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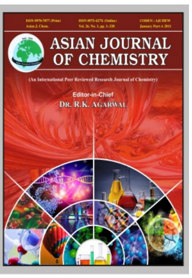

Room-Temperature Magnetic Liquid Complexes of 2-Hexyldecanoato Ligand with Cu(II), Ni(II) and Co(II) Ions

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Three new complexes $[Cu_2(L)_4(LH)_2]$ (**1**), $[Ni_2(L)_4(EtOH)_2(H_2O)_2].H_2O.CHCl_3$ (**2**) and $[Co_2(L)_4(H_2O)_4].3H_2O$ (**3**), were obtained as coloured viscous liquids at room temperature (30 ºC) and in good yields from the reaction of sodium 2-hexyldecanoate (NaL) with the corresponding MCl_2 (M = Cu, Ni or Co). The structural formulae of these complexes were indirectly deduced by a combination of analytical results and additionally for **1**, inferred from that of $[Cu_2(CH_3(CH_2)_5COO)_4]$ (**4**) obtained as single crystals under similar synthetic conditions. Complexes **1**-**3** were paramagnetic with weak antiferromagnetic interactions between the two M(II) centres, while **4** has a significantly stronger antiferromagnetic interaction. Complex **3** was also high spin. These complexes were thermally stable: **1** and **2** decomposed at 200 ºC, **3** at 150 ºC and **4** at 280 ºC. However, they were redox inactive in the potential range -1.5 V to + 1.5 V, while only **1** was mesogenic with a hexagonal columnar mesophase (Col_h) at -23.2 ºC.

Keywords: 2-Hexyldecanoate, Cu(II), Ni(II), Co(II), Magnetic, Thermal.

INTRODUCTION

Most of transition metal(II) carboxylates were reported to exist as multinuclear complexes due to the multibinding modes of the ligands[1,2]. For example, most of the copper(II) carboxylates were dinuclear with the paddle-wheel structure[3-7], while other metal(II) complexes (Mn, Co, Ni and Zn) were found to form polymeric structures[8-11]. Hence, these complexes are attracting the interests of many researchers in various fields, such as catalysis, molecular electronics and molecular magnetism. 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. However, these complexes are yet to be commercially used as functional materials due to physical limitations, such as insolubility, high-melting and low-decomposition temperatures.

Currently, our research group is focused on designing, synthesizing and characterizing thermally stable and low melting temperatures magnetic metal(II) carboxylates to function as molecular magnetic, photonic and electronic materials and as precursors for functional coordination polymers.

This paper reports the synthesis, structural, magnetic, thermal, optical and redox properties of three complexes of 2-hexyldecanoato ligand (L) with Cu(II) (**1**), Ni(II) (**2**) and Co(II) (**3**). These complexes were obtained as room-temperature viscous liquids from the reaction of NaL with the corresponding MCl_2. It also reports the single-crystal structure of $[Cu_2(CH_3(CH_2)_5COO)_4]$ (**4**) used to ascertain the structure of **1**. The ligand L was specifically chosen as the branched long alkyl chains would allow for the formation of low melting temperature complexes, hence minimising thermal degradation. The metal(II) ions were chosen as they have unpaired electron(s) and hence expected to form magnetic complexes to allow for the use of low energy magnetic field for structural alignment. Additionally, Cu(II) and Ni(II) centres have readily available axial positions for the formation of coordination polymers using ditopic ligands, such as 4,4'-bipyridine and pyrazine [12,13], while Co(II) complexes were potential spin crossover materials useful as sensors and in information storage[14].

