An Interpretation of the Circular Dichroism and Electronic Spectra of Salicylaldimine Complexes of Square-Coplanar Diamagnetic Nickel(II)

B. Bosnich

Contribution from the William Ramsay and Ralph Forster Laboratories, University College, London W.C. 1, England. *Received August 21, 1967*

Abstract: The electronic absorption spectrum and the associated circular dichroism of the complex N,N′-bis(salicylidene)-(−)-propylenediaminonickel(II), [Ni(−)pn(sal)$_2$], have been measured. The circular dichroism absorption reveals electronic transitions which are not resolved in the ordinary absorption spectrum and, in addition, allows for the identification of magnetic dipole transitions. A comparison of the two types of spectra shown by the free ligand (N,N′-bis(salicylidene)-(−)-propylenediamine) and its zinc complex with that of the nickel complex suggests a consistent explanation for the electronic provenance of the transitions in both the ligand and its metal complexes.

The electronic absorption spectra of square-coplanar salicylaldimine transition metal complexes have been the subject of a number of recent investigations[1−4] which have been mainly concerned with the assignment of the d–d absorption bands. It has been found that certain difficulties arise in the interpretation of the crystal field bands due, possibly, to the fact that intense absorption bands appear in the d–d absorption regions. In this note we outline what is believed to be a consistent interpretation of the d–d transitions, the charge-transfer transitions, and the first (complexed) ligand transition of the two square-coplanar diamagnetic nickel complexes, N,N′-bis(salicylidene)-(−)-propylenediaminonickel(II), [Ni(−)pn(sal)$_2$], and *trans*-bis(N-methylsalicylaldimino)nickel(II), *trans*-[Ni(mesal)$_2$]. Further, we wish to show the usefulness of circular dichroism spectra in revealing electronic transitions which are not resolved in the ordinary absorption spectra and also in assigning the nature of the electronic transitions.[5] For the purposes of assigning the spectra of the nickel complexes, we shall first discuss the electronic absorption and circular dichroism spectra of the free ligand and its zinc complex so that the effect of the divalent nickel ion on the absorption spectrum can be clearly distinguished from that of the ligand. Finally the assignments will be checked by comparing the spectra of the [Ni(−)pn(sal)$_2$] and *trans*-[Ni(mesal)$_2$] complexes.

1. The Electronic Absorption Spectrum and Circular Dichroism of the Ligand

The near-ultraviolet absorption spectrum and the associated circular dichroism of a methanol solution of the free ligand, N,N′-bis(salicylidene)-(−)-propylenediamine, derived from (−)-propylenediamine, is shown in Figure 1. It can be seen that there are two absorption bands below 35,000 cm^{-1}, both of which carry negative circular dichroism. As yet no rigorous spectroscopic assignments of these bands in salicylaldimines have been made, although molecular orbital calculations[6,7] indicate that the band at around 25,250 cm^{-1} is the n → π^* transition involving the promotion of one of the lone-pair electrons of the nitrogen atom to the antibonding π orbital associated with the azomethene group, while the 32,000-cm^{-1} band involves a $\pi \rightarrow \pi^*$ transition which includes the π-orbital functions of the azomethene group. We shall adopt these assignments here.

The reasons for assigning the 25,250-cm^{-1} band to a n → π^* transition are the following. Usually n → π^* transitions involving nitrogen atoms occur at lower energies and are less intense than the $\pi \rightarrow \pi^*$ transitions.[8] In acid solutions, the 25,250-cm^{-1} band "disappears"[9] (moves to higher energies). The behavior is characteristic of n → π^* transitions.[10] It is likely that strong internal hydrogen bonding[9] occurs in salicylaldimines, and it is possible to explain the observed solvent shifts of the 25,250-cm^{-1} band on this basis. In alcohols this band is clearly discernible; in dioxane it shifts to higher energies; in hexane it is "absent."[11] If it is assumed that the solvent can "compete" for the internal hydrogen atom connecting the hydroxyl group with the nitrogen lone pair, then we might expect that, in hydrogen-bonding solvents such as alcohols and, to a lesser extent, ethers, the amount of internal hydrogen-bond disruption would be greater than for inert solvents such as hexane. Thus we anticipate, as is observed, a correlation between the hydrogen-bonding capacity of the solvent and the position of the n → π^* transition. Finally, as we shall see in the next section, the 25,250-cm^{-1} band is "absent" in the zinc complex. This is expected on the grounds that complex formation, in a similar way to hydrogen bonding, will stabilize the energy of the lone pair of electrons.

