Articles

Studies of Thermotropic Properties and the Mesophase of Mixtures of *n*-Alkanoates and Perfluoro-*n*-alkanoates of Dimolybdenum (M_2^{4+})

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Mixtures of $Mo_2(O_2C(CH_2)_nCH_3)_4$, where $n = 6$ (=Oct) and 7 (=Non), form a columnar mesophase upon heating and the crystal-to-liquid crystal phase transition temperatures differ little from those predicted by the Shroder−van Laar equation for an ideal mixture. The XRD of the solid sample obtained from cooling a 1:1 mixture of $Mo_2(Oct)_4$ and $Mo_2(Non)_4$ conformed to a triclinic cell with lattice parameters intermediate between those of the pure compounds. Similarly in the mesophase the intercolumnar separation (d) was an intermediate distance. The phase behavior of mixtures of $Mo_2(non)_4$ and $Mo_2(O_2C(CH_2)_{10}CH_3)_4$ [$Mo_2(Dod)_4$] were more complex, but in all instances a mesophase was observed whereas that of the pure $Mo_2(Dod)_4$ shows only a crystalline solid to isotropic phase transition. Mixtures of $Mo_2(Oct)_4$ and $Mo_2(O_2C(CF_2)_6CF_3)_4$ [$Mo_2(Oct^f)_4$] were also shown to form a columnar mesophase with an intercolumnar separation intermediate between that of the pure compounds. The mesophase is an optically positive material with the largest component of the index of refraction coincident with the columnar axis. The solid to mesophase transition temperatures varied significantly from that predicted for an ideal mixture. These results are discussed on the basis of facile carboxylate scrambling to produce $Mo_2(O_2CR)_{4-n}(O_2CR')_n$, where $n = 0-4$ in both the mesophase and the resultant solid solution.

Introduction

All applications in liquid crystalline displays and other devices employ mixtures.[2] No single compound fulfills the requirements of even the simplest application in LC technology. As the field of metallomesogens[3] emerges (metal-containing liquid crystalline materials) it will become important to understand how mixtures (combinations of metallomesogens, combinations of metallomesogens with organic mesogens and dyes, or solvents which yield lyotropic phases) behave. Mixtures can have vastly different properties in viscosity, dielectric anisotropy, electric polarization and susceptibility, and magnetization and magnetic susceptibility, all of which influence physical behavior and response parameters. In predicting the behavior of mixtures it is often assumed that the mixtures act as ideal solutions, since in this limit it is a relatively easy matter to compute melting temperature as a function of composition. Although simple to apply, such a model is not always adequate to describe the behavior and we provide one example of this in the following work. There are many potential causes for departure from ideal solution behavior, but in this case we suggest that a facile ligand scrambling may be responsible for the discrepancies seen in this study and the miscibility of a hydrocarbon and fluorous phase.

The thermal behavior of ideal nematic mixtures was described in detail by Hsu and Johnson using the example of *p*-azoxyanisole and *p*-azoxyphenetole.[4] Typically three endothermal transitions were observed for binary mixtures: (i) the transition from the crystalline solid mixture to two phases, the comesophase and excess pure solid; (ii) the transition from the two phase region to a one phase region in which the two compounds were completely miscible, the pure nematic comesophase; and (iii) the transition to an isotropic liquid where both components are again completely miscible. A schematic phase diagram for the thermotropic behavior of an ideal

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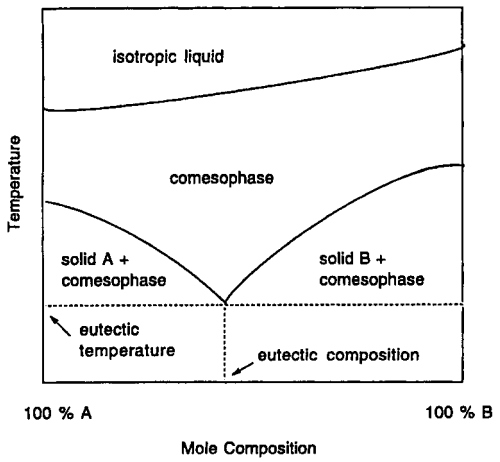

