

Synthesis, characterization and magnetic properties with mesogenic of single-molecule (copper(II) palmitate) with 2,2'-bipyridine and 4,4'-bipyridine

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Abstract—Single molecule magnets and magnetic properties of advanced low-dimensional materials, especially for spintronic applications. They may be constructed from copper (II) ion and ditopic ligands, such as 2,2'-bipyridine and 4,4'-bipyridine. This paper reports the synthesis and characterization of a single molecule magnet, $[\text{Cu}_2(\eta^2\text{-(OOCR)}_2)(\eta^1\text{-(OOCR)}_2)(2,2'\text{-bpy})_2]$ (Complex 1), and a coordination polymer, $[\text{Cu}_2(\eta^2\text{-(OOCR)}_2)(\eta^1\text{-(OOCR)}_2)(2,2'\text{-bpy})(4,4'\text{-bpy})\text{EtOH}]$ (Complex 2), where $\text{R} = \text{CH}_3(\text{CH}_2)_{14}$. These complexes are characterized by elemental analyses, FTIR and UV-vis spectroscopies, magnetic susceptibility, Thermogravimetry and optical polarized microscopy (OPM). Both complexes showed weak ferromagnetic interactions between the square pyramidal Cu(II) centres, and exhibit mesomorphisms.

Keywords— Cu(II) palmitate, 2,2'-bipyridine, 4,4'-bipyridine, Magnetic, Mesomorphism

I. Introduction

The bipyridine ligand is extensively used in coordination chemistry because it produces metal complexes of noted thermal and kinetic stability [1]. Such metal complexes often possess useful photonic and electronic materials, which arise from the interaction of the orbitals of the metal and a bipyridine ligand. Many searches have focused on changing the functionality of the bipyridine ligand toward the end of predictably altering the electronic properties of metal complexes that are prepared from them [2].

The above-mentioned properties make bipyridine metal complexes versatile molecules that have been used in metal-organic polymers [3,4]. The coordination polymers bearing bipyridine ligands have been shown to form a wide range of interesting network topologies, for example, chains, ladders, grids, and adamantoid networks [5], and bipyridine is very popular for the construction of porous organic/inorganic hybrid solids with potential applications as catalytic, gas adsorption, or molecular sieve materials [6]. One-dimensional (1-D) chain compounds have been the focus of very active research because of their special and excellent physicochemical properties [7]. Although transition metal complexes with bipyridine have shown many interesting networks 3d [8]. Most of transition metal (II) are reported to exist as multinuclear complexes due to the multibinding modes of the ligands [9,10]. For example, most of Cu (II) carboxylates are dinuclear with the paddle-wheel structure [11-12]. The main reason is because they are easily prepared from relatively low cost, nontoxic and readily accessible starting materials and readily characterized by conventional analytical methods. Cu (II) palmitate complexes are obtained as room-temperature solid from the reaction of NaOH with the corresponding $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The ligand is specifically chosen as the branched long alkyl chains would allow for the formation of low melting temperature complexes, hence minimizing thermal degradation. Synthesis, characterization of the coordination polymers in the family of copper (II) palmitate with 2,2'-bipyridine and 4,4'-bipyridine to study magnetic properties is the main aim of this paper

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II. Experimental

Palmitic acid and all other chemicals were commercially available and used as received. The elemental analyses were carried out on a Perkin-Elmer CHNO/S 2400 Series II elemental analyser. The FTIR spectra were recorded in the 4000–400 cm^{-1} region for neat samples sandwiched between two NaCl plates on a Perkin-Elmer Spec-trum 400 spectrometer. The electronic spectra were recorded for samples dissolved in CHCl_3 on a Shimadzu UV-VIS-NIR1600 spectrophotometer. The room-temperature magnetic susceptibility measurements were taken on a Sherwood auto magnetic susceptibility balance by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. The molar susceptibility was corrected for the diamagnetism of the constituent atoms using Pascal's constants. The thermogravimetric analysis (TGA) was done on a Perkin-Elmer Pyris Diamond TG/DTA thermal instrument in the temperature range 50–900 $^\circ\text{C}$, under N_2 at a flow rate of $10\text{cm}^3\text{min}^{-1}$ and scan rate of $20^\circ\text{C min}^{-1}$. The optical textures are observed using an Olympus polarizing microscope equipped with a Mettler Toledo FP90 central processor and FN82HT hot stage. A minute amount of the sample is sandwiched between two microscope slides, and then heated at the rate of $5\text{--}10^\circ\text{C min}^{-1}$, and cooled at the rate of $2\text{--}5^\circ\text{C min}^{-1}$.

