rhodium and also suggests a more systematic synthesis of cone-shaped trinuclear complexes, by reaction of suitable binuclear precursors with binucleating ligands *cis*-[ML_2X_2], in which the anionic groups X would act as donor atoms.

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Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, positional parameters, bond distances, and bond angles (9 pages); a table of structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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(6) Crystal data for **3**: fw = 975.5, monoclinic, space group $C2/c$, a = 33.804 (3) Å, b = 10.038 (3) Å, c = 23.348 (2) Å, β = 121.95 (1)°, V = 6722.6 (7) Å^3, Z = 8, d_{calc} = 1.928 g cm^{-3}, Mo Kα radiation, μ = 18.1 cm^{-1}, Enraf-Nonius CAD4 diffractometer, θ–2θ scan method at 25 °C, quadrant of data with $1° < \theta < 30°$ measured, 10796 unique reflections, absorption correction based on ψ scans, structure solved by heavy-atom methods. Full-matrix least-squares refinement converged to R = 0.032 and R_w = 0.034 for 407 variables and 6098 observations with $I > 3\sigma(I)$. All H atoms were found, but refinement used calculated positions with fixed isotropic displacement parameters.

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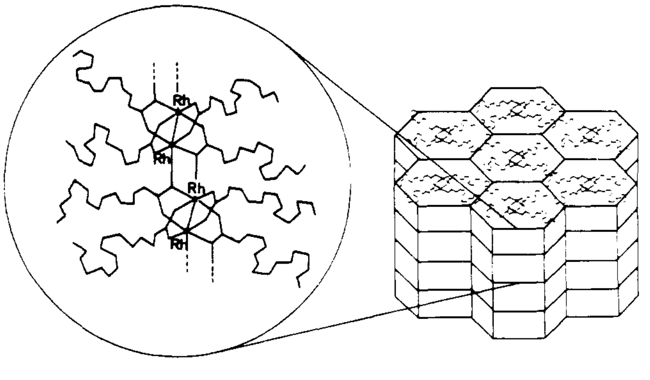
Raman Spectroscopy as a Convenient Probe of Solid–Liquid Crystal Phase Transitions in Binuclear Rhodium(II) *n*-Alkanoates

Phase transitions from lamellar crystalline lattices to columnar liquid crystalline mesophases, shown as



have been observed for several bimetallic complexes of fatty acids.[1,2] Because of their potential as molecular materials for electronics,[3] considerable interest in this type of compound has developed, and numerous complexes have been prepared for study including those of Cu(II),[1] Rh(II),[4] and Ru(II)[5] with carboxylate ligands derived from fatty acids of varying lengths. Whereas the phase transitions of classical organic mesogens usually are followed by hot-stage polarizing microscopy, differential scanning calorimetry, and low-angle X-ray scattering, the presence in metallomesogens of heavy atoms and/or of unpaired electron density allows additional experimental techniques to be used for the characterization of their transitions into and through their various mesophases, e.g. EXAFS,[6,7] magnetic susceptibility measurements,[5,8-11] and EPR spectroscopy.[10-15] In the course of our studies[4] of the metal–metal-bonded dirhodium(II) tetrakis(*n*-alkanoates)[16] using vibrational spectroscopy, we have discovered that Raman spectroscopy is a highly sensitive probe of the phase transitions exhibited by this class of mesogens. Moreover, this probe is extremely convenient, as it has no need of an independent heat source.

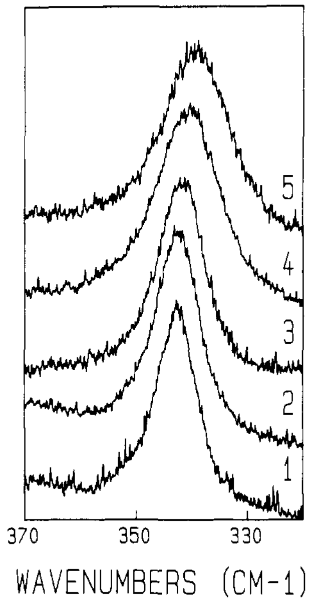


Figure 1. Raman spectra (514.5-nm excitation, 30 mW) of dirhodium tetrakis(hexanoate) in the 320–370-cm^{-1} region as a function of the sample temperature: 1, 325 K; 2, 340 K; 3, 360 K; 4, 400 K; 5, 450 K.