Figure 1. A typical binary phase diagram for an ideal mesogenic mixture.

nematic mixture is shown in Figure 1. A eutectic composition exists where only two transitions are observed, namely those for the solid mixture to the comesophase and the comesophase to the isotropic liquid mixture. The nature of the comesophase can be determined for ideal mixtures by the Schroder−van Laar equation,[5] (eq 1), where H_A and H_B are the heats of fusion and transition temperatures T_A and T_B are for the pure components A and B from the crystalline-solid to the mesophase. T is the transition temperature for a two-component system containing X_A, the mole fraction of A, and R is gas constant.

$$\ln X_A = \frac{H_A}{R}\left(\frac{1}{T^A} - \frac{1}{T}\right) \quad (1)$$

For mixtures of *p*-azoxyanisole and *p*-azoxyphenetole, experimental data showed excellent agreement with the theory, demonstrating that the system conformed well to an ideal solution.[4] This was not surprising in view of the similar structures of the compounds and the small differences in heat capacities of the solids and the mesophases. However, even in a hypothetical ideal liquid mixture consisting of hard rectangular molecules of different sizes, the mixing entropy often deviates from idealility. Thus correlations between experimental data and that predicted by the Schroder−van Laar equation are not expected to be always perfect, and the physical constants of pure compounds determined by extrapolation from mixed systems (and vice versa) may be inaccurate.

We describe here our studies of the thermotropic behavior and properties of mixtures of tetracarboxylates of dimolybdenum, $Mo_2(O_2CR)_4$. The selection of carboxylates follows from our earlier studies which established a hexagonal disordered columnar mesophase for certain R within a temperature range being bracketed by the crystalline and isotropic phases.[6] In this work the selection of R has been made in order to satisfy three criteria: (i) the mixing of two very like complexes, namely R = octanoate and nonanoate; (ii) the mixing of a compound known to have a thermally accessible mesophase, R = octanoate, with one that merely undergoes a crystal to isotropic phase transition, R = dodecanoate, and (iii) a mixture of an *n*-alkanoate with its perfluoro counterpart (designated with a superscript f), both of which are known to have thermally accessible mesophases but are expected to behave as nonideal mixtures, since fluorocarbons and hydrocarbons C_nX_{2n+2}, where X = H or F, are typically immiscible.

The only previous study that we are aware of that in any way relates to the current work is by Marchon et al.,[7] who examined mixtures of $Cu_2(O_2C(CH_2)_5CH_3)_4$ and $Rh_2(O_2(CH_2)_5CH_3)_4$. In the latter study the compounds were cocrystallized from heptane and studied by X-ray diffraction and EXAFS. Upon heating, the mesogens formed separately to produce two distinct columnar phases which merged into a homogeneous and stable columnar phase over a short time. From EXAFS studies the authors concluded that the mesogenic mixture consisted of randomly distributed pure copper and pure rhodium columns. We shall return to this matter later. Here we examine only the influence of differing carboxylate ligands with a common dinuclear center.

Results and Discussion

Sample Preparation. The pure compounds $M_2(O_2CR)_4$ and $M_2(O_2CR')_4$ were mixed in the solid state in specific mole ratios, heated until they formed an isotropic solution, and then allowed to cool and solidify. The subsequent studies were performed on samples prepared in this manner. It is pertinent to note that when dissolved in a solution such as benzene-d_6 ligand scrambling of the type shown in eq 2 has been previously noted to be facile for R = ^{t}Bu, R′ = ^{n}Bu[8] and R = CF_3, R′ = H.[9] We also observe that when $Mo_2(Oct)_4$ and $Mo_2(Oct^f)_4$ are heated in benzene-d_6, a similar scrambling is indicated by NMR spectroscopy.

$$M_2(O_2CR)_4 + M_2(O_2CR')_4 \rightleftharpoons M_2(O_2CR)_{4-n}(O_2CR')_n \quad (n = 0, 1, 2, 4) \quad (2)$$

