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Thermotropic Mesomorphism of Soft Materials Bearing Carboxylate-Supported μ_4-Oxo Tetracupric Clusters

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A new ligand containing long alkyl (octadecyl) chains was used to obtain the mesogenic complex $[L_2Cu_4(\mu_4\text{-}O)(OAc)_4]\cdot EtOH$ (**1**). This complex was thoroughly characterized and had its molecular structure solved by X-ray diffraction (XRD). Mesomorphic properties were demonstrated by means of polarized microscopy, differential scanning calorimetry, and XRD.

A great deal of interest surrounds metal-containing soft materials. Metallopolymers,[1] metallosurfactants,[2] and metallomesogens[3] take advantage of geometric, redox, and magnetic properties of transition metals to build up organized supramolecular architectures based on organic scaffolds. Similarly, recent advances point to successful applications of these materials toward molecular electronics and magnetic films.[4] Despite this growing interest, systems bearing three-dimensional clusters remain largely unexplored because flat multinuclear cores are favored by commonly used ligands that fail to provide support for cluster formation.[5] This constraint can be overcome by the use of preassembled dimers or clusters. These species can interact with properly designed ligands that will confer specific properties to the final assembly. In this regard, formation of carboxylate-supported clusters[6] has been observed for several ($\text{-}C_{28}H_{37}$) transition-metal ions and can be an important starting point in the incorporation of such clusters to mesogenic and amphiphilic ligands. Our interest toward molecular electronics focuses on the understanding of asymmetric metal/organic junctions[7] and ground-state switching.[8] Soft materials can pave the road to the design of stimulus-responsive liquid-crystalline mesophases and films relevant to storage and display technologies.[9] In this Communication, we describe a new N_2O terdentate ligand HL with bilateral octadecyl chains and its (μ_4-O)Cu_4-containing mesogen $[L_2Cu^{II}_4(\mu_4\text{-}O)(OAc)_4]\cdot EtOH$ (**1**).

Although the μ_4-oxo motif has been observed in similar chelates,[10,11] the introduction of octadecyl side chains in the ligand design is an excellent way to confer mesomorphic behavior to the referred clusters. The ligand, shown in Chart 1, was synthesized by the treatment of 2,6-diformyl-4-*tert*-butylphenol with 1-octadecylamine and was analyzed by

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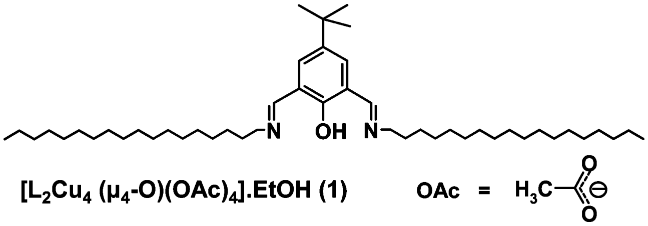
Chart 1