In both the N-aryl and the N-alkyl anils, molecular orbital calculations[12] indicate that the lowest energy $\pi \rightarrow \pi^*$ transition involves molecular orbitals which originate from the C=N group and the benzene rings rather than those molecular orbitals which are essentially localized on the benzene rings. The first $\pi \rightarrow \pi^*$ transition[12] of the N-methyl anil occurs at around

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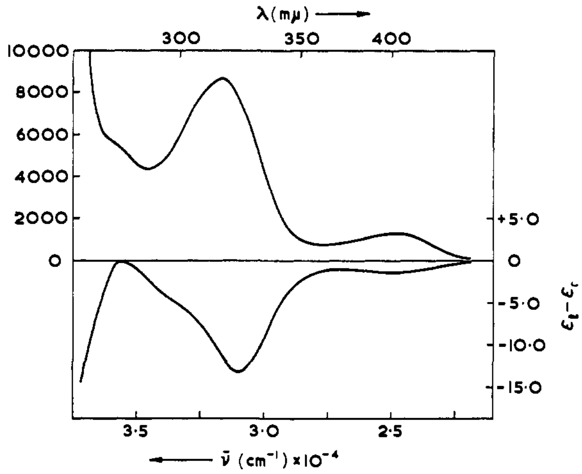

Figure 1. The absorption spectrum and the associated circular dichroism of the ligand N,N′-bis(salicylidene)-(−)-propylenediamine in methanol solution.

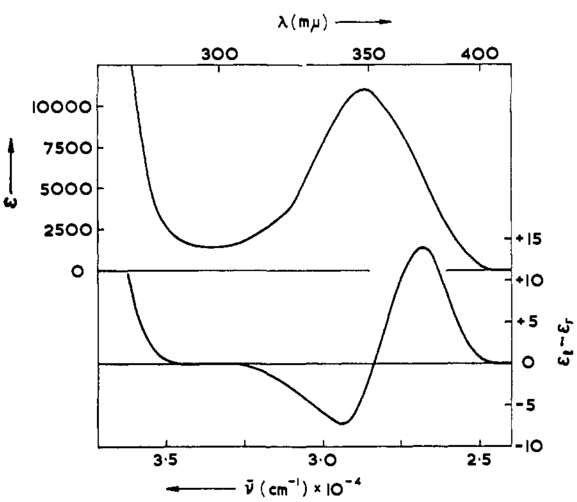

Figure 2. The absorption spectrum and the associated circular dichroism of the [Zn(−)pn(sal)$_2$] complex in methanol solution. The small shoulder at 32,000 cm^{-1} is most probably due to the free ligand which has partly (≈5%) dissociated from the zinc atom.

38,500 cm^{-1}. However, the N-alkylsalicylaldimines, possibly due to tautomerism,[9] display spectra[11] which are bodily shifted to lower energies; it is for this reason, together with the calculations that have been performed, that we assign, despite its appearance at somewhat low energies, the 32,000-cm^{-1} band to a $\pi \rightarrow \pi^*$ transition involving the azomethene group. It will be seen later that this assignment provides a consistent hypothesis for the interpretation of the spectra of salicylaldimine complexes. The absorption bands over 35,000 cm^{-1} are most probably those associated with the phenolic chromophore.

The highest point group to which N-alkyl salicylaldimine compounds can belong is C_s, and thus both the $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ transitions will be simultaneously electric and magnetic dipole allowed, but in both cases the electric and magnetic transition dipole vectors are orthogonal and thus their pseudo-scalar products vanish. In asymmetric molecules, however, the electric transition moment can be associated with a small parallel magnetic transition moment, and the magnetic dipole transitions can be associated with small parallel electric dipole moments. Thus, small rotational strengths are expected for both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

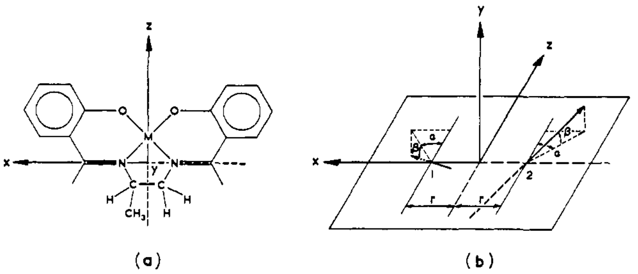

Figure 3. (a) A schematic structure of the N,N′-bis(salicylidene)-(−)-propylenediaminometal complex and the coordinate frame referred to in the text and (b) a pictorial representation of the transition dipole moments of the $\pi \rightarrow \pi^*$ transitions in one coupling mode. The other combination may be represented by reversing the direction of one arrow.

The circular dichroism shown by the ligand (Figure 1) undoubtedly arises from this second-order asymmetric perturbation by the asymmetric "center."