$Mo_2(Oct^f)_4$ is essentially insoluble in benzene-d_6, but upon heating with $Mo_2(Oct)_4$, it dissolves as reaction 2 occurs. For compounds of formula $Mo_2(O_2CR)_2(O_2CR')_2$, there are two isomers, cis and trans, reflecting the disposition of the two pairs of carboxylates about the M-4-M bond, and at least for R = CF_3 and R′ = H, the 1:1 mixture of compounds leads to an essentially statistical distribution of all six $Mo_2(O_2CR)_{4-n}(O_2CR)_n$ compounds, where n = 0, 1, 2 (cis + trans), 3, and 4.[9] The reaction 2 and the facile equilibration of $Mo_2(O_2CR)_{4-n}(O_2(CR)_n$ compounds may occur by intermolecular (bimolecular) ligand exchange through μ-O_2CR groups or by acid catalysis. We mention the facility of 2 because it bears on the findings reported below.

$Mo_2(Oct)_4$ + $Mo_2(Non)_4$. The phase transition temperature for the solid-to-mesophase transition for various mole fractions of $Mo_2(Oct)_4$ is shown in Figure 2, where a comparison with that predicted from the Schroder−van Laar equation is also given. As can be

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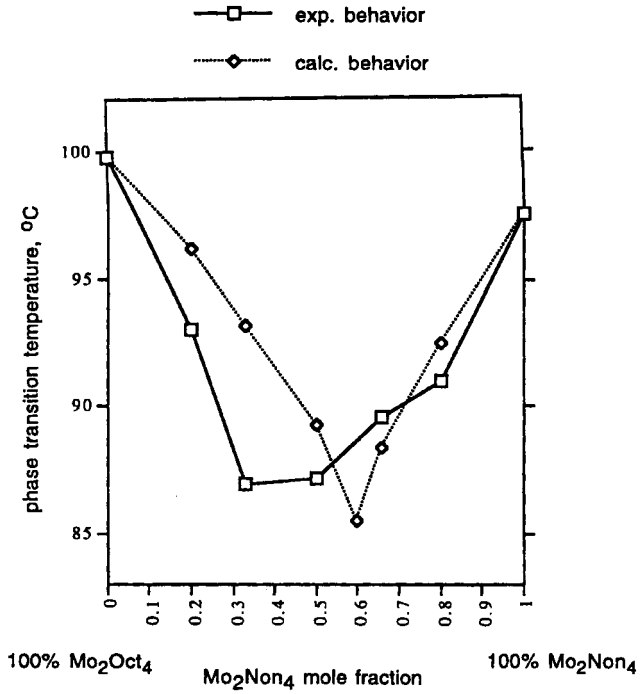

Figure 2. Phase diagram of a binary mixture of $Mo_2(O_2C(CH_2)_nCH_3)_4$, where $n = 6$ (Oct) and 7 (Non). Only the crystal-to-mesophase transition is shown.

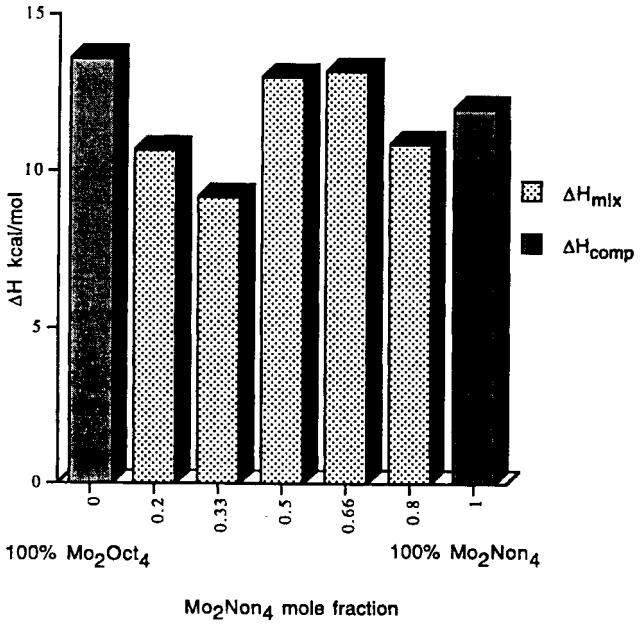

Figure 3. Comparison of the ΔH_{mix} values for the crystal-to-mesophase transitions of binary mixtures of $Mo_2(O_2C(CH_2)_n-CH_3)_4$, where $n = 6$ (Oct) and 7 (Non), to the crystal-to-mesophase transition enthalpies of the pure components.

