smaller contact shifts for hydrogen must result from smaller values for  $|\psi_{(0)}|^2$ . There are two effects which could produce smaller values for  $|\psi_{(0)}|^2$  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  $|\psi_{(0)}|^2$  for the 2s atomic orbital of <sup>13</sup>C, <sup>14</sup>N, and <sup>17</sup>O than for the 1s atomic orbital of <sup>1</sup>H. 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 Eu(dpm)<sub>3</sub>(py)<sub>2</sub>.<sup>63</sup> The second effect is probably responsible for the generally larger<sup>13</sup>C contact shifts because even if the <sup>1</sup>H and <sup>13</sup>C s orbital coefficients are comparable, as they often are, the larger values of  $|\psi_{(0)}|^2$  for the <sup>13</sup>C 2s atomic orbital will tend to make the contact shift larger for <sup>13</sup>C. It has been pointed out<sup>65,66</sup> that values of  $|\psi_{(0)}|^2$  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.<sup>67</sup>

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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  $-150^{\circ}$  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  $Eu(dpm)_3(3-pic)_2$  is solvent dependent, being 18 ppm in CS<sub>2</sub> but only 8 ppm in  $CCl_2F_2$  at  $-120^{\circ}$ , 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

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

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.<sup>1-6</sup> 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.<sup>7-10</sup> In this paper, we report

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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-(salicylaldimine)nickel(II),<sup>11</sup> bis(salicylaldoxime)nickel(II),<sup>12</sup> bis-(*N*-methylsalicylaldimine)nickel(II),<sup>13</sup> bis(*N*-phenylsalicylaldimine)-nickel(II),<sup>14</sup> bis(*N*-o-tolylsalicylaldimine)nickel(II),<sup>14</sup> bis(*N*-m-tolylsalicylaldimine)nickel(II),<sup>14</sup> bis(*N*-m-tolylsalicylaldimine)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 elipticity (defined as in natural optical activity in degree deciliter decimeter<sup>-1</sup> mole<sup>-1</sup>) per gauss in the direction of the light beam.  $\epsilon$  is the molar extinction coefficient. The magnitudes in the region 5000-20,000 cm<sup>-1</sup> 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  $\epsilon$  in the region 5000-20,000 cm<sup>-1</sup> are shown on the right for chloroform solution and on the left for pyridine solution.



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

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



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)ethylenediiminenickel(II).

previously.<sup>16,17</sup> 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<sup>-1</sup>. 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.<sup>18</sup> It has been established that the paramagnetism results from the reaction

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of the diamagnetic complex with two molecules of pyridine to form an octahedral bispyridine adduct.<sup>2,19</sup> The absorption spectra of Ni(Sal-N-(o)Tol)<sub>2</sub> and Ni-(Sal-N-Me)<sub>2</sub> show two d-d bands of the nickel(II) ion at around 10,000 and 17,000 cm<sup>-1</sup>, which suggests that the nickel atom is octahedrally coordinated. The observed MCD spectra (Figures 1 and 2) for the band at ca. 17,000 cm<sup>-1</sup> are similar to the MCD spectra of the transition  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  observed in some octahedrally coordinated nickel(II) complexes;<sup>20</sup> the sign of  $[\theta]_{M}$  is negative, and the minimum point of the MCD spectrum is red shifted in comparison with the peak of the corresponding absorption band. The magnitude of  $[\theta]_{M}$  is also in good agreement. This allows us to assign the band at ca. 17,000  $cm^{-1}$  to the transition  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ . The band at around 10,000 cm<sup>-1</sup> corresponds to the transition  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$ . The MCD of the high-intensity band at ca. 26,000  $cm^{-1}$ shows the negative sign of  $[\theta]_M$ , and the minimum point of the MCD is at the same frequency with the peak of the corresponding absorption band. The characteristic property will be available to distinguish the paramagnetic octahedral species from the diamagnetic planar or the paramagnetic tetrahedral species. This high-intensity band is an allowed transition  ${}^{3}A_{2g} \rightarrow$  ${}^{3}T_{1u}$ , but the character is not clear and a satisfactory answer must await further investigation.