EXPERIMENTAL

2-Hexyldecanoic acid (HL), heptanoic 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 Spectrum 400 spectrometer. The electronic spectra were recorded for samples dissolved in $CHCl_3$ on a Shimadzu UV-VIS-NIR 1600 spectrophotometer. The room-temperature magnetic susceptibility measurements were taken on a Sherwood automagnetic susceptibility balance by the Gouy method, using Hg[Co(SCN)$_4$] as the calibrant. The molar susceptibility was corrected for the diamagnetism of the constituent atoms using Pascal's constants. The diffraction data for single crystals was collected at 100(2) K on a Bruker SMART APEX II fitted with MoKα radiation so that λ_{max} was 28.4°. The data set was corrected for absorption based on multiple scans[15] and reduced using standard methods[16]. The structure was solved by direct method with SHELXS-97[17] and refined by a full-matrix least-squares procedure on F^2 using SHELXL-97 with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.2108P]$ where $P = (F_o^2 + 2F_c^2)/3)$. All hydrogen atoms were included in the final refinement in their calculated positions. The thermogravimetric analysis (TGA) was done on a Perkin-Elmer Pyris Diamond TG/DTA thermal instrument in the temperature range 50-900 ºC, under N_2 at a flow rate of 10 cm^3 min^{-1} and scan rate of 20 ºC min^{-1}. The differential scanning calorimetry (DSC) was done on a Mettler Toledo DSC 822 instrument, with the scans recorded for two consecutive heating-cooling cycles, from 30-50 ºC and then cooled to -30 ºC, under N_2 at a flow rate of 20 cm^3 min^{-1} and scan rate of 10 ºC min^{-1}. The optical textures were inferred from the photomicrographs captured on either an Olympus polarizing or Nikon-H600L eclipse microscopes, both equipped with a Mettler Toledo FP90 central processor and a Linkam THMS 600 hot stage. The heating and cooling rates were 5 ºC and 2 ºC min^{-1} respectively and the magnification was 50X. The cyclic voltammetric scans (CV) were mainly recorded on a Gamry Instrument Reference 600 potentiostat/galvanostat/ZRA. A three-electrode cell consisting of glassy carbon as the working electrode, saturated calomel electrode (SCE) as the reference electrode and platinum wire as the counter electrode were used. The supporting electrolyte was tetrabutylammonium tetrafluoroborate (TBATFB, 0.05 M). The samples (0.005 M) were dissolved in THF or CHCl$_3$ and the solutions were bubbled with N_2 for *ca.* 1 min. The potential range was -1.5 V to +1.5 V and the scan rates were 50-150 mV s^{-1}.

Synthesis

[Cu$_2$(L)$_4$(LH)$_2$] (1): A solution of Na_2CO_3 (5.42 g, 51.1 mmol) in distilled H_2O (150 mL) was added to a solution of LH (26.22 g, 102.3 mmol) in EtOH (95 %, 100 mL). The cloudy suspension formed was magnetically stirred and gently heated on a hot plate until a clear colourless solution formed (2 h). The solvents were removed on a rotary evaporator to give NaL as a colourless viscous liquid. The yield was 25.61 g (90 %). FTIR (cm^{-1}): 3366 (m, br), 2956 (m), 2924 (vs), 2855 (s), 1540 (vs), 1459 (m), 1409 (s).

NaL (12.67 g, 45.5 mmol) was then dissolved in hot aqueous EtOH (1:1, 200 mL). $CuCl_2.2H_2O$ (3.88 g, 22.8 mmol) was gradually added to the solution and the mixture magnetically stirred, heated for 0.5 h and left to cool to room temperature. The oily dark green product formed was extracted using CHCl$_3$ and the solvent evaporated off on a rotatory evaporator. The viscous dark green liquid obtained was further dried in an oven at 60 ºC. The yield was 7.71 g (61 %). Anal. calcd. (%) for $C_{97}H_{192}O_{12}Cu_2$: C, 69.4; H, 11.4. Found (%): C, 69.5; H, 11.1. FTIR (cm^{-1}): 3393 (w), 2955 (s), 2855 (s), 1706 (m), 1609 (s), 1580 (m), 1455 (s), 1419 (s), 462 (vs).