A. Syntheses

Reaction complex 1

A solution of copper(II) palmitate was prepared as [13] (1 g, 8.7×10^{-4} mol) in ethanol (50 ml) is added 2,2'-bipyridine (0.27 g, 1.73×10^{-3} mol) to the suspension. The mixture is heating on a hot plate for 30 min. The suspension is filtered hot and discard any solid. Allow the solvent to slowly evaporate off from the filtrate. The light blue solid formed from the filtrate is filtered. The yield is 1.2 g (94%). Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{70}\text{O}_4\text{CuN}_2$ (730.56 g mol^{-1}): C, 69.05; H, 9.66; N, 3.83. Found. (%): C, 69.46; H, 10.54; N, 3.92.

Reaction complex 2

A solution of copper (II) palmitate -2,2'-bpy (0.3365 g, 2.3×10^{-4} mol) dissolved in ethanol (50 ml). Added 4,4'-bipyridine (0.0359 g, 2.3×10^{-4} mol) to the solution at room. The mixture is stirred on heating for 10 min,

allowed the solvent to slowly evaporate off from the reaction mixture. The light blue solid is filtered and dried. The yield is 0.24 g (69%). This is new step to study of magnetic coordination polymers with mesogenic properties. Anal. Calcd. (%) for $\text{C}_{86}\text{H}_{146}\text{Cu}_2\text{N}_4\text{O}_9$ ($1507.20\text{ g mol}^{-1}$): C, 68.53; H, 9.76; N, 3.72. Found. (%): C, 68.97; H, 10.57; N, 3.28. are in excellent agreement with those calculated from the chemical formula.

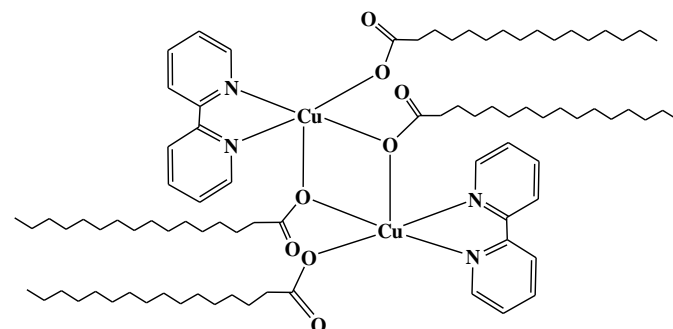


Fig 1. Structure formula $[\text{Cu}_2(\text{C}_{15}\text{H}_{31}\text{COO})_4]\text{-}2,2'\text{-bpy}$ [22].

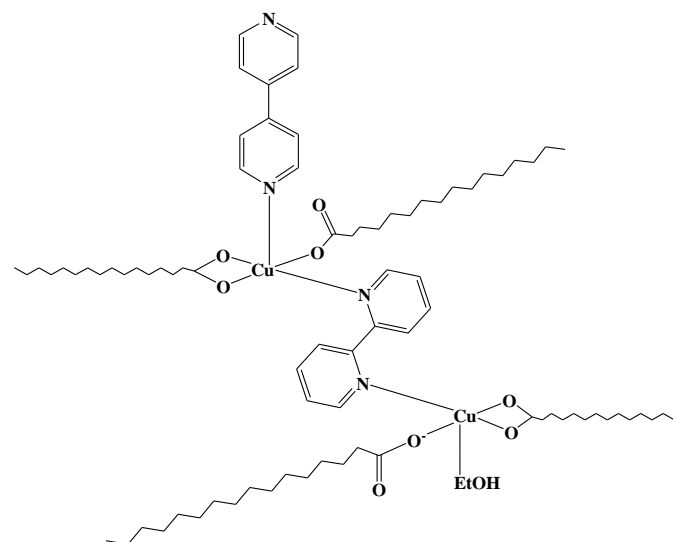


Fig 2. Proposed structural formula $[\text{Cu}_2(\text{C}_{15}\text{H}_{31}\text{COO})_4\text{EtOH}]\text{-}2,2'\text{-bpy-}4,4'\text{bpy}$

III. Results and discussion

Fourier transform infrared spectroscopy (FTIR)

Complex 1

FTIR spectrum shows two strong peaks at 2917cm^{-1} and 2849cm^{-1} for asymmetric and symmetric CH_2 vibrations respectively, the presence of all of the expected functional groups as discussed previously, and additional peaks due to 2,2'-bpy at 1626cm^{-1} (C=C) and 778cm^{-1} ($\nu_{\text{C-H}}$). The Δ_{COO} values, calculated from values of $\nu_{\text{asymCOO}} = 1599\text{cm}^{-1}$ and $\nu_{\text{symCOO}} = 1466$ and 1374cm^{-1} , are 133cm^{-1} and 225cm^{-1} , suggesting bridging monodentate and monodentate carboxylates. This result is identical with $[\text{Cu}_2(\text{RCOO})_4(\text{RCOOH})_2] + 2,2'$ -bipyridine [14].

