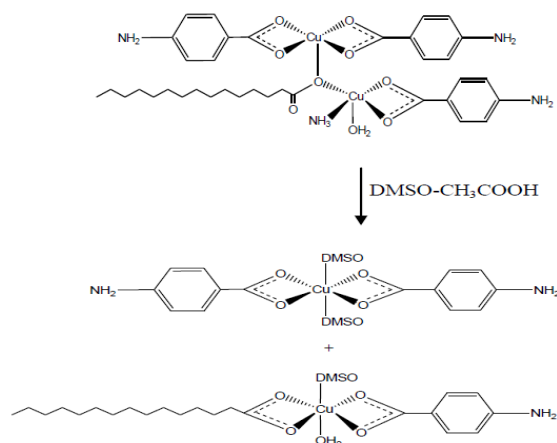


Figure 3. Proposed reaction mechanism of **Complex 1** in DMSO-CH₃COOH solution

CONCLUSIONS

One-pot synthesis was found to be suitable for preparing copper(II) mixed-carboxylate complex since it gave the desired product namely Cu₂C₃₇H₅₄N₄O₉ (**Complex 1**) with FW 825.1 g/mol. The ligands binding mode are chelating and bridging (monoatomic, syn-anti) which can be inferred that **Complex 1** is a binuclear complex with square pyramidal geometry at Cu(II). Dissolution of **Complex 1** in DMSO:CH₃COOH underwent rearrangement producing symmetrical mononuclear complex (D_{2h} symmetry) and an unsymmetrical mononuclear complex (C₁ symmetry).

REFERENCES

- Giroud-Godquin, A. M. and P. M. Maitlis (1991). "Metallomesogens: metal complexes in organized fluid phases." *Angewandte Chemie International Edition in English* 30(4): 375-402.
- Paschke, R., et al. (2002). "Lowering melting points in asymmetrically substituted Salen-copper (II) complexes exhibiting mesomorphic behavior. Structure of the mesogen Cu (5-hexyloxySalen)." *Inorganic chemistry* 41(7): 1949-1953.
- Rajendiran, K., et al. (2021). "An Overview of liquid crystalline mesophase transition and photophysical properties of "f block," "d block," and (SCO) spin-crossover metallomesogens in the optoelectronics." *Journal of Molecular Liquids* 321: 114793.

Surat kami : 700-KPK (PRP.UP.1/20/1)

Tarikh : 20 Januari 2023

Prof. Madya Dr. Nur Hisham Ibrahim
Rektor
Universiti Teknologi MARA
Cawangan Perak



Tuan,

PERMOHONAN KELULUSAN MEMUAT NAIK PENERBITAN UiTM CAWANGAN PERAK MELALUI REPOSITORI INSTITUSI UiTM (IR)

Perkara di atas adalah dirujuk.

2. Adalah dimaklumkan bahawa pihak kami ingin memohon kelulusan tuan untuk mengimbas (*digitize*) dan memuat naik semua jenis penerbitan di bawah UiTM Cawangan Perak melalui Repositori Institusi UiTM, PTAR.

3. Tujuan permohonan ini adalah bagi membolehkan akses yang lebih meluas oleh pengguna perpustakaan terhadap semua maklumat yang terkandung di dalam penerbitan melalui laman Web PTAR UiTM Cawangan Perak.

Kelulusan daripada pihak tuan dalam perkara ini amat dihargai.

Sekian, terima kasih.

“BERKHIDMAT UNTUK NEGARA”

Saya yang menjalankan amanah,

SITI BASRIYAH SHAIK BAHARUDIN
Timbalan Ketua Pustakawan

nar

Setuju.

27.1.2023

PROF. MADYA DR. NUR HISHAM IBRAHIM
REKTOR
UNIVERSITI TEKNOLOGI MARA
CAWANGAN PERAK
KAMPUS SERI ISKANDAR