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Renal Backov [a], A. Nicole Morgan [b], Sarah Lane [a], Eduardo E. Perez-Cordero [a], Kathryn Williams [a], Mark W. Meisel [b], Clement Sanchez [c] & Daniel R. Talham [a]

[a] Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida, 32611-7200, USA

[b] Department of Physics, University of Florida, P.O Box 118440, Gainesville, FL, 32611-8440, USA

[c] Laboratoire de Chimie de la Matière Condensée, UMR 7574 CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, Paris, 75252, France

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Lyotropic Phase From Hybrid Organic-Inorganic Layered Copper Hydroxides

RENAL BACKOV[a], A. NICOLE MORGAN[b], SARAH LANE[a], EDUARDO E. PEREZ-CORDERO[a], KATHRYN WILLIAMS[a], MARK W. MEISEL[b], CLEMENT SANCHEZ[c] and DANIEL R. TALHAM[a,*]

[a]*Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200 USA;*
[b]*Department of Physics, University of Florida, P.O Box 118440, Gainesville, FL, 32611-8440 USA;*
[c]*Laboratoire de Chimie de la Matière Condensée, UMR 7574 CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris, France*
[*]*Authors to whom correspondence should be addressed.*

Lyotropic liquid crystalline suspensions have been observed for organic/inorganic layered copper(II) hydroxycarboxylates dispersed in organic solvents such as toluene. Polycrystalline powders of the lamellar phases $Cu_2(OH)_{4-x}(C_nH_{2n+1}COO)_x$ were prepared for the octanoate (n = 7), stearate (n = 17), eicosanoate, (n = 19), and docosanoate (n = 21), and dispersions of each show lyotropic phase behavior when viewed under cross polarized microscopy. The dispersions form a birefringent gel at higher weight percent. The birefringence results from the lyotropic liquid crystals alignment of submicron flattened needles of the organic/inorganic layered solid. Similar behavior is observed for Ni(II) and Co(II)hydroxycarboxylates. The gel phases can be cast onto solid supports, and after solvent evaporation, oriented films of the starting powder are formed. In the case of the nickel film, magnetic order, characteristic of the starting powder, is retained in the oriented film.

Keywords: complex fluids; mineral liquid crystals; layered hydroxides

INTRODUCTION

The field of inorganic lyotropic mesophases has seen renewed interest in the past decade.[1,2] These complex suspensions of anisotropic inorganic particles are sometimes called "mineral liquid crystals," because of the phase behavior and optical properties that parallel molecule and polymer-based liquid crystals. Examples of particle-based lyotropic phases include aqueous suspensions of vanadium pentoxide[3] or aluminum oxyhydroxide (boehmite) polymeric rods,[4,5] gels of montmorillonite clays[6] and nickel(II) hydroxide platelets.[7] The renewed interest in this class of materials is partially inspired by the recent discovery of nematic phase behavior of the synthetic solid $LiMo_3Se_3$[8,9] when exposed to *N*-methylformamide. The electronic and chemical structures of inorganic extended solids could lead to hybrid materials that combine liquid crystalline behavior with traditional solid-state properties,[1,2] such as conductivity or magnetism, which can be tuned through chemical synthesis.

We report here a new class of lyotropic mesophases based on the family of layered metal hydroxides, $Cu_2(OH)_{4-n}X_n$, where X is an anionic ligand. When X is an alkylcarboxylate, then organic suspensions exhibit nematic phase behavior. The layered copper hydroxycarboxylates form as very small flat needles, a micron or less in length. The surface of the particles is hydrophobic as a result of the alternating organic/inorganic layered structure. The particles can be taken up in organic solvents, such as toluene, to yield anisotropic suspensions that exhibit nematic behavior. The mixed organic/inorganic nature of the family of metal hydroxycarboxylates provides an opportunity to demonstrate the idea of combining properties into a single-phase material, as some examples are magnetic. We show that the complex suspensions can be cast into transparent, anisotropic magnetic films.

EXPERIMENTAL SECTION

Copper Hydroxycarboxylates

The lamellar phases $Cu_2(OH)_{4-x}(C_nH_{2n+1}COO)_x$ with n = 7, 17, 19 and 21 were prepared directly, or by ion exchange starting from the acetate, in accordance with published methods.[10,11] For the direct