Complex 2

FTIR spectrum is different from that of complex 1. It shows the presence of peaks due to coordinated 2,2'-bpy and 4,4'-bpy (a medium band at 1602cm^{-1} for C=N coincident, at 1622cm^{-1} weak band for C=C, small band at 1162cm^{-1} for 'ring breathing' and a medium band at 778 for para ring), The $\Delta\nu$ value is 192cm^{-1} (calculated from the values of 1610cm^{-1} for ν_{asymCOO} and 1418cm^{-1} for ν_{symCOO}). suggesting monodentate coordination mode of the palmitate ligand. This result is different with $[\text{Cu}_2(\text{RCOO})_4(\text{RCOOH})_2] + 4,4'$ -bipyridine, it appeared chelating bidentate coordination mode [15].

UV-visible spectroscopy

Complex 1

UV-vis spectrum in CHCl_3 shows a broad *d-d* band at 689nm ($\epsilon_{\text{max}} = 84\text{M}^{-1}\text{cm}^{-1}$), a shoulder at about 801nm ($\epsilon_{\text{max}} = 63\text{M}^{-1}\text{cm}^{-1}$), and another shoulder at 390nm ($\epsilon_{\text{max}} = 53\text{M}^{-1}\text{cm}^{-1}$). These suggest a binuclear complex with square pyramidal Cu(II) centers. This result is excellent compared with distorted square pyramidal to $[\text{Cu}_2(\text{RCOO})_4(\text{RCOOH})_2] + 2,2'$ -bipyridine [16].

Complex 2

UV-vis spectrum in chloroform shows a broad *d-d* band at 667nm ($\epsilon_{\text{max}} = 207\text{M}^{-1}\text{cm}^{-1}$). These suggest a binuclear complex with square pyramidal geometry at Cu(II) while $[\text{Cu}_2(\text{RCOO})_4(\text{RCOOH})_2] + 4,4'$ -bipyridine is mononuclear complex with square pyramidal geometry at Cu(II) [17].

Magnetic susceptibility

Complex 1

The value of μ_{eff} , calculated from its proposed chemical formula ($\text{FM} = 730.56\text{g mol}^{-1}$), and the values of χ_{g} ($0.156 \times 10^{-5}\text{c.g.s}$), χ_{M} (1.14×10^{-3}), $\chi_{\text{M}}^{\text{corr}}$ (1.607×10^{-3}), and χ_{dia} ($-467.7 \times 10^{-6}\text{c.g.s}$), is 1.99B.M. at 298K .

The experimental value is slightly higher than the expected spin only value for one unpaired electrons (1.73BM). This explains complex 1 supports the proposed mononuclear complex. The magnetic of complex 1 is ferromagnetic interaction between the two Cu(II) centers.

Complex 2

The μ_{eff} value, calculated as before from its chemical formula ($\text{FM} = 1507.2\text{g mol}^{-1}$) and the values of χ_{g} ($0.156 \times 10^{-5}\text{c.g.s}$), χ_{dia} ($-952.98 \times 10^{-6}\text{c.g.s}$), χ_{M} ($2.351 \times 10^{-3}\text{c.g.s}$) and $\chi_{\text{M}}^{\text{corr}}$ ($3.304 \times 10^{-3}\text{c.g.s}$), is 2.83B.M at 298K . It was calculated using the equation: $\mu_{\text{eff}} = 2.83[T(\chi_{\text{M}}^{\text{corr}} - N\alpha)]^{1/2}$, where $\chi_{\text{M}}^{\text{corr}}$ is the corrected molar magnetic susceptibility, T is the absolute temperature (298K) and $N\alpha$ is the temperature-independent paramagnetism of Cu(II) ($120 \times 10^{-6}\text{cm}^3\text{mol}^{-1}$ per dinuclear complex). The experimental value is slightly exactly the same of the expected spin-only value for two unpaired electrons (2.83BM) from a dinuclear Cu(II) complex (d^9). This suggesting complex 2 supports the proposed binuclear complex. The magnetic of complex 2 is paramagnetic interaction between the two Cu(II) centers.

