

smaller contact shifts for hydrogen must result from smaller values for $|\psi_{(O)}|^2$. There are two effects which could produce smaller values for $|\psi_{(O)}|^2$ for hydrogen: (1) a larger coefficient in the unpaired electron wave function for the 2s orbital of the heavy element than for the 1s orbital of hydrogen, (2) the larger value of $|\psi_{(O)}|^2$ for the 2s atomic orbital of ^{13}C , ^{14}N , and ^{17}O than for the 1s atomic orbital of ^1H . The first effect will certainly dominate whenever the nucleus being examined is the donor atom, since the wave function of the unpaired electron on the metal will mix predominantly with the ligand lone pair orbital which will have a large contribution from the donor atom. This probably accounts for the apparent contact shift observed for ^{14}N in $\text{Eu}(\text{dpm})_3(\text{py})_2$.⁶³ The second effect is probably responsible for the generally larger ^{13}C contact shifts because even if the ^1H and ^{13}C s orbital coefficients are comparable, as they often are, the larger values of $|\psi_{(O)}|^2$ for the ^{13}C 2s atomic orbital will tend to make the contact shift larger for ^{13}C . It has been pointed out^{65,66} that values of $|\psi_{(O)}|^2$ for valence s

orbitals increase as the atomic number increases. Therefore there is good reason to believe that proton shifts will be largely free from contamination by a Fermi contact contribution but that this may not be true for heavier nuclei.⁶⁷

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(67) NOTE ADDED IN PROOF. Recent experiments with the substrates pyridine, 4-methylpyridine, and 3,5-dimethylpyridine in Freon 12 at temperatures as low as -150° fail to reveal doubling of the ortho peaks or any splitting of the chelate protons. These results suggest that the barrier to rotation model we had advocated earlier [R. E. Cramer and R. Dubois, *J. Chem. Soc., Chem. Commun.*, 936 (1973)] may not be correct. The doubling observed for the ortho peaks of 3-pic may instead be due to a Fermi contact interaction. However the fact that the separation of the ortho peaks of $\text{Eu}(\text{dpm})_3(3\text{-pic})_2$ is solvent dependent, being 18 ppm in CS_2 but only 8 ppm in CCl_2F_2 at -120° , suggests that the splitting may be due to unequally populated conformers. Further experiments are in progress to resolve this matter.

Magnetic Circular Dichroism of Some Complexes of Nickel(II) with Schiff Bases

Hajime Katô* and Takashi Sakamoto

Contribution from the Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657, Japan. Received August 16, 1973

Abstract: Magnetic circular dichroism (MCD) data of bis(*R-N*-salicylaldehyde)nickel(II) complexes ($\text{R} = \text{H}, \text{OH}, \text{Me}, \text{Ph}, o\text{-tolyl}, m\text{-tolyl}, p\text{-tolyl}$) and bis(salicylaldehyde)ethylenediaminenickel(II) in chloroform and pyridine solutions are presented and analyzed. The MCD of an allowed transition ${}^3\text{A}_{2g} \rightarrow {}^8\text{T}_{1u}$ of the paramagnetic and octahedral bispyridine adduct shows the negative sign of $[\theta]_M$ at *ca.* 26,000 cm^{-1} . The MCD of the high-intensity bands of $\text{Ni}(\text{Sal-}N\text{-}o\text{)Tol}_2$ in chloroform, which is diamagnetic planar, shows a negative *A* term pattern at *ca.* 29,500 cm^{-1} and a positive *B* term pattern at *ca.* 23,000 cm^{-1} . On the basis of the analysis on the sign and magnitude of the MCD, the band at *ca.* 29,500 cm^{-1} is assigned to the transition ${}^1\text{A}_g \rightarrow {}^1\text{B}_u(\sigma, x), {}^1\text{B}_u(\sigma, y); e_u(\sigma) \rightarrow b_{1g}-(d_{x^2-y^2})$ and the band at *ca.* 23,000 cm^{-1} is assigned to the transition ${}^1\text{A}_g \rightarrow {}^1\text{A}_u(\pi^*, z); a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*, z)$.

