The Single-Molecule Origin of the Green Absorption Band in Solid Nickel Dimethylglyoxime. A Comparative Study of the Solution and Solid-State Spectra of the Nickel(II) Glyoximates[1a]

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Abstract: Polarized single-crystal, liquid-nitrogen-temperature colloid, and room-temperature solution spectra have been obtained for the bisdimethylglyoxime, -ethylmethylglyoxime, and -heptoxime complexes of nickel(II). These data have led to the first precise characterization of the striking spectral changes that typically accompany solid formation in the nickel glyoximates. It has thus been possible to trace what has heretofore appeared to be a "new" band in the solid to its origin in the charge-transfer region of the single-molecule spectrum. Assignments for this "color band" and for the other transitions observed have been made in terms of a reasonable energy-level diagram suitable for planar complexes that possess intraligand π bonds. Insights have thus been gained into the electronic structures of both the isolated molecules and the crystals involved in this work.

Nickel dimethylglyoxime (NiDMG) and related complexes have long been the object of spectroscopic study, largely as a result of the unusual solid-state optical properties they commonly display relative to their solution spectra.[2-4] For instance, in the case of NiDMG itself a series of weak absorptions in the blue part of the spectrum leads to a pale yellow solution color, while a relatively strong green crystal transition causes the solid material to have a red body color and to possess a green sheen when the light specularly reflected from an appropriate crystal face is observed. The appearance of this band seems to be associated with the fact that the substance crystallizes in chains in which the metal atoms fall one on top of the other, in that analogous phenomena are observed in Magnus' green salt,[5,6] alkaline earth salts of $Pt(CN)_4^{2-}$,[7] and most other complexes between nickel, palladium, and platinum and the *vic*-dioximes, all of which have similar crystal structures in respect to the formation of "metal chains."[6-11]

The fact that the crystal transition in question is polarized perpendicularly to the molecular planes (*i.e.*, along the metal chains) in each of the cases cited has led to speculation that it is associated with metal-metal interactions in the crystals.[2,5,8,12-14] With the exception of several recent studies,[6,7,15] however, single-crystal spectral investigations on these substances have been at best qualitative in nature and thus have not provided a detailed experimental picture of the situation. As a result attempts to rationalize the crystal effects have been severely hampered. The present work was therefore undertaken with the aim of characterizing as accurately as possible the solid-state absorption of NiDMG and a series of closely related complexes, comparing this absorption to that of their solutions, and reaching some conclusions about the nature of the solid-state effects.

NiDMG and its relatives are of interest from another point of view, in that they are examples of planar complexes, which are somewhat less well understood than other types and have been the object of considerable discussion.[6,16-21] Although the d-d transitions are largely obscured in the nickel glyoximates by the allowed bands, these substances do present a rich and fairly well-resolved group of charge-transfer and other higher intensity transitions whose study can yield information concerning both the metal and the ligand orbitals.

The work reported here concerns NiDMG itself and the Ni(II) complexes of ethylmethylglyoxime and heptoxime (cycloheptanedione dioxime). These three compounds have almost identical solution spectra, but the saturated ligand substituents give rise to varying interplanar spacings in the crystal and thus allow one to study the spectral effects of varying this parameter. Fortunately, one modification of nickel ethylmethylglyoxime has a crystal structure in which the metal atoms do not form a chain structure.[22] One thus has a situa-

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tion where the "oriented-gas model" may apply and polarized single-crystal studies provide information concerning the properties of the isolated complex which will allow one to ascertain more clearly the nature of the solid-state effects noted in the other cases.

The spectroscopic aspects of this work have included solution absorption, polarized single-crystal absorption and reflection, and colloid absorption studies. In addition to yielding information of relevance to the understanding of the electronic structure of the specific molecules and crystals in question, the results presented, when compared to those of previous studies, provide an excellent example of the extreme care that must be exercised in working with even moderately highly absorbing substances in order to obtain accurate solid-state spectra. In this regard, the complementary nature of crystal reflection and absorption, and, where obtainable, other supporting evidence, is clearly brought out. Moreover, what is thought to be a rather novel and potentially quite useful method of preparing very small crystallites finely dispersed in a nonabsorbing medium, in such a fashion that accurate comparison of the solution and solid-state absorption spectra may be made, has been developed in the course of this work.

Experimental Section

Preparation of Materials. Dimethylglyoxime (Mallinckrodt) and heptoxime (Hach Chemical Co., Ames, Iowa) were obtained commercially. Ethylmethylglyoxime was synthesized by treating 2,3-pentanedione (Eastman) with hydroxylamine hydrochloride.[23a] This procedure did *not* produce a significant amount of the desired material, but when it was repeated on the initially formed product, which was presumedly composed largely of monoximes, a good yield of the dioxime was obtained. The final product was purified by vacuum sublimation. The melting point of the purified material (172°) compared well with the literature value (170–171°).[23b]

A given metal complex was obtained by treating stoichiometric amounts of $NiSO_4 \cdot 6H_2O$ (Fisher Certified) with the appropriate ligand in a 50% water-alcohol solution. The complexes were dried and purified either by vacuum sublimation or two crystallizations from chloroform solution.

The preparation of samples sufficiently thin to allow direct absorption measurements presented a serious problem here, and in general a variety of approaches was tried in each case. The nickel heptoxime (NiHept) and monoclinic nickel ethylmethylglyoxime (NiEMG) spectra were obtained on small crystals grown from saturated chloroform solutions. A crystalline film of NiDMG suitable for study was prepared by vacuum sublimation onto a quartz plate. This sample consisted of a mosaic of extremely small oriented areas. A modification of NiEMG differing from the monoclinic type described by Frasson and Panattoni[22] and apparently containing the "column stacking" characteristic of the other complexes studied was obtained by the evaporation of a small amount of a chloroform solution directly on a quartz slide.

For reflection work large crystals of course do not ordinarily lead to complications and, in general, are desirable. Detailed reflection studies were made only in the case of NiDMG and monoclinic NiEMG. For this purpose crystals of the former substance were prepared by vacuum sublimation and the latter by cold room evaporation of chloroform solutions. The approximate NiHept reflection data used to correct the absorption measurements were also obtained on crystals grown by slow evaporation of chloroform solutions.

Colloid Absorption Studies. In an attempt to improve the resolution of the solution absorption spectra of these substances, a series of rigid-glass, liquid-nitrogen temperature absorption studies was undertaken. On cooling the solutions, however, it was found that the color changed dramatically and the absorption spectrum became that of the solid as a result of the precipitation of the solute as small crystallites dispersed throughout the glass. This situation presented the possibility of measuring the absorption spectrum of the solid over a relatively extended spectral range and in such a way that very careful comparisons of the solid and solution spectra could be made.

The general procedure followed was to dissolve the complex in a suitable glass-forming solvent, place the resulting solution in a quartz dewar equipped with an aluminum heat exchanger, and take the solution spectrum using a Cary recording spectrophotometer with a suitably modified cell compartment. Liquid nitrogen was then poured on top of the sample and the spectrum taken again after the glass had formed. Both room-temperature and glass base-line spectra of the solvent were obtained and appropriate optical densities subtracted to give the true spectra. To ensure that constant effective path lengths were used throughout a given experiment, the cell holder was adjusted so that optical density measurements in the transparent part of the spectrum matched whenever the dewar was replaced in the light path after having been removed from it. Care was also taken to maintain the dewar's orientation during such operations. Independent measurements were made of those solution extinction coefficients not already known and of the low-temperature contraction factor for the solvents used. The solution spectra then allowed one to ascertain the effective path length in a given experiment and thus, taking proper account of the contraction of the glass, one could compute the solid extinction coefficients. The spectra so obtained are referred to here, perhaps in a somewhat nonrigorous fashion, as "colloid" spectra.

Polarized Single-Crystal Reflection and Absorption. The single-crystal measurements reported here were carried out on a microspectrophotometer developed in these laboratories. This instrument, which has been described in some detail elsewhere,[24] consists of a Leitz Ortholux microscope suitably modified and augmented so as to allow one to carry out spectral studies throughout the quartz ultraviolet. The configuration of the instrument for reflection measurements was essentially that outlined previously.[25] For absorption studies a system of mirrors deflected the beam so that instead of passing through the microscope's vertical illuminator arrangement it traversed the usual path followed in transmission microscopy. Here the standard Ortholux condenser system was replaced by a duplicate of the objective being used, as is the usual practice in ultraviolet microscopy. Two features of the present apparatus that were particularly useful in this work were the existence of a series of diaphragms in the optical system that allow one to select very small crystal areas for study and the use of a trinocular microscope tube that permits careful visual examination of the precise area being investigated during the course of an actual run.