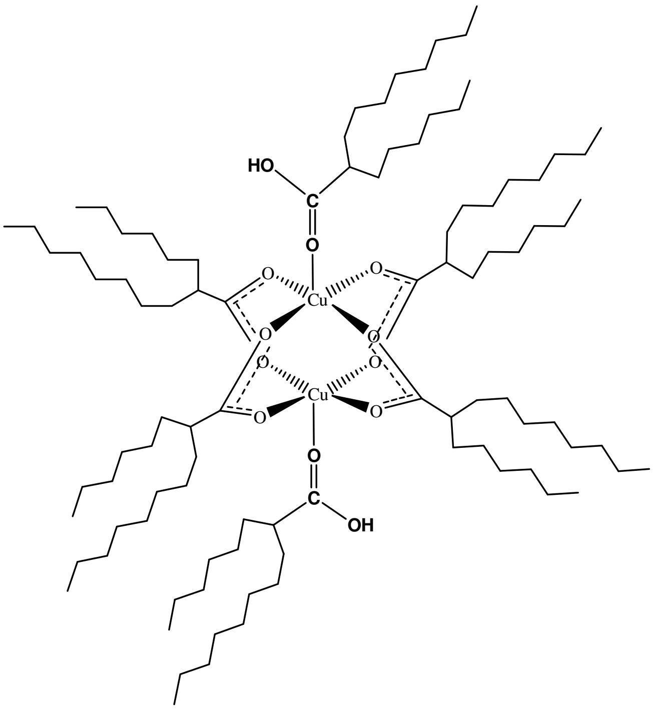
[Ni$_2$(L)$_4$(EtOH)$_2$(H$_2$O)$_2$].H$_2$O.CHCl$_3$ (2): The synthetic method was similar to that of **1**, using NaL (6.08 g, 21.9 mmol) and $NiCl_2.6H_2O$ (2.59 g, 10.9 mmol). The product was a pale green viscous liquid and the yield was 3.82 g (62 %). Anal. calcd. (%) for $C_{70}H_{147}O_{13}Cl_3Ni_2$: C, 59.1; H, 10.4 ; found (%): C, 58.6; H, 10.8. FTIR (cm^{-1}): 3368 (w), 2955 (s), 2855 (s), 1685 (s), 1610 (m), 1587 (s), 1465 (m), 1414 (s), 485 (vs).

[Co$_2$(L)$_4$(H$_2$O)$_4$].3H$_2$O (3): The synthetic method was similar to that of **1**, using NaL (3.01 g, 10.8 mmol) and $CoCl_2.6H_2O$ (0.70 g, 5.40 mmol). The product was a dark blue viscous liquid and the yield was 0.98 g (59 %). Anal. calcd. (%) for $C_{64}H_{138}O_{15}Co_2$: C, 60.7; H, 11.0; found (%): C, 60.8; H, 11.1. FTIR (cm^{-1}): 3383 (w), 2925 (s), 2856 (s), 1682 (s), 1607 (m), 1465 (s), 1459 (s), 1410 (s), 446 (vs), 436 (vs).

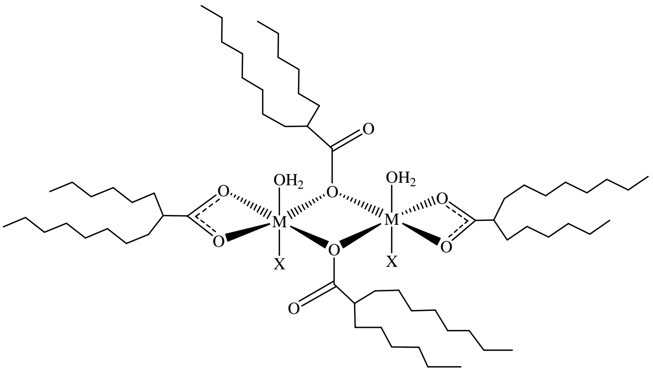
[Cu$_2$(CH$_3$(CH$_2$)$_5$COO)$_4$] (4): The synthetic method was similar to that of **1**, using $CH_3(CH_2)_5COONa$ (1.64 g, 10.8 mmol) and $CuCl_2.2H_2O$ (0.92 g, 5.40 mmol). The product was a greenish-blue powder and the yield was 1.28 g (65 %). The powder formed greenish-blue crystals on recrystallization from THF-MeOH (2:1). FTIR (cm^{-1}): 3448 (w), 2927 (s), 2871 (s), 1589 (vs), 1416 (s).