seen from this figure, the experimental temperatures did not correspond exactly to those predicted by eq 1. The calculated T_{min} was 85.5 °C at a mole ratio of 40% $Mo_2(Oct)_4$ and 60% $Mo_2(Non)_4$, while the experimental minimum was observed at $T = 87$ °C for 67% $Mo_2(Oct)_4$: 33% $Mo_2(Non)_4$. Although the eutectic parameters do not dramatically deviate from theory, the slope of the curve as well as the minimum transition temperature indicate a significant difference from ideal behavior of the mixture. A comparison of the observed values of ΔH_{mix} for the solid-to-mesophase transition of the mixtures to the enthalpies of the pure components, ΔH_{comp}, for the same phase transition is given in Figure 3. The observed values are in reasonable agreement with the theoretical prediction for ideal mixtures. However, the deviations must arise from a combination of factors including facile ligand scrambling which undoubtedly influences the entropy of mixing.

The clearing temperatures (mesophase to isotropic liquid) were slightly lower for the mixtures than for the pure compounds but showed only small variations with concentration change. (This type of behavior is typical for mesogenic binary mixtures.)

A 1:1 molar mixture of $Mo_2(Oct)_4$:$Mo_2(Non)_4$ was heated to the isotropic liquid state for 5 min, cooled to room temperature, and examined by XRD. Upon comparing the X-ray pattern observed with those obtained from the individual components,[6] it is clear that in the solid state the mixture forms the triclinic phase. This behavior is similar to that seen for $Mo_2(Non)_4$ and the pure $Mo_2(Oct)_4$. The solid that forms from the mixture is crystalline but rather disordered, particularly along the (010) axis, as indicated by the breadth of peaks other than the (h00) series. The width of the (010) peaks suggests a coherence length of no more than 11 nm along this direction in the crystal, while the (h00) peaks indicate coherence along this direction over at least 80 nm. Due to the weak intensity and width of many of the peaks, it is not possible to determine accurate lattice constants for the mixture in the solid phase. A reasonable estimate for some of the lattice parameters may be obtained by taking the average values for the separate triclinic phases of the pure materials (giving a =22.00 Å, b = 8.19 Å, c = 5.55 Å, $\alpha = 97.8°$, $\beta = 87.9°$, and $\gamma = 87.1°$). Even allowing for reasonable departures from the expected values for the cell angles (±5°), the positions of the (h00) peaks are consistently at larger angles than one would expect on the basis of these cell parameters. This suggests that the actual value for the major dimension of the unit cell is no more than 22.7 Å in size. The difference between the best estimate for the lattice constant a and the expected value is only about 10% of the difference between the values of this parameter in the two pure phases. This indicates that Vergard's law holds rather well for this mixture.[10] This observation is consistent with either a random solid solution of the original species or a random mixture of several species resulting from ligand scrambling.

$Mo_2(Oct)_4 + Mo_2(Oct^f)_4$. Although both compounds are known to form mesophases, the $Mo_2(Oct^f)_4$ compound is essentially insoluble in hydrocarbon solvents. However, solid samples prepared from the melt show the formation of homogeneous mesophases. The phase transition temperatures for the solid-to-mesophase with varying molar composition are shown in Figure 4. The observed concave curve contrasts with the convex curve predicted by the Schroder−van Laar equation (eq 1). Moreover the clearing temperatures of all mixtures were higher than those of either component. Thus the $Mo_2(Oct)_4/Mo_2(Oct^f)_4$ mixtures lead to a greater range of temperature for the mesophase. Such behavior is not observed for ideal mesogenic binary mixtures and very