For absorption measurements the crystal or film being examined was simply placed on a microscope slide, while in the case of reflection studies the sample was usually mounted atop a Supper eucentric goniometer head. The positioning, alignment, and rotation of the samples in the light beam were accomplished by using standard microscope stages augmented in some cases, especially those involving reflection measurements, by special goniometric modifications. The apparatus was operated in its single-beam mode.

Reflection data were collected as in previous studies.[24,25] The procedure followed in obtaining absorption data was analogous to that used in reflection, a set of readings first being collected with the crystal in position and a series of reference readings then being obtained under exactly the same conditions with the crystal removed. The absorption spectra were corrected for reflection losses at the crystal surface using the detailed data reported in the Results section for NiDMG and α-NiEMG and approximate data collected especially for this purpose for NiHept and β-NiEMG. The crystals were sufficiently highly absorbing and their reflectivities sufficiently low, however, that these corrections were not particularly significant.

Polarized crystal spectra are generally recorded with the electric vector of the light vibrating parallel to the extinction, or principal, directions for the face being studied. Since in absorption studies it can often be extremely important to have the alignment of the crystal such that the light is polarized as precisely as possible along the crystal extinction directions,[24] the determination of these directions was routinely made on each sample with the two Glan prisms in a "crossed" position. In the case of reflection, where precise alignment is not so crucial, principal directions were found either by finding the positions of extinction between the crossed prisms, as in absorption, or else by simply finding the rotational

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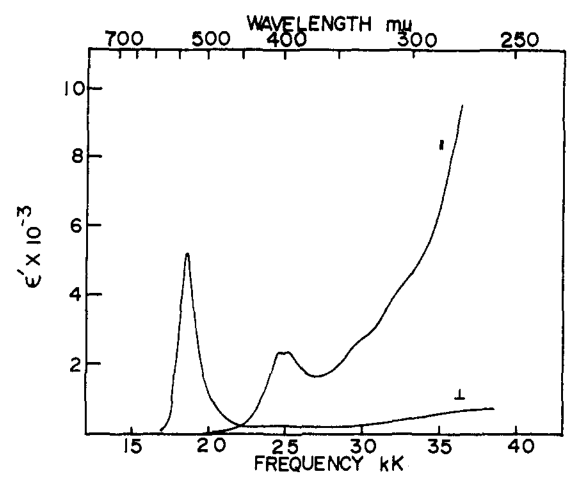

Figure 1. The polarized absorption spectra obtained for an oriented film of nickel dimethylglyoxime. The ∥ and ⊥ labels indicate that the curves are believed to have been obtained with the incident radiation so polarized that its electric vector vibrates parallel or perpendicular to the molecular planes, respectively. The extinction coefficients shown are based on the results of a Kramers–Kronig analysis of the out-of-plane reflection data of Figure 3 (see text) and have been scaled as outlined in ref 26.

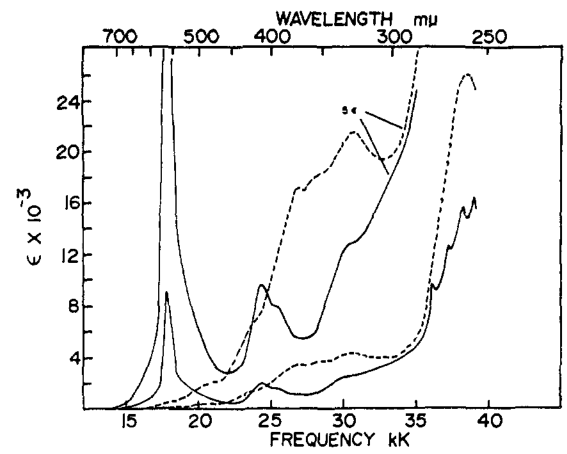

Figure 2. Glass (———) and solution (- - - -) absorption spectra of nickel dimethylglyoxime. The solvent was composed of a volume ratio of five parts of ethanol to three parts of chloroform.

positions of maximum and minimum reflectivity. In either mode of operation the spectra were recorded with the polarizers parallel.

Results

Nickel Dimethylglyoxime. NiDMG forms needle-like orthorhombic crystals in which the needle, or *c* crystallographic, axis corresponds to the out-of-plane molecular direction, and directions perpendicular to this axis are in-plane in nature.[8] The fact that adjacent molecules in a given molecular stack are rotated by 90°, however, causes all "in-plane" crystallographic directions (*i.e.*, all directions perpendicular to the *c* axis) to be spectroscopically equivalent and contain equal contributions from both in-plane molecular directions. Thus, although the selection rules appropriate to the D_{2h} symmetry of NiDMG indicate that a given molecular transition should be polarized either out-of-plane or along one of the two in-plane symmetry axes, single-crystal measurements do not allow one to distinguish between the latter and are limited to indicating that a given absorption is either in-plane or out-of-plane.

Figure 1 presents the polarized oriented film absorption spectra obtained for NiDMG. Although this film has not been subjected to X-ray studies, it and the crystal are thought to be isomorphous on the basis of the correspondence, brought out below, of the single-crystal reflection spectra to those anticipated if this were the case. Moreover, as is expected for an orthorhombic crystal, the film showed no dispersion of its principal directions. The film directions along which the incident radiation was polarized in obtaining the curves of Figure 1 have thus been labeled ∥ and ⊥ to indicate that they are believed to correspond to in-plane and out-of-plane polarization, respectively. It should also be noted that the spectra of Figure 1 have been reported in terms of "equivalent solution extinction coefficients"[26] and that the ϵ' labeling of the ordinate axis reflects the fact that these extinctions have not been measured directly but have rather been obtained through a Kramers–Kronig analysis of the reflection data.

It is immediately apparent that the spectra of Figure 1 differ from those previously reported for NiDMG single crystals,[2,3] as has been illustrated by the first figure in ref 24, where a portion of Figure 1 has been compared with two typical sets of previous data. The low-energy band that has been the object of considerable speculation is seen to be, despite recent assertions to the contrary,[3] highly dichroic, polarized almost exclusively along the needle axis, and of moderately high intensity. Moreover, a great deal more detail is brought out here, and as a result it becomes clear that the "appearance" of the "new" band has associated with it changes in the high-energy part of the spectrum. The rigid-glass colloid spectra reported in Figure 2, which covers a somewhat more extended spectral range, show more clearly the nature of this high-energy alteration, which is seen to consist essentially of intensity losses in the charge-transfer and ligand absorption regions.

The spectra of Figures 1 and 2 are quite consistent. It has been conjectured, however, that single-crystal absorption is not accurately characterized by the spectra of polycrystalline material in suspension or in salt pellets.[2b,3] Such a view might cause one to take the position that the absorption spectra shown in Figure 1, which were obtained on an oriented area of a polycrystalline film, are not truly characteristic of the bulk crystal and correspond only to the absorptive properties of the crystallites studied in the colloid. Figure 3, however, shows the reflection spectra obtained on a side face of a large NiDMG crystal, and these are seen to be those that one would expect on the basis of the absorption spectra of Figure 1.[27] In particular the sharpness, highly dichroic nature, and out-of-plane polarization of

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(26) Consideration of the orthorhombic crystal structures dealt with here indicates for incident radiation polarized along the needle axis the out-of-plane direction of every molecule will be favorably oriented for absorption to take place, while for light polarized along the ∥ direction an in-plane transition moment will be favorably oriented effectively half the time. In solution a given molecular direction is similarly favorably oriented one-third of the time. Thus, in order that the intensities of colloid and solution spectra may readily be compared to those of the crystal absorption spectra, the optical densities and extinction coefficients for ⊥ crystal directions have been divided by 3 and those for ∥ directions multiplied by $^2/_3$ for most spectra of orthorhombic crystals reported here.

(27) For examples and discussions of the connection between reflectivity and crystal absorption, see ref 24 and 25 and (a) B. G. Anex and A. V. Fratini, *J. Mol. Spectry.*, **14**, 1 (1964); (b) B. G. Anex and R. S. Umans, *J. Am. Chem. Soc.*, **86**, 5026 (1964).

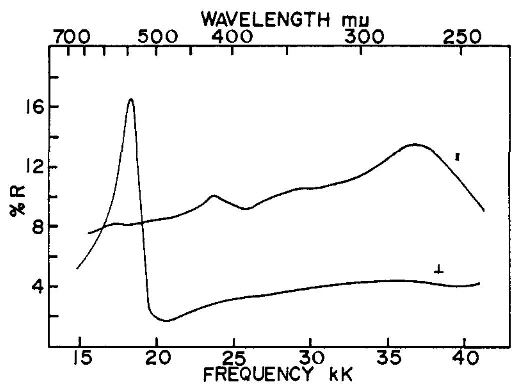

Figure 3. Polarized single-crystal reflection spectra obtained from a side face (*i.e.*, a face corresponding to a plane in the (*hk*0) zone) of a nickel dimethylglyoxime single crystal. The ∥ and ⊥ labels distinguish between the curves measured with the incident radiation's electric vector vibrating parallel and perpendicular to the molecular planes, respectively. (Thus the ⊥ spectrum is that obtained when the electric vector of the incident radiation vibrates parallel to the needle axis.)

the low-energy peak in the ⊥ spectrum, hereafter referred to as the "color band," are certainly confirmed.