Schiff base complexes of nickel(II) are of particular interest because of the variety of spatial configurations and multiplicities of the ground state, and a number of studies on these complexes have been reported.¹⁻⁶ However, the interpretation of spectra, especially of the strong absorption bands, is insufficient and left unsettled. The usefulness of MCD in assigning the nature of electronic transitions has been extensively demonstrated.⁷⁻¹⁰ In this paper, we report

* Ramsay Fellow.

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the MCD spectra of some complexes of nickel(II) with Schiff bases in "noncoordinating" solvent, chloroform, and in "coordinating" solvent, pyridine. The sign and magnitude of MCD will help considerably in assigning the transitions and in interpreting the electronic structure.

Experimental Section

The following compounds used in this study were prepared and recrystallized according to previously reported procedures: bis(salicylaldehyde)nickel(II),¹¹ bis(salicylaldehyde)nickel(II),¹² bis(*N*-methylsalicylaldehyde)nickel(II),¹³ bis(*N*-phenylsalicylaldehyde)nickel(II),¹⁴ bis(*N*-*o*-tolylsalicylaldehyde)nickel(II),¹⁴ bis(*N*-*m*-tolylsalicylaldehyde)nickel(II),¹⁴ bis(*N*-*p*-tolylsalicylaldehyde)nickel-

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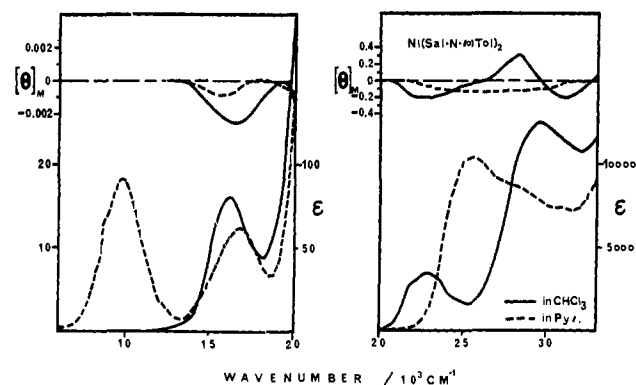


Figure 1. MCD and absorption spectra of bis(*N*-*o*-tolylsalicylaldimine)nickel(II) in chloroform and pyridine at room temperature. $[\theta]_M$ is molar ellipticity (defined as in natural optical activity in degree decimeter⁻¹ mole⁻¹ per gauss in the direction of the light beam). ϵ is the molar extinction coefficient. The magnitudes in the region 5000–20,000 cm^{-1} are shown on the right for chloroform solution and on the left for pyridine solution.

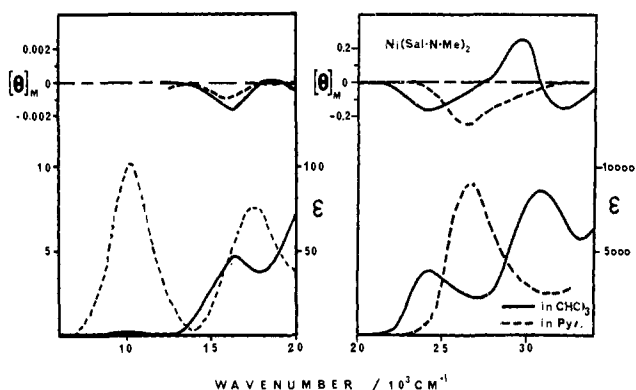


Figure 2. MCD and absorption spectra of bis(*N*-methylsalicylaldimine)nickel(II). The magnitudes of ϵ in the region 5000–20,000 cm^{-1} are shown on the right for chloroform solution and on the left for pyridine solution.

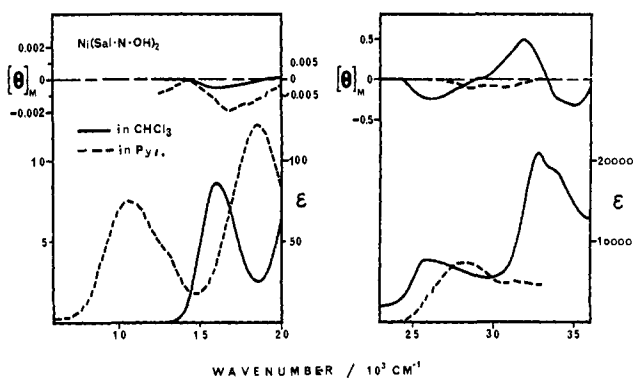


Figure 3. MCD and absorption spectra of bis(salicylaldoxime)nickel(II). The magnitudes of $[\theta]_M$ and ϵ in the region 5000–20,000 cm^{-1} are shown on the right for chloroform solution and on the left for pyridine solution.