RESULTS AND DISCUSSION

Synthesis and structural elucidation: There were several methods reported in the literature for the synthesis of metal(II) carboxylates[18-20]. All complexes in this paper were obtained in good yields (> 50 %) from the reaction of sodium alkanoate (either 2-hexyldecanoate or heptanoate) with the corresponding metal(II) chloride. The structural formulae for complexes **1**-**3** (Fig. 1) were deduced from a combination of CHN elemental analyses, FTIR and UV-VIS spectroscopies and room-temperature magnetic susceptibility data. Additionally, the structural formula of **1** was ascertained by comparison with the analytical data obtained from crystals of **4**.



(a)



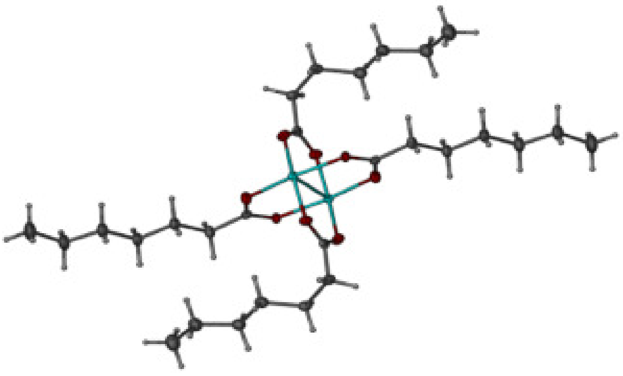
(b)

Fig. 1. Proposed structural formulas: (a) **1** ($[Cu_2(L)_4(LH)_2]$), (b) **2** (M = Ni(II), X = EtOH) and **3** (M = Co(II), X = H_2O. The solvent molecules are not shown

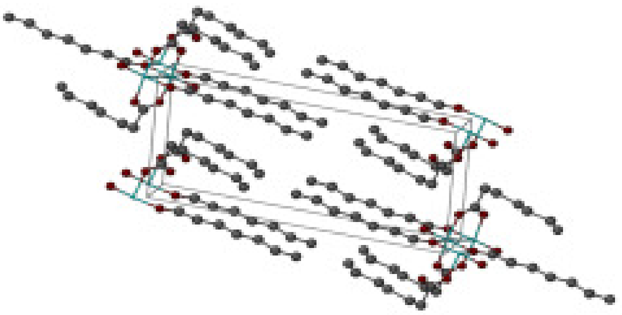
For **1**, the chemical formula deduced from the elemental analytical data is $[Cu(L)_2(LH)]$. Its FTIR spectrum shows peaks (in cm^{-1}) for $-CH_2$ at 2955 (ν_{asym}) and 2855 (ν_{sym}), -COO at 1609 (ν_{asym}) and 1455 (ν_{sym}) and for intramolecularly H-bonded -COOH at 3393 and 1706. Accordingly, the Δ_{COO} value ($\Delta_{COO} = \nu_{as,COO} - \nu_{s,COO}$) is 154 cm^{-1}, suggesting a bridging carboxylate ligand[1,2] when compared to that of NaL (Δ_{COO} = 131 cm^{-1}). Its UV-visible spectrum shows a broad *d-d* band at 667 nm (ε_{max} = 436 $M^{-1} cm^{-1}$), a weak shoulder at 860 nm (ε = 131 $M^{-1} cm^{-1}$) and another shoulder at 375 nm (ε = 144 $M^{-1} cm^{-1}$). The result suggest a square pyramidal binuclear Cu(II) complex[21]. The electronic transitions, based on the C_{4v} point group at each Cu(II) centre, are assigned to $^2B_2 \rightarrow {}^2B_1$, $^2A_1 \rightarrow {}^2B_1$ and $^2E \rightarrow {}^2B_1$, respectively[19]. The value of its effective magnetic moment (μ_{eff}) was 2.6 BM. It was calculated using the equation: $\mu_{eff} = 2.83[T(\chi_M^{corr} - N\alpha)]^{1/2}$, where χ_M^{corr} is the corrected molar magnetic susceptibility, T is the absolute temperature (298 K) and $N\alpha$ is the temperature-independent paramagnetism of Cu(II) (120×10^{-6} cm^3 mol^{-1} per dinuclear complex). The experimental value is slightly lower than the expected spin-only value for two unpaired electrons (2.83 BM) from a dinuclear Cu(II) complex (d^9), suggesting a weak antiferromagnetic interaction between the two Cu(II) centres. From the above analytical results, it is proposed that **1** may adopt the paddle-wheel structure similar to other Cu(II) carboxylates[18,19], but with a 2-hexyldecanoic acid molecule at each axial position (Fig. 1a).