2. Absorption Spectrum and Circular Dichroism of the N,N′-Bis(salicylidene)-(−)-propylenediaminozinc(II) Complex

The near-ultraviolet spectrum of the complex N,N′-bis(salicylidene)-(−)-propylenediaminozinc(II), [Zn(−)-pn(sal)$_2$], in methanol is shown in Figure 2. It will be noticed that (a) the $n \rightarrow \pi^*$ of the ligand is "absent," (b) that the first $\pi \rightarrow \pi^*$ transition of the ligand is shifted to lower energies, and (c) the $\pi \rightarrow \pi^*$ at around 28,700 cm^{-1} is unsymmetrical. Gaussian analysis of the 28,700-cm^{-1} band indicates that it is constituted of two absorption bands. This is confirmed by the associated circular dichroism which, unlike the free ligand, shows positive and negative differential absorption in this region. The split $\pi \rightarrow \pi^*$ transition and the nearly equal positive and negative circular dichroism suggests the presence of exciton[13–15] (Davydov) interactions. We shall use this formalism in order to rationalize the spectra of the [Zn(−)pn(sal)$_2$] complex and certain bands that appear in the nickel complexes.

The crystal structure[16] of aquo-N,N′-bis(salicylidene)ethylenediaminozinc(II) shows that the two nitrogen atoms and two oxygen atoms are in one plane and that, as is true for all known structures[17] of *cis*-bis(salicylaldimine) complexes, the two azomethene groups are essentially collinear (Figure 3). If the azomethene groups were isolated from the benzene rings, the transition dipole moment vector of the $\pi \rightarrow \pi^*$ transition would be polarized along the carbon–nitrogen internuclear bond axis. However, interaction with the benzene ring will cause the vector to be skewed away from the carbon–nitrogen bond axis. We define this horizontal (x,z plane) angle as α, and, if the azomethene groups are not coplanar, we define the vertical (y,z plane) angle as β (see Figure 3b).

The ground-state wave function, Ψ_0, for the two azomethene chromophores is

$$\Psi_0 = \varphi_1\varphi_2 \tag{1}$$

where φ_1 and φ_2 represent the ground-state wave func-

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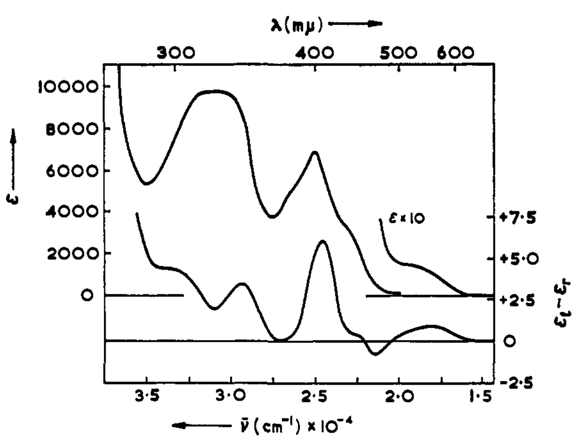

Figure 4. The absorption spectrum and associated circular dichroism of the [Ni(−)pn(sal)$_2$] complex in methanol solution.

tions for the chromophores 1 and 2, respectively (Figure 3b). The two excited state wave functions are

$$\begin{aligned}\Phi_1 &= \varphi_1'\varphi_2 \\ \Phi_2 &= \varphi_1\varphi_2'\end{aligned} \qquad (2)$$

where the primes represent the excited-state wave functions. These two excited-state functions may be combined, giving, assuming zero overlap, the two wave functions

$$\Psi_A = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2) \qquad (3)$$

$$\Psi_B = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2) \qquad (4)$$

In Figure 3b we show pictorially the transition dipole moments of the excitation $\Psi_0 \rightarrow \Psi_A$. Transitions occur between the totally symmetric ground state Ψ_0 and the excited states Ψ_A and Ψ_B. The $\Psi_0 \rightarrow \Psi_A$ transition is z polarized and the $\Psi_0 \rightarrow \Psi_B$ transition is x,y polarized.

The dipole strength in the z direction, D_z, is given by

$$D_z = 2p^2 \cos^2\beta \cos^2\alpha \qquad (5)$$

where p is the transition dipole moment of one "azomethene" chromophore. For the particular absolute configuration of the chromophores shown in Figure 3b, the rotational strength in the z direction, R_z, is given by

$$R_z = -2\pi\bar{\nu}rp^2 \cos\alpha \cos\beta \sin\beta \qquad (6)$$

where $\bar{\nu}$ is the frequency in wave numbers of the $\pi \rightarrow \pi^*$ transition of the monomeric unit and r is half the distance (radius) between the "centers" of the two excitation moments. Similarly, the dipole strength $D_{x,y}$ and the rotational strength $R_{x,y}$ in the x,y plane are given by

$$D_{x,y} = 2p^2(\cos^2\beta \sin^2\alpha + \sin^2\beta) \qquad (7)$$

and

$$R_{x,y} = +2\pi\bar{\nu}rp^2 \cos\alpha \cos\beta \sin\beta \qquad (8)$$

It will be seen that when $\beta = 0$ and/or $\alpha = 90°$, the exciton rotational strengths vanish.

