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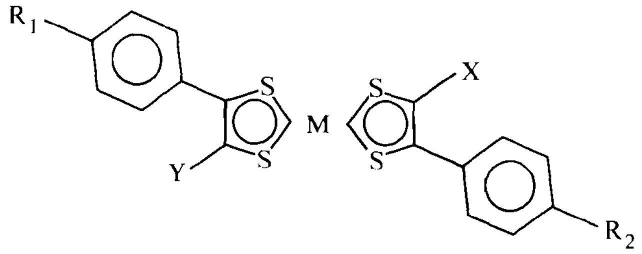
2.B Near-Infrared Dichroism of a Mesogenic Transition Metal Complex and Its Solubility in Nematic Hosts

Introduction

The use of dichroic dyes in guest-host liquid-crystal displays has received a great deal of attention in recent years. Numerous literature references[1-7] can be found regarding the order parameter, dichroism, solubility, and stability of a wide variety of dyes in nematic and smectic hosts for electro-optical applications in the visible region of the spectrum. Little information is available, however, regarding applications in the near-infrared region of the spectrum,[8] such as the blocking or modulation of diode or YAG laser sources. One reason for this lack of information is the limited availability of dyes with strong electronic absorption bands in this region. One class of materials that displays strong near-infrared absorption bands with molar extinction coefficients (ϵ) for these bands of nearly 30,000 is the square-planar transition metal dithiene complexes[9] generically shown in Fig. 33.22.

The position of the absorption band in these materials can vary from 750 to 1075 nm, depending on the molecular structure of the ligands and, to a much lesser extent, on the particular central metal atom in the complex.[9] A well-known example of this class of compounds is the laser dye bis(dimethylaminodithiobenzil)nickel [Fig. 33.23(a)], which possesses an absorption maximum at 1064 nm. Several of the dithiene transition-metal complexes display mesomorphic behavior; Ohta *et al.*[10] have reported discotic mesomorphism in the bis[1,2-di(*p*-*n*-alkoxyphenyl)ethane-1,2-dithione]nickel complexes [Fig. 33.23 (b)], and Giroud-Godquin *et al.* have reported the occurrence of nematic[11-13] and smectic[11-16] phases in the bis(*p*-*n*-alkylstyryl-1,2-dithiolato)nickel and platinum complexes [Fig. 33.23(c)].



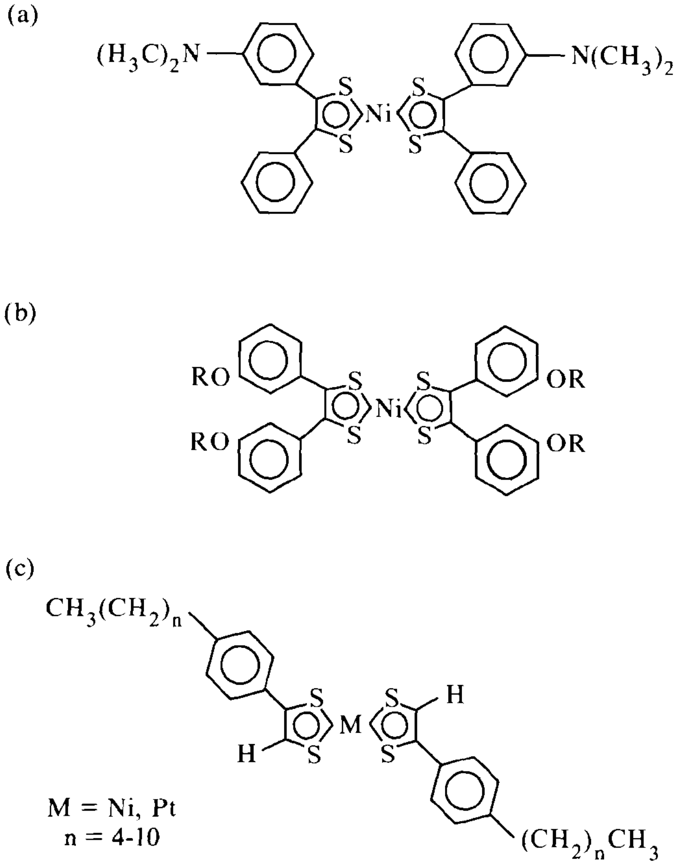
M = Ni, Pt, Pd, Cu

X and Y = H or substituted phenyl

R_1 and R_2 = alkyl, alkoxyl, alkylamino, cyano, etc.

G2113

Fig. 33.22
General molecular structure of the transition metal dithienes.



M = Ni, Pt
n = 4-10

G2114

Fig. 33.23
Molecular structures of various dithiene complexes. (a) bis(dimethylaminodithiobenzil)nickel; (b) bis[1,2-di(*p*-*n*-alkoxyphenyl)ethane-1,2-dithione]nickel; (c) bis(*p*-*n*-alkylstyryl-1,2-dithiolato)nickel and platinum.