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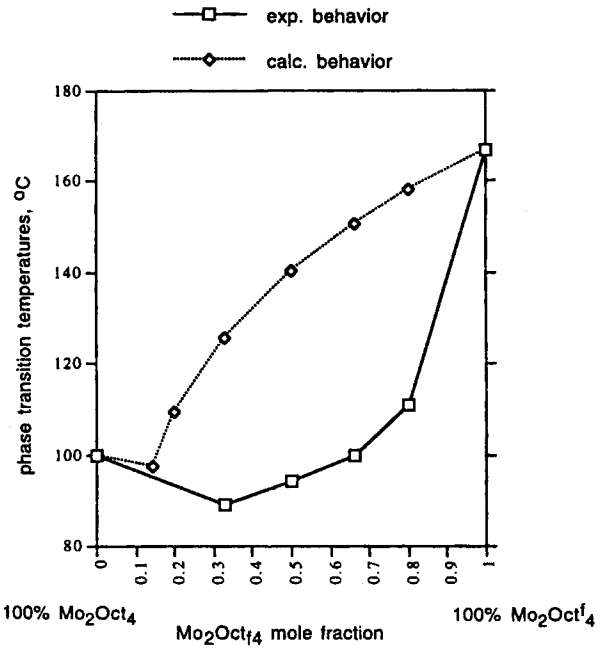

Figure 4. Phase diagram for the solid-to-liquid crystal transition of the binary mixture of $Mo_2(Oct)_4$ and $Mo_2(Oct^f)_4$. From left to right is the mole fraction of $Mo_2(Oct^f)_4$. The heating and cooling curves are shown by the bottom and top traces, respectively.

likely reflects the occurrence of a chemical reaction in this system, namely ligand scrambling (eq 2).

The $Mo_2(Oct)_4/Mo_2(Oct^f)_4$ system was also studied by DSC and XRD. The DSC of a 2:1 mixture of $Mo_2(Oct)_4$ to $Mo_2(Oct^f)_4$ crystallized from the neat melt. Under an inert atmosphere, He, enantiotropic behavior was observed with the endotherm at 89 °C, corresponding to the solid-to-mesophase transition, and the much smaller endotherm at 207 °C, corresponding to the clearing temperature. On cooling the exotherms at 203 and 52 °C correspond to the reverse phase changes and reflect a hysteresis typical of these systems with a heating rate of ca. 3−5 °C per min. The relatively sharp endotherms and exotherms for the mesophase-to-solid-phase transitions implies that phase separation leading to $Mo_2(Oct)_4$ and $Mo_2(Oct^f)_4$ crystalline domains is not occurring.

When examined by polarized microscopy the $Mo_2(Oct)_4/Mo_2(Oct^f)_4$ mesophase appears homogeneous and shows conical or fan-shaped textures typical of hexagonal columnar mesophases. When a sample was prepared by allowing the neat liquids of $Mo_2(Oct)_4$ and $Mo_2(Oct^f)_4$ to meet between two microscope slides, there was no evidence for phase separation or immiscibility. Indeed the two formed a miscible liquid and a homogeneous comesophase. The optical textures of one such mixture are shown in Figure 5.

Of note are the colored bands (blue and mauve) which arise from the alignment of the columnar axes at 45 °C to the cross polarizers.

The colors seen in this picture are changed by inserting $\lambda/4$ or λ wave plates between the crossed polarizers and lined up at 45° with respect to the polarizer axes. The extra retardation introduced by the wave plates either adds or subtracts from that introduced by the liquid crystal itself, leading to the observed shift in colors. Matching these observed shifts with a polarization color chart allowed us to determine that the largest