The favorable visual correlation of the reflection and absorption spectra of Figures 1 and 3 may be verified through a Kramers–Kronig analysis of the reflection data.[24,25] The results of applying such an analysis to the out-of-plane spectrum of Figure 3 are summarized in Figure 4. As the caption indicates, one of the derived curves shown in Figure 4 is obtained using essentially just the experimental reflection data, while the second utilizes additional input for an "effective" transition that is intended to compensate for the effects of the reflectivities in the inaccessible vacuum ultraviolet.[24,25] As is commonly the case for strong bands, which tend to dominate the dispersion in their own frequency range, the inclusion of the effective transition is seen to have little influence on the color band, in respect both to its shape and maximum molar extinction coefficient ($\epsilon_{\max}$). Moreover, when the directly measured absorption spectrum is assigned an $\epsilon_{\max}$ value corresponding to the Kramers–Kronig result, the derived and directly measured bands almost coincide. Thus, on the basis of these observations and previous successes in this laboratory in deriving crystal optical constants from reflectivity measurements,[24,25] the film absorption spectra for NiDMG were placed on an absolute scale by accepting the Kramers–Kronig $\epsilon_{\max}$ as being correct.

It is thus seen that all three approaches employed here to study the absorption of NiDMG in the solid state have yielded results that are in essential qualitative and quantitative agreement. Even the relatively higher intensity of the colloid's long wavelength absorption peak is in accord with, as will be seen later, its red shift in comparison to the related single-crystal band, and is probably correlated with low-temperature contraction reducing the interplanar spacings in the colloid.

As pointed out elsewhere,[24] the serious inaccuracies in the previously reported NiDMG single-crystal spectra are indicative of the extreme care that must be exercised in such measurements and of the value of having specular reflection and other supporting studies[2b,3,4,28] that

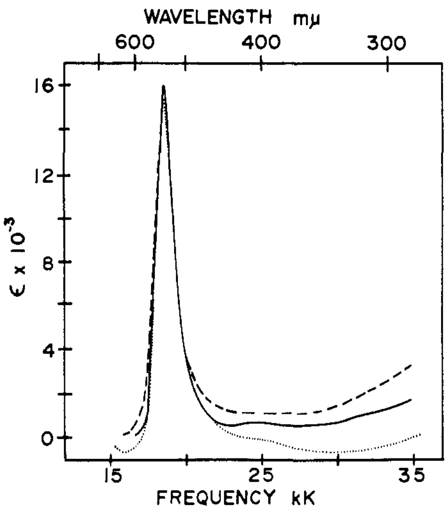

Figure 4. Comparison of the absorption curves obtained through a Kramers–Kronig analysis of the out-of-plane reflection spectrum of Figure 3 with the corresponding directly measured absorption spectrum of Figure 1: (· · · ·) the Kramers–Kronig curve obtained making no approximations for the nonaccessible reflectivities other than those built into the relevant computer program;[24] (– – – –) the Kramers–Kronig curve obtained with the assumption of an appropriate "effective" vacuum ultraviolet reflection band; (———) the measured absorption spectrum scaled so that its $\epsilon_{\max}$ corresponds to that computed for the Kramers–Kronig curves. The intensities are reported here in terms of true crystal extinction coefficients which have *not* been corrected as outlined in ref 26.

will allow one to ascertain whether the single-crystal work is at least qualitatively correct. Although there are many possible sources of error in single-crystal studies, experience in this laboratory with a variety of substances indicates that previous workers' difficulties with NiDMG probably stemmed from studying crystals that were much too thick. Such a situation results in one measuring stray light of various kinds over much of the absorbing region instead of the properly transmitted radiation of the desired polarization and wavelength and is consistent with the extinctions that have been reported[3] being low by over an order of magnitude.

In addition to exercising care in sample preparation in the present studies, other precautions were taken that were designed to allow one to measure reasonably high optical densities on highly absorbing and highly dichroic crystals. For instance, two monochromators were employed to reduce to a minimum radiation of wavelengths other than that intended being involved in a given measurement, and the second Glan prism was used to minimize the effects of instrumental depolarization and scattering within the crystal. In spite of these procedures, which have allowed the measurement of optical densities of up to 3, it has not generally been possible to obtain measurements in the more intense ultraviolet bands. In view of this circumstance it is unfortunate that the reflection spectra have not proven to be better resolved (with the exception of the first ⊥ band) and thus more informative. Low-temperature measurements may help remedy this situation, however.

α-Nickel Ethylmethylglyoxime. That the crystals produced by slow evaporation of chloroform solutions of NiEMG were in fact the monoclinic modification discribed by Frasson and Panattoni,[22] referred to here as

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(28) (a) R. J. H. Clark, *J. Chem. Educ.*, **41**, 488 (1964); (b) R. J. Magee and F. Nasouri, *Microchem. J.*, **9**, 324 (1965). These authors present and compare colloid and diffuse reflectance spectra for nickel diphenylglyoxime.

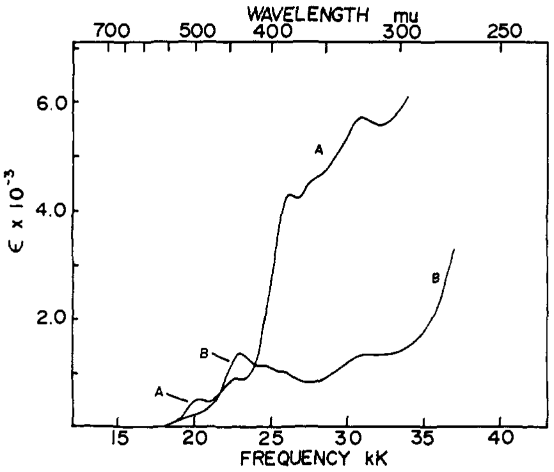

Figure 5. Polarized single-crystal absorption spectra for the (011) face of α-nickel ethylmethylglyoxime. The A and B curves are those for the corresponding principal directions defined in the text. The reported optical densities are those actually obtained for the crystal and have *not* been scaled as outlined in ref 26, since the more complex crystal structure encountered here precludes a simple conversion.

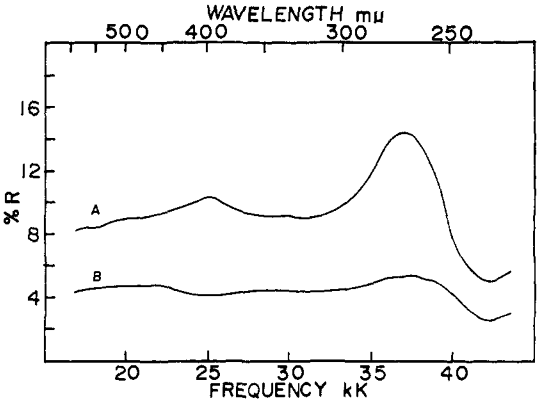

Figure 6. The crystal reflection spectra for the (011) face of monoclinic α-nickel ethylmethylglyoxime. The A and B curves have the same significance as in Figure 5.

α-NiEMG, was verified by an X-ray examination of a representative specimen. The angles between the reciprocal axes and the intensities associated with the (*h*00), (0*k*0), and (00*l*) reflections were found to be those expected on the basis of the published crystal data. Moreover, the *a* crystallographic axis was shown to be parallel to the four side faces studied spectroscopically, and the *b* and *c* axes were found to point approximately at the intersection of these faces. The fact that the observed interfacial angles (91.2 and 89.2°) compared well with those calculated for "(011)-type" faces was taken as confirming the identification suspected on the basis of the X-ray work. The symmetry operations of the $P2_1/c$ space group to which this crystal belongs carry the (011)-type faces into one another, and thus each of these side faces must be spectroscopically equivalent to all the others.

The low symmetry of these crystals raises the possibility of dispersion of the principal directions when the face in question is not parallel to the *b* axis.[27a] A careful study of the principal directions as a function of wavelength was thus undertaken, which revealed that, except for inversions of 90° which occur in the 430-mμ region when the spectra obtained with light polarized along the two directions cross, the principal directions disperse a maximum of 9° between 300 and 600 mμ. The spectra shown in Figure 5 were taken along a fixed direction at an extreme value within this range, direction *B* being approximately 49° clockwise from horizontal when the (011) face is viewed with the positive *a* axis directed upward. Obtaining the measurements along this fixed set of principal directions, which correspond to those appropriate at about 390 mμ, was found to be acceptable since, as will be discussed shortly, the projections of molecular axes on the true principal directions do not vary greatly over the range of the dispersion.