Although several references[11,15,17] suggest the potential usefulness of these metal complexes in mixtures with themselves or with other liquid-crystal materials for near-infrared switching applications, there has been to date no report of the dichroic behavior of these metal complexes in nematic host materials. Complexes of structure (c) (see Fig. 33.23) would be of particular interest for this application for several reasons:

1. The elongated rodlike structure of these metal complexes, combined with the extensive electron delocalization afforded by the metal dithiene core, would be expected to promote the occurrence of positive dichroism in the strong near-infrared absorption band of these materials.
2. The high solubility of these complexes in nonpolar solvents such as hexane[11,14,15] indicates they may be highly soluble in the relatively nonpolar liquid-crystal hosts, which themselves display a high solubility in hydrocarbon-like solvents. Typical guest-host and laser dyes are soluble to a great extent only in such polar solvents as methanol or chloroform, and display little if any solubility in nonpolar solvents. As a result, the maximum stable dye concentration obtainable with most dichroic dyes in liquid-crystal hosts is typically around 1% to 2% by weight.[1,2]
3. The presence of a stable nematic phase with a wide mesomorphic range (117°C–178.6°C in the *n*-butyl derivative)[16] would allow the addition of large quantities of the metal complex to increase mixture absorbance without causing the major reduction in the mixture transition temperature and order parameter that would occur with a large addition of a non-mesogenic dye of equivalent solubility.

We have undertaken the synthesis of one of the members of this interesting series, bis(*p*-*n*-butylstyryl-1,2-dithiolato)nickel (abbreviated as C_4-Ni), and studied its behavior in the well-known nematic liquid crystals K15 (BDH Chemicals) and MBBA (Aldrich Chemical Co.). The solubility, optical absorption characteristics in the 800-nm to 1100-nm region, and stability of the mesogenic metal complex in these nematic hosts were determined and compared to similar data obtained for the laser dye bis(dimethylaminodithiobenzil)nickel (DMADB-Ni, Eastman Kodak Co.) in K15. We have also observed what we belive to be the first reported evidence of positive near-infrared dichroism in mesomorphic metal dithiene complexes in a nematic host.

Experimental

Liquid-crystal phase characterization and transition temperature measurements were determined using a Leitz Orthoplan Pol polarizing microscope and a Mettler FP-52 hot stage. Infrared spectra were obtained with a Nicolet 20SXC FTIR spectrometer. A Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer was used for absorption measurements of the metal complex and mixtures, and for the measurement of the dichroic ratio.

1. Synthesis

The liquid-crystal metal complex C_4-Ni was synthesized by a method described by Giroud-Godquin and Mueller-Westerhoff.[11,15] The synthesis scheme is outlined in Fig. 33.24. The ratio of dioxane to water in the reaction mixture during complex formation had a considerable effect on the formation of product; initial yields of 1%-2% obtained with only small amounts of water in the reaction mixture were improved to 10% by using a dioxane/water ratio of 1:1. The use of a nitrogen purge during the reaction of *p*-*n*-butylphenacyl bromide with phosphorous pentasulfide, and the subsequent reaction with nickel chloride, helped to minimize the formation of tarry side products. Isolation of the product was accomplished by extracting the reaction mixture several times with a 1:1 toluene-hexane mixture. After evaporation of the extracts under vacuum, hexane was added to the residue and the soluble portion was chromatographed on silica gel, with hexane as the eluent. The dark green fraction was collected and the solvent evaporated. A dark green residue was obtained, which was recrystallized several times from hexane to yield shiny, nearly black needles. The product exhibited a C-N (crystalline-nematic) transition at 117°C; an irreversible nematic-isotropic transition occurred at 178.7°C due to thermal decomposition of the complex. These results are consistent with those reported earlier for this material.[11,14-17] The purity of the product was qualitatively assessed by thin-layer chromatography on plates of silica gel with hexane as the eluent. Only one spot was observed after development of the plates with iodine vapor. The infrared spectrum of the complex in KBr showed extremely strong bands at 1365 and 1198 cm^{-1}, which were assigned to perturbed $C = C$ and $C = S$ stretching caused by bond formation between the central metal atom and the sulfur ligands.[9] The visible-NIR spectrum of a 1-cm path length of a 50-ppm solution of the complex in hexane displayed the strong near-infrared absorption band (optical density = 2.81) characteristic of this class of compounds, which for this material occurs at 860 nm.[9,11,14-17] The molar extinction coefficient ϵ of $\sim$28,000 was calculated for the complex based on the above absorbance data using the Beer-Lambert law, $A = \epsilon bc$, where A is the absorbance in optical density units, b is the path length in centimeters, and c is the concentration expressed in moles per liter.

2. Mixture Preparation

Mixtures of various concentrations (0%-10% wt/wt) of C_4-Ni in the nematic hosts K15 and MBBA were prepared by dissolving the complex in the host material at 50°C and stirring the resulting mixture for one hour. The host materials were used as supplied without further purification. The mixtures were cooled and were allowed to stand at 20°C for several days to avoid supersaturation. All samples were filtered through Teflon membrane filters (0.5-μm pore size) prior to making absorption spectroscopy measurements, in order to remove insoluble foreign material and precipitated dye crystals. Absorption measurements were repeated on samples stored in glass vials for one month after filtration through 0.5-μm-pore Teflon membrane filters. The above procedure was also used for the preparation of mixtures of the near-IR laser dye DMADB-Ni in K15.

