These observations described above demonstrate that a variety of anionic surfactant microstructures become available upon addition of macrocyclic complexing agents. Addition of such complexing agents to polyelectrolytes, nucleic acids, and proteins should alter physical and chemical properties of these macromolecules and may prove useful as a separation technique.

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## **Discotic Mesophases of Dirhodium Tetracarboxylates**

#### Anne-Marie Giroud-Godguin, Jean-Claude Marchon,\*

Laboratories de Chimie/Chimie de Coordination (UA 1194), Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble Cedex, France

#### **Daniel Guillon, and Antoine Skoulios**

Institut Charles Sadron, CNRS, 67083 Strasbourg, France (Received: July 17, 1986)

The synthesis of dirhodium tetraoctanoate and dirhodium tetradodecanoate is described. Both complexes exhibit a thermotropic discotic mesophase that was characterized by optical microscopy, differential scanning calorimetry, and X-ray diffraction. A two-dimensional hexagonal columnar lattice was observed in which each column is made of stacked metal-metal bonded dirhodium units with a period of ca. 4.6 Å.

#### Introduction

The study of thermotropic transition-metal mesogens (i.e., complexes exhibiting a liquid crystalline phase above a certain temperature) is a rapidly expanding new field of research. The design of discotic mesophases giving a one-dimensional array of closely spaced metal atoms, with possible ferromagnetic or electron-transport properties,<sup>1-9</sup> is of particular interest. Recent work in our laboratories<sup>7</sup> has shown that copper(II) laurate (dicopper tetradodecanoate) exhibits a discotic mesophase in the temperature range 107-250 °C. This mesophase is characterized by a twodimensional hexagonal lattice with an intercolumnar distance of about 20 Å; each column is made of stacked binuclear units with a thickness of 4.7 Å (Figure 1, M = Cu). Magnetic susceptibility measurements indicate that a slight modification of the coordination shell, which retains the binuclear structure of the complex, occurs at the solid-discotic transition temperature.8 Further work has demonstrated that the same thermotropic behavior is found throughout an extended series of binuclear complexes of copper(II) with linear chain ( $C_6$  to  $C_{22}$ ) and substituted fatty acids.<sup>9</sup>

The so-called "lantern" structure of copper(II) acetate, in which four bidentate carboxylato groups bridge the two metal atoms, is also found in many other transition-metal acetates and in rhodium(II) acetate in particular.<sup>10,11</sup> Provided that the higher

TABLE I: Temperature Variation of the Intercolumnar Distance in the Discotic Mesophases of Dirbodium Tetracarboxylates

compd	temp, °C	intercolumnar dist, Å
rhodium(II) caprylate	150	16.7
	230	16.7
rhodium(II) laurate	168	19.9
	196	20.6

homologues<sup>12</sup> retain this "lantern" structure, it can be expected that they might exhibit discotic mesophases as well. In this letter, we report the synthesis of rhodium(II) caprylate (dirhodium tetraoctanoate) and rhodium(II) laurate (dirhodium tetradodecanoate) and the characterization by X-ray diffraction of their thermotropic discotic mesophases. These complexes are the first examples of metal-metal bonded binuclear mesogens.

#### **Results and Discussion**

Ligand exchange between dirhodium tetraacetate and the appropriate fatty acid was obtained upon heating the mixture at 120 °C for 2 h. The green products were recrystallized from heptane. Satisfactory elemental analyses were obtained. Caprylate, C<sub>32</sub>-H<sub>60</sub>O<sub>8</sub>Rh<sub>2</sub>, Calcd/found: C, 49.36/48.49; H, 7.77/7.67; Rh, 26.43/26.88. Laurate, C<sub>48</sub>H<sub>92</sub>O<sub>8</sub>Rh<sub>2</sub>, Calcd/found: C, 57.48/ 57.39; H, 9.24/9.10; Rh, 20.52/20.45.

Hot-stage polarizing microscopy and differential scanning calorimetry (DSC) were used to detect and characterize the thermotropic mesophases of these materials.<sup>13</sup> A phase change to a birefringent fluid was observed at ca. 100-110 °C for both

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rhodium single bond in rhodium(II) carboxylates is well documented.<sup>10</sup>

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<sup>(15)</sup> Note Added in Proof: Synthesis and characterization by DSC of similar complexes have been carried out independently at the University of Sheffield. We thank Dr. Duncan Bruce for communicating this information prior to publication.



Figure 1. Schematic view of the stacking of dicopper (M = Cu) and dirhodium (M M = Rh-Rh) tetracarboxylates in their discotic mesophases.

complexes. The mesophases were stable in a large temperature range, and they started to decompose only above 220 °C. DSC curves showed an endothermic peak at 95 °C ( $\Delta H = 8.5 \text{ cal/g}$ ) for rhodium(II) caprylate and at 100 °C ( $\Delta H = 13.6 \text{ cal/g}$ ) after a full heating-cooling cycle for rhodium(II) laurate.