The interpretation of the polarized spectra for α-NiEMG is less straightforward than for the other compounds studied in that the spatial relationships between the two molecules in the unit cell are more complicated here.[22] Molecular axes were therefore defined and a series of projections made that would allow one to characterize the crystal absorption in molecular terms. The in-plane *x* and *y* molecular axes were taken as the lines that bisect the angles formed by the nickel–nitrogen bonds, the *x* axis being that one which cuts the ligand carbon–carbon bond, and the *z* axis taken as the perpendicular to the plane of the molecule. The squared projections, averaged over the two molecules present in the unit cell, of unit vectors directed along these axes were then obtained for each of the extreme sets of principal directions found in the dispersion studies. Since the two sets of results did not differ appreciably, they in turn were averaged to give

	A	*B*
x axis	0.511	0.072
y axis	0.463	0.212
z axis	0.026	0.718

Thus the *A*-direction spectrum of Figure 5 corresponds to almost completely in-plane absorption, while the *B*-direction is largely out of plane.

In order to place the measured spectra of Figure 5 on an absolute scale, one once again required a knowledge of the crystal extinction coefficient at at least one point in the spectrum. In this instance the crystal reflection spectra, which are shown in Figure 6, did not appear to hold great promise in regard to a Kramers–Kronig analysis. It was therefore fortunate that in some instances an interference pattern was observed as a result of interaction between the radiation directly transmitted and that transmitted after two internal reflections. Thus, if λ_1 and λ_2 are the wavelengths at which successive maxima or minima occur for light polarized along a given principal direction, the thickness of the crystal may be estimated from

$$2d(n_2\lambda_1 - n_1\lambda_2) = \lambda_1\lambda_2$$

where *d* is the thickness and n_1 and n_2 are the indices of refraction for the principal direction in question at λ_1 and λ_2, respectively. The indices of refraction required here were obtained from the measured reflectivities for the wavelengths in question using Fresnel's formula for a nonabsorbing region[29]

$$R = (n - 1)^2/(n + 1)^2$$

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[29] The crystal indices of refraction were measured directly at the sodium D lines and found to correspond quite closely (within 2%) to the values derived from the reflectivity.

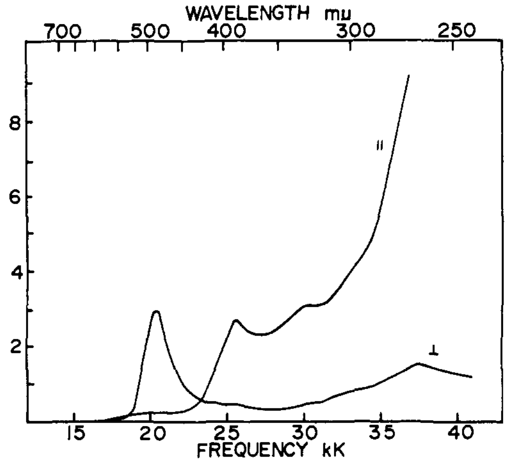

Figure 7. The polarized crystalline film absorption spectra for β-nickel ethylmethylglyoxime. The ‖ and ⊥ labeling refers to the principal directions and has the same significance as in Figure 1. The ε values have been estimated as outlined in the text and scaled as indicated in ref 26.

Once one knows the thickness of a given crystal, the extinction coefficients may be computed from a knowledge of the optical density and the molar concentration of absorbers present.

β-Nickel Ethylmethylglyoxime and Nickel Heptoxime. As was noted previously, a second crystal modification of NiEMG, referred to here as β-NiEMG, was prepared by evaporating a chloroform solution directly on a quartz slide. The spectra obtained for this form, typical examples of which are shown in Figure 7, are consistent with its possessing the orthorhombic crystal structure described by Sharpe and Wakefield.[30] This identification is supported by the relationship between the intensity and position of the low-energy out-of-plane crystal absorption for this compound, as will be seen later.

Attempts to prepare low-temperature colloids of NiEMG resulted in the formation of suspended solid material, but the complexity of the spectra obtained suggested that one had a mixture of orthorhombic and monoclinic forms, or, alternatively, the orthorhombic form had precipitated incompletely.

Figures 8 and 9, which complete the presentation of the data for this series of compounds, show the rigid-glass colloid and polarized single-crystal absorption spectra of NiHept, whose crystal structure is isomorphous with that of NiDMG.[2b] As precise reflection data were not obtained for NiHept and β-NiEMG and the crystal absorption spectra did not show interference patterns, these spectra were placed on an absolute scale by consideration of the absorption occurring in the 380- to 400-mμ region (bands B(1) and B(2) in subsequent tables and discussion). Since this absorption shows relatively little change in its equivalent solution $\epsilon_{\max}$ in going from α-NiEMG[31] ($\epsilon_{\max}$ 2940) to NiDMG ($\epsilon_{\max}$ 2360), and since β-NiEMG and NiHept both possess intermediate nickel–nickel spacings, it was assumed that the $\epsilon_{\max}$ for the latter compounds in this region was the average of those measured for the former and this value used to compute the ε values reported in Figures 7 and 9. This indirect determination of ε is indicated here, as it was for NiDMG, by the ε′ labels used for the ordinate axes.

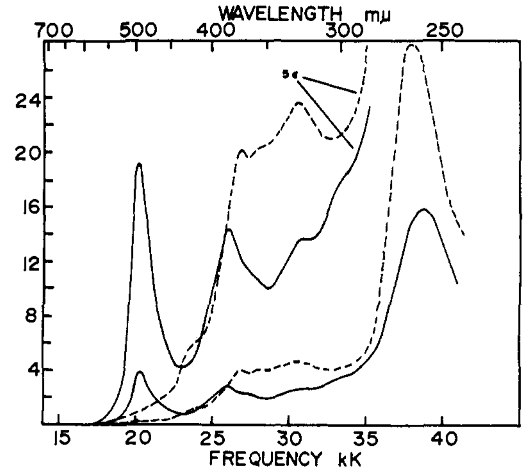

Figure 8. Glass (———) and solution (- - - -) absorption spectra for nickel heptoxime. The solvent was composed of a volume ratio of five parts of ethanol to two parts of chloroform.

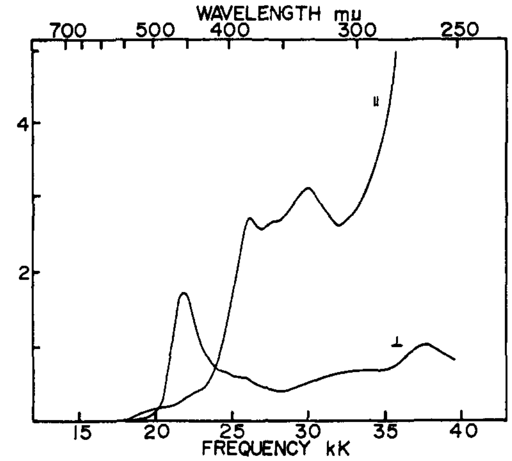

Figure 9. Polarized single-crystal absorption spectra obtained for a side face of nickel heptoxime. The ‖ and ⊥ notation has the same significance as in Figure 3. The ε values have been estimated as outlined in the text and scaled as indicated in ref 26.

Summary of Results. Tables I and II summarize the solution, colloid, and single-crystal absorption data accumulated in the course of this work, the solution data for NiEMG, which are essentially the same as those for NiDMG, having been omitted from Table I. The various observed bands listed have been assigned labels to facilitate later discussions and to indicate the correlations that are thought to be apparent in the spectra. Included in Table II are data for a series of weak and faintly resolved bands occurring in the ⊥ spectra of the orthorhombic crystals and roughly paralleling the in-plane absorption systems. Although the possibility of vibronically allowed components of the in-plane bands being involved here exists, it is felt likely that these bands arise simply from the incident radiation being scattered and depolarized within the crystal, since such effects have been quite common in many of the crystals examined in this laboratory.

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[30] A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 281 (1957).

[31] When it has been found necessary to compute equivalent solution extinctions for α-NiEMG, it has been assumed that principal direction *A* is completely "in-plane" in nature and that the complex absorbs equally along its two in-plane axes.