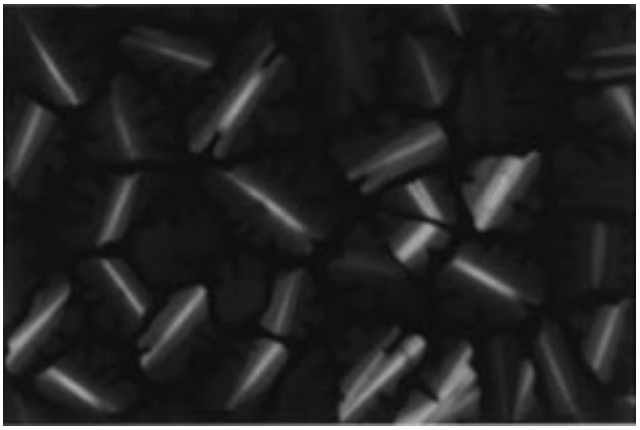

Figure 5. The optical textures of the mesophase formed by diffusion of $Mo_2(Oct)_4$ and $Mo_2(Oct^f)_4$ showing the homogeneous nature of the mesophase.

component of the index of refraction for the mesophase is coincident with the columnar axis (i.e. the mesophase is an optically positive uniaxial material). Typical discotic liquid crystals are optically negative due to greater polarizability normal to the columnar axis.[3] The unusual property of the mesophase of the $Mo_2(O_2CR)_4$ compounds may be attributed to the highly polarizable quadruple bond between the Mo atoms. In this regard, it is worth noting the others have recently reported on the unusually large third-order nonlinear optical susceptibility of M−M quadruple bonds.[11]

With increasing concentrations of $Mo_2(Oct^f)_4$:$Mo_2(Oct)_4$, specifically when the $Mo_2(Oct^f)_4$ concentration was greater than 50 mol %, heating the solid sample formed by cooling a fused melt revealed shoulders on the endotherms/exotherms associated with the solid-to-mesophase transition. This broadening of the endotherms/exotherms never resulted in the formation of separate peaks and is no doubt related to the incongruent melting behavior in this area of the phase diagram (see Figure 1). At high concentrations of any one component there will be a solid to comesophase transition where some of the solid of one of the components is still present.

This behavior is confirmed in XRD measurements on these mixtures, which show the mesophase coexisting with the solid phase over a range of temperatures. X-ray diffraction studies of the mesophase at the 1:1 composition show an intercolumnar spacing which is roughly midway between those seen in the individual mesophases.

$Mo_2(Non)_4$ + $Mo_2(Dod)_4$. Mixtures of these two *n*-alkanoates [Non = $(CH_2)_7$ and Dod = $(CH_2)_{10}$] showed somewhat more complex behavior. A 9:1 mixture of $Mo_2(Dod)_4$:$Mo_2(Non)_4$ showed only a clearing temperature at ca. 90 °C, reduced by some 20 °C from that of pure $Mo_2(Dod)_4$. However, for mole ratios of $Mo_2(Dod)_4$:$Mo_2(Non)_4$ below 8:1 a mesophase was observed. The phase transition temperature diagram is shown in Figure 6. Again a significant departure from idealized behavior is seen and this is now further demonstrated by the DSC studies. As the ratio of $Mo_2(Dod)_4$, which as a pure compound does not show a mesophase, increases the solid-to-mesophase transition first develops a shoulder and then splits into two distinct endotherms and exotherms upon the heating and cooling