Microcrystalline samples of dirhodium butyrate, hexanoate, and octanoate were prepared from dirhodium acetate by ligand exchange followed by slow recrystallization from the neat fatty acid. While investigating the Raman spectra of these complexes,

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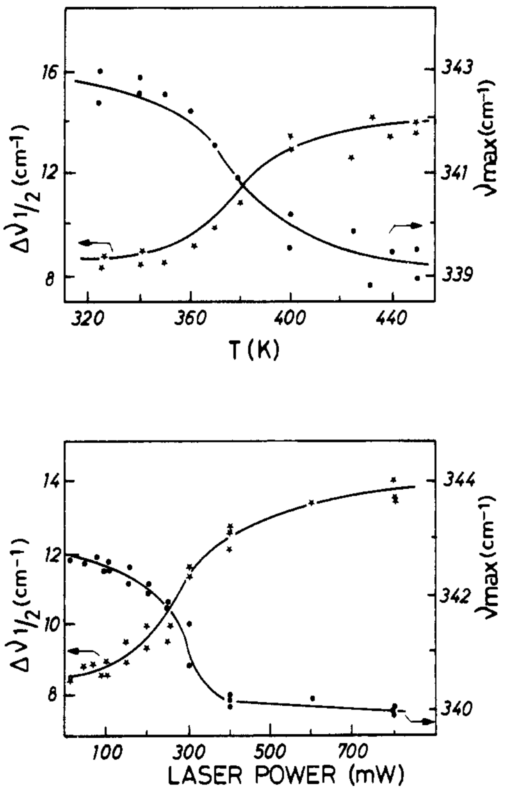

Figure 2. Top: Effect of the temperature on the frequency (dots) and half-width (stars) of the Raman band due to the Rh–Rh bond strength in dirhodium tetrakis(hexanoate) (514.5-nm excitation, 30 mW). Bottom: Effect of the laser power (514.5-nm excitation) on the frequency (dots) and half-width (stars) of the Raman band due to the Rh–Rh bond stretch in dirhodium tetrakis(hexanoate) (sample at 300 K).

we observed regular variations in the positions and half-widths of the Rh–Rh stretching mode as a function of the laser power. As the latter is increased, the frequency maximum of the Rh–Rh stretch moves continuously to lower values while its half-width increases. The process appears to be completely reversible, and there is no evidence of sample decomposition.

In our initial experiments, the Raman spectra of these compounds were recorded in the 250–500-cm^{-1} region with several different visible probe excitations (514.5, 496.5, 488.0, and 476.5 nm) and for various temperatures in the 295–450 K range. The sample (ca. 5 mg) was placed in a thin-glass tube (2-mm o.d.) and heated in an oil bath that was specifically designed for Raman measurements. The temperature was regulated with a copper–constantan thermocouple, and the Raman scattering was recorded on a triple-monochromator spectrometer (Dilor RTI). In all cases, the spectra are dominated by a strong signal in the 340–350-cm^{-1} range, which can be ascribed to the rhodium–rhodium bond stretch by analogy with the careful assignments reported by Clark et al.[17] for $Rh_2(O_2CCH_3)_4$ and related complexes. Figure 1 shows typical spectra obtained for the hexanoate complex at various temperatures between 325 and 450 K. As can be readily seen in Figure 2 (top), the band maximum and half-width for the Rh–Rh stretch of this species vary with the temperature, and their temperature evolution shows inflection points at ca. 380 K. This result is in good agreement with the temperature for the mesophase transition of the hexanoate, which has been found to occur at 402 K from differential scanning calorimetry, if local overheating by the laser (ca. 20 °C) is taken into account (see below). A comparable temperature dependence of the Raman spectrum is observed with the octanoate complex. The Raman inflection point at ca. 370 K can also be related to its phase transition (T = 390 K). In the case of the butyrate complex, the Raman spectrum is more complicated and will not be analyzed in detail here. The main signal appears broadened and split into two components at ca. 345 and 352 cm^{-1}, each of which has a different temperature dependence. However the frequency variation of the former component is similar to that found for the hexanoate compound (Figure 2 (top)) and is characterized by an inflection point near 420 K, i.e. in a temperature region close to the mesophase transition temperature (447 K). In all cases, the rhodium–rhodium stretching mode shifts to lower wavenumbers, indicating a weaker Rh–Rh bond in the mesophase, possibly related to a slight change in axial binding energy. On the other hand, the notable band broadening that parallels this frequency shift reflects significant fluctuation of the Rh–Rh bond strength. The latter probably results from the stronger disorder of the alkyl chains in the liquid crystalline phase.