It is now well established that bis(R-N-salicylaldimine)nickel(II) complexes (R = n-alkyl and aryl)groups) become partially paramagnetic in inert solvents as a result of molecular association.<sup>4,14,21</sup> The spectra of the paramagnetic solutions of these complexes present bands at 10,000, 12,800, and 16,300 cm<sup>-1</sup> which are considered characteristic of the octahedral structure achieved by intermolecular association.<sup>22</sup> It was demonstrated that  $Ni(Sal-N-(o)Tol)_2$  is weakly paramagnetic in inert solution<sup>14</sup> and that the diamagnetic and monomeric species are dominant. No characteristic band of the paramagnetic associated species is found in the absorption spectra (Figure 1). The absorption spectra in chloroform were measured at a concentration of  $2 \times 10^{-2}$  M for low-intensity bands in the region 5000–20,000 cm<sup>-1</sup>. The paramagnetic associated species decrease with dilution. Therefore, the observed MCD and absorption spectra of high-intensity bands, which were measured at a concentration of  $1 \times 1$  $10^{-4}$  M, are essentially those of the planar, diamagnetic monomer. The MCD and absorption spectra of Ni-(Sal-N-Me)<sub>2</sub> and Ni(Sal-N-OH)<sub>2</sub> (Figures 2 and 3) are very similar to that of Ni(Sal-N-(o)Tol)<sub>2</sub> (Figure 1), and these complexes are supposed to be nearly identical in configurational and electronic structure. The concentration dependence of molar susceptibility of Ni(Sal-N-Me)2 in chloroform<sup>21</sup> also supports that almost all molecules of Ni(Sal-N-Me)<sub>2</sub> are diamagnetic planar in the chloroform solution as dilute as  $10^{-4}$  M. At this concentration, the MCD and absorption spectra of the high-intensity bands were measured.

It has been shown by the analysis of the polarized

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single-crystal absorption spectra<sup>23</sup> of Ni(Sal-N-Me)<sub>2</sub> that the band at 16,500 cm<sup>-1</sup> is assigned to the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{1g}(d_{xy} \rightarrow d_{x^{2}-y^{2}})$  and that the shoulder at 19,600 cm<sup>-1</sup> is assigned to the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{3g}$ - $(d_{zy} \rightarrow d_{x^2-y})$ . Therefore, the bands of Ni(Sal-N-(0)Tol)<sub>2</sub>, Ni(Sal-N-Me)<sub>2</sub>, and Ni(Sal-N-OH)<sub>2</sub> in chloroform at ca. 16,000 cm<sup>-1</sup> are assigned to the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{1g}(d_{xy} \rightarrow d_{x^{2}-y^{2}})$ . The sign of  $[\theta]_{M}$  at *ca*. 16,000  $cm^{-1}$  is negative, and the minimum point of the MCD is at the same frequency with the peak of the corresponding absorption band. This character is different from that of the MCD of the transition  ${}^{3}A_{2g} \rightarrow$  ${}^{3}T_{1g}(F)$  observed in paramagnetic octahedral species in pyridine solution.

On the other hand, the studies on the assignment of the high-intensity bands have not been so many. Bosnich<sup>24</sup> proposed an assignment of the absorption spectrum of Ni(Sal-N-Me)<sub>2</sub> complex dissolved in methanol solution. The spectrum is markedly similar to the spectrum observed in pyridine solution. This fact suggests the formation of an octahedral bismethanol adduct.<sup>19</sup> Thus, methanol acts as "a coordinating solvent" rather than "a noncoordinating solvent" to Ni(Sal-N-Me)<sub>2</sub> and this molecule is in equilibrium of predominantly paramagnetic form

Therefore, the assignment of high-intensity bands proposed by Bosnich<sup>24</sup> is not appropriate because the ground state was assumed to be diamagnetic. As we have shown above, the MCD and absorption spectra of high-intensity bands of Ni(Sal-N-Me)<sub>2</sub> and Ni(Sal-N-(o)Tol)<sub>2</sub> in chloroform were measured in small concentration, and the results may be interpreted as due to the diamagnetic planar species. The observed MCD spectra show a characteristic sign of  $[\theta]_M$ , and this fact will give us useful information for the spectroscopic assignment of the transitions.