(II),¹⁴ and bis(salicylaldehyde)ethylenediiminickel(II).¹⁵ These are abbreviated hereafter as Ni(Sal-*N*-H)₂, Ni(Sal-*N*-OH)₂, Ni(Sal-*N*-Me)₂, Ni(Sal-*N*-Ph)₂, Ni(Sal-*N*-*o*Tol)₂, Ni(Sal-*N*-*m*-Tol)₂, Ni(Sal-*N*-*p*-Tol)₂, and Ni(Sal₂en). The absorption and MCD spectra of these compounds in solvents, pyridine and chloroform, were measured at room temperature in a manner described

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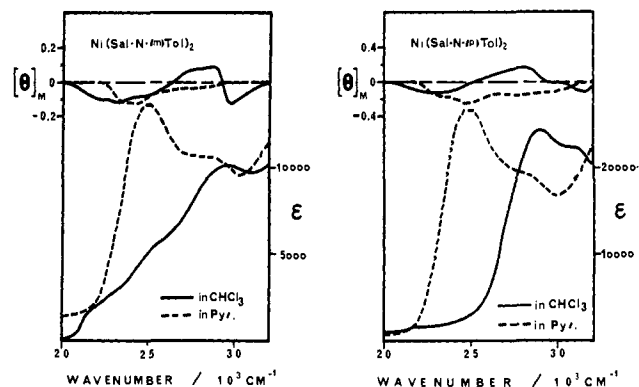


Figure 4. MCD and absorption spectra of bis(*N*-*m*-tolylsalicylaldimine)nickel(II) and bis(*N*-*p*-tolylsalicylaldimine)nickel(II).

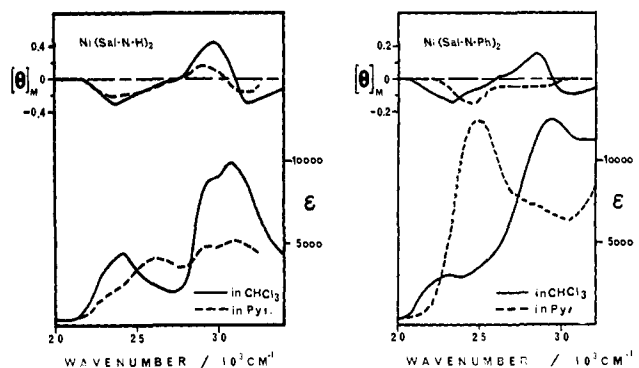


Figure 5. MCD and absorption spectra of bis(salicylaldehyde)nickel(II) and bis(*N*-phenylsalicylaldimine)nickel(II).

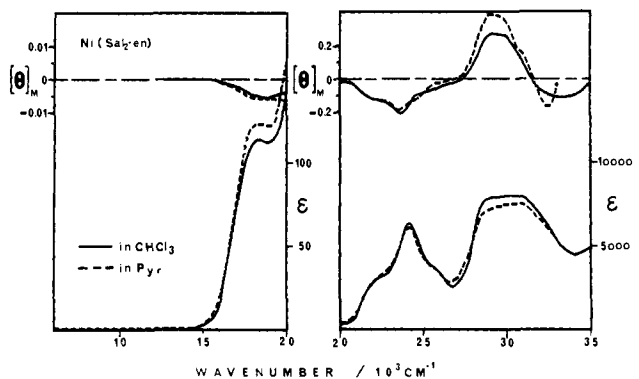


Figure 6. MCD and absorption spectra of bis(salicylaldehyde)ethylenediiminickel(II).

previously.^{16,17} These results together with the corresponding absorption spectra measured on a JASCO J-10 spectrometer are displayed in Figures 1–6. Because of our instrumental restriction, we could not measure the MCD spectra in the frequency region lower than 12,500 cm^{-1} . The MCD data should be accurate to better than $\pm 20\%$ since the signal-to-noise ratio was not so favorable in these spectra.