$[L_2Cu_4(\mu_4\text{-}O)(OAc)_4]\cdot EtOH$ (1) **OAc = H_3C**

NMR and IR spectroscopy and electrospray ionization mass spectrometry (ESIMS). A multiplet peak at 1.31 ppm in the NMR spectrum confirms the presence of 60 protons, as expected for the combined C−H groups from the *tert*-butyl and alkyl chains. The imine nature of the ligand is verified by the presence of a C═N group at 1641 cm^{-1} in the IR spectrum as well as an MS peak at *m*/*z* 771 for $[HL + H]^+$. Complex **1** was synthesized by treatment of HL with an ethanolic solution of "copper(II) acetate" in a 1:2 (L/Cu) molar ratio. Evidence of the complex formation is given by ESIMS data at different cone voltages, with peaks related to $[\mathbf{1} - OAc]^+$. These peaks show the expected isotopic distribution associated with Cu ions, and the microanalysis showed good agreement with the described structures. Structural characterization by single-crystal X-ray diffraction (XRD) was obtained and is shown with selected average bonds in Figure 1. Bond lengths and angles are given in Table T2 of the Supporting Information. Complex **1** is composed of neutral molecules consisting of two deprotonated ligands L^-, each of them delivering a set of N_2O donor atoms to a cluster of four Cu^{II} centers μ_4-bridged by a distorted tetrahedral O atom. Four acetato coligands complete the coordination sphere. Each of the two O atoms from the phenolate ring bridges two Cu^{II} ions that lie at about 3.0 Å from each other. The $Cu-O_{phenolate}-Cu$ angles span about 98.8°, and the four $Cu-N_{imine}$ bonds are ca. 1.97 Å in length. These distances are in good agreement with previously reported values.[10,11] Each Cu ion is further coordinated to the O atoms of two bridging acetato groups, fostering a five-coordinate geometry around the metal centers. A distorted square-pyramidal geometry can be inferred from a τ value[12] ranging from 0.011 to 0.103. Carboxylate-supported[10b,c] μ-oxo Cu cores are considerably less usual than the related halogeno-bridged[11] μ-oxo counterparts. The latter tend to have a more pronounced trigonal-bipyramidal character.[11b] The pattern of the acetato bridges is symmetric,[10b] with two acetate groups linking Cu1 and Cu4 and the other two linking Cu2 and Cu3. The $Cu-O_{acetato}$ bond lengths range from 1.94 to 2.38 Å. It can be seen from the unit cell representations (Figures 1c and S1 in the Supporting Information) that the alkyl chains of vicinal molecules align, forming a layered ladderlike structure. This arrangement in the solid suggests the formation of columnar mesophases, as is commonly found in metallomesogens.[13] Differential scanning calorimetry (DSC) of **1** demonstrated phase transitions at 77 and 109 °C. The crystal structure and elemental analysis of **1** show the presence of an ethanol molecule that has a boiling point of 78.5 °C, thus very close to the phase transition temperature. To ensure that the phase transition at 77 °C is not related to ethanol evaporation, DSC was repeated after grinding and drying of the powder for 36 h in a high vacuum at 40 °C. The result was found to be identical. Visual observations in the polarizing microscope showed the transition at 109 °C to be melting to an isotropic liquid. Characterization of the mesophase at 77 °C revealed limited visual signs of the transition with no apparent spontaneous flow observed in organic mesogens. Nonetheless, metallomesogenic phases are usually viscous, and if a columnar liquid crystal were to form prior to melting, spontaneous flow would be difficult to detect. Indeed, this proved to be the case, as revealed by subsequent shearing experiments. During viewing of the sample sandwiched between a cover slip and a microscope slide, a thin stick was pressed against the cover slip. No shearing at all was observed near room temperature, but above 50 °C, it was found that the sample could be sheared, returning to its original position after the shearing force was removed. This elastic response, although weakened with heating, persisted up to about 77 °C. Above this temperature, the sample behaved viscously; it flowed when it was sheared and showed no signs of returning to its original position when the force was removed. Thus, we infer that the phase existing between 77 and 109 °C is a viscous mesophase, and a photomicrograph is shown in Figure 2.

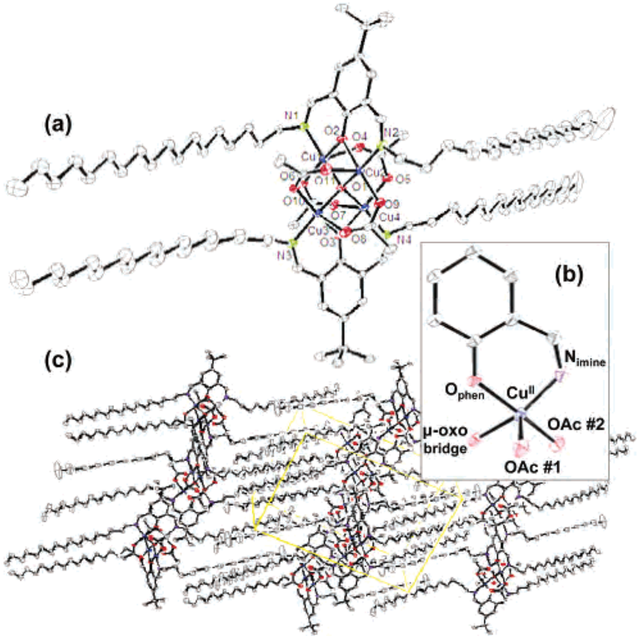


Figure 1. ORTEP diagrams for **1** at the 40% probability level. (a) View of the single molecule. Selected average bonds (Å): $Cu-O_{oxo} = 1.917$; $Cu-O_{acetate} = 1.94-2.38$; $Cu-O_{phenolate} = 1.986$; $Cu-N_{imine} = 1.972$; $Cu1\cdots Cu2 = 3.0132$; $Cu3\cdots Cu4 = 3.0199$; $C-C_{ring} = 1.40$; $C-C_{alkyl\ chain} = 1.52$. (b) Local coordination for the Cu^{II} centers. (c) Packing of the alkyl chains and columnar arrangement.

