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ABSTRACT

This research project is focused on the synthesis and characterization of copper(II) mixed carboxylates of general formula, $[\text{Cu}_2(\text{RCOO})_n(\text{R}'\text{COO})_{4-n}]$, where $\text{R} = p\text{-H}_2\text{NC}_6\text{H}_4$, $\text{R}' = \text{CH}_3(\text{CH}_2)_{14}$, and $n = 1\text{--}3$. These mixed carboxylates were specially designed to be low-temperature and thermally stable magnetic and redox-active metallomesogens.

A total of six binuclear copper(II) mixed-carboxylates were successfully prepared by the one-pot reaction, and their thermal, metallomesogenic, magnetic and redox properties reported. The instrumental analyses used to characterize these complexes were CHN elemental analyses, FTIR and UV-vis spectroscopies, molar conductivity, thermogravimetry, differential scanning calorimetry, optical polarized microscopy, magnetic susceptibility by the Gouy method, and cyclic voltammetry.

All complexes, except for $[\text{Cu}_2(p\text{-H}_3\text{NC}_6\text{H}_4\text{COO})_3\text{Cl}]\text{Cl}_3\cdot\text{NH}_3\cdot 3\text{H}_2\text{O}$ (**Complex 4**), were non-electrolytes. **Complex 4** was a 1:1 electrolyte. Their geometry was square-pyramidal involving *syn-syn* or *syn-anti* bridging and/or chelating carboxylates, their thermal stabilities were higher than 200°C, and the melting point ranges from about 118°C, except for **Complex 6** which melted at a higher temperature of 166°C.

The complex exhibiting thermotropic metallomesogenic properties was $[\text{Cu}_2(p\text{-H}_2\text{NC}_6\text{H}_4\text{COO})_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(\text{H}_2\text{O})(\text{CH}_3\text{CH}_2\text{OH})]$ (**Complex 1**) with smectic C mesophase. They were either antiferromagnet or ferromagnet, with μ_{eff} and 2J values from 2.11 to 3.72 B.M. and from -200 to 109 cm^{-1} ,

respectively. All complexes were redox active. The redox reactions were quasi-reversible involving extensive structural reorganization and chemical reactions (the EC mechanism).

ABSTRAK

Penyelidikan ini adalah fokus untuk mensintesis dan mencirikan kompleks kuprum(II) karboksilat campuran dengan formula umum, $[\text{Cu}_2(\text{RCOO})_n(\text{R}'\text{COO})_{4-n}]$, di mana $\text{R} = p\text{-H}_2\text{NC}_6\text{H}_4$, $\text{R}' = \text{CH}_3(\text{CH}_2)_{14}$, dan $n = 1\text{--}3$. Kompleks-kompleks ini direka khas sebagai metalomesogen bersuhu rendah, stabil haba, magnetik dan aktif redoks.

Sebanyak enam kompleks telah berjaya disintesis dengan menggunakan tindak balas satu kelalang, dan sifat terma, metalomesogen, magnetik dan redoks dilaporkan. Peralatan yang digunakan untuk mencirikan kompleks-kompleks adalah analisis unsur CHN, spektroskopi FTIR dan UV-vis, kekonduksian molar, termogravimetri, kalorimetri pembeza imbasan, mikroskop cahaya terkutub, kerentanan magnet dengan kaedah Gouy, dan voltametri siklik.

Semua kompleks, kecuali $[\text{Cu}_2(p\text{-H}_3\text{NC}_6\text{H}_4\text{COO})_3\text{Cl}]\text{Cl}_3\cdot\text{NH}_3\cdot 3\text{H}_2\text{O}$ (**Kompleks 4**) adalah bukan elektrolit. **Kompleks 4** adalah elektrolit 1:1. Geometri kompleks adalah piramid segi empat yang melibatkan karboksilat titian *syn-syn* atau *syn-anti* dan/atau kelat. Kestabilan terma kompleks-kompleks tersebut adalah lebih tinggi daripada 200°C , dengan takat lebur sekitar 118°C , kecuali **Kompleks 6** yang melebur pada suhu 166°C .

Kompleks yang menunjukkan sifat metalomesogen termotropik adalah $[\text{Cu}_2(p\text{-H}_2\text{NC}_6\text{H}_4\text{COO})_2(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2(\text{H}_2\text{O})(\text{CH}_3\text{CH}_2\text{OH})]$ (**Kompleks 1**), dengan mesofasa smektik C. Kompleks-kompleks ini sama ada anti-feromagnet atau feromagnet dengan nilai μ_{eff} dan $2J$ masing-masing dari 2.11 hingga 3.72 B.M., dan -200 hingga 109 cm^{-1} . Semua kompleks adalah aktif redoks. Tindak

balas redoks adalah kuasi-berbalik yang melibatkan pengolahan semula struktur secara ekstensif dan tindak balas kimia (mekanisme EC).

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