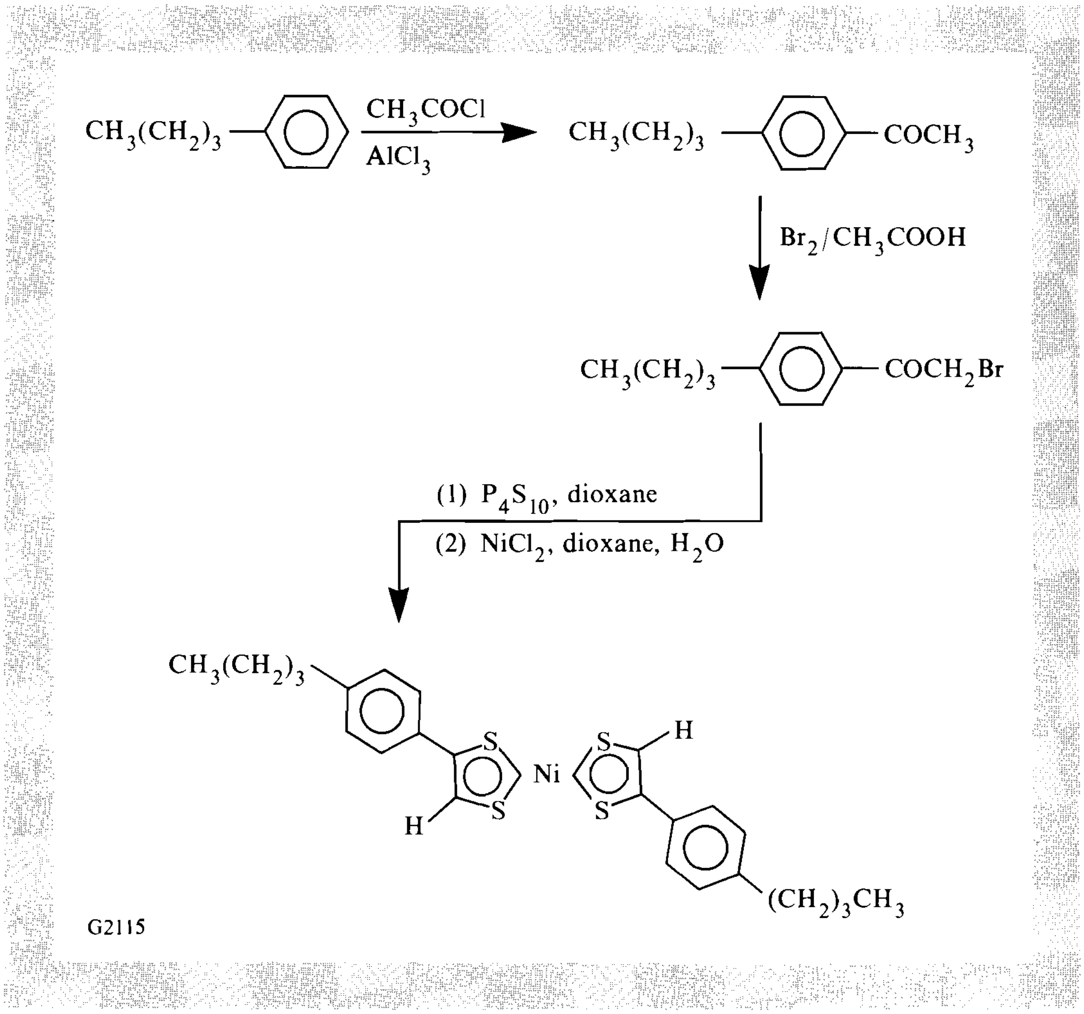


Fig. 33.24
Synthesis method for the preparation of bis(*p*-*n*-butylstyryl-1,2-dithiolato)nickel.

3. Absorption Spectroscopy

The visible and near-IR absorption characteristics of the mixtures in the isotropic state were determined in 100-μm-path-length quartz spectrophotometer cells at 50°C in a heated sample compartment in the spectrophotometer. This method, rather than the addition of solvent diluents, was used to eliminate optical scatter produced by the unaligned bulk liquid-crystal material, since complications such as dilution errors, solvent effects on absorbance maxima positions, and introduction of impurities into the mixtures are avoided. The near-infrared spectra displayed inherent lead sulfide detector noise at optical density (OD) values of 3 or greater. The raw spectral data was used without additional smoothing.

4. Dichroism Measurement

The dichroism of the NIR absorption band was determined in a homogeneously aligned cell containing a 1% wt/wt mixture of C_4-Ni in K15. The homogeneous alignment condition was obtained using a rubbed PVA alignment layer, which was applied to indium tin oxide (ITO) conductive-coated substrates (2 cm × 2 cm) by spin deposition. The cell was assembled with the rub directions antiparallel and filled by capillary action, with the fluid gap of 24 μm controlled by Mylar spacers. Measurements of absorption in the homogeneous and homeotropic orientations were made in the spectrophotometer sample chamber, with the cell rub axis parallel to a Corning Glass 8612 IR polarizer aligned parallel to the inherent spectrophotometer beam polarization. Switching into the homeotropic orientation was accomplished by the application of a 10-V, 100-KHz-square wave provided by a Tektronix FG-508 function generator. Absorption spectra, corrected for Fresnel and ITO coating absorption losses, were obtained after subtraction of a stored background spectrum of two index-matched ITO-coated plates from the raw absorbance data.