Discussion

Some Schiff base complexes of nickel(II), which are diamagnetic in the solid state, were observed to be paramagnetic in pyridine solution.¹⁸ It has been established that the paramagnetism results from the reaction

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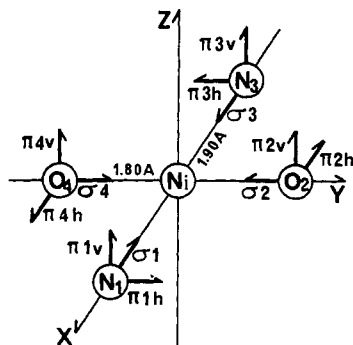


Figure 7. Geometry and coordinate system for the σ - and π -molecular orbitals of NiN_2O_2 .

pected to be contiguous to each other. As the two states are close in energy, the B term for the transition to one of the states should arise principally from the mixing of the other neighboring state.

Let us now calculate the largest contribution to the B term, which arises from the mixing of only one level closest to the excited state. Then, $[\theta]_M$ for each transition is approximately given by

$$[\theta(^1A_g \rightarrow ^1B_u(x))]_M = - (72Nf_2/\hbar c) (1/3) \text{Im} \{ \langle ^1B_u(x) | \mu_z | ^1B_u(y) \rangle \langle ^1A_g | P_x | ^1B_u(x) \rangle \times \langle ^1B_u(y) | P_y | ^1A_g \rangle / \delta E(^1B_u(y) - ^1B_u(x)) \} \quad (1)$$

$$[\theta(^1A_g \rightarrow ^1B_u(y))]_M = - [\theta(^1A_g \rightarrow ^1B_u(x))]_M \quad (2)$$

$$[\theta(^1A_g \rightarrow ^1A_u(z))]_M = - (72Nf_2/\hbar c) \times (1/3) \text{Im} \{ \langle ^1A_u(z) | \mu_y | ^1B_u(x) \rangle \langle ^1A_g | P_z | ^1A_u(z) \rangle \times \langle ^1B_u(x) | P_x | ^1A_g \rangle / \delta E(^1B_u(x) - ^1A_u(z)) - \langle ^1A_u(z) | \mu_x | ^1B_u(y) \rangle \langle ^1A_g | P_z | ^1A_u(z) \rangle \langle ^1B_u(y) | P_y | ^1A_g \rangle / \delta E(^1B_u(y) - ^1A_u(z)) \} \quad (3)$$

where N , P , μ , and f_2 are defined in ref 16.

In order to predict the absolute sign of $[\theta]_M$ for each transition, it is necessary to evaluate the matrix elements in eq 1-3. The structure of the diamagnetic $\text{Ni}(\text{Sal-N-Me})_2$ molecule has been determined by X-ray methods.²⁵ The Ni-O and Ni-N bond lengths are 1.80 and 1.90 Å, respectively. The O-Ni-N angle is 96°. In setting up molecular orbitals for the ligand, let us consider only four atoms which are bonded directly to the central Ni(II) ion. We assume the geometry and the orbital coordinate as shown in Figure 7. The following types of the charge transfer can occur in general: the metal to ligand transitions ($M \rightarrow L$) $^1A_g \rightarrow ^1B_u(\pi^*, x): e_g(d_{xz}) \rightarrow a_{2u}(\pi^*, z)$, $^1A_g \rightarrow ^1B_u(\pi^*, y): e_g(d_{yz}) \rightarrow a_{2u}(\pi^*, z)$, $^1A_g \rightarrow ^1A_u(\pi^*, z): a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*, z)$; the ligand to metal transitions ($L \rightarrow M$) $^1A_g \rightarrow ^1B_u(\sigma \text{ or } \pi, x): e_u(\sigma \text{ or } \pi, x) \rightarrow b_{1g}(d_{x^2-y^2})$, $^1A_g \rightarrow ^1B_u(\sigma \text{ or } \pi, y): e_u(\sigma \text{ or } \pi, y) \rightarrow b_{1g}(d_{x^2-y^2})$, $^1A_g \rightarrow ^1A_u(\pi, z): b_{2u}(\pi, z) \rightarrow b_{1g}(d_{x^2-y^2})$, where $e_u(\sigma, x) = (\sigma_1 - \sigma_3)/\sqrt{2}$, $e_u(\sigma, y) = (\sigma_2 - \sigma_4)/\sqrt{2}$, $e_u(\pi, x) = (\pi_{2h} - \pi_{4h})/\sqrt{2}$, $e_u(\pi, y) = (\pi_{1h} - \pi_{3h})/\sqrt{2}$, $b_{2u}(\pi, z) = (\pi_{1v} - \pi_{2v} + \pi_{3v} - \pi_{4v})/2$, and $a_{2u}(\pi^*, z) = (\pi^*_{1v} + \pi^*_{3v})/\sqrt{2}$. For the 3d orbital of the Ni atom, we use the one obtained by Clementi and Raimondi.²⁶ For the 2p orbitals of oxygen and nitrogen, we use Slater orbitals. Then, the magnitude