Thus we expect on this model that the $\pi \rightarrow \pi^*$ transition should split into two components and that each component should carry equal but opposite rotational strength. For the particular absolute configuration of the chromophores shown in Figure 3b, the point-dipole point-dipole approximation,[18] which is correct as far as direction (as opposed to total magnitude) is concerned, gives the z-polarized component occurring at higher energies than the x,y-polarized component.

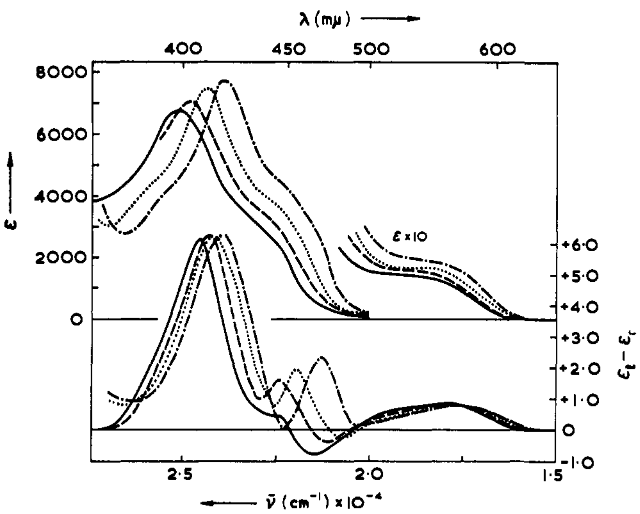

Figure 5. The absorption spectrum and associated circular dichroism of the [Ni(−)pn(sal)$_2$] complex dissolved in various solvents. The curves are (——) methanol, (---) nitromethane, (· · · ·) dichloromethane, and (—·—) benzene.

Inspection of Figure 2 will reveal that the expectations of the exciton theory for the first $\pi \rightarrow \pi^*$ transition are essentially borne out with respect to both dipole and rotational spectra. The fact that the negative component is weaker than the lower energy positive circular dichroism is probably due to overlap with positive high-energy circular dichroism absorptions. This exciton interpretation suggests that the [Zn(−)pn(sal)$_2$] complex in methanol solution is not coplanar but in a somewhat distorted tetrahedral structure, the molecular framework of which, when viewed down the z axis (Figure 3), presents essentially a sinistral chirole.

3. Absorption Spectrum and Circular Dichroism of the N,N′-Bis(salicylidene)-(−)-propylenediaminonickel(II) Complex

The electronic absorption spectrum and associated circular dichroism of a methanol solution of the [Ni(−)-pn(sal)$_2$] complex is shown in Figure 4. There are five intense absorption bands (not all fully resolved) and a weak low-energy band. A comparison of the spectra of the free ligand and its zinc complex suggests that the two (unresolved) bands at around 31,000 cm^{-1} originate from the first $\pi \rightarrow \pi^*$ transition of the ligand. If, as is probable, the [Ni(−)pn(sal)$_2$] complex is planar in solution, the strong positive–negative exciton circular dichroism should not appear because the angle β will be close to zero (eq 6 and 8). It can be seen that the two bands around 31,000 cm^{-1} are probably both positive and their rotational strengths are of an order of magnitude less than the corresponding bands of the zinc complex. The symmetric and antisymmetric exciton coupling modes, however, give nonzero values to the dipole strength, the transition moments of which are in the z and x directions (Figure 3). On the point-dipole point-dipole approximation the z-polarized transition should occur at higher energies than the x-polarized transition. The ratio of the dipole strengths is given by

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[18] E. G. McRae and M. Kasha, "Physical Processes in Radiation Biology," Academic Press Inc., New York, N. Y., 1964, p 23.

$$D_z/D_x = \cos^2 \alpha/\sin^2 \alpha \quad (9)$$

and since the two $\pi \rightarrow \pi^*$ transitions at around 31,000 cm^{-1} have approximately the same intensity, we conclude that the transition dipole vector of this transition is inclined at an angle (α) of about 45°.

