

ABSTRACT

The objective of this research was to study the correlation between structure and physical properties of copper(II)-cyclam-alkylcarboxylate complexes, and the electronic effect of a substituent on the aromatic ring of copper(II)-cyclam-arylcarboxylate complexes. The alkylcarboxylate ligands were $C_nH_{2n+1}COO$ ($n = 6, 7, 9, 11, 13, 15$) and $CH_3(CH_2)_7CH((CH_2)_5CH_3)$, while the arylcarboxylate ligands were $p-XC_6H_4COO$ ($X = NH_2, OH, OCH_3, CH_3, C\equiv N, H$) and C_6F_5COO .

A total of fourteen complexes were successfully synthesized and their structural formulas (**Table 1.0**) deduced from either single crystal XRD (for crystals) or a combination of instrumental analyses.

Table 1.0 Structural formulas of complexes

Complex	Structural Formula
1	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_5COO)_2 \cdot 2H_2O$
2	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_6COO)_2 \cdot 7H_2O$
3	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_8COO)_2 \cdot 2H_2O$
4	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{10}COO)_2 \cdot 2H_2O$
5	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{12}COO)_2 \cdot 2H_2O$
6	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{14}COO)_2 \cdot 2H_2O$
7	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_2 \cdot 5C_2H_5OH$
8	$[Cu(p-H_2NC_6H_4COO)_2(C_{10}H_{24}N_4)] \cdot 2H_2O$
9	$[Cu(p-HOC_6H_4COO)_2(C_{10}H_{24}N_4)]$
10	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3OC_6H_4COO)_2 \cdot 2H_2O$
11	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3C_6H_4COO)_2 \cdot H_2O$
12	$[Cu(p-N\equiv CC_6H_4COO)(C_{10}H_{24}N_4)(H_2O)](p-N\equiv CC_6H_4COO) \cdot 3H_2O$
13	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6H_5COO)_2 \cdot 2H_2O$
14	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6F_5COO)_2 \cdot 2H_2O$

The neutral cyclam ligand formed the molecular planar array which is defined by the four *aza*-N stereocentres. Cyclam in all complexes adopted the most stable *trans*-III configuration. The axial positions of Cu atom of the alkylcarboxylate complexes (**1** – **7**) were preferentially occupied by H₂O molecules, which bridged the metal centres and the alkylcarboxylates through hydrogen bonding.

The *p*-H₂NC₆H₄COO and *p*-HOC₆H₄COO ligands (in complexes **8** and **9**) were coordinated to both axial positions of Cu atom. The rest of the arylcarboxylate complexes, except **12**, were ionic. Complex **12** has a H₂O molecule and a *p*-N≡CC₆H₄COO ligand coordinated at each of the axial positions of its Cu atom.

There was a significant antiferromagnetic interaction between the Cu centres ($\mu_{\text{eff}} = 1.43$ BM) in **1**, while there was no magnetic interaction in the other complexes ($\mu_{\text{eff}} \sim 1.73$ BM).

The melting temperatures (T_m) of the alkylcarboxylate complexes were lower than 82 °C, and increased with the number of carbon atoms in the alkyl chain. Complex **7** was a liquid at room temperature. All complexes were thermally stable at temperatures about 200 °C in an inert atmosphere ($T_{\text{dec}} \sim 196 - 270$ °C).

Based on a Hartree-Fock Self-Consistent Field (HF/6-311G(d,p) calculations for complexes **1**, **8**, **9** and **10**, the binding energies were more exothermic for their respective actual structures compared to their simulated structures (where the Cu atom was theoretically bonded to the competing ligand).

The findings of this research were published in six ISI journals, and presented in two international conferences and one departmental symposium (**Appendix 1**).