Results and Discussion

1. Physical Properties of the Mixtures

A series of mixtures containing C_4-Ni in K15 and MBBA ranging in concentration from 0.5% to 10% wt/wt was prepared as described in the experimental section. Mixtures of the laser dye DMADB-Ni in K15 and MBBA were prepared by the same method for use as a benchmark for the comparison of solubility and absorption properties. Mixtures containing amounts as large as 5% and 10% wt/wt of C_4-Ni in K15 showed no apparent signs of separation of the dye complex, even after storage at 20°C for one month. No precipitation or separation of the dye component was observed either in the containers or upon observation of agitated samples of the mixtures by polarizing microscopy at 100X magnification. In contrast, a mixture of DMADB-Ni in K15 began to show signs of separation immediately after cooling to room temperature, and a nearly complete precipitation of the dye was observed after the mixture had been allowed to stand for several days. The stable concentration limit of DMADB-Ni in K15 was determined to be 0.05% wt/wt, by making absorption spectroscopy measurements of filtered samples and comparing the results against known standards. We attribute this large disparity in solubility between C_4-Ni and DMADB-Ni in the nematic hosts to be due in part to differences in the molecular structures of the two complexes. Referring to Fig. 33.23, the rodlike nature and alkyl terminal groups of C_4-Ni [structure (c)] would be expected to promote solubility in the hydrocarbonlike nematic materials. The terminal dimethylamino groups of DMADB-Ni [structure (a)] introduce a high degree of polarity due to the unshared electron pair on the nitrogen atom, and, thus, should favor solubility in polar solvent matrices (e.g., chloroform or methanol). The presence of the two additional phenyl groups give DMADB-Ni a disklike structure, which would not fit as well as C_4-Ni into the nematic liquid-crystal matrix.

The effect of the concentration of C_4-Ni in K15 and in MBBA on the mixture transition temperatures can be observed in Fig. 33.25. The presence of the nematic metal complex causes a gradual increase in mixture transition temperature with increasing concentration, as would be expected due to the large mesomorphic range and high N-I transition temperature (117°C–178°C) of C_4-Ni. The slope of the transition temperature versus concentration curve for the K15 mixtures is considerably larger than for MBBA mixtures at the same concentration, causing us to speculate that an interaction was taking place between MBBA and C_4-Ni. This speculation was confirmed when, after examination of samples, which had been stored in glass vials under ambient conditions for one month, it was discovered that the MBBA mixtures had changed color from dark green to reddish brown, with a black, tarry precipitate evident in the 5% and 10% wt/wt samples. The K15 mixtures stored under the same conditions appeared unchanged. In Figs. 33.26(a) and 33.26(b), the transition temperatures of the new and one-month-old mixtures of C_4-Ni in K15

Fig. 33.25
Dependence of mixture N-I transition temperature on metal complex concentration for various compositions of C_4-Ni in K15 and MBBA.

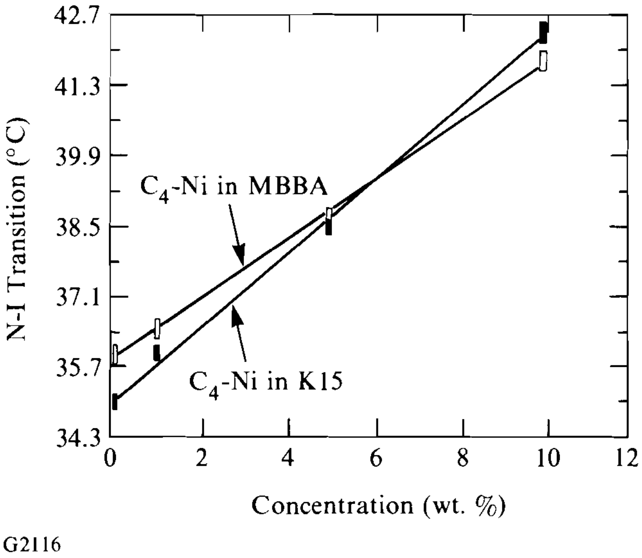
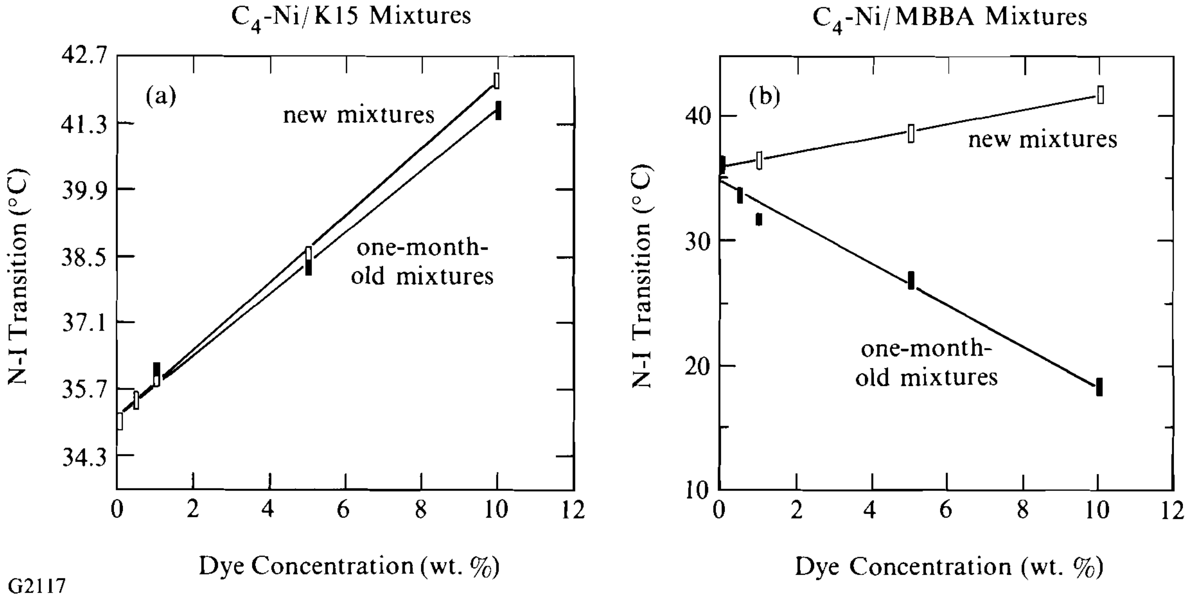