In order to extract more useful information, it is necessary to interpret the experimental MCD spectra from theoretical grounds. The ground state of the Ni(Sal-N-Me)<sub>2</sub> molecule, which has been proved to have a trans structure with  $C_{2h}$  symmetry<sup>25</sup> and to be diamagnetic in chloroform, is  ${}^{1}A_{g}$ . The allowed transitions are  ${}^{1}A_{g} \rightarrow {}^{1}A_{u}(z)$ ,  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(x)$ , and  ${}^{1}A_{g} \rightarrow$  ${}^{1}B_{u}(y)$  (where x, y, and z in the parentheses are the direction of polarization of each transition). In the present case, since the ground state and the excited states are nondegenerate, only the B term is possible. The Bterm arises from the mixing by the magnetic field of each ground and excited state, to which transition occurs, with all other states connected by a magnetic transition dipole. The magnitude of the contribution to a B term is inversely proportional to the energy difference of the states which are mixed. The doubly degenerate state  ${}^{1}E_{u}(x,y)$  in a  $D_{4h}$  field splits into  ${}^{1}B_{u}(x)$ and  ${}^{1}\mathbf{B}_{u}(y)$  in a  $C_{2h}$  field. The local symmetry about the nickel(II) ions of four-coordinated trans-planar complexes will not be reduced much from  $D_{4h}$  symmetry and the energy separation between the states  ${}^{1}B_{u}(x)$  and  ${}^{1}B_{u}(y)$  will be small, and these states are ex-

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Figure 7. Geometry and coordinate system for the  $\sigma$ - and  $\pi$ molecular orbitals of NiN2O2.

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

$$\begin{array}{l} [\theta({}^{1}\mathbf{A}_{g} \rightarrow {}^{1}\mathbf{B}_{u}(x))]_{M} = \\ -(72Nf_{2}/\hbar c)({}^{1}/_{3})Im\{\langle {}^{1}\mathbf{B}_{u}(x)|\mu_{z}|{}^{1}\mathbf{B}_{u}(y)\rangle\langle {}^{1}\mathbf{A}_{g}|P_{z}|{}^{1}\mathbf{B}_{u}(x)\rangle \times \\ \langle {}^{1}\mathbf{B}_{u}(y)|P_{y}|{}^{1}\mathbf{A}_{g}\rangle/\delta \mathbf{E}({}^{1}\mathbf{B}_{u}(y) - {}^{1}\mathbf{B}_{u}(x))\} \quad (1) \end{array}$$

$$[\theta({}^{1}\mathrm{A}_{g} \rightarrow {}^{1}\mathrm{B}_{u}(y))]_{\mathrm{M}} = -[\theta({}^{1}\mathrm{A}_{g} \rightarrow {}^{1}\mathrm{B}_{t_{i}}(x))]_{\mathrm{M}}$$
(2)

$$\begin{bmatrix} \theta({}^{1}\mathbf{A}_{g} \rightarrow {}^{1}\mathbf{A}_{u}(z)) \end{bmatrix}_{M} = -(72Nf_{2}/\hbar c) \times \\ ({}^{1}/_{3})Im\{\langle {}^{1}\mathbf{A}_{u}(z) | \mu_{y} | {}^{1}\mathbf{B}_{u}(x) \rangle \langle {}^{1}\mathbf{A}_{g} | P_{z} | {}^{1}\mathbf{A}_{u}(z) \rangle \times \\ \langle {}^{1}\mathbf{B}_{u}(x) | P_{x} | {}^{1}\mathbf{A}_{g} \rangle / \delta E({}^{1}\mathbf{B}_{u}(x) - {}^{1}\mathbf{A}_{u}(z)) - \\ \langle {}^{1}\mathbf{A}_{u}(z) | \mu_{x} | {}^{1}\mathbf{B}_{u}(y) \rangle \langle {}^{1}\mathbf{A}_{g} | P_{z} | {}^{1}\mathbf{A}_{u}(z) \rangle / {}^{1}\mathcal{G}_{u}(y) | P_{y} | {}^{1}\mathbf{A}_{g} \rangle / \\ \delta E({}^{1}\mathbf{B}_{u}(y) - {}^{1}\mathbf{A}_{u}(z)) \}$$
(3)