Table I. Solution and Rigid Glass Data[a]

	Nickel dimethylglyoxime						Nickel heptoxime					
	Solution			Glass			Solution			Glass		
	Position		ϵ_{max},	Position		ϵ_{max},	Position		ϵ_{max},	Position		ϵ_{max},
Band	mμ	kK	cm^{-1} M^{-1}	mμ	kK	cm^{-1} M^{-1}	mμ	kK	cm^{-1} M^{-1}	mμ	kK	cm^{-1} M^{-1}
A	481	20.8	300	...	...	...	476	21.0	300	...	...	...
Color	435	23.0	1,000	565	17.8	9,100	429	23.3	1,000	495	20.2	3,800
B(1)	373	26.8	3,400	410	24.4	2,000	373	26.8	3,900	385	26.0	2,800
B(2)	355	28.2	3,800	392	25.5	1,600	355	28.2	4,000	366	27.3	2,100
C	326	30.7	4,300	331	30.2	2,500	326	30.7	4,600	326	30.7	2,600
D	...	...	...	302	33.1	3,500	...	...	...	302	33.1	3,500
E	259	38.6	26,100	257	39.0	16,300	264	38.0	27,900	258	38.7	15,800

[a] Many of the bands reported here overlap badly, and this situation must be borne in mind in connection with any interpretation of the ϵ values listed (see Figures 2 and 8).

Table II. Crystal Data for Nickel Dimethylglyoxime and Related Complexes[a]

	Nickel dimethylglyoxime			β-Nickel ethylmethylglyoxime			Nickel heptoxime			α-Nickel ethylmethylglyoxime		
Band and polarization[b]	Position mμ	kK	Equiv soln ϵ_{max},[26] cm^{-1} M^{-1}	Position mμ	kK	Equiv soln ϵ_{max},[26] cm^{-1} M^{-1}	Position mμ	kK	Equiv soln ϵ_{max},[26] cm^{-1} M^{-1}	Position mμ	kK	Measd crystal ϵ_{max}, cm^{-1} M^{-1}
A ∥	...	...	...	...	...	...	498	20.1	143	495	20.2	512
Color ∥	...	...	...	...	...	...	446	22.4	400	439	22.8	910
B(1) ∥	408	24.5	2330	391	25.6	2680	382	26.2	2680	382	26.2	4290
B(2) ∥	397	25.2	2390	...[c]	...[c]	...[c]	361	27.7	2620	365	27.4	4540
C ∥	337	29.7	2520	~329	~30.4	3090	333	30.0	3070	324	30.9	5710
D ∥	311	32.2	4030	~303	~33.0	3940	...	...	..	...	...	...
A ⊥	...	...	...	...	...	...	...	...	...	495	20.2	255
Color ⊥	538	18.6	5340	488	20.5	2970	457	21.9	1700	435	23.0	1370
B(1) ⊥[d]	410	24.4	Small	413	24.2	487	405	24.7	634	405	24.7	1140
B(2) ⊥[d]	395	25.3	Small	385	26.0	487	386	25.9	552	385	26.0	1030
C ⊥[d]	...	...	...	~328	~30.5	406	317	32.5	655	323	31.0	1340
D ⊥[d]	...	...	...	~303	~33.0	447	...	...	..	...	...	...
E ⊥[d]	...	...	...	265	37.8	773	265	37.7	1000	...	...	...

[a] Many of the bands reported here overlap badly and this situation must be borne in mind in connection with any interpretation of the ϵ_{max} values listed (see Figures 1, 5, 7, and 9). [b] The ⊥ and ∥ designations are not really appropriate for α-NiEMG and in this case refer to the *A* and *B* directions defined in the text. [c] Band B does not appear as a doublet in β-NiEMG. [d] The ⊥ spectra of the orthorhombic crystals show a series of weak bands for which data are listed here but which may well be a result of part of the incident radiation being scattered into the ∥ direction (see text).

Discussion

In this section attention will first be centered on the low-energy out-of-plane crystal absorption that has attracted much attention to these compounds. After the general nature of this absorption has been established, the other observed bands occurring in the spectra will be examined and the effects of solid formation on them summarized. At that point one will be in a position to suggest a reasonable set of assignments for the transitions observed for the isolated complexes and to examine the solid-state effects in terms of these assignments.

The Nature of the Low-Energy Crystal Band. As noted in the introductory section, α-NiEMG does not possess the chain stacking found in the orthorhombic crystals. This substance thus plays a crucial role in defining the nature of the spectral effects seen in the latter cases. The nearest nonbonded atom to the nickel atom in α-NiEMG is an oxygen lying 3.44 A away, and the shortest nickel–nickel distance is 4.75 A, as compared to 3.25, 3.4, and 3.60 A, respectively, for NiDMG,[8] β-NiEMG,[30] and NiHept.[2b] This situation, coupled with the fact that the crystal spectra of α-NiEMG strongly resemble that of its solution (compare the spectra of Figure 5 with the solution spectra of Figures 2 and 8), suggests that the crystal spectrum may reasonably be taken to characterize the absorption of the isolated complex. This "oriented-gas" nature of the α-NiEMG spectrum is further substantiated by Figure 10, which compares the solution spectrum of α-NiEMG to a hypothetical spectrum based on the oriented-gas assumption, the spectra of Figure 5, and the average projections of the molecular axes on the principal directions listed previously.[31] The degree of agreement between the two curves of Figure 10 is certainly within that expected when one recalls the two different types of measurements being compared here and the difficulties associated with obtaining accurate crystal extinction coefficients, especially in regions of high absorption. These results thus support the oriented-gas assumption and, incidentally, provide an additional internal check on the mechanics of the projection procedures.

With the identification established above and recalling that direction *B* of α-NiEMG is predominantly out of plane in character, one may take the curves shown in Figure 5 as indicating that the isolated molecules of the complexes studied here possess an out-of-plane absorption at 435 mμ. Furthermore, the glass and crystal spectra, taken in their entirety, indicate this band to be the single-molecule origin of the band that in NiDMG, for instance, appears to have "arisen" in the solid, this out-of plane absorption shifting to the red and increasing dramatically in intensity as the interplanar distance

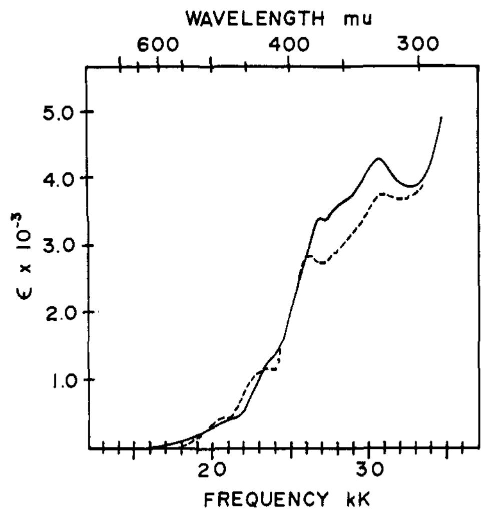

Figure 10. A comparison of the "equivalent solution spectrum" computed from the crystal spectra of Figure 5 as outlined in the text (- - - -) with the observed solution spectrum (————).

decreases. Figure 11 emphasizes this point, tracing the development of the green NiDMG band from the 435-mμ α-NiEMG band by displaying a portion of the out-of-plane crystal spectra for each complex in question. It should be emphasized that careful scrutiny of the experimental data indicates that for the orthorhombic crystals these appear to be the only out-of plane absorptions that can be related to the 435-mμ absorption of α-NiEMG.

In order to examine the quantitative aspects of the intensity changes of the color band on solid formation in this series, the absolute values of the transition moments associated with it have been evaluated through the appropriate graphical integration and application of the expression[25]

$$\int \epsilon d \log \lambda = (3.270 \times 10^{19})|q|^2$$

The results are summarized in Table III[32] and indicate an approximate eightfold intensity increase on solid formation, a conclusion which cannot be reached, as a consequence of the pronounced sharpening of the band with decreasing Ni–Ni spacing, merely from comparison of extinction coefficients.

Table III

Compound	Ni–Ni spacing, A	$\|q\|^2$, A^2
α-NiEMG	4.75	0.0230[a]
NiHept	3.60	0.0820
β-NiEMG	3.4	0.140
NiDMG	3.25	0.178

[a] See ref 32.

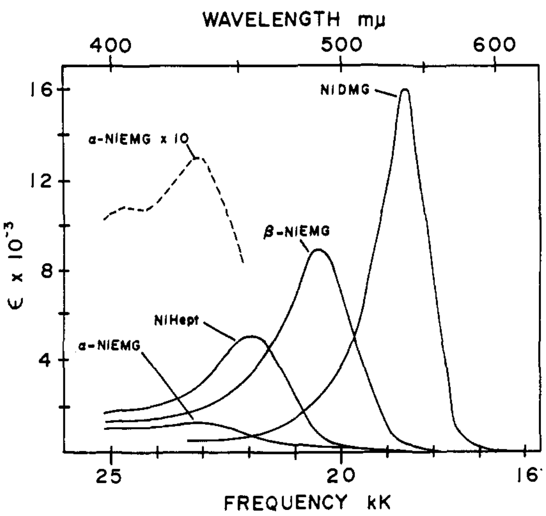

Figure 11. Portions of the out-of-plane spectra obtained for the nickel glyoximates studied in this work plotted so as to illustrate the development of the color band as the Ni–Ni spacing decreases. (The α-NiEMG spectrum is actually that for the *B* principal direction, and thus also contains a small amount of in-plane character.)