(26) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

of $[\theta]_M$ for each possible transition is given by

$$[\theta(^1A_g \rightarrow ^1B_u(\pi^*, x))]_M = - (0.08/\delta E(^1B_u(\pi^*, y) - ^1B_u(\pi^*, x))) f_2 \quad (4)$$

$$[\theta(^1A_g \rightarrow ^1B_u(\pi^*, y))]_M = (0.08/\delta E(^1B_u(\pi^*, y) - ^1B_u(\pi^*, x))) f_2 \quad (5)$$

$$[\theta(^1A_g \rightarrow ^1A_u(\pi^*, z))]_M = - (0.27/\delta E(^1B_u(\pi^*, x) - ^1A_u(\pi^*, z)) + 0.09/\delta E(^1B_u(\pi^*, y) - ^1A_u(\pi^*, z))) f_2 \quad (6)$$

$$[\theta(^1A_g \rightarrow ^1B_u(\sigma, x))]_M = (1.29/\delta E(^1B_u(\sigma, y) - ^1B_u(\sigma, x))) f_2 \quad (7)$$

$$[\theta(^1A_g \rightarrow ^1B_u(\sigma, y))]_M = - (1.29/\delta E(^1B_u(\sigma, y) - ^1B_u(\sigma, x))) f_2 \quad (8)$$

$$[\theta(^1A_g \rightarrow ^1B_u(\pi, x))]_M = - (0.18 \times 10^{-3}/\delta E(^1B_u(\pi, y) - ^1B_u(\pi, x))) f_2 \quad (9)$$

$$[\theta(^1A_g \rightarrow ^1B_u(\pi, y))]_M = (0.18 \times 10^{-3}/\delta E(^1B_u(\pi, y) - ^1B_u(\pi, x))) f_2 \quad (10)$$

$$[\theta(^1A_g \rightarrow ^1A_u(\pi, z))]_M = - (0.35 \times 10^{-1}/\delta E(^1B_u(\pi, x) - ^1A_u(\pi, z)) + 0.04 \times 10^{-1}/\delta E(^1B_u(\pi, y) - ^1A_u(\pi, z))) f_2 \quad (11)$$

in units of $72 \times 10^{-4} N\mu_B e^2 [\text{Å}^2]/c$. $\delta E(j - a)$ represents the energy difference; the energy of state j minus the energy of state a .