preparation, the products are precipitated by titration of a methanolic solution containing copper nitrate and the corresponding carboxylic acid with 0.1M NaOH in methanol. The precipitation is performed at 10 °C to discourage formation of copper oxides during the titration. The final product is collected by centrifugation, washed with methanol, and air-dried. In the case of the docosanoate (n=21) the precipitation is obtained with a solution of ethanol/decane (50/50). In the ion exchange preparations, $Cu_2(OH)_3(CH_3COO)\cdot H_2O$ is dispersed in a methanol solution containing a 3-5 fold excess of the appropriate acid. The dispersion is stirred for 12 hours and the final product is isolated as described above. Combustion analysis for C, H, and N provided the following stoichiometry for the copper based materials $Cu_2(OH)_3(CH_3COO)_1\cdot H_2O$; $Cu_2(OH)_{1.7}(CH_3(CH_2)_6COO)_{2.3}$; $Cu_2(OH)_{1.0}(CH_3(CH_2)_{16}COO)_{3.0}$; $Cu_2(OH)_{1.0}(CH_3(CH_2)_{18}COO)_{3.0}$ $Cu_2(OH)_{1.0}(CH_3(CH_2)_{20}COO)_{3.0}$. Thermogravimetric analyses (TGA), performed in air for each copper compound, do not show any weight loss until 210 °C, verifying the anhydrous nature of these materials. In each case, X-ray diffraction shows that monophasic lamellar phases are formed.

Nickel Hydroxystearate and Cobalt Hydroxystearate

These solids were prepared by direct precipitation, starting with the appropriate divalent metal salts. Combustion analysis yields the stoichiometries $Co_2(OH)_{1.9}(CH_3(CH_2)_{16}COO)_{2.1}\cdot H_2O$ and $Ni_2(OH)_{2.1}(CH_3(CH_2)_{16}COO)_{1.9}\cdot H_2O$.

Organic Suspensions

The solids are easily dispersed in a non-polar solvent such as toluene in the concentration range 0.2%-6% by weight. In a typical preparation the toluene is added to the powders and the resulting suspension is sonicated for 4 hours and stirred overnight.

Film Formation

Particle suspensions in the concentration range 2%-3% by weight were spread on Mylar sheets by simply dropping from a Pasteur pipette. Evaporation of solvent in ambient laboratory conditions yielded the free-standing films.

RESULTS AND DISCUSSION

Characterization of Lyotropic Suspensions

Polycrystalline powders of the copper(II) hydroxycarboxylates can be dispersed in organic solvents such as toluene, xylene, or benzene. The resulting mixtures show different phase behavior that depends on the concentration range and temperature. The general trend for the copper(II) hydroxystearate particles dispersed in toluene at ambient temperature, is shown in Figure 1. At low concentration, below about 1.5%, the particles do not disperse throughout the solvent, but rather there is segregation of the suspended particle phase and the clear, pure solvent. If viewed through cross polarizers, the suspended particle phase is birefringent, while the pure solvent phase is isotropic. As the concentration of polycrystalline solid is increased, a gelatinous phase results that is also birefringent (Fig. 1).

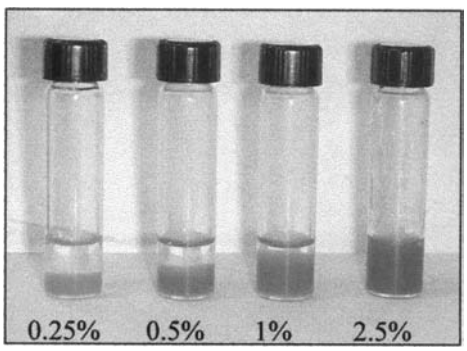

FIGURE 1. Copper(II) hydroxystearate suspension in toluene at different weight percents.

An optical micrograph of the gel phase, observed through untreated glass plates and obtained through crossed polarizers, is shown in Figure 2. The optical birefringence shows a marble texture characteristic of a liquid crystalline phase.[12,13] Upon heating either the biphasic or gel phases, an isotropic solution is obtained above a clear point. For the copper(II) hydroxystearate the clear point is 70 °C ± 1 for all compositions. The birefringent domains are recovered upon cooling through the clear point. Also consistent with the characteristic

fluidity associated with liquid crystalline behavior, the birefringent domains change shape and size in response to external stimuli such as shear or uneven pressure.

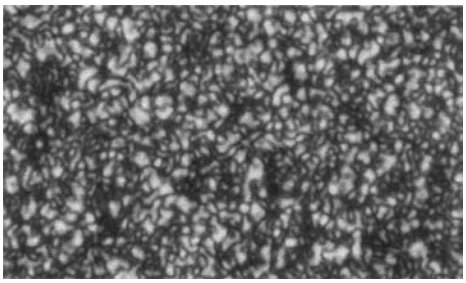

FIGURE 2. Crossed polarized micrograph of a copper hydroxystearate gel (5% weight). A marble texture with black domain boundaries can be seen. The picture area has dimensions 97 x 58 μm^2.