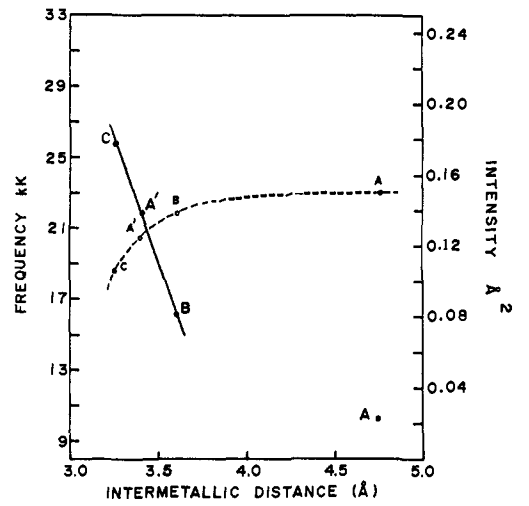

Figure 12. The frequency (- - - -) and intensity, $|q|^2$ (————), of the color band of the nickel glyoximates studied in this work plotted *vs.* the Ni–Ni separation in the crystal. The points labeled A, A′, B, and C represent, respectively, α-nickel ethylmethylglyoxime, β-nickel ethylmethylglyoxime, nickel heptoxime, and nickel dimethylglyoxime.

The relationship that exists between both the intensity and the position of the out-of-plane solid absorption and the interplanar spacing is shown in Figure 12, where it is seen that a smooth curve is obtained for each function (the α-NiEMG points of Figure 12 are actually based on the Ni–Ni separation found in this crystal, but they are best thought of as simply fixing the limiting intensity and energy for large nickel separation). These curves may in fact be used to estimate the interplanar spacings in closely related nickel *vic*-dioxime complexes of undetermined crystal structure, as was done for β-NiEMG before it was realized that crystal data existed for this compound. It was thus concluded from the energy curve that the interplanar spacing in this crystal was 3.4 A, this number providing an excellent value for comparison to the observed intensity from the intensity curve. Sharpe and Wakefield[30] in fact obtain a value of about 3.4 A for this spacing.

Other Spectral Characteristics. The behavior of the color band is only one of the changes that accompany solid formation in the case of the orthorhombic crystals studied here, and, in fact, the entire remainder of the

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(32) The color-band intensity for α-NiEMG was obtained by constructing an out-of-plane spectrum from the data of Figure 5 under the assumptions of ref 31.

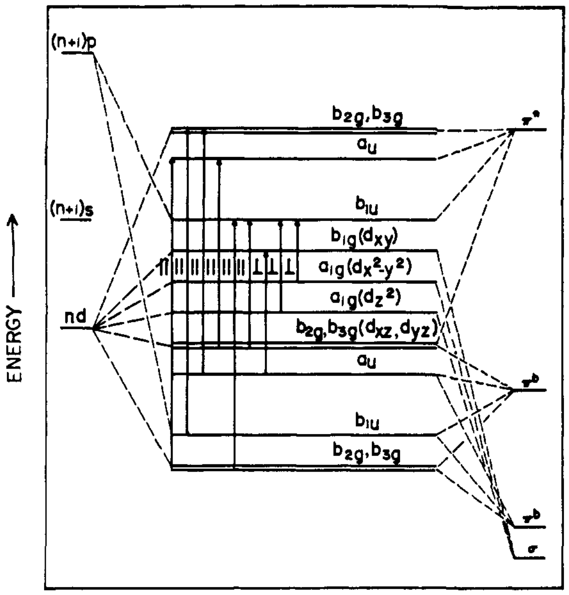

Figure 13. Proposed one-electron molecular orbital level scheme for the nickel glyoximates in D_{2h} symmetry. The allowed transitions and their polarizations are indicated, the ⊥ and ∥ notations indicating whether the transition is allowed out-of-plane or in-plane, respectively.

spectrum, which is essentially in-plane in character, is affected. In order of increasing energy the remaining bands have been designated A, B, C, . . ., etc., and, as indicated above, in this section the behavior of each of them that coincides with nickel "chain formation" will be summarized.

Band A, which occurs at 20.2 kK in α-NiEMG, is the weakest resolved in-plane transition observed here. This band appears not to undergo any shift as the nickel–nickel distance shortens, but does lose intensity, as is evidenced by the fact that it is clearly observed in α-NiEMG, not so clearly seen in NiHept, and definitely not observed in NiDMG. In β-NiEMG some intensity is found in the ∥ direction around 20 kK, but this absorption could very well be associated with the ⊥ band in this region, either as a result of the ∥ radiation being scattered into the ⊥ direction or else through a vibronic mechanism. Similarly, the weak band falling under the color band in α-NiEMG and also faintly apparent in NiHept (see Figures 5 and 7) could be associated with the color band itself, and has been in Table II, although an independent weak ∥ absorption whose behavior parallels that of band A cannot be ruled out.

Between about 25 and 32 kK the solution spectra reveal a series of three peaks of moderate intensity, which have been designated B(1), B(2), and C. B(1) and B(2) show very similar behavior and undergo a red shift of about 2 kK with decreasing nickel–nickel spacing, while the position of the band C does not appear to vary significantly. There is a general decrease in intensity in this whole region with decreasing intermetallic distance, but the overlapping of these bands among themselves and with their neighbors makes it difficult to separate native changes in intensity from the effects of changes in overlap. Clearly, however, either the B "doublet," or C, or both undergo a true intensity loss here.

The highest energy band observed is the intense band E, which occurs at 38.6 kK in the solution spectrum of NiDMG. As can be clearly seen in Figures 2 and 8, this band suffers a sharp reduction in intensity in the orthorhombic forms. The much more pronounced appearance of this band in the α-NiEMG reflection spectrum of Figure 6 in comparison to that for NiDMG in Figure 3 confirms that this intensity loss is associated with "chain formation" and not merely with the solid state in general. One also sees a development of vibronic structure in the NiDMG colloid spectrum, which also may be present as the slight, but reproducible, structure noted in the *B*-direction reflection spectrum of α-NiEMG.

As a general decrease in intensity of the in-plane directions takes place, another band, designated as D, seems to appear as a shoulder on the steeply rising edge of band E. It of course is difficult to characterize band D in any detail, if it is indeed real.

In light of the trends outlined above, it becomes clear that differences noted between the colloid and crystal spectra can be related to the low-temperature contraction, and consequent shortening of the intermetallic distances, in the crystallites studied in the glass work. Thus, the color band in the colloids is characteristically shifted to lower energies and more intense. Likewise, the NiHept colloid spectrum's similarity to the solid-state spectra of β-NiEMG and NiDMG rather than that of its crystal is correlated with the colloid Ni–Ni spacing being quite close to that of β-NiEMG, as is indicated by both the position and the intensity of the color band in the colloid of NiHept.

Assignment of the Single-Molecule Transitions. The fact that the phenomena observed here clearly concern the ligand, as well as the metal orbitals, and that they are quite sensitive to the nature of the ligands involved,[33] suggests the consideration of a molecular orbital approach which takes explicit account of the nature of the pertinent ligand orbitals. Gray and Ballhausen's molecular orbital theory of square-planar complexes,[19] which emphasizes the importance of ligand unsaturation in situations where such exists, thus appears to be a plausible starting point for an interpretation of the presently observed spectra. The level diagram presented by these authors (Figure 3 of ref 19) must be modified here, however, to reflect the fact that the glyoxime complexes differ from the cyanides in at least two important ways: they do not have D_{4h} symmetry and their ligands do not involve in-plane π orbitals. The central portion of the orbital diagram that results from these and various other[35] considerations is shown in Figure 13. The symmetry utilized here is D_{2h}, which is strictly appropriate for NiDMG within the accuracy limits of the crystallographic determination,[8] very nearly appropriate for α-NiEMG if one does not consider the ethyl and methyl groups,[22] and although detailed X-ray crystallographic studies have not been carried out on the other two complexes, is, on the basis of the spectral regularities observed, felt to be adequate here also.

It will also be noted in Figure 13 that three sets of ligand orbitals, two bonding and one antibonding, are

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(33) A recent study of the single-crystal reflection and absorption spectra of orthorhombic nickel N-methylsalicylaldiminate, for instance, which possesses a crystal structure similar to that of NiDMG,[34] shows no out-of-plane absorption analogous to that of the color band of the NiDMG crystal in the region from 700 to 220 mμ: L. Furtado and B. G. Anex, unpublished.

(34) J. Ferguson, *J. Chem. Phys.*, 34, 611 (1961).