In order to ascertain the proposed structural formula of **1**, a reaction was carried out between $CH_3(CH_2)_5COONa$ and $CuCl_2 \cdot 2H_2O$ under similar conditions. Bluish-green crystals of $[Cu_2(CH_3(CH_2)_5COO)_4]$ (**4**) deposited from a solution of the powder obtained in THF-MeOH (2:1). Its structure and packing diagram are shown in Fig. 2 and the crystal data and structure refinement details are shown in Table-1.

The X-ray data for complex **4** clearly shows the expected paddle-wheel structure. Its FTIR (Δ_{COO} = 173 cm^{-1}) and UV-visible (λ_{max} = 671 nm, ε_{max} = 375 $M^{-1} cm^{-1}$) spectral results are similar to those of **1**. Hence, we are quite confident that both complexes have similar structure. The significantly lower μ_{eff} value for **4** (1.6 BM) compared to **1** (2.6 BM) may arise from the coordination of 2-hexyldecanoic acid molecules at the two axial positions in the latter complex, leading to a more planar geometry at both Cu(II) centres.



(a)



(b)

Fig. 2. (a) Crystal structure and (b) packing diagram of $[Cu_2(CH_3(CH_2)_5COO)_4]$ (**4**)

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT DETAILS FOR COMPLEX 4

Formula	$C_{14}H_{26}O_4Cu$
Formula weight	321.89
Crystal system	Triclinic
Space group	P-1
T (K)	100(2)
a (Å)	5.1486(3)
b (Å)	8.3829(5)
c (Å)	18.6623(11)
α (°)	81.5410(10)
β (°)	83.5910(10)
γ (°)	76.1890(10)
Z	2
V (Å³)	771.21(8)
$F_{(000)}$	342
θ range (°)	1.11 - 28.37
Goodness-of-fit on F^2	1.140
Final R indices [I > 2σ(I)]	R_1 = 0.0231, wR_2 = 0.0726
R indices (all data)	R_1 = 0.0274, wR_2 = 0.0836

For complex **2**, the structural formula proposed from the combined analytical data is $[Ni_2(L)_4(EtOH)_2(H_2O)_2].H_2O.CHCl_3$ (Fig. 1b). Its FTIR spectrum shows the expected peaks (in cm^{-1}) for -OH at 3368, $-CH_2$ at 2955 (ν_{asym}) and 2855 (ν_{sym}), -COO at 1610 (ν_{asym}), 1587 (ν_{asym}), 1465 (ν_{sym}) and 1414 (ν_{sym}). Accordingly, the Δ_{COO} values are 122 and 196 cm^{-1}, suggesting bidentate chelating and monodentate bridging carboxylate, respectively. Its UV-visible spectrum shows a weak *d-d* band at 681 nm (ε_{max} = 7.3 $M^{-1} cm^{-1}$), suggesting a highly symmetrical octahedral geometry at Ni(II) centres [22]. The μ_{eff} value of 4.6 BM at 298 K is slightly lower than the expected spin-only value for four unpaired electrons (4.89 BM) from a dinuclear Ni(II) octahedral complex (d^8). This indicates a weak antiferromagnetic interaction between the two metal centres. The analytical results seem to suggest that 2-hexyldecanoato ligand exerted a weak ligand field effect on the *d* orbitals of Ni(II) in this complex.