The phase behavior of the n = 7, n = 19, and n = 21 compounds are each similar to the stearate case. The clear points increase with the number of carbons in the fatty acid tail. The observed values are 54 °C ± 1 °C for n =7, 76 °C ± 1 °C for n = 19, and 83 °C ± 1 °C for n = 21. The clear points are also relatively independent of solvent. For example, in the case of the stearate, in benzene, toluene, and xylene, the clear points range from 70° to 72° C. The analogous nickel(II) hydroxystearate and cobalt(II) hydroxysteatrate also form lyotropic phases in toluene. The clear point of the nickel and cobalt analogs in toluene are 55° and 65°, respectively, which is lower than the 70° observed for the copper(II) hydroxystearate, perhaps because of differences in the in-plane packing density of the alkylcarboxylates in the three materials.

X-ray diffraction and AFM indicate that the suspended objects responsible for the anisotropic phases are submicron crystallites. X-ray diffraction from the starting copper hydroxystearate powder and from the birefringent gel in toluene show identical interlayer spacings, indicating that the layers are not expanded upon suspension in the solvent. The crystal structure in the gel is the same as the structure in the solids. AFM images demonstrate that the particles have a flat needle-like shape with typical size of 0.4μm x 0.03μm x 0.06μm.

It is these anisotropic particles that align in the suspension to form the lyotropic mesophase.

Oriented Films

The suspensions can be cast onto a surface that, after solvent evaporation, leaves an oriented thin film. For example, casting the copper(II) or nickel(II) hydroxystearate suspensions onto Mylar, followed by lifting off of the surface, results in self-standing, flexible, transparent films (Figure 3a). Since the solvent has been removed, the thin films are comprised of only the starting powder, but are now transparent because the individual crystallites are aligned, leading to decreased scattering. A scanning electron microscope image (Figure 3b) shows that the texture of the film is very homogeneous, and the particles show a preferential orientation with the long axis parallel to the surface of the film.

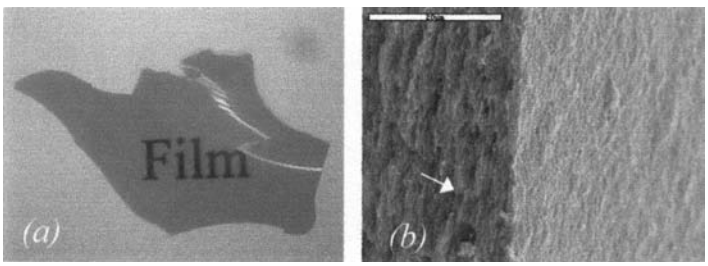

FIGURE 3. (a) A free-standing film of copper(II) hydroxystearate set on top of the word "film." The film was cast from a nematic gel in toluene. (b) an SEM image of the edge of a copper(II) hydroxystearate film showing texture that results from the alignment of the particles parallel to the surface, the scale bar corresponds to 20 μm.

Magnetic Properties

The nickel(II) hydroxystearate powdered solid orders ferromagnetically near 7K. This property is retained in the processed film. A plot of magnetization *vs* temperature for the cast film shows the phase transition around 7K (Fig 4a). The magnetic ordering is shown more clearly in the plot ΔM vs T ($\Delta M = M_{FC} - M_{ZFC}$) (Fig. 4b) where long range order is shown to result in spontaneous magnetization, characteristic of ferromagnetic ordering.

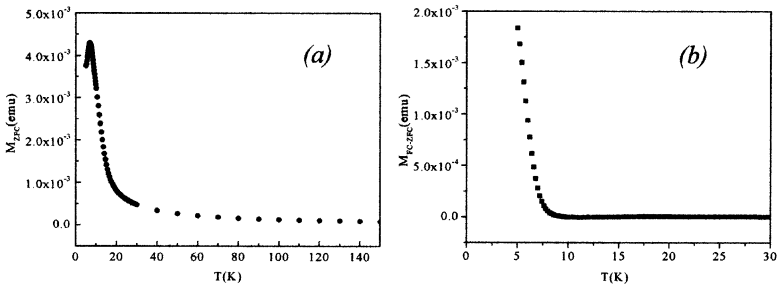

FIGURE 4. Magnetization measurements on a nickel(II) hydroxystearate film cast from a gel. (a) magnetization vs temperature, and (b) $\Delta M_{(FC-ZFC)}$ vs T.

CONCLUSIONS

The series of mixed organic/inorganic transition metal hydroxycarboxylates provide an interesting combination of physical phenomena that derive from the combination of organic and inorgainc networks in a single-phase material. The powdered solids order ferromagnetically, a property of the inorganic network, while organic suspensions form lyotropic phases. The texture and shape of the particles are characteristic of an inorganic solid, yet they suspend in organic solvents because of the organic nature of their surface. In addition to the interesting behavior that these suspensions exhibit, they can be used to generate oriented films of the organic/inorganic extended solids. Additional combinations of physical properties should be possible through synthetic modification of either the organic or inorganic networks to produce new hybrid materials.

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