Fig. 33.26
Effect of aging on the N-I transition temperature of C_4-Ni/K15 and C_4-Ni/MBBA mixtures as a function of metal complex concentration. (a) New and one-month-old mixtures in K15; (b) new and one-month-old mixtures in MBBA.



and MBBA mixtures are plotted as a function of metal complex concentration. The K15 mixtures show a slight decrease in transition temperature with time (a maximum of 0.8°C for the 10% wt/wt mixture), while large reductions in the N-I transition are evident for even the most dilute C_4-Ni/MBBA mixtures. The transition temperature of the most concentrated C_4-Ni/MBBA mixture (10% wt/wt) was depressed by over 23°C from its original value, rendering it isotropic at room temperature. The change observed in the visible and near-IR spectra of the one-month-old MBBA mixtures (discussed in detail in the following sections) and the radical reduction in transition temperature for the C_4-Ni/MBBA mixtures indicate a chemical reaction has apparently occurred between these compounds, resulting in the formation of isotropic reaction products. The nature of this reaction is the subject of current investigations. The dianions of these complexes have been reported by Schrauzer[9] and others[18] to readily undergo nucleophilic substitution reactions with other materials; this suggests that reduction of the metal complex may be an important step in the degradation process.

2. Absorbance Spectroscopy

The effect of the solvent matrix on the position of the absorption maximum for C_4-Ni is illustrated in Fig. 33.27. A bathochromic shift is observed for freshly prepared samples of C_4-Ni in K15 and MBBA scanned in the isotropic phase (50°C), as compared to a 50-ppm solution of the complex in hexane. The reduced absorption band for the C_4-Ni/MBBA mixture, as compared to an equivalent C_4-Ni/K15 mixture at the same concentration (0.5%), indicates that the reaction between the metal complex and MBBA may begin upon initial mixing. The absorption curves of new and aged samples of C_4-Ni in the

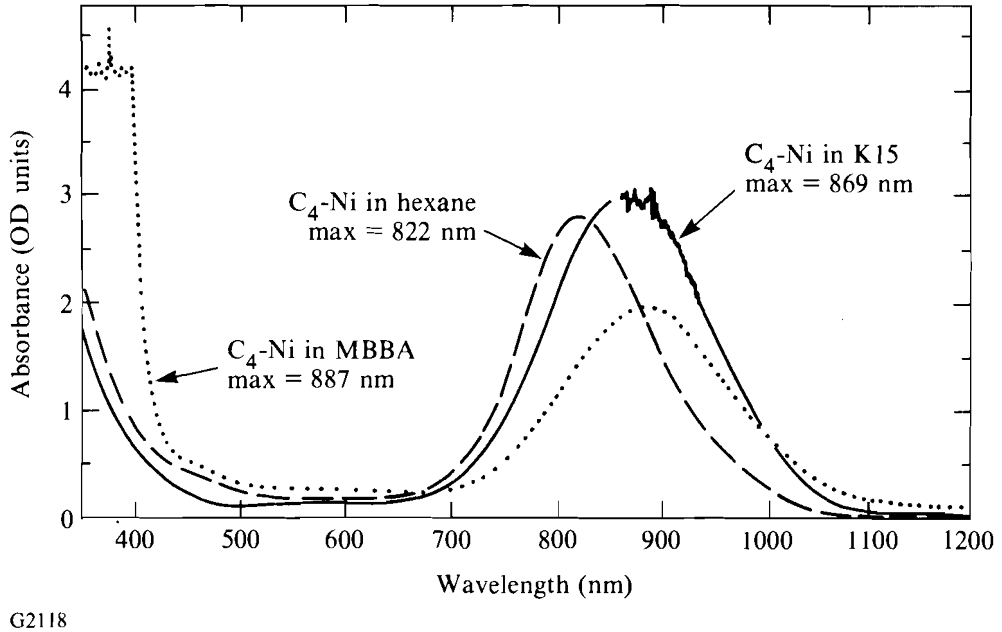


Fig. 33.27
Effect of the solvent matrix on the position of the near-infrared absorption maximum of C_4-Ni. The curve for the complex in hexane was determined in a 1-cm path length for a 50-ppm solution; the curves for K15 and MBBA were determined in 100-μm paths for 0.5% wt/wt of the complex in mixtures held in the isotropic state (50°C).