Following these experiments, a series of spectra were recorded at a fixed local temperature (295 K) but with varying excitation wavelengths and probe intensities (10–800 mW). Once again we observed regular changes in both band maxima and half-widths that paralleled those found by changing the temperature of the oil bath. Figure 2 (bottom) shows the frequency and half-width dependence of the hexanoate complex as a function of the laser power with 514.5-nm excitation. One cannot determine the exact temperature of the phase transition, since the local temperature of the sample within the laser beam depends upon the wavelength of the excitation. However, the phase transition is readily observed (see Figure 2 (bottom)).

Previous studies of liquid-crystalline phase transitions by Raman spectroscopy[18] have been confined to the investigation of molecular orientational order[19] and of side-chain disordering processes.[20] The work described in the present communication seems to be the first direct investigation of a liquid-crystalline transition using Raman spectroscopy as a probe of a mesogen core vibration.

In summary, the laser provides both a heat source that brings about local transition from a crystalline lattice to a columnar mesophase in dirhodium tetrakis(n-alkanoate) complexes and a convenient means for following this phase transition by Raman scattering. The assignment of the bands observed in the butyrate complex warrants further study and is currently under detailed examination in our laboratories. Extension of these investigations to multiply metal–metal bonded mesogens such as diruthenium(II) tetracarboxylates[5] is under way.

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Evidence for Photoinduced Heterolytic Bond Cleavage in Iodotrimethylstannane

In contrast to the extensive literature on the photochemistry of transition-metal compounds, relatively little attention has been given the photochemistry of main-group-metal compounds, particularly those of tin. In a recent summary of selected examples, Vogler and co-workers have shown that the observed reactivity correlates with the orbital nature of the excited state,[1] although in some cases charge transfer is accompanied by reductive elimination.[2] Similar correlations have yet to be developed for organotin compounds, but scattered observations have led to the generally accepted idea that UV excitation of R_3SnX (R = alkyl, X = halogen) leads to homolytic cleavage of the Sn-X bond.[3-9] Our interest has focused on volatile organotin compounds, since these reagents offer a means of using standard photolithographic techniques to change the refractive index and, in some cases, the structure of glass and glass gels.[10-12] Utilizing these techniques as routes to integrated optics[12] and nonlinear photonic materials,[13] however, requires a detailed understanding of the photochemistry. Here, we describe a series of experiments which show that, under certain conditions, $(CH_3)_3SnI$ exhibits a different mode of photoreactivity.