Thermogravimetry

Complex 1

The TGA shows that complex 1 is thermally stable on heating up to 230°C . Thus, its thermal stability was lower than $[\text{Cu}_2(\text{CH}_3(\text{CH}_2)_5\text{COO})_4]$ is found to decompose at a higher temperature of 280°C , reported by Yasameen (2013) [18]. Hence, it may be suggested that both complexes started to decompose soon after bpy molecules dissociated from the axial positions. 63

The total weight loss from 230 °C to 680 °C, of 88.9% is assigned to the decomposition of the decarboxylation of RCOO ligand (expected, 89.1%). The amount of residue at temperatures above 700 °C is 11.1. However, the expected value, assuming that is pure CuO 10.9%.

Complex2

The TGA scan shows that complex 2 is thermally stable on heating up to 230 °C. The initial weight loss of 3.53.0% from 100 °C to 230 °C is due to evaporation of lattice and coordinated EtOH molecules (expected 3.1%). The final weight loss of 85.6% from 230 °C to 750 °C is due to the decarboxylation of RCOO ligand (expected 86.3%). The amount of residue at temperatures above 750 °C is 10.9%. However, the expected value, assuming that is pure CuO 10.6%. In comparison, $[\text{Cu}_2(\text{RCOO})_4(4,4'\text{-bpy})]$ is found to decompose at a lower temperature of 220 °C, reported by Yasameen (2013) [19].

Polarizing Optical Microscopy

Complex1

Viewed under a polarising optical microscope (POM), the photomicrographs of the filament texture [20] mesophase of the powder complex at -136.1 °C and 113.5 °C are shown in (Figure 3).

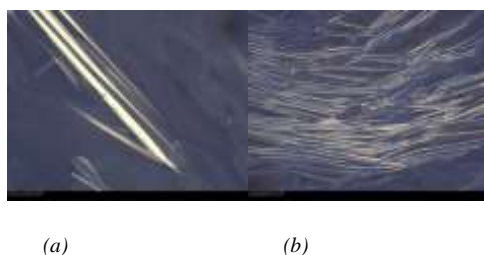


Fig 3. The mesophases of Complex 1 during the second cooling cycle at: (a) 136.1 °C; (b) 113.5 °C

Complex 2

Is done for two heating-cooling cycles starting from room temperature to 147.7 °C. It is observed to melt at 74.1°C, and formed an isotropic liquid at 140.2 °C. On cooling, an optical texture (D_h) started to form at 77.9 °C and continue to grow until room temperature. On re-heating, the solid started to melt at 140 °C, and formed an isotropic liquid at 130.3 °C. On cooling, similar optical texture is formed but at a lower temperature of 49.2 °C. This

texture coalesced to give a filament texture [21] on further cooling to room temperature (Figure 4).

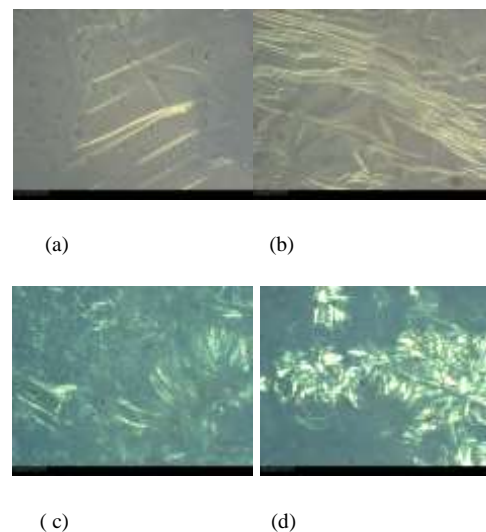


Fig 4. The mesophases of Complex 2 during the two cooling cycle at: (a) 134.6 °C; (b) 77.9 °C; (c) 70.1 °C; (d) 49.2 °C.

Conclusion

The coordination chemistry of 2,2-bipyridine and 4,4-bipyridine ligand with transition metal Cu (II) is investigated. Using different auxiliary ligands and metal ions lead to a series of 1D chain structures with different coordination modes of bridging ligands and coordination geometry of metal centers. These complexes are dinuclear, ferromagnetic for (complex 1) and paramagnetic for (complex 2) interactions between the two metal Cu(II) centres. Additionally, they are exhibit mesomorphism, thermally and electrochemically stable.

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