In the lower energy region the circular dichroism spectrum reveals more transitions than are resolved in the ordinary absorption. We have been able to investigate this apparent discrepancy more closely by observing the effects that occur in various solvents. Figure 5 shows the absorption and circular dichroism spectra of the [Ni(−)pn(sal)$_2$] complex in various solvents, and it can be seen that there is a general red shift of both spectra with decreasing polarity of the solvent. Of particular interest is the region of the circular dichroism between 20,000 and 23,000 cm^{-1} where, as the spectra shift to the red, the positive peak increases at the expense of the negative peak. This information allows us to attempt the Gaussian analysis of the circular dichroism spectrum which is shown in Figure 6, where it is clear that there are at least six absorption bands in this spectral region. Since none of these transitions occurs in either the free ligand or its zinc complex, we ascribe their origin to excitations within the d-electron manifold of the nickel atom (d–d transitions) and to excitations involving both the metal and the ligand (charge-transfer transitions). By making these assumptions about the general provenance of the transitions shown resolved in Figure 6, symmetry theory and certain rudimentary energy arguments allow us to discuss their detailed origins and positions.

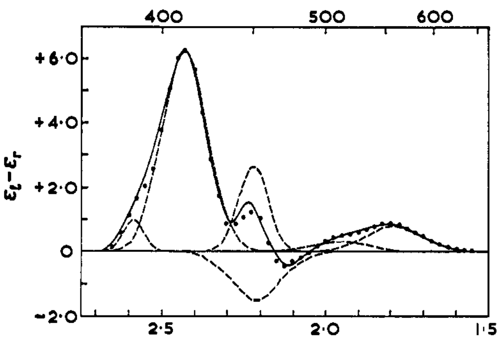

Figure 6. A Gaussian analysis of the circular dichroism spectrum of the complex [Ni(−)pn(sal)$_2$] in methanol solution. The solid curve is the measured spectrum; the dashed curves are the Gaussian components; the dots represent the Gaussian summations. The discrepancy between the summed curve and the measured curve is within the experimental errors.

If only the donor atoms are considered, the [Ni(−)pn(sal)$_2$] complex belongs to the point group C_{2v} and the complex *trans*-[Ni(mesal)$_2$], whose spectrum we shall discuss presently, belongs to the D_{2h} point group. In order that the transitions between orbital states may be discussed in a consistent way, it is convenient to refer the d orbitals in the C_{2v} and D_{2h} point groups to those which are defined by the point group D_{4h}. Table I shows how the original D_{4h} d orbitals form irreducible representations of C_{2v} and D_{2h}. For this purpose we have used the reference frames shown in Figure 7.

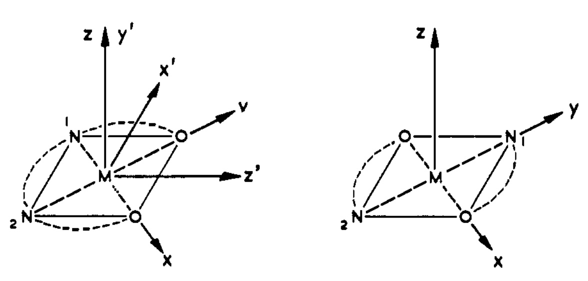

Figure 7. Schematic drawings of (a) the [Ni(−)pn(sal)$_2$] complex and (b) the *trans*-[Ni(mesal)$_2$] complex. The coordinates X, Y, Z are those of the D_{4h} and D_{2h} point groups and the X', Y', Z' coordinates refer to those of the C_{2v} point group. These coordinates have been used in constructing Table I, and the numbering of the nitrogen atoms is that used in constructing the ligand group orbitals.

Approximate molecular orbital calculations[19,20] and the crystal field theory[21] both predict that, in square-coplanar diamagnetic d^8 complexes, the d orbitals should lie in the following energy order: $d_{x^2-y^2} > d_{xy} > d_{yz}, d_{xz}$. These positions of the four orbitals have been confirmed by experimental studies[22–24] on the [PtCl$_4$]$^{2-}$ ion. The position of the d_{z^2} orbital, however, remains uncertain, although it is likely that it is close to the d_{xz}, d_{yz} pair.

Table I. Transformation Properties of the D_{4h} d Orbitals in the Point Groups C_{2v} and D_{2h}[a]

D_{4h}		C_{2v}		D_{2h}	
Rep	d orbital	Rep	d orbital	Rep	d orbital
a_{1g}	d_{z^2}	a_1	d_{z^2}	a_g	d_{z^2}
b_{1g}	$d_{x^2-y^2}$	b_1	$d_{x^2-y^2}$	a_g	$d_{x^2-y^2}$
b_{2g}	d_{xy}	a_1	d_{xy}	b_{1g}	d_{xy}
	d_{xz}	a_2	$1/\sqrt{2}(d_{xz} - d_{yz})$	b_{2g}	d_{xz}
e_g	d_{yz}	b_2	$1/\sqrt{2}(d_{xz} + d_{yz})$	b_{3g}	d_{yz}

[a] See Figure 7 for coordinate convention.