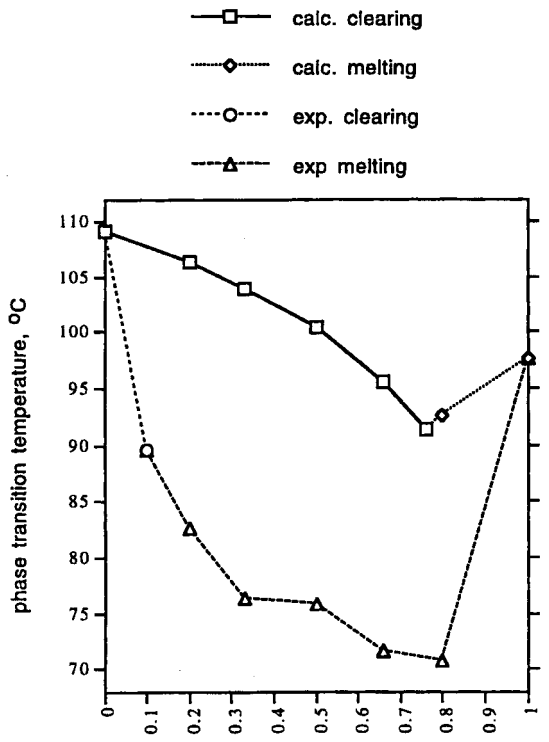

Figure 6. Phase behavior for the first transition of binary mixtures containing $Mo_2(Non)_4$ and $M_2(Dod)_4$. The mole percent of $Mo_2(Non)_4$ increases from left to right.

cycle, respectively. The endotherms and exotherms associated with the mesophase-to-isotropic liquid transition remain sharp though this temperature and the magnitude of ΔH varies with molar composition. Representative DSC cycles are shown in Figure 7.

The temperature dependence of the splitting of the solid-to-mesophase transition cannot be explained in terms of ideal eutectic binary mixtures, as outlined in the hypothetical phase diagram for the ideal two-component system in Figure 1. In the case of eutectic binary mixtures (Figure 1), the first endotherm on heating corresponds to the solid-to-comesophase transition with an excess of the solid of one component being present. The second endotherm arises as the solid component melts into the comesophase, which then no longer has the eutectic composition. Thus in an ideal binary system forming a comesophase the temperature of the first endothermm on the heating cycle (or the temperature of the last exotherm on the cooling cycle) should remain constant. As is evident from an inspection of Figure 7 this is not the case for mixtures of $Mo_2(Non)_4$ and $Mo_2(Dod)_4$.

Concluding Remarks

The thermotropic behavior of the mixtures of $Mo_2(O_2CR)_4$ and $Mo_2(O_2CR')_4$ do not conform to expectations based on the mixing of ideal mesogens. The miscibility of the $Mo_2(Oct)_4$:$Mo_2(Oct^f)_4$ systems and its columnar mesophase are quite striking. We attribute these interesting properties to the facile carboxylate exchange reaction (eq 2), which has been repeatedly observed in solution.[8,9] We are not able to offer proof that this occurs in the neat melt of the mixtures reported here and is thus responsible for the properties of the mesophases. A potential proof was sought by mass spectrometry, but the high molecular weights and low volatilities of these compounds did not allow the identification of the expected $Mo_2(O_2CR)_{4-n}(O_2(CR')_n^+$ ions. However, for the lower molecular mass mixtures obtained from a melting of $Mo_2(O_2CMe)_4$ with $Mo_2(O_2C(CH_2)_2CH_3)_4$, the molecular ions of $Mo_2(O_2CMe)_{4-n}(O_2C(CH_2)_2CH_3)_n^+$ were observed.