X-ray diffraction measurements were carried out with either a Guinier focusing camera equipped with a bent quartz monochromator (Cu K $\alpha_1$  radiation) or a Searle camera equipped with an Elliott optics (toroidal mirror) and a Mettler FP52 heating

stage (Ni-filtered Cu radiation). For both compounds, a series of sharp Bragg reflections was observed in the small-angle region, with reciprocal spacings in the ratios  $1:3^{1/2}:4^{1/2}:7^{1/2}$ , characteristic of a two-dimensional hexagonal array of columns, similar to that found earlier in the discotic mesophases of copper(II)-fatty acid complexes.<sup>7,9</sup> The intercolumnar distance (Table I) varies slightly with temperature. In the wide-angle region, the diffraction patterns showed a broad band corresponding to a distance of 4.65 Å for rhodium caprylate, whereas for rhodium laurate a diffuse band was observed at about 4.6 Å. These distances are in fair agreement with the stacking period of binuclear copper(II) units (4.7 Å) observed earlier in the discotic mesophase of copper(II) laurate.7 The columnar stacking of binuclear rhodium(II) units (Figure 1, M M = Rh-Rh) appears to be fairly well ordered for rhodium(II) caprylate but liquidlike for rhodium(II) laurate.

## Conclusion

In summary, this Letter shows that the thermotropic columnar mesophase observed earlier in binuclear copper(II) alkanoates is also found in isostructural rhodium(II) alkanoates.<sup>15</sup> This observation suggests that many other 3d, 4d, and 5d binuclear transition-metal alkanoates might exhibit the same thermotropic behavior, including the multiple metal-metal bonded Cr, Mo, Ru, Os, etc., congeners. The synthesis of these complexes and the search for extended metal-metal interactions along the columns in their discotic mesophases are continuing in our laboratories.

# Excited-State Proton-Transfer Reactions in 2-(2'-Hydroxyphenyl)benzoxazole. Role of **Triplet States**

## A. Mordziński<sup>†</sup> and K. H. Grellmann<sup>\*</sup>

Max-Planck-Institut für Biophysikalische Chemie, Abteilung Spektroskopie, D-3400 Göttingen, Federal Republic of Germany (Received: July 24, 1986)

The fluorescence of 2-(2'-hydroxyphenyl)benzoxazole (HBO) is strongly Stokes-shifted due to intramolecular proton transfer in the excited singlet state by which the enol form ( ${}^{1}E^{*}$ ) of HBO is converted into the keto form ( ${}^{1}K^{*}$ ). At room temperature the decay of  ${}^{1}K^{*}$  is dominated by a thermally activated radiationless transition. At lower temperatures fluorescence and intersystem crossing are the main deactivation processes. In the triplet state of the keto tautomer proton back-transfer to the enol triplet state, <sup>3</sup>E\*, takes place. At high triplet-state concentrations the transient decay is mainly governed by triplet-triplet annihilation. This process was used to determine the extinction coefficients of the triplet-triplet absorption. In contrast to other work the singlet ground-state absorption of the keto tautomer,  ${}^{1}K$ , was not observed.

### Introduction

In carefully dried nonpolar solvents 2-(2'-hydroxyphenyl)benzoxazole (HBO) exhibits a fluorescence spectrum with a large Stokes shift. It is generally accepted that this shift is due to an intramolecular proton-transfer reaction in the first excited singlet state,  ${}^{1}E^{*}$ , by which the enol form (E) of HBO is converted into the keto form (K). The latter,  ${}^{1}K^{*}$ , is the only strongly emitting species, which in its ground state, <sup>1</sup>K, returns back to the thermodynamically more stable enol form,  ${}^{1}E$ . The kinetics of this reaction have been studied recently in a number of laboratories.<sup>1</sup> The lifetime  $(\tau_i)$  of <sup>1</sup>K\* has been determined as a function of the temperature,<sup>2</sup> and attempts have been made,<sup>3</sup> to detect the ground-state absorption of the unstable keto tautomer in order to measure the rate constant of the hydrogen back-transfer process, i.e., the decay of  ${}^{1}K$  into  ${}^{1}E$ .

Surprisingly little is known about the triplet state of HBO. In this Letter we will show that its population can become a major and very interesting pathway in the decay of  ${}^{1}K^{*}$ .

#### Results

The fluorescence spectrum of a carefully dried and degassed 10<sup>-4</sup> M solution of HBO in methylcyclohexane (MCH) or isopentane/cyclopentane (4:1 by volume, IP) consists of a broad and intense band with a maximum at  $\lambda_{max} = 490 \text{ nm}$  (quantum yield  $\phi_f(296 \text{ K}) = 0.017$ ) and a very weak band with  $\lambda_{max} = 380 \text{ nm}$  $(\phi_f(296 \text{ K}) < 10^{-4})$ . The latter is presumably due to a rotamer<sup>1</sup> of HBO where the hydroxy group forms a hydrogen bond with the oxygen atom of the heterocycle. The (uncorrected) intensity ratio of the two maxima is  $I_{490}/I_{380} > 70$  at 296 K. In glassy solutions at 77 K the enol form phosphoresces<sup>2</sup> with a quantum yield of  $\phi_p = 0.002$ .

Flash excitation of a degassed HBO solution yields transient spectra that change strongly with the temperature between 296

<sup>&</sup>lt;sup>†</sup>Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland.

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