The low-energy absorption band of [Ni(−)pn(sal)$_2$] occurring as a shoulder at around 18,000 cm^{-1} (Figure 4) is weak in intensity and carries strong circular dichroism in the sense that the dissymmetry factor[25] is large. This band, therefore, is most probably a magnetic dipole-allowed d–d transition. The polarized spectrum[1] of the *trans*-[Ni(mesal)$_2$] complex and the theoretical calculations[19–21] all support our assumption that this band should be assigned to the $d_{xy} \rightarrow d_{x^2-y^2}$ ($^1A_1 \rightarrow {}^1B_1$) transition. There are, within the d-electron manifold, two more magnetic dipole-allowed transitions which should exhibit circular dichroism of comparable magnitude, namely, the transitions $(1/\sqrt{2})(d_{xz} - d_{yz}) \rightarrow d_{x^2-y^2}$ ($^1A_1 \rightarrow {}^1B_2$) and $(1/\sqrt{2})(d_{xz} + d_{yz}) \rightarrow d_{x^2-y^2}$ ($^1A_1 \rightarrow {}^1A_2$). The semiempirical molecular orbital theory of Yamatera,[26] when applied to square-coplanar complexes, indicates that these two transitions should be essentially degenerate in the [Ni(−)pn(sal)$_2$] complex. In addition, experimental studies[27] on the platinum(II) complexes have shown that the splitting

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(19) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

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(26) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(27) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

of the "$^1A_{1g} \rightarrow {}^1E_g$ transition" in these complexes must be less than the band width. Square-coplanar diamagnetic nickel(II) complexes all show[28] a band (the "yellow band") at around 22,000 cm^{-1} which is magnetic dipole allowed.[29] We therefore assign the negative circular dichroism band at around 22,000 cm^{-1} (Figure 6) to the two-component magnetic dipole-allowed transition $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ which is not resolved in the ordinary spectrum of [Ni(−)pn(sal)$_2$]. It seems unlikely that this band originates from the charge-transfer transitions since, with solvent changes, this band remains relatively constant in position, while the three positive circular dichroism bands shift correspondingly with the three intense bands in this region (Figure 5). At around 19,500 cm^{-1} the weak positive band is not seen in the ordinary absorption but is clearly seen in the circular dichroism spectrum (Figure 6). There are two possible assignments for this transition; either it is the $d_{z^2} \rightarrow d_{x^2-y^2}$ ($^1A_1 \rightarrow {}^1B_1$) transition or it is a single–triplet-state transition. We have no firm evidence to support either assignment, but if it were a spin-"forbidden" transition, we might expect to find other singlet–triplet-state transitions resolved in the spectrum. It is because of the apparent absence of other spin-forbidden bands in the spectrum that we prefer to assign this 19,500-cm^{-1} band to the spin-allowed $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation which can borrow magnetic dipole character by mixing with the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in the presence of the C_{2v} field.

We are now left with the assignment of the three intense bands which, in methanol, occur at around 22,250, 24,250, and 25,750 cm^{-1}. Their intensity indicates that they are electric dipole-allowed and not d–d transitions; a comparison of the spectrum of the free ligand and its zinc complex suggests that they occur because of the presence of the nickel atom, and their positions are highly dependent upon solvent. All these observations suggest that these three transitions are charge-transfer bands which involve both the nickel atom and the ligand. There are two possible types of charge-transfer spectra in the [Ni(−)pn(sal)$_2$] complex; (a) excitation of the lone-pair electrons of the donor oxygen atoms to higher unfilled levels, (b) the excitation of filled d-orbital electrons to the empty antibonding π orbitals of the "azomethene chromophore." The first possibility seems unlikely, since these types of charge-transfer spectra usually occur[30] at much higher energies than three intense bands occurring in the region 21,000–27,000 cm^{-1} in the [Ni(−)pn(sal)$_2$] complex. We therefore assign these bands as $d \rightarrow \pi^*$ charge-transfer transitions. In order to be more precise in these assignments, we need to define the upper states more closely.

If we assume that the two nitrogen atoms are equivalent in [Ni(−)pn(sal)$_2$], and we define the empty π orbitals (which are part of a molecular orbital) on the nitrogen atoms as ϕ_1 and ϕ_2, we obtain, after neglecting overlap, the two combined orbitals Ψ_{a_2} and Ψ_{b_2}

$$\Psi_{a_2} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$$\Psi_{b_2} = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

The subcripts a_2 and b_2 refer to the irreducible representations of C_{2v} under which the orbitals transform and the subscripts 1 and 2 refer to the convention in Figure 7. These two wave functions can combine with the nickel d orbitals which are of the same symmetry (Table I). We shall assume that the *relative* energy positions of the final two molecular orbitals formed by $d\pi$–$p\pi$ overlap can be defined by a single resonance integral β as

$$\beta = \langle d | H | p \rangle$$

where d and p represent the appropriate d-orbital and ligand-orbital wave function, respectively, and H is the appropriate Hamiltonian. Then it is readily shown, or seen by inspection, that the two final states, in this approximation, are essentially degenerate. We are now in a position to specify the three charge-transfer bands.

