The Circular Dichroism and Magnetic Circular Dichroism Spectra of Bis(stilbenediamine) nickel(II) Complexes

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The temperature dependence of the absorption and circular dichroism spectra for $[Ni((+)\text{-stien})_2](ClO_4)_2$ is indicative of the equilibrium between the square planar (yellow) and tetragonal (violet) species in acetone solutions. On the other hand, the square planar species is predominant in a methanol solution, even at room temperature, in the case of $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$. The Cl^- as a counter anion favored an equilibrium slightly displaced to the tetragonal species. The analysis of the CD and MCD bands suggests an ordering of the d-orbital energy levels of $d_{x^2-y^2} \gg d_{z^2} > d_{xz}, d_{yz} > d_{xy}$.

Despite considerable efforts, the spectra exhibited by d^8 square planar complexes are still imperfectly understood. It was only recently that some workers[1–4] have demonstrated the usefulness of magnetic circular dichroism (MCD) studies in obtaining spectroscopic information about the d^8 square planar complexes. The main features of the theory of the dispersion of MCD through absorption (AB) bands have previously been reviewed.[5–7] For AB bands which are too broad to assign, MCD is definitely superior, so the MCD spectra of $[Ni(\textit{meso-}$ and $(+)\text{-stien})_2]X_2$, where X=Cl and ClO_4, were measured in this study.

On the other hand, the optical rotatory dispersion and circular dichroism (CD) spectra for the violet and yellow forms of $[Ni((-)\text{-stien})_2]^{2+}$ have been measured by Lifschitz *et al.*[8] and Bosnich *et al.*[9] respectively. Bosnich and his colleagues analyzed the electronic structure of the yellow complexes and suggested an energy scheme.

It is well known[10] that Lifschitz's complexes with the general fomula of $[Ni(\textit{meso}\text{-stien})_2]X_2$, where X is the anion of an organic acid, are present as equilibrium mixtures of the blue or violet and yellow forms under a variety of conditions.

In this study, we found that the equilibrium between the violet and yellow forms occurs more easily in an acetone solution of optically-active $[Ni((+)\text{-stien})_2](ClO_4)_2$, than in a methanol solution of optically-inactive $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$.

Experimental

Materials. The *meso*-stilbenediamine(*meso*-stien) (Calcd for $C_{14}H_{16}N_2$: C, 79.32; H, 7.61; N, 13.21%. Found: C, 79.16; H, 7.67; N, 12.58%) and (+)-stien ($[\alpha]_D=185°$ (in ether)) were prepared by the methods of Irving and Parkins[11] and of Lifschitz and Bos[12] respectively. The $[Ni(\textit{meso}\text{-stien})_2]Cl_2$ (Calcd for $NiC_{28}H_{32}N_4Cl_2$: C, 60.75; H, 5.83; N, 10.12%. Found: C, 60.81; H, 5.82; N, 9.98%), $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ (Calcd for $NiC_{28}H_{32}N_4Cl_2O_8$: C, 49.34; H, 4.73; N, 8.22; Cl, 10.40%. Found: C, 49.19; H, 4.67; N, 8.15; Cl, 10.02%), and $[Ni((+)\text{-stien})_2](ClO_4)_2$ (Calcd for $NiC_{28}H_{32}N_4Cl_2O_8$: C, 49.34; H, 4.73; N, 8.22; Cl, 10.40%. Found: C, 49.21; H, 4.72; N, 8.25; Cl, 9.97%) were prepared by the method of Lifschitz, Bos, and Dijkema.[8]

Measurements. The CD and MCD measurements were made with a JASCO model 20A dichrograph equipped with an electromagnet. The magnetic field was set at 12500 G in the case of the MCD measurements. The electronic absorption spectra were measured by using a Hitachi EPS-3T recording spectrophotometer. The spectra at 0.8 °C were measured by using jacketed cells regulated with circulating water held at a constant temperature. The spectra at −75 °C were measured by the use of a quartz-Dewar designed in our laboratory. The temperatures were measured directly using a thermometer.

Results and Discussion

The Temperature Dependence of the AB and CD Spectra of Bis((+)-stien)nickel (II) Diperchlorate in an Acetone Solution. The temperature dependence of the AB spectrum for $[Ni((+)\text{-stien})_2](ClO_4)_2$ in an acetone solution is shown in Fig. 1. The AB bands at 22500, 11300, 18000, and 28000 cm^{-1} are denoted as AB bands—Y, V_1, V_2, and V_3 respectively. As the temperature of the $[Ni((+)\text{-stien})_2](ClO_4)_2$ acetone solution is raised, the intensity of the Y AB band increases, while that of the V_1 AB band decreases. The lack of isosbesticity and the variation in the intensity of the V_2 and V_3 bands may be due to experimental errors. It is well known that the V_1, V_2, and V_3 AB bands are attributable to the violet paramagnetic species, while the Y AB band is due to the yellow diamagnetic species. The temperature dependence and reversibility of the variation in intensity for each AB band lead us to expect the occurrence of the following equilibrium for $[Ni((+)\text{-stien})_2](ClO_4)_2$ in an acetone solution:

$$[Ni((+)\text{-stien})_2]^{2+} + 2S \rightleftarrows [Ni((+)\text{-stien})_2\cdot 2S]^{2+} \quad (1)$$

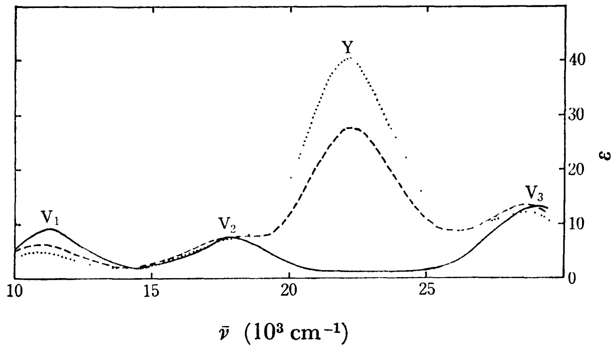

Fig. 1. AB spectra for $[Ni((+)\text{-stien})_2](ClO_4)_2$ in an acetone solution at +21 (······), +0.8 (– – –), and −75 °C (——). Y and V denote the AB bands ascribed to the yellow and violet complexes, respectively.

where S is an acetone molecule. As the temperature increases, the equilibrium in Eq. (1) is shifted to the left side. Thus, the relative quantity of the violet species of the nickel(II) complex decreases with a rise in the temperature. It should be added that [Ni((+)-stien)$_2$]$^{2+}$ gives the violet species in a methanol solution, even at room temperature,[13