As similarly argued for **1** and **2**, the proposed structural formula for **3** is $[Co_2(L)_4(H_2O)_4]\cdot 3H_2O$. The Δ_{COO} values of 147 and 217 cm^{-1} from its FTIR spectrum suggest bidentate chelating and monodentate bridging carboxylate, respectively. The broad *d-d* band at 617 nm (ε_{max} = 215 $M^{-1}cm^{-1}$) from its UV-visible spectrum suggest that Co(II) has similar geometry as **2** (Fig. 1b). The μ_{eff} value of 6.46 BM at 298 K is slightly lower than the expected spin value for six unpaired electrons (6.93 BM) for a dinuclear high-spin Co(II) octahedral complex (d^7). Accordingly, there is also a weak antiferromagnetic interaction between the two Co(II) centers[22].

Thermal properties: The TGA trace for **1** shows that its decomposition temperature was 200 ºC, with a total weight loss of 89.7 % (calculated, 89.8 %). The excellent agreement between the experimental and calculated values further supports the proposed formula for the complex. In comparison, **4** was found to decompose at a higher temperature of 280 ºC, which was similar to that of $[Cu_2(C_6H_5COO)_4(H_2O)_2]$ (T_{dec} = 280 ºC) reported by Siqueira *et al.*[23]. The lower thermal stability of **1** is likely due to the condensation of H_2O from the axially coordinated 2-hexyldecanoic acid molecules. As expected from a viscous liquid sample, its DSC trace does not show any peaks in the temperature range -30 ºC to 50 ºC. However, it is noted that a needle-like growth developed in the liquid after six months at room temperature. This may be due to crystallization from the isotropic liquid. Viewed under a polarising optical microscope (POM), the photomicrographs of the needles and the Col$_h$ mesophase of the viscous liquid at -23.2 ºC are shown in Fig. 3.

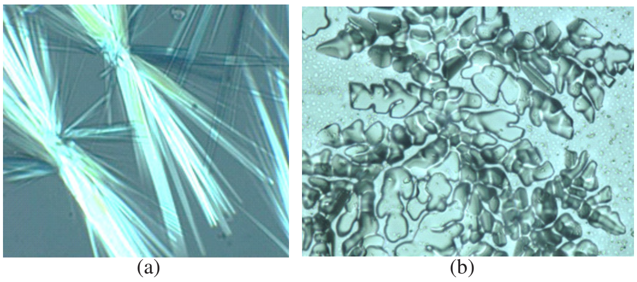

(a) (b)

Fig. 3. Photomicrographs of **1**: (a) after six months, (b) the Coh$_h$ mesophase at -23.2 ºC

The complex **2** was found to decompose at about the same temperature as **1** (200 ºC), with a total weight loss of 88.2 % (calculated: 89.5 %). It is noted that its decomposition temperature is lower than that reported for $[Ni(C_6H_5COO)_2]$ (T_{dec} = 230 ºC)[23]. In contrast, **3** decomposed at a lower temperature (150 ºC) with a total weight loss of 92.3 % (calculated: 92.4 %). The DSC traces for both complexes do not show any peaks, while the POM did not detect any mesophases on cooling from room temperature to -30 ºC. These results further support the proposed isotropic structures as shown in Fig. 1b.

Redox properties: The cyclic voltammetric studies (CV) for complexes **1-4** were performed repeatedly in two different solvents (THF and $CHCl_3$) with different concentrations, under different experimental conditions and using two different instruments. Surprisingly in all cases, neither cathodic nor anodic peaks were detected. It is infered from these results that the structures of these complexes were stable in these solvents and that the 2-hexyldecanoato ligand was an effective 'insulating shield', preventing the central metal(II) ions from being electrochemically reduced or oxidized.

Conclusion

Complexes formed from 2-hexyldecanoato ligand with Cu(II) (**1**), Ni(II) (**2**) and Co(II) (**3**) ions existed as coloured viscous liquids at room temperature (30 ºC). These complexes were dinuclear, paramagnetic with weak antiferromagnetic interactions between the two metal(II) centres and thermally and electrochemically stable. Complex **3** was high spin, while **1** was mesogenic exhibiting a hexagonal columnar mesophase (Col$_h$) at -23.2 ºC.

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