(35) F. K. Krist, Thesis, Yale University, 1966.

included. This reflects the assumption made here, based on the observation that the bond lengths obtained in the NiDMG and α-NiEMG crystal structure determinations indicate that there is little conjugation between the oxime groups within a given ligand in these complexes,[36] that one can approximate the ligand orbitals with those appropriate to an allyl-type (–O–N–CH–) fragment. The model that then emerges is, on the assumption of no direct interaction between these ligand units, one of three sets of fourfold degenerate π-electron levels. Although one thus has a reasonable concrete framework within which to discuss the nature of the electronic structure of these complexes, it is to be emphasized that the validity of the subsequent discussions does not rest on this precise view of the ligand structure, as all that is invoked there is the existence of a low-lying unfilled ligand orbital of appropriate symmetry.

The assignments will begin with a consideration of the color band, the only clearly observed out-of-plane transition. Figure 13, which also indicates, along with their expected polarizations, a number of transitions that may enter into the assignments, reveals three color band possibilities. One of these is ligand to metal and the other two metal to ligand. The present discussion will focus attention from the outset on the metal-to-ligand assignments for the low-lying charge-transfer bands. Justification of this approach may be drawn in part from the similar assignments made for systems containing unsaturated ligands that one would hope would bear some analogy to the present case[19,37] and, perhaps more importantly, from the rather pleasing over-all interpretation that will be seen to follow from such a procedure. If one thus first examines the two metal-to-ligand possibilities suggested by Figure 13 it will be noted that, although both are formally allowed in D_{2h} symmetry, the ($d_{x^2-y^2}, \sigma \rightarrow p_z, \pi^*$) promotion is orbitally forbidden in D_{4h}. Since, as will be pointed out below, many of the practical consequences of the deviations from D_{4h} symmetry do not appear to be particularly strong here, it would seem reasonable to accept as a working hypothesis that the color band is associated with the ($d_{z^2}, \sigma \rightarrow p_z, \pi^*$) transition.

A self-consistent argument for this assignment may be made through a more formal consideration of the intensities associated with the three suggested out-of-plane transitions. These intensities cannot be examined in a straightforward manner at present because of a lack of knowledge of the mixing of the metal and ligand orbitals in the molecular orbitals involved. The procedure that has been followed, therefore, has been to assume that the (d_{z^2}, σ) orbital, which is expected to be highly metallic in nature, consists of about 90% d_{z^2}, as measured by the square of its mixing coefficient in the molecular orbital. The amount of metal–ligand mixing in the (p_z, π^*) orbital was then varied until the calculated intensity of the ($d_{z^2}, \sigma \rightarrow p_z, \pi^*$) transition corresponded to about that listed in Table III for α-NiEMG, the atomic orbitals involved being approximated by Slater orbitals. The intensities expected for the ($\pi^b \rightarrow d_{xy}, \sigma$) and ($d_{x^2-y^2}, \sigma \rightarrow p_z, \pi^*$) transitions were then computed using in the second instance the (p_z, π^*) orbital thus obtained and assuming that the ligand–metal mixing in the strongly "d" orbitals is proportional to the ligand–metal overlap.[38] The values of the squares of the transition moments obtained were smaller by one and two orders of magnitude, respectively, than that of the ($d_{z^2}, \sigma \rightarrow p_z, \pi^*$) transition. Although one cannot attach any great significance to the exact numbers obtained in this way, the calculation does seem to indicate that the assignment of the color band to the latter transition is consistent with the other two charge-transfer transitions not being clearly observed in the out-of-plane spectra, especially in view of the fact that if the ($\pi^b \rightarrow d_{xy}, \sigma$) transition occurs at higher energies, it is likely to be lost in the general background of perpendicular absorption observed in that region.

If one assigns the color band as indicated, then a pair of transitions associated with the same excited orbital as the color band and originating from the orbitals that are strongly d_{xz} and d_{yz} in character are expected to occur in the same energy region with in-plane polarization. The bands B(1) and B(2), which, as noted previously, appear to be closely connected with each other in their behavior, may be reasonably assigned to these transitions. The rather small splitting observed, of the order of 1 kK, reflects the relatively small influence of the departure from D_{4h} symmetry in this respect, which is consistent with the low intensity computed for the ($d_{x^2-y^2}, \sigma \rightarrow p_z, \pi^*$) charge-transfer transition, the low value computed for the ($d_{x^2-y^2}, \sigma$) group overlap integral (about 0.03),[35] which would be zero in D_{4h} symmetry, and the successful computation of the effective solution curve of Figure 10, which assumed identical absorption along the x and y axes.

The assignment of bands B(1) and B(2) to the lowest energy predicted in-plane absorptions leads one to conclude that the in-plane intensity of band A must be "forbidden" in nature. It will be noted that if one associates band A with the formally out-of-plane, but very weakly allowed ($d_{x^2-y^2}, \sigma \rightarrow p_z, \pi^*$) transition, one has a situation where the lowest three transitions observed here have precisely the characteristics predicted by Gray and Ballhausen[19] for the metal-to-ligand system of absorptions in planar d^8 complexes with unsaturated ligands. Thus one has three predicted and observed bands, that of lowest energy being quite weak (predicted to be forbidden in square-planar geometry), the second somewhat stronger and polarized out of plane, and the third (predicted to be a degenerate transition in D_{4h} and split in the present case) still stronger and allowed in plane. The over-all drop in ϵ_{max} values observed here in comparison to the analogous bands in the cyanides[19] may at least in part be related to the fact that the π* orbitals are delocalized over at least three centers here, instead of two, and thus the excited orbital occupies to a greater extent a different region of space than the ground-state orbital. If one accepts this picture, then

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(36) For instance, L. L. Merritt and E. Lanterman (*Acta Cryst.*, **5**, 811 (1952)) give a value 1.44 A for the distance between the nitrogen-bearing carbons in the free DMG ligand, while ref 8 gives a value of 1.53 A for the comparable distance in the NiDMG complex.

(37) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

(38) Richardson functions,[39] instead of Slater orbitals, were used to compute the ($d_{x^2-y^2} \rightarrow \pi^*$) and ($\pi^b \rightarrow d_{xy}$) transition moment contributions appearing in these intensity calculations. The excited orbital that finally gave an adequate accounting of the color-band intensity was composed of about 4% 4p_z, where the square of the orbital coefficient in the molecular orbital is again taken as a measure of its contribution.

(39) (a) J. W. Richardson, *J. Chem. Phys.*, **35**, 1829 (1961); (b) J. W. Richardson, W. C. Nieuwport, R. R. Powell, and W. F. Edgell, *ibid.*, **36**, 1057 (1962); (c) J. W. Richardson, R. R. Powell, and W. C. Nieuwport, *ibid.*, **38**, 796 (1963).

the implication is that band A gains its intensity through a borrowing mechanism, in which case its preponderantly in-plane polarization would simply be related to there being much more in-plane intensity available from which to borrow. One actually finds that attempts to resolve the α-NiEMG spectra of Figure 5 into in-plane and out-of-plane curves lead to a small amount of out-of-plane intensity being associated with band A, which could reflect either its native intensity or its borrowing from the color band, or both.

Another possibility for band A is that it is a d–d transition, similarly allowed by a vibronic mechanism. One might also wish to consider a similar assignment for the weak parallel band that falls under the color band in α-NiEMG and NiHept. Regardless of these assignments, however, the color-band polarization, the polarization and splitting of bands B(1) and B(2), and the relative color-band and B-band intensities give strong support to the metal-to-ligand charge-transfer nature of the color band and bands B(1) and B(2) and thus, assuming that the ordering of the spectroscopically determined state energies reflects that of the relevant orbitals, confirm the positioning of the d_{z^2} orbital above d_{xz}, d_{yz}. Of course, if band A were in fact the weakly allowed charge-transfer band suggested above, the d-orbital ordering would be $d_{xy} > d_{x^2-y^2} > d_{z^2} > d_{xz}, d_{yz}$. This would support at least some current thinking on this matter.[40] The potential importance of using charge-transfer spectra to fix this ordering is pointed up by recent studies that indicate a possible change in geometry for some excited states reached by d–d transitions in complexes with square-planar ground states.[21d,41] This situation can lead to an apparent breakdown of the vibronic selection rules that greatly complicates the interpretation of the "crystal-field" spectra obtained.

Turning now to the higher energy transitions, one finds that band C appears to possess reasonably high intensity in the solution spectra and the crystal spectra of α-NiEMG and NiHept. The nature of this absorption is, however, as noted previously, difficult to ascertain as a result of its being severely overlapped by its neighbors, and one notes that in the glass spectra and in the crystal spectra of NiDMG it simply appears as a shoulder on the side of band E. It would thus seem that it, and band D, might appropriately be assigned to forbidden bands, several transitions shown in Figure 13 being in energetically acceptable positions.