ABSTRAK

Matlamat penyelidikan ini adalah untuk mengkaji hubungan antara struktur dan sifat fizik kompleks kuprum(II)-siklam-alkilkarboksilat, dan kesan elektronik kumpulan pengganti pada gelang aromatik ke atas kompleks kuprum(II)-siklam-arilkarboksilat. Ligan alkilkarboksilat adalah $C_nH_{2n+1}COO$ ($n = 6, 7, 9, 11, 13, 15$) dan $CH_3(CH_2)_7CH((CH_2)_5CH_3)$, manakala ligan arilkarboksilat adalah $p-XC_6H_4COO$ ($X = NH_2, OH, OCH_3, CH_3, C\equiv N, H$) dan C_6F_5COO .

Empat belas kompleks telah berjaya disintesis dan formula struktur kesemuanya (**Jadual 1.0**) dideduksikan melalui kaedah XRD hablur tunggal atau gabungan analisis beralatan.

Jadual 1.0 Formula struktur kompleks

Kompleks	Formula Struktur
1	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_5COO)_2 \cdot 2H_2O$
2	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_6COO)_2 \cdot 7H_2O$
3	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_8COO)_2 \cdot 2H_2O$
4	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{10}COO)_2 \cdot 2H_2O$
5	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{12}COO)_2 \cdot 2H_2O$
6	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{14}COO)_2 \cdot 2H_2O$
7	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_2 \cdot 5C_2H_5OH$
8	$[Cu(p-H_2NC_6H_4COO)_2(C_{10}H_{24}N_4)] \cdot 2H_2O$
9	$[Cu(p-HOC_6H_4COO)_2(C_{10}H_{24}N_4)]$
10	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3OC_6H_4COO)_2 \cdot 2H_2O$
11	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3C_6H_4COO)_2 \cdot H_2O$
12	$[Cu(p-N\equiv CC_6H_4COO)(C_{10}H_{24}N_4)(H_2O)](p-N\equiv CC_6H_4COO) \cdot 3H_2O$
13	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6H_5COO)_2 \cdot 2H_2O$
14	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6F_5COO)_2 \cdot 2H_2O$

Ligan siklam neutral membentuk susunan molekul sesatah menerusi empat pusat stereo atom *aza*-N. Ligan siklam dalam kesemua kompleks membentuk konfigurasi *trans*-III. Kedudukan paksian atom Cu bagi kompleks alkilkarboksilat (**1** – **7**) diisi oleh molekul H₂O, yang menghubungkan atom pusat logam dengan kumpulan alkilkarboksilat melalui ikatan hidrogen.

Ligan *p*-H₂NC₆H₄COO dan *p*-HOC₆H₄COO (dalam kompleks **8** dan **9**) terkoordinat pada atom Cu. Kompleks arilkarboksilat lain, kecuali **12**, adalah ionik. Kompleks **12** mempunyai molekul H₂O dan ligan *p*-N≡CC₆H₄COO terkoordinat pada setiap kedudukan paksian atom Cu.

Terdapat saling tindakan antiferomagnet yang ketara antara pusat Cu ($\mu_{\text{eff}} = 1.43$ BM) bagi **1**, manakala tiada saling tindakan magnet bagi kompleks-kompleks yang lain ($\mu_{\text{eff}} \sim 1.73$ BM).

Suhu lebur (T_m) bagi kompleks alkilkarboksilat adalah kurang daripada 82 °C, dan meningkat dengan bilangan atom karbon dalam rantai alkil. Kompleks **7** adalah cecair pada suhu bilik. Kesemua kompleks adalah stabil secara terma pada suhu sekitar 200 °C dalam atmosfera lengai ($T_{\text{urai}} \sim 196 - 270$ °C).

Berdasarkan pengiraan *Hartree-Fock Self Consistent Field* bagi kompleks **1**, **8**, **9** dan **10**, tenaga ikatan bagi struktur sebenar kompleks tersebut didapati adalah lebih eksotermik berbanding struktur yang disimulasikan (di mana atom Cu secara teori terikat kepada ligan yang bersaing).

Hasil penemuan penyelidikan ini telah diterbitkan dalam enam jurnal ISI, dan dibentangkan di dua persidangan antarabangsa dan satu simposium jabatan (**Lampiran 1**).