where  $N, P, \mu$ , 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 Ni(Sal-N-Me)<sub>2</sub> molecule has been determined by X-ray methods.<sup>25</sup> 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 bounded 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  $(M \rightarrow L) {}^{1}A_{g} \rightarrow {}^{1}B_{u}$  $(\pi^*, x): e_g(d_{xz}) \rightarrow a_{2u}(\pi^*, z), \ {}^1A_g \rightarrow {}^1B_u(\pi^*, y): e_g(d_{yz}) \rightarrow$  $a_{2u}(\pi^*,z), \ ^1A_g \rightarrow \ ^1A_u(\pi^*,z):a_{1g}(d_z^2) \rightarrow a_{2u}(\pi^*,z); \ \text{the}$ ligand to metal transitions (L  $\rightarrow$  M)  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma \text{ or}$  $\begin{array}{l} \pi, x): \mathrm{e}_{\mathrm{u}}(\sigma \text{ or } \pi, x) \rightarrow \mathrm{b}_{\mathrm{1g}}(\mathrm{d}_{x^2 - z^2}), \ \mathrm{^{1}A_g} \rightarrow \ \mathrm{^{1}B_{\mathrm{u}}}(\sigma \text{ or } \pi, y): \mathrm{e}_{\mathrm{u}}\\ (\sigma \text{ or } \pi, y) \rightarrow \mathrm{b}_{\mathrm{1g}}(\mathrm{d}_{x^2 - y^2}), \ \mathrm{^{1}A_g} \rightarrow \ \mathrm{^{1}A_{\mathrm{u}}}(\pi, z): \mathrm{b}_{\mathrm{2u}}(\pi, z) \rightarrow \end{array}$  $b_{1g}(d_{x^2-y^2})$ , where  $e_u(\sigma, x) = (\sigma_1 - \sigma_3)/\sqrt{2}$ ,  $e_u(\sigma, y) = (\sigma_1 - \sigma_3)/\sqrt{2}$  $(\sigma_2 - \sigma_4)/\sqrt{2}, e_u(\pi, x) = (\pi_{2h} - \pi_{4h})/\sqrt{2}, e_u(\pi, y) =$  $(\pi_{1h} - \pi_{3h})/\sqrt{2}, b_{2u}(\pi, z) = (\pi_{1v} - \pi_{2v} + \pi_{3v} - \pi_{4v})/2,$ 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.<sup>26</sup> For the 2p orbitals of oxygen and nitrogen, we use Slater orbitals. Then, the magnitude of  $[\theta]_{M}$  for each possible transition is given by

$$[\theta({}^{1}A_{i_{0}} \rightarrow {}^{1}B_{u}(\pi^{*}, x))]_{M} = -(0.08/\delta E({}^{1}B_{u}(\pi^{*}, y) - {}^{1}B_{u}(\pi^{*}, x)))f_{2} \quad (4)$$

$$[\theta({}^{1}A_{a} \rightarrow {}^{1}B_{u}(\pi^{*}, y))]_{M} =$$

$$(0.08/\delta E({}^{1}B_{u}(\pi^{*},y) - {}^{1}B_{u}(\pi^{*},y)))f_{2} \quad (5)$$

$$[\theta({}^{1}A_{g} \rightarrow {}^{1}A_{u}(\pi^{*},z))]_{M} = -(0.27/\delta E({}^{1}B_{u}(\pi^{*},x) - {}^{1}A_{u}(\pi^{*},z)) + 0.09/\delta E({}^{1}B_{u}(\pi^{*},y) - {}^{1}A_{u}(\pi^{*},z)))f_{2} \quad (6)$$

$$[\theta({}^{1}\mathrm{A}_{g} \rightarrow {}^{1}\mathrm{B}_{\mathrm{u}}(\sigma, x))]_{\mathrm{M}} =$$

$$(1.29/\delta E({}^{1}B_{u}(\sigma,y) - {}^{1}B_{u}(\sigma,x)))f_{2}$$
 (7)