The high intensity and position of band E suggests that it is closely related to the $\pi \rightarrow \pi^*$ transition that occurs in the free ligands at 226 mμ in ethanol solution. Drawing a strict comparison is precluded, of course, by the strong mixing of ligand and metal orbitals implied by the interpretation thus far set forth. Moreover, dimethylglyoxime itself has an *s-trans* configuration in its single crystal, and probably in solution, while the ligand is *s-cis* in the complex and, as noted previously, has undergone a very appreciable change in its central carbon–carbon bond length.[36] Nevertheless, band E doubtlessly contains strong $\pi \rightarrow \pi^*$ components.

Solid-State Effects. In the foregoing assignments the color band in the free molecule has been associated with a one-electron excitation from the d_{z^2} orbital to an orbital composed of a mixture of the $4p_z$ and a linear combination of the ligand π^* orbitals, weighted heavily in favor of the ligand contribution. The observed solid-state effects can be rationalized in this picture if one assumes that some, for now nonspecific, interaction causes the $4p_z$ orbital to be greatly stabilized—to the extent that the transition leading to the B_{1u} excited state becomes strongly metallic in nature. Since the intensity calculations indicate that the major component of the transition moment for this excitation is $d_{z^2} \rightarrow 4p_z$, one would thus expect a sharp increase in intensity in this situation. Actually, if one approximates the atomic orbitals with Slater orbitals, a value of 0.225 A^2 is obtained for the $|q|^2$ value associated with the $3d_{z^2} \rightarrow 4p_z$ transition. One thus has ample intensity available from this mechanism to account for the value of 0.178 A^2 listed in Table III for NiDMG.[42] Moreover, as noted previously, much of the apparent sharp increase in the intensity of this band arises from its sharpening in the solid. This characteristic would of course also be typical of increasing metallic character in the transition, which would reduce the amount of antibonding character introduced into the ligands, thus reducing possible changes in the force constants and resultant Franck–Condon effects. Such stabilization of the p_z orbital would also explain at least in part the large red shift observed for the color band in the crystal.

It has been suggested previously that the NiDMG color band absorption might arise from $3d \rightarrow 4p_z$ promotions,[4,8,43,44] but the strong supporting evidence provided by the present work was of course lacking. Refutations of this assignment, based mainly on arguments stemming from the somewhat misleading crystal spectra discussed previously, have thus been presented.[3] The suggestion put forth by Zahner and Drickamer in fact corresponds rather closely to the proposal made here that in the solid one obtains a strongly $d_{z^2} \rightarrow 4p_z$ transition, although these workers were not in a position to be specific regarding the d orbital concerned. Zahner and Drickamer also suggest that the crystal perturbation may have its origin in electrostatic effects. Although one cannot explore this possibility in detail without a knowledge of the charge distribution in the complex, the observation for Magnus' green salt, where the alternating positive and negative ions in the molecular columns provide a clear possibility of such a mechanism, of an ultraviolet band whose energy variation with intermetallic distance is quite analogous to that of the color band of NiDMG[15] lends credence to such a view.

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[40] H. B. Gray (in "Transition Metal Chemistry," Vol. 1, R. C. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1965) reviews much of the evidence relevant to the ordering of the d orbitals in square-planar complexes. See ref 6 and 21 for more recent investigations that have a bearing on this problem.

[41] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, 4, 514 (1965).

[42] Drickamer and Zahner[43] have also reported a computed oscillator strength, which corresponds to a $|q|^2$ value of 0.24 A^2 for the $3d_{z^2} \rightarrow 4p_z$ transition, and indicate that this corresponds to about twice the intensity obtained for the color band in nickel nioxime in a sodium chloride pellet measurement. (Nickel nioxime is closely related to NiDMG, possessing a nickel–nickel spacing of 3.237 A and having its color-band absorption at 18.2 kK, according to Drickamer and Zahner.)

[43] H. G. Drickamer and J. C. Zahner, *Advan. Chem. Phys.*, 4, 161 (1962).

[44] Moncuit[7] also proposes a $d_{z^2} \rightarrow p_z$ transition to account for the "color band" in the rare earth platinocyanides and invokes an exciton shift to account for the crystal perturbations observed. Although the present work lends support to the basic assignment, it does not appear that exciton theory would provide an adequate mechanism for the intensity growth noted with decreasing interplanar spacing in the nickel glyoximates.

One may also inquire as to how this mechanism accounts for the changes seen in the in-plane spectrum on solid formation. The most logical bands to examine first in this respect are B(1) and B(2), which in the scheme put forth here involve the same excited orbital as the color band. As assigned here these absorptions may be expected to derive much of their intensity from the $\pi \rightarrow \pi^*$ components in their transition moments,[35] whose decrease as the b_{1u} excited orbital becomes more metallic would result in the observed decrease in intensity in the solid. One difficulty that arises in this connection, however, is that if a perturbation of the b_{1u} level accounts for the energy shift of the color band, then band B should shift a comparable amount which it does not. It may thus be that part of the energy perturbation of the color band arises from ground-state destabilization of the d_{z^2} orbital by similar filled orbitals on adjacent complexes. It is also possible, of course, that one is asking too much of a one-electron theory to give a quantitative accounting of this nature.

The loss of intensity in A is consistent with the general loss of in-plane intensity and this band borrowing from the other in-plane transitions. Its nonappearance in NiDMG could then be a combination of this effect and changes in the situation with respect to overlap with its neighbors. One may also note that a similar explanation will account for band C's intensity loss if it is in fact a forbidden transition. Finally, if the mixing of metal and ligand orbitals is sensitive to the solid-state perturbations, it is quite reasonable that band E should suffer intensity changes in the process.

As noted in the introduction, some form of intermetallic bonding has often in the past been invoked to account for the optical properties of NiDMG and related complexes. The present work has cast strong doubts on the assertion that the color band is unique to the crystal, which has been the most salient piece of evidence that has been put forth for such interaction. It may further be noted that nothing observed here requires, at the present level of our understanding at least, that one invoke such a mechanism. It may be noted in this respect that previous authors have reviewed other evidence for metal–metal interaction and found none of it compelling.[3,5] The most important points to be made in this regard are (1) there is nothing "unusual" about bands being polarized perpendicular to the molecular plane if one is dealing with other than strictly p_z molecular orbitals, (2) the "column-stacking" and low solubility of many square-planar complexes may simply be favored by electrostatic and packing considerations, regardless of any metal–metal effects, and (3) the striking optical properties of NiDMG may be a side effect of the stacking, not a necessary consequence of it,[33] and could in fact reflect antibonding, instead of, or as well as, bonding effects.

It may also be noted that the calculation of overlap integrals for various pairs of metal orbitals centered on adjacent nickel atoms in the NiDMG columns shows that, as one would expect, the 3d orbital overlap is quite small for the range of metal–metal distances encountered in this series, a circumstance which argues against "bond" formation in the ground state. Indeed, the observed Ni–Ni spacing of 3.25 A in NiDMG is considerably larger than that (2.30 A) which one would estimate from the covalent radii listed for Ni by Pauling[45] and metal–metal distances found in instances where direct metal–metal interaction is thought to occur.[46] If one examines the $4p_z$–$4p_z$ (σ) overlap, however, sufficiently large values are found to admit the possibility of some degree of delocalization in the excited state, although it is to be emphasized once again that no evidence for such effects is currently apparent.[47] Mixed crystal spectra of the type reported by Banks and Barnum[2b] and Basu, *et al.*,[3] could have an important bearing on this aspect of the problem, especially if they could be obtained in better resolution by using, for instance, single-crystal techniques.

Conclusion

The experimental situation that obtains with respect to these complexes has been greatly clarified by the work presented here, both with regard to the "single-molecule" spectra and those of the orthorhombic crystals. The interpretation of the free complex absorption has provided rather striking confirmation of the importance of low-energy metal-to-ligand charge-transfer transitions in complexes that possess unsaturation and the insights into the electronic structure of the complex that can be gained through their study, especially in the single crystal.

Although there are many aspects of the solid-state phenomena that remain to be explained, the present study has certainly brought out their nature in considerable detail and removed a number of misconceptions. Moreover, an explanation of the broad outlines of these effects has been put forth that can provide the basis for further study, both interpretive and experimental.

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(45) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(46) See, for example, F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965); and F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

(47) L. L. Ingraham (*Acta Chem. Scand.*, **20**, 283 (1966)) recently reported the results of a molecular orbital calculation on NiDMG. His findings support the contentions put forth in this paper concerning the possibilities of Ni–Ni interactions, in that he reports that they are at best slight in the ground state, but may occur in some excited states. It should be noted, however, that his assignments of band A and the color band differ sharply from those made in the present work and in the case of the color band the assignment is clearly incompatible with the polarization reported here. This again indicates the difficulties that surround *ab initio* calculations on complex systems such as these and emphasizes the need for accurate experimental assignments as a guide to the proper theoretical approach.