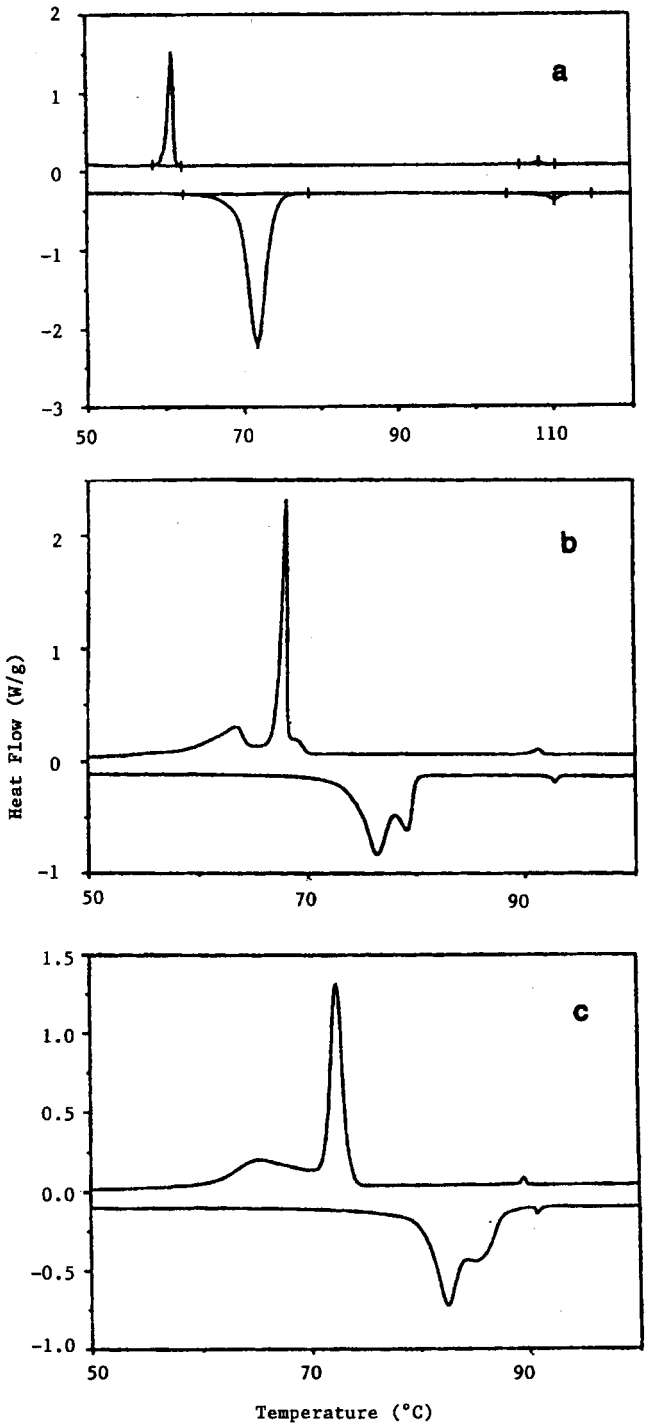

Figure 7. Differential scanning calorimetry studies of a binary mixture of $Mo_2(Non)_4$ and $Mo_2(Dod)_4$ (a) in 2:1 ratio, respectively, (b) in 1:2 ratio, and (c) in 1:4 ratio. The heating and cooling curves are shown by the bottom and top traces, respectively.

The mixtures of $Mo_2(Oct)_4/Mo_2(Oct^f)_4$ yield a significant increase in the mesophase temperature range. Thus with alkyl group side branching, as noted before,[6] we should be able to access a mesophase from ambient

temperature to ca. 200 °C. The incorporation of functional substituents that influence MLCT transitions[12] and the optical properties of these highly anisotropic molecules within an aligned mesophase will be the subject of a future study.

Experimental Section

The compounds $Mo_2(Oct)_4$, $Mo_2(Non)_4$, $Mo_2(Dod)_4$, and $Mo_2(Oct^f)_4$ were prepared as previously described.[6] The predictions based on eq 1 are made using the ΔH values previously reported. The triclinic cell constants and the *d* spacing in the mesophase have also been reported.

DSC measurements were performed on a duPont Instruments 910 differential scanning calorimetry. The hermetically sealed samples (A1 cells) were heated under a He flow gas at a rate of 5 °C/min.

Variable temperature and powder XRD studies were made by using a Scintag XDS 2000 $\theta-\theta$ goniometer fitted with a model HT2000 high-temperature stage. Details of data collection and temperature calibration were as reported previously.[6] Additional XRD were obtained using Cu Kα radiation on an Inel CPS 120 position-sensitive detector with a XRD 2000 generator, a fine focus X-ray tube, and a house-built heating stage. The temperature was regulated with a Minco CT 137 controller with ±1 °C stability. The detector was calibrated using mica and silicon standards obtained from the National Bureau of Standards.

Optical characterization was performed using covered microscope slides on a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS 46 Photoautomat along with a Mettler FP82 HT hot stage and a Mettler FP 80 HT central processor. Inserting $\lambda/4$ and λ wave plates at 45° angles with respect to the polarizers caused a shift in color of the linear birefringent defects. These shifts were matched with a polarization color chart. It was thereby determined that the uniaxial materials were optically positive, with the largest component of the refractive index coincident with the columnar axis.

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