nematic hosts are shown in Figs. 33.28(a) and 33.28(b). An optical density of 3 is readily obtainable in either host material for a concentration of 0.5%–1% wt/wt and a cell path length of 100 μm. The high solubility of C_4-Ni in the nematic hosts would allow equivalent blocking extinctions to be obtained for thinner path lengths by increasing the concentration of metal complex in the mixtures. A decrease in absorbance with time at 860 nm is observed for a 0.5% solution of the C_4-Ni complex in K15 [Fig. 33.28(a)], indicating that

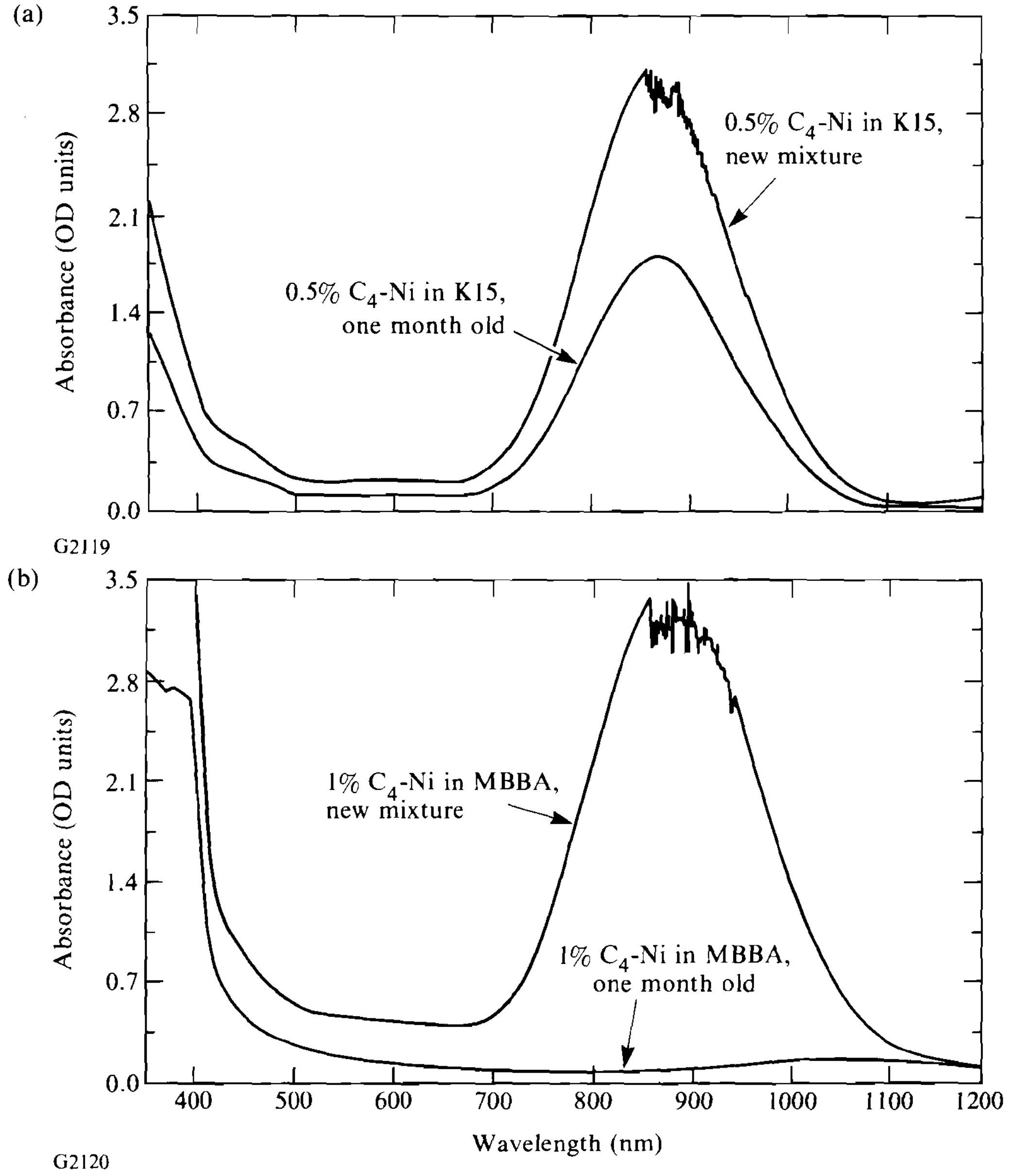


Fig. 33.28
Change in absorbance of mixtures of C_4-Ni in K15 and MBBA after storage for one month. The spectra are for 100-μm path lengths at 50°C.