XRD experiments were performed in both small- and wide-angle ($2\theta = 0-13°$) configurations. In each case, the sample was heated well into the isotropic phase and then cooled. In the small-angle configuration, a single broad

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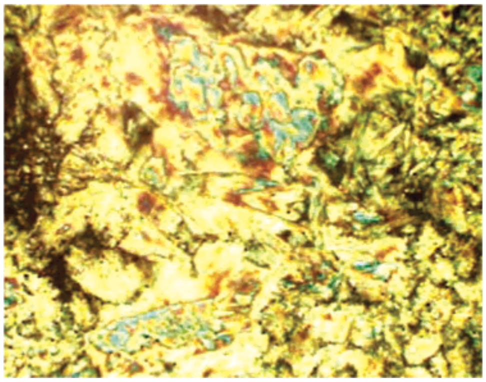

Figure 2. Micrograph of the mesophase observed for **1**.

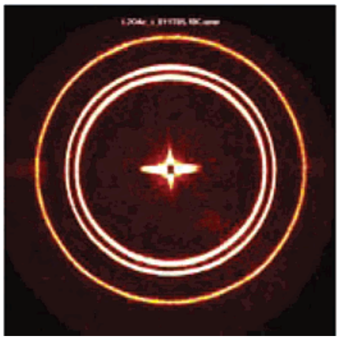

Figure 3. XRD of the columnar oblique phase in **1**.

diffraction ring was observed in the isotropic phase. Upon cooling into the mesophase, this feature split into two sharp rings and was joined by a third ring (Figure 3). The positions and intensities of these three rings remained relatively unchanged upon further cooling. Wide-angle diffraction in the mesophase showed an additional six or seven rings in the $2\theta = 0.5-13°$ range. Such peaks are observed in columnar phases with high-density contrast variations.[14] The low symmetry of the diffraction pattern is common in metallomesogens,[15] and the optical texture does not allow immediate phase identification. However, the observation of viscous flow and the molecular packing of the solid-state crystal in Figures 1c and S1 in the Supporting Information suggest a columnar liquid-crystal phase. The observed peaks do not relate to square, rectangular, or hexagonal lattices but can be indexed to an oblique two-dimensional lattice with $a = 26.0$ Å, $b = 29.7$ Å, and $\gamma = 84.0°$. No peaks were observed in the $2\theta = 17-25°$ range characteristic of ordered columnar crystals. Oblique columnar unit cells have been reported in Cu-containing[16] and organic[17] mesogens and may reflect the presence of several competing molecular interactions. Dispersive van der Waals forces can be identified as the driving reason for the multiple C_{18} alkyl chains to be held together, forming layered structures. Similarly, it could be expected that the phenolate rings of vicinal L^- ligands would present π stacking,[18] but closer analysis shows that no significant interaction involves the rings that are too far apart. The Cu···O interactions observed in square-planar mesogens[19] are not relevant because the Cu^{II} ions in **1** already adopt a favored Jahn−Teller distorted square-pyramidal geometry. Although a lack of π stacking is not unusual,[20] vicinal C=N bonds (3.364−3.566 Å) may contribute to columnar formation because the alkyl chains are relatively far apart. The closest C−C distances of ca. 4.2 Å indicate that only weaker attractions between two juxtaposed layers are expected. Upon heating, the weaker van der Waals interactions will collapse as a result of thermal vibration, and displacement of adjacent layers can occur, making the imine π stacking the dominant interaction related to the Co_{ob} phases observed.

In summary, we have developed a new ligand capable of conferring mesogenic properties to bulky transition-metal clusters due to the presence of long alkyl chains. To the best of our knowledge, we obtained the first carboxylate-supported tetracupric complex that exhibits mesomorphic properties. The complex was characterized by several spectroscopic techniques and single-crystal XRD and had its mesomorphic behavior clearly demonstrated by means of polarized microscopy, DSC, and XRD of the oblique mesophase. Current efforts focus on the generalization of the synthetic methods for other carboxylate-containing coligands such as benzoates, as well as the behavior of these species toward electric and magnetic fields. Because these species also behave as metallosurfactants, ongoing research in our laboratories involves surface deposition and the formation of [Cu_4-bridge-Cu_4]-extended one-dimensional polymeric films, as well as the replacement of the alkyl chains by other functional moieties.

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Supporting Information Available: Experimental details (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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