Remembering that we have assigned the filled d orbitals in the following order $d_{xy} > d_{z^2} > (1/\sqrt{2})(d_{xz} - d_{yz}), (1/\sqrt{2})(d_{xz} + d_{yz})$, of which the last two are essentially degenerate, we assign the three charge-transfer bands in the following way. The band at around 22,250 cm^{-1} is ascribed to the transitions $d_{xy} \rightarrow \Psi_{a_2}, \Psi_{b_2}$ ($^1A_1 \rightarrow {}^1A_2$, $^1B_2$). The band at around 24,250 cm^{-1} is ascribed to the transitions $d_{z^2} \rightarrow \Psi_{a_2}, \Psi_{b_2}$ ($^1A_1 \rightarrow {}^1A_2$, $^1B_2$). Finally, the band at around 25,750 cm^{-1} is assigned to the transitions $(1/\sqrt{2})(d_{xz} - d_{yz}), (1/\sqrt{2})(d_{xz} + d_{yz}) \rightarrow \Psi_{a_2}, \Psi_{b_2}$ ($^1A_1 \rightarrow {}^1A_1$, $^1B_1$, $^1B_1$, $^1A_1$). It will be noted that in each of these groups of transitions there is always one component which is formally electric dipole allowed. In making these assignments of the charge-transfer bands, we have assumed that configuration interaction is sufficiently small so as not to alter the ordering or cause a splitting of the orbital states which is greater than the detectability of these measurements. A consideration of the band widths and the extensive overlap which occurs in these transitions suggests that the configurational interactions would have to be somewhat greater than 2000 cm^{-1} to be detected clearly. A value of this order of magnitude, however, is perhaps not unreasonable[31] for these transitions, and we need further supporting evidence in order to make the assignments plausible. For this purpose we have chosen the complex *trans*-[Ni(mesal)$_2$] which should be electronically similar to the [Ni(−)pn(sal)$_2$] system, but which imposes certain stringent symmetry conditions upon both the exciton and charge-transfer transitions.

4. The Electronic Spectrum of the *trans*-Bis(N-methylsalicylaldimino)nickel(II) Complex

The square-coplanar diamagnetic complex [Ni(mesal)$_2$] has its donor nitrogen and oxygen atoms *trans*, and the N-methylsalicylaldimine ligands are essentially planar in the crystal.[32] The solution and solid spectra are very similar, which suggests that the geometry (D_{2h}) is the same in solution as it is in the solid.

As in the case of the [Ni(−)pn(sal)$_2$] complex, the $\pi \rightarrow \pi^*$ transition of the ligand will have two exciton coupling modes; namely, an in-phase combination ($A_g \rightarrow B_{3u}$) and an out-of-phase combination ($A_g \rightarrow$

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[28] See, for example, B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 4, 1109 (1965).

[29] B. Bosnich, J. H. Dunlop, and R. D. Gillard, *Chem. Commun.*, 274 (1965).

[30] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

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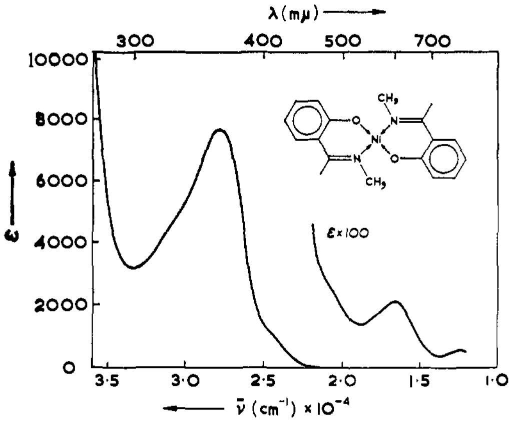

Figure 8. The absorption spectrum of the *trans*-[Ni(mesal)$_2$] complex dissolved in methanol solution. The structure of the complex is shown in the inset.

B_{1g}) which will occur at lower and higher energies, respectively. Only one of these ($A_g \rightarrow B_{3u}$) is electric dipole allowed, and thus, unlike the [Ni(−)pn(sal)$_2$] complex, we expect to find only one strong exciton transition in the *trans*-[Ni(mesal)$_2$] complex. An analogous symmetry restriction is placed upon the charge-transfer bands.