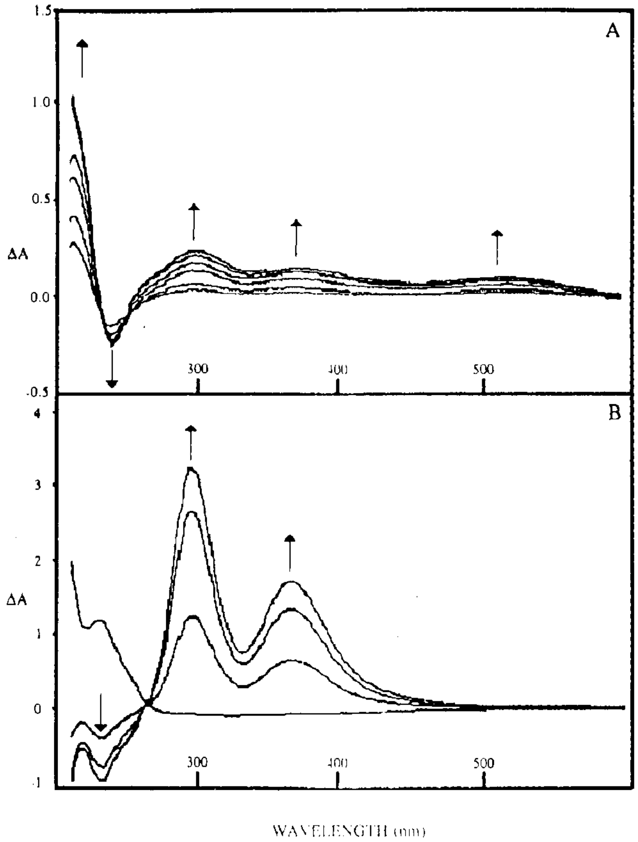

Figure 1. Difference spectra recorded during 254-nm photolysis of 7.37 × 10^{-4} M $(CH_3)_3SnI$ in (A) *n*-hexane and (B) ethanol.

In the 200–800-nm range, the electronic spectrum of $(CH_3)_3SnI$ in *n*-hexane consists of a single absorption with maximum at 234 nm ($\epsilon = 3.45 \times 10^3$ M^{-1} cm^{-1}). A 254-nm photolysis of a 7.37 × 10^{-4} M *n*-hexane solution of $(CH_3)_3SnI$ causes a decline in the 234-nm band and concurrent appearance of an intense band at 211 nm and weaker bands at 290, 365, and 520 nm (Figure 1A). The 211-nm band agrees with that of $((CH_3)_3Sn)_2$, while the 520-nm band indicates I_2 formation. The bands at 290 and 365 nm are due to the formation of I_3^-. Although the larger absorbance gives the impression that I_3^- is a major photoproduct, the amount formed is always less that 2% of the amount of I_2 formed, and extrapolations to zero irradiation time indicate that I_3^- is a secondary photoproduct. The spectral changes exhibit isosbestic points at 224 and 252 nm, which are maintained through 50 and 100% of the reaction, respectively. Consequently, all photolyses were limited to ≤50% conversion. Under these conditions, the quantum yield of $(CH_3)_3SnI$ dissappearance is 0.32 ± 0.01 with 254-nm excitation and declines to 0.060 ± 0.006 with 310-nm excitation and ≤0.01 with 350-nm excitation. Stoichiometric measurements yield 0.50 ± 0.05 mol of $((CH_3)_3Sn)_2$ formed/mol of $(CH_3)_3SnI$ consumed and 0.50 ± 0.05 mol of I_2 formed/mol of $(CH_3)_3SnI$ consumed. In short, the results are in exact agreement with previous observations which suggest that the primary photochemical event is homolytic cleavage of the Sn-I bond.

Experiments were also carried out in polar solvents, principally ethanol, as a way to mimic in fluid solution the behavior that might occur on the polar, hydroxylated surface of porous glass or glass gels. The electronic spectrum of $(CH_3)_3SnI$ in ethanol is similar to that in *n*-hexane except that the band maximum shifts to 218 nm ($\epsilon = 1.54 \times 10^4$ M^{-1} cm^{-1}). This was initially thought to be a solvent shift, but the photochemical behavior is quite different. A 254-nm photolysis of an ethanol solution 7.37 × 10^{-4} M in $(CH_3)_3SnI$ causes a decline in the 218-nm absorbance (Figure 1B) and a concurrent growth of peaks at 290 and 360 nm. There is no indication of the higher energy absorption attributable to $((CH_3)_3Sn)_2$ or a lower energy absorption, ca. 450 nm, attributable to I_2. Raman spectra recorded periodically during photolysis yield similar results. A progressive decline in the intensity of the 167-cm^{-1} Sn-I vibration occurs without any indication of the appearance of the 186-cm^{-1} Sn-Sn vibration of $((CH_3)_3Sn)_2$. Rather, the 290- and 360-nm absorptions agree precisely with the

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