$$[\theta({}^{1}\mathbf{A}_{g} \rightarrow {}^{1}\mathbf{B}_{u}(\sigma, y))]_{M} = -(1.29/\delta E({}^{1}\mathbf{B}_{u}(\sigma, y) - {}^{1}\mathbf{B}_{u}(\sigma, x)))f_{2} \quad (8)$$

$$[\theta({}^{1}A_{g} \rightarrow {}^{1}B_{u}(\pi, x))]_{M} = -(0.18 \times 10^{-3}/\delta E({}^{1}B_{u}(\pi, y) - {}^{1}B_{u}(\pi, x)))f_{2}$$
 (9)

$$[\theta({}^{1}A_{g} \rightarrow {}^{1}B_{u}(\pi, y))]_{M} = (0.18 \times 10^{-3} / \delta E({}^{1}B_{u}(\pi, y) - {}^{1}B_{u}(\pi, x)))f_{2} \quad (10)$$

$$\begin{bmatrix} \theta({}^{1}A_{g} \rightarrow {}^{1}A_{u}(\pi,z)) \end{bmatrix}_{M} = -(0.35 \times 10^{-1} / \delta E({}^{1}B_{u}(\pi,x) - {}^{1}A_{u}(\pi,z)) + 0.04 \times 10^{-1} / \delta E({}^{1}B_{u}(\pi,y) - {}^{1}A_{u}(\pi,z))) f_{2} \quad (11)$$

in units of  $72 \times 10^{-4} N \mu_{\rm B} e^2 [\text{\AA}^2]/c$ .  $\delta E(j - a)$  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,  ${}^{1}A_{g} \rightarrow$  ${}^{1}B_{u}(x)$  and  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(y)$ , 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  ${}^{1}A_{g} \rightarrow {}^{1}E_{u}$  in  $D_{4h}$  symmetry. In fact, the MCD of Ni(CN)<sub>4</sub><sup>2-</sup> shows a positive A term pattern corresponding to the absorption band at 37,200 cm<sup>-1</sup>, and it is assigned to the transition  ${}^{1}A_{g} \rightarrow {}^{1}E_{u}(d_{xz}, d_{yz} \rightarrow$  $\pi^*$ ).<sup>27,28</sup> Kobayashi and Daszkiewicz<sup>29</sup> also observed the same pattern of MCD at 35,500 cm<sup>-1</sup> in the study on nickel(II) complexes with 1,4,8,11-tetraazacyclotetradecane derivatives, and assigned it to the transition  ${}^{1}A_{g} \rightarrow {}^{1}E_{u}(d_{xz}, d_{yz} \rightarrow \pi^{*})$ . Equations 4 and 5 and 9 and 10 show that the MCD spectra of the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\pi^{*},x), {}^{1}B_{u}(\pi^{*},y):e_{g}(d_{xz},d_{yz}) \rightarrow a_{2u}(\pi^{*},z)$  and  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\pi, x), {}^{1}B_{u}(\pi, y):e_{u}(\pi) \rightarrow b_{1g}(d_{x^{2}-y^{2}})$  are expected to show a positive A term pattern formed by overlapping B terms. The MCD of Ni(Sal-N-(o)Tol)<sub>2</sub> in chloroform shows an A term pattern corresponding to the absorption band at ca. 29,500 cm<sup>-1</sup>. However, the observed MCD shows a negative A term pattern. Equations 7 and 8 show that the MCD of the transitions  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma, x), {}^{1}B_{u}(\sigma, y):e_{u}(\sigma) \rightarrow b_{1g}(d_{x^{2}-y^{2}})$  is expected to show a negative A term pattern. Therefore, we assign the band at  $ca. 29,500 \text{ cm}^{-1}$  to the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma, x), {}^{1}B_{u}(\sigma, y):e_{u}(\sigma) \rightarrow b_{1g}(d_{x^{2}-y^{2}}).$  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  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(x)$  and  ${}^{1}A_{g} \rightarrow$ 

<sup>(27)</sup> P. J. Stephens, A. J. McCaffery, and P. N. Schatz, Inorg. Chem., 7, 1923 (1968).

<sup>(28)</sup> 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,

<sup>(26)</sup> E. Clementi and D. L. Raimondi, J. Chem. Phys., 38, 2686 (1963).

 ${}^{1}B_{u}(y)$ , 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  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma, x)$  and  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma, y)$ .