The two π orbitals on the nitrogen atoms can be combined into two ligand molecular orbitals; namely, $\Psi_{b3g} = (1/\sqrt{2})(\phi_1 - \phi_2)$ and $\Psi_{b1u} = (1/\sqrt{2})(\phi_1 + \phi_2)$. (The symbolism is analogous to that used for the [Ni(−)pn(sal)$_2$] system and refers to the convention shown in Figure 7.) Reference to Table I shows that only the Ψ_{b3g} orbital is capable of bonding with the metal d orbitals; the Ψ_{b1u} orbital is nonbonding as far as d orbitals are concerned. Thus, unlike the [Ni(−)pn(sal)$_2$] case, the higher empty orbitals involved in the charge-transfer transitions of *trans*-[Ni(mesal)$_2$] should be split. However, this splitting is expected to be small since, as has been shown,[27] the splitting of the appropriate d orbitals is small. The nature of the charge-transfer transitions can now be defined in a similar way to that used in the [Ni(−)pn(sal)$_2$] complex.

Excitations from the even d orbitals to the Ψ_{b3g} level are all electric dipole forbidden and therefore would not be expected to be observed in the charge-transfer region. The transitions, $d_{z^2} \rightarrow \Psi_{b1u}$ ($^1A_g \rightarrow {}^1B_{1u}$) and d_{xz}, $d_{yz} \rightarrow \Psi_{b1u}$ ($^1A_g \rightarrow {}^1B_{3u}$, $^1B_{2u}$) are all electric dipole allowed, but the transition $d_{xy} \rightarrow \Psi_{b1u}$ ($^1A_g \rightarrow {}^1A_u$) is not. If the splitting of the d_{xz} and d_{yz} orbitals is less than the band width of the transitions, we should expect, in contrast to the [Ni(−)pn(sal)$_2$] complex, only two strong charge-transfer transitions. Since the average ligand field is the same for the two complexes *trans*-[Ni(mesal)$_2$] and [Ni(−)pn(sal)$_2$], we expect that the d → d transitions should occur in very similar positions.

In Figure 8 we show the absorption spectrum of *trans*-[Ni(mesal)$_2$] in methanol solution. It will be evident that the general appearance of the spectrum is considerably different from that displayed by the [Ni(−)pn(sal)$_2$] complex. The weak band at around 12,000 cm^{-1} is assigned to a singlet–triplet-state transition ($^1A_g \rightarrow {}^3B_{1g}$) which is related to the orbital excitation $d_{xy} \rightarrow d_{x^2-y^2}$. We have not been able to detect this spin-"forbidden" band in the [Ni(−)pn(sal)$_2$] complex. It has been shown[1] that the transition at around 16,500 cm^{-1} is the $^1A_g \rightarrow {}^1B_{1g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) d–d excitation and that the shoulder at around 20,000 cm^{-1} represents the $^1A_g \rightarrow {}^1B_{3g}$ transition. However, the latter assignment is less definite because of the overlap with the charge-transfer system, and it is probable, for reasons outlined previously, that the weak shoulder at around 20,000 cm^{-1} represents the two-component transition $^1A_g \rightarrow {}^1B_{2g}$, $^1B_{3g}$. Thus, as expected, the d–d transitions of the *trans*-[Ni(mesal)$_2$] occur in similar positions to those of the [Ni(−)pn(sal)$_2$] complex. It is in the charge-transfer region and in the region of the first ligand transition that differences are expected to occur between the two complexes.

A Gaussian analysis of the strong absorptions in the region from 22,000 to 33,000 cm^{-1} of the *trans*-[Ni(mesal)$_2$] complex shows that the absorption manifold can be identically reproduced by assuming that only three strong absorption bands occur in this region. The peak maxima of the Gaussian curves correspond roughly in position to the central peak and the two wing shoulders seen in the unresolved spectrum. From the foregoing arguments, this is exactly the number of strong bands expected for this complex, and we assign them in the following way. The transition at around 24,000 cm^{-1} is ascribed to the $d_{z^2} \rightarrow \Psi_{b1u}$ ($^1A_g \rightarrow {}^1B_{1u}$) excitation. The band at around 27,500 cm^{-1} is ascribed to the two-component excitation d_{xz}, $d_{yz} \rightarrow \Psi_{b1u}$ ($^1A_g \rightarrow B_{3u}$, $^1B_{2u}$). Finally, the band at around 30,500 cm^{-1} is assigned to the electric-dipole-allowed exciton coupling mode ($A_g \rightarrow B_{3u}$) which arises from the "azomethene" $\pi \rightarrow \pi^*$ excitations.

Experimental Section

The ligand N,N′-bis(salicylidene)-(−)-propylenediamine and its zinc and nickel complexes[33] and the *trans*-[Ni(mesal)$_2$] complex[34] were prepared and purified by methods described elsewhere. The Gaussian curves were constructed with the aid of mathematical tables.[35] The absorption spectra were measured using a Unicam S.P. 800B (recording) spectrophotometer, and the circular dichroism spectra were measured using a Roussel-Jouan Dichrographe (sensitivity 1.5 × 10^{-4}).

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