the metal complex may be decomposing slightly even in K15. This slow decomposition could be initiated by the presence of impurities in the metal complex, and, thus, may not be an indication of a lack of stability of the complex itself. The reduction of the photochemical and thermal stability of various liquid-crystal materials due to the presence of trace impurities is well known and has been extensively documented by Yamagishi *et al.*,[19] and more recently by Lackner, Margerum, and Van Ast.[20] The other possible explanation, separation of the dye complex from solution, seems very unlikely since mixtures with higher concentrations of C_4-Ni have not shown any signs of separation. In the case of mixtures of C_4-Ni in MBBA [Fig. 33.28(b)], the absorption band at 860 nm has completely disappeared, and a new band at 1050 nm is observed. The intensity of this new band is greatly pronounced in mixtures containing a high concentration of the nematic metal complex (Fig. 33.29), and, thus, may be a primary absorption band of a new chemical species resulting from the interaction of C_4-Ni and MBBA.

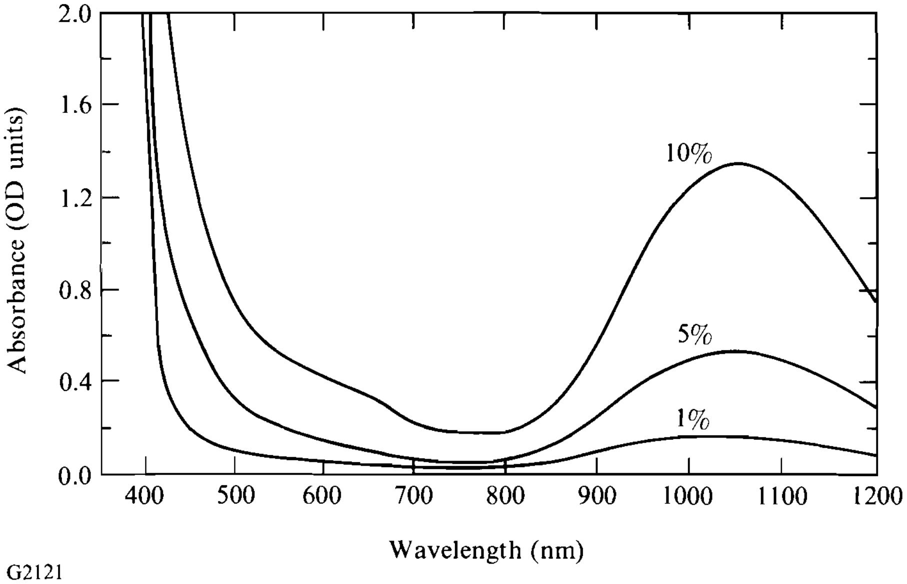


Fig. 33.29
Dependence of the absorbance at 1000 nm–1100 nm on the original metal complex concentration in 100-μm path lengths of one-month-old C_4-Ni/MBBA mixtures. The measurement temperature was 50°C.

The importance of good dye solubility in the liquid-crystal matrix for device applications, such as passive blocking filters or guest-host shutters or modulators, becomes readily apparent upon comparison of the relative blocking efficiencies of C_4-Ni and DMADB-Ni in K15 at their respective peak maxima. The absorption curve for a fresh mixture of 0.5% C_4-Ni in K15, shown in Fig. 33.28(a), is plotted in Fig. 33.30 against the absorption spectrum of the maximum stable concentration of DMADB-Ni (0.05%) in the same host for an equivalent path length. Although the two metal complexes possess similar molar extinction coefficients (~30,000), the poor solubility of

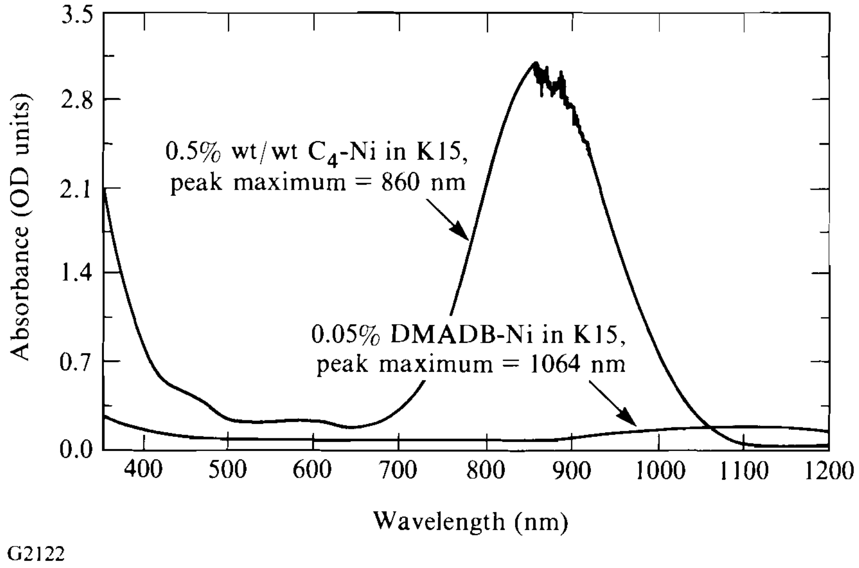


Fig. 33.30
Comparison of the absorption at their respective peak maxima for mixtures of C_4-Ni (0.5% wt/wt) in K15 and DMADB-Ni (0.05% wt/wt) in K15 for 100-μm path lengths.