These results, *i.e.*, eq 4 and 5, 7 and 8, and 9 and 10, predict that the MCD spectra of the transitions, $^1A_g \rightarrow ^1B_u(x)$ and $^1A_g \rightarrow ^1B_u(y)$, which are close in energy, are equal in magnitude and opposite in sign. This corresponds to the fact that the A term is dominant in the transition $^1A_g \rightarrow ^1E_u$ in D_{4h} symmetry. In fact, the MCD of $\text{Ni}(\text{CN})_4^{2-}$ shows a positive A term pattern corresponding to the absorption band at 37,200 cm^{-1} , and it is assigned to the transition $^1A_g \rightarrow ^1E_u(d_{xz}, d_{yz} \rightarrow \pi^*)$.^{27, 28} Kobayashi and Daszkiewicz²⁹ also observed the same pattern of MCD at 35,500 cm^{-1} in the study on nickel(II) complexes with 1,4,8,11-tetraazacyclotetradecane derivatives, and assigned it to the transition $^1A_g \rightarrow ^1E_u(d_{xz}, d_{yz} \rightarrow \pi^*)$. Equations 4 and 5 and 9 and 10 show that the MCD spectra of the transition $^1A_g \rightarrow ^1B_u(\pi^*, x)$, $^1B_u(\pi^*, y): e_g(d_{xz}, d_{yz}) \rightarrow a_{2u}(\pi^*, z)$ and $^1A_g \rightarrow ^1B_u(\pi, x)$, $^1B_u(\pi, y): e_u(\pi) \rightarrow b_{1g}(d_{x^2-y^2})$ are expected to show a positive A term pattern formed by overlapping B terms. The MCD of $\text{Ni}(\text{Sal-N-(O)Tol})_2$ in chloroform shows an A term pattern corresponding to the absorption band at *ca.* 29,500 cm^{-1} . However, the observed MCD shows a negative A term pattern. Equations 7 and 8 show that the MCD of the transitions $^1A_g \rightarrow ^1B_u(\sigma, x)$, $^1B_u(\sigma, y): e_u(\sigma) \rightarrow b_{1g}(d_{x^2-y^2})$ is expected to show a negative A term pattern. Therefore, we assign the band at *ca.* 29,500 cm^{-1} to the transition $^1A_g \rightarrow ^1B_u(\sigma, x)$, $^1B_u(\sigma, y): e_u(\sigma) \rightarrow b_{1g}(d_{x^2-y^2})$. It should be noted that the sign of the A term pattern formed by overlapping B terms does not depend on the order of transition energies of $^1A_g \rightarrow ^1B_u(x)$ and $^1A_g \rightarrow$

(27) P. J. Stephens, A. J. McCaffery, and P. N. Schatz, *Inorg. Chem.*, **7**, 1923 (1968).

(28) S. B. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Amer. Chem. Soc.*, **91**, 5994 (1969).

(29) H. Kobayashi and B. K. Daszkiewicz, *Bull. Chem. Soc. Jap.*, **45**, 2485 (1972).

${}^1B_u(y)$, as is easily found from eq 4 and 5, 7 and 8, and 9 and 10. As the result, we cannot decide the order of energy of the transitions ${}^1A_g \rightarrow {}^1B_u(\sigma, x)$ and ${}^1A_g \rightarrow {}^1B_u(\sigma, y)$.

Equations 6 and 11 show that the MCD spectra of the transitions, ${}^1A_g \rightarrow {}^1A_u(\pi^*, z)$ and ${}^1A_g \rightarrow {}^1A_u(\pi, z)$, are expected to show a positive B term pattern. Since the sign of the MCD of these two transitions is in accord with the observed MCD corresponding to the absorption band at *ca.* 23,000 cm^{-1} , we cannot assign the band only from the sign of MCD. However, judging from the magnitude of the calculated $[\theta]_M$, it seems to be plausible to assign the band as the transition ${}^1A_g \rightarrow {}^1A_u(\pi^*, z): a_{1g}(d_{z^2}) \rightarrow a_{2u}(\pi^*, z)$. This assignment is consistent with the assignment of the lowest energy allowed transition observed in $\text{Ni}(\text{CN})_4^{2-}$. The reason why the second allowed transition of $\text{Ni}(\text{Sal-}N\text{-}(o)\text{Tol})_2$ is different from that of $\text{Ni}(\text{CN})_4^{2-}$ will be explained as follows. The σ -orbital $e_u(\sigma)$ in $\text{Ni}(\text{Sal-}N\text{-}(o)\text{Tol})_2$ is essentially nonbonding and the orbital energy of the σ -ligand orbital is higher than that of the π -ligand orbital. As the result, the molecular orbital energy level scheme is different from that proposed by Gray and Ballhausen,³⁰ and it seems that the transition ${}^1A_g \rightarrow {}^1B_u(\sigma, x)$, ${}^1B_u(\sigma, y)$ is observed at the lower energy region than the transition ${}^1A_g \rightarrow {}^1B_u(\pi^*, x)$, ${}^1B_u(\pi^*, y)$.