Equations 6 and 11 show that the MCD spectra of the transitions,  ${}^{1}A_{g} \rightarrow {}^{1}A_{u}(\pi^{*},z)$  and  ${}^{1}A_{g} \rightarrow {}^{1}A_{u}(\pi,z)$ , 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  $\text{cm}^{-1}$ , 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  ${}^{1}A_{g} \rightarrow$  ${}^{1}A_{u}(\pi^{*},z):a_{1g}(d_{z^{2}}) \rightarrow a_{2u}(\pi^{*},z)$ . This assignment is consistent with the assignment of the lowest energy allowed transition observed in Ni(CN)42-. The reason why the second allowed transition of Ni(Sal-N-(o)Tol)<sub>2</sub> is different from that of Ni(CN)42- will be explained as follows. The  $\sigma$ -orbital  $e_u(\sigma)$  in Ni(Sal-N-(o)Tol)<sub>2</sub> is essentially nonbonding and the orbital energy of the  $\sigma$ ligand orbital is higher than that of the  $\pi$ -ligand orbital. As the result, the molecular orbital energy level scheme is different from that proposed by Gray and Ballhausen,<sup>30</sup> and it seems that the transition  ${}^{1}A_{g} \rightarrow$  ${}^{1}B_{u}(\sigma,x), {}^{1}B_{u}(\sigma,y)$  is observed at the lower energy region than the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\pi^{*}, x), {}^{1}B_{u}(\pi^{*}, y)$ .

The MCD and absorption spectra of Ni(Sal-N-Me)<sub>2</sub> and Ni(Sal-N-OH)<sub>2</sub> are very similar to that of Ni(Sal-N-(o)Tol)<sub>2</sub>. It is therefore reasonable to extend the assignment proposed for Ni(Sal-N-(o)Tol)<sub>2</sub> to Ni(Sal-N-Me)<sub>2</sub> and Ni(Sal-N-OH)<sub>2</sub>. The bands at 31,000 and 33,000 cm<sup>-1</sup> of Ni(Sal-N-Me)<sub>2</sub> and Ni(Sal-N-OH)<sub>2</sub>, respectively, which show a negative A term pattern of MCD, are assigned to the transition  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma,x)$ ,  ${}^{1}B_{v}(\sigma,y)$ . The bands at 24,000 and 26,000 cm<sup>-1</sup> of Ni(Sal-N-Me)<sub>2</sub> and Ni(Sal-N-OH)<sub>2</sub>, respectively, which show a positive B term pattern of MCD, are assigned to the transition  ${}^{1}A_{g} \rightarrow {}^{1}A_{u}(\pi^{*},z)$ . In the same way, we can extend the assignment to the other compounds by using the characteric 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.<sup>14</sup> 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 data<sup>14</sup> 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 Ni(Sal-N-(m)-Tol)<sub>2</sub> is a little different from the others. The absorption band of the chloroform solution at *ca*. 25,000 cm<sup>-1</sup> 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 Ni(Sal-N-H)<sub>2</sub> and Ni(Sal<sub>2</sub>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  $Ni(Sal-N-H)_2$  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<sup>-1</sup> is assigned to  ${}^{1}A_{g} \rightarrow {}^{1}A_{u}(\pi^{*},z)$ , and the absorption bands at 29,000 and 31,000 cm<sup>-1</sup> are assigned  ${}^{1}A_{g} \rightarrow {}^{1}B_{u}(\sigma, x), {}^{1}B_{u}(\sigma, y)$ , which are ascribed to the presence of a diamagnetic form. On the other hand, an absorption band at 26,000 cm<sup>-1</sup> is assigned to the allowed transition  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2u}$ , which is ascribed to the presence of a paramagnetic and octahedral bispyridine adduct. The structure of Ni(Sal<sub>2</sub>en) can only be tetrahedral or cis planar because of the steric constraint of the ethylene bridge between chelating nitrogen atoms.<sup>31</sup> We cannot observe any absorption band in the 6000-7000 cm<sup>-1</sup> region which is characteristic of the tetrahedral nickel(II) complexes,<sup>22</sup> 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 Ni(Sal<sub>2</sub>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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