DMADB-Ni in K15 and the resulting weak absorbance renders this material essentially useless for applications in a liquid-crystal matrix at its peak maximum of 1064 nm.

3. Dichroism and Order Parameter

The positive dichroism in the near-infrared absorption band of C_4-Ni is shown in the absorbance spectra in Fig. 33.31. The measurements were conducted using a 24-μm-thick, homogeneously aligned sample containing 1% wt/wt of C_4-Ni in K15. No difficulty was encountered in producing high-quality homogeneous alignment at this concentration level. A high-frequency ac field (100 KHz) was used to switch the cell to reduce the mixture conductance that occurred at lower frequencies and interfered with the measurements. The maximum transmission was obtained with a 10-V applied field, although switching was observed with fields slightly less than 2 V. The dichroic, or contrast, ratio for C_4-Ni was calculated using corrected absorbance values at 860 nm obtained from the spectra in Fig. 33.31 for the parallel and perpendicular orientations of the metal complex according to the equation:[6]

$$\mathrm{CR} = \frac{A_{\parallel}}{A_{\perp}} = 2.43/0.488 = 4.97 \qquad (1)$$

The percent transmission values for the parallel and perpendicular alignment states were 0.29% and 31.8%, respectively. The order parameter S for C_4-Ni in K15 was calculated using the above absorbance values from the expression[6]

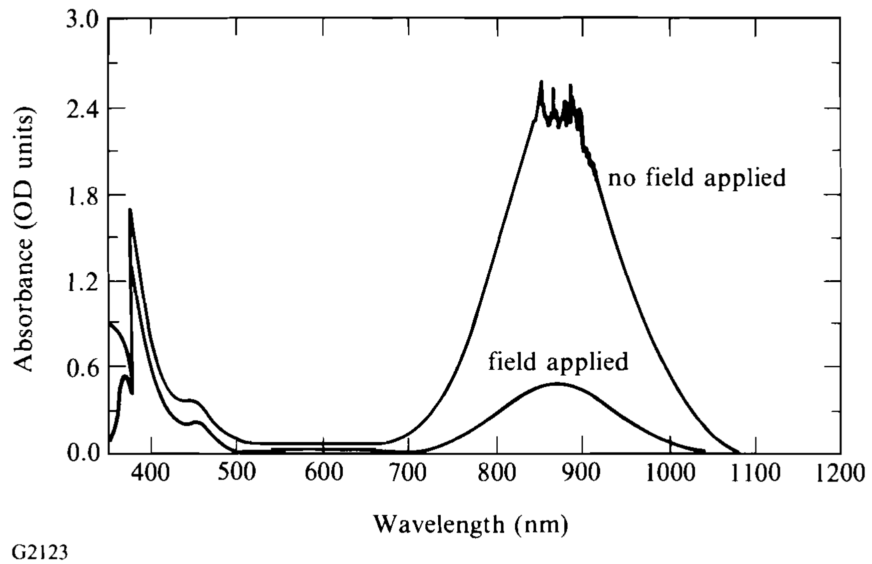


Fig. 33.31
Dichroism of the near-infrared absorption band of C_4-Ni, as measured in a homogeneously aligned, 24-μm-thick cell containing a 1% wt/wt mixture of the complex in K15. Switching between the homogeneous and homeotropic orientations was accomplished with a 10-V, 100-KHz ac field.

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \quad . \tag{2}$$

A value for S in K15 of 0.57 was obtained, which is very near the reported maximum range of 0.6–0.8 for S in a nematic liquid crystal.[21] Both the order parameter and dichroic ratio compare favorably to those reported for conventional guest-host dyes for visible region applications.[3-7] To our knowledge, this is the first reported measurement of near-infrared dichroism for a transition metal complex in a nematic host.

Conclusion

The potential of the nematic metal complex bis(*p*-*n*-butylstyryl-1,2-dithiolato)nickel as a near-infrared dichroic dye for use in active and passive liquid-crystal devices for lasers operating near 800 nm has been demonstrated. The high solubility, large optical extinction coefficient, and wide mesomorphic range of these materials are valuable assets in the construction of such devices. Several issues, however, remain to be resolved. The purity of the nematic metal complex may have an effect on its stability in mixtures, and should be more thoroughly investigated. Purification techniques such as preparative high-performance liquid chromatography may be useful for producing samples of well-defined purity. A more rigorous investigation of the solubility of C_4-Ni in K15 and other nematic liquid crystals needs to be undertaken in order to determine the most effective concentration and temperature ranges of mixtures for device applications. The effect of metal complex concentration on the electrooptic threshold, response time, and dielectric anisotropy of the doped host mixture should also be investigated. The isolation and identification of the species responsible for the 1050-nm peak in aged mixtures of C_4-Ni in MBBA would be of great interest and is currently being investigated. Finally, complexes of other transition metals, such as platinum, palladium, or copper, with ligands of different molecular structures should be prepared and characterized to obtain additional highly soluble dichroic mesogens for applications involving near-infrared laser sources at longer wavelengths.

ACKNOWLEDGMENT

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