The MCD and absorption spectra of $\text{Ni}(\text{Sal-}N\text{-Me})_2$ and $\text{Ni}(\text{Sal-}N\text{-OH})_2$ are very similar to that of $\text{Ni}(\text{Sal-}N\text{-}(o)\text{Tol})_2$. It is therefore reasonable to extend the assignment proposed for $\text{Ni}(\text{Sal-}N\text{-}(o)\text{Tol})_2$ to $\text{Ni}(\text{Sal-}N\text{-Me})_2$ and $\text{Ni}(\text{Sal-}N\text{-OH})_2$. The bands at 31,000 and 33,000 cm^{-1} of $\text{Ni}(\text{Sal-}N\text{-Me})_2$ and $\text{Ni}(\text{Sal-}N\text{-OH})_2$, respectively, which show a negative A term pattern of MCD, are assigned to the transition ${}^1A_g \rightarrow {}^1B_u(\sigma, x)$, ${}^1B_u(\sigma, y)$. The bands at 24,000 and 26,000 cm^{-1} of $\text{Ni}(\text{Sal-}N\text{-Me})_2$ and $\text{Ni}(\text{Sal-}N\text{-OH})_2$, respectively, which show a positive B term pattern of MCD, are assigned to the transition ${}^1A_g \rightarrow {}^1A_u(\pi^*, z)$. In the same way, we can extend the assignment to the other compounds by using the characteristic signs of $[\theta]_M$.

It has been found that upon alteration of the R substituent in bis(R-*N*-salicylaldimine)nickel(II) complexes, as R = *o*-tolyl, phenyl, *p*-tolyl, and *m*-tolyl, large increases in the solution paramagnetism in inert solvents are produced.¹⁴ However, any essential change was not observed in the MCD spectra of the high-intensity bands in chloroform solution (Figures 1, 4, and 5). Inspection of the solution magnetic data¹⁴ has revealed that all these complexes except *o*-tolyl complex are

(30) H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, **85**, 260 (1963).

strongly paramagnetic in solution. However, the measurement was done at high concentrations ($>1 \times 10^{-2} M$). On the other hand, the measurement of the MCD and absorption spectra of high intensity bands was done at $1 \times 10^{-4} M$. It seems that the molecular association is deduced in such a dilute solution and the MCD spectra show the situation. Of these complexes, the MCD and absorption spectrum of $\text{Ni}(\text{Sal-}N\text{-}(m)\text{Tol})_2$ is a little different from the others. The absorption band of the chloroform solution at *ca.* 25,000 cm^{-1} is in accord with the absorption band of the pyridine solution, and the corresponding MCD spectra also suggest the coexistence of considerable paramagnetic species with diamagnetic species in chloroform solution.

The MCD and absorption spectra in pyridine solutions of $\text{Ni}(\text{Sal-}N\text{-H})_2$ and $\text{Ni}(\text{Sal}_2\text{en})$ (Figures 5 and 6) are different from those of the other compounds which are found to be completely paramagnetic in pyridine. The spectrum of $\text{Ni}(\text{Sal-}N\text{-H})_2$ in pyridine is of the form expected for equilibrium between diamagnetic and paramagnetic forms. According to the analysis of the MCD spectra discussed above, an absorption band at 23,500 cm^{-1} is assigned to ${}^1A_g \rightarrow {}^1A_u(\pi^*, z)$, and the absorption bands at 29,000 and 31,000 cm^{-1} are assigned ${}^1A_g \rightarrow {}^1B_u(\sigma, x)$, ${}^1B_u(\sigma, y)$, which are ascribed to the presence of a diamagnetic form. On the other hand, an absorption band at 26,000 cm^{-1} is assigned to the allowed transition ${}^3A_{2g} \rightarrow {}^3T_{2u}$, which is ascribed to the presence of a paramagnetic and octahedral bispyridine adduct. The structure of $\text{Ni}(\text{Sal}_2\text{en})$ can only be tetrahedral or *cis* planar because of the steric constraint of the ethylene bridge between chelating nitrogen atoms.³¹ We cannot observe any absorption band in the 6000–7000 cm^{-1} region which is characteristic of the tetrahedral nickel(II) complexes,²² and the structure will be *cis* planar. This compound is known to be diamagnetic in the solid state and also in pyridine solution. The spectrum in pyridine is very similar to that in chloroform. The signs and the magnitudes of the MCD of $\text{Ni}(\text{Sal}_2\text{en})$ are very similar to those of the other diamagnetic trans-planar complexes. Therefore it seems that the MCD of the compounds in the present paper is not sensitive to the local symmetry, such as *cis* or *trans*, and can be interpreted by the assumption that the effective field around the nickel(II) ion is approximately of D_{4h} symmetry.

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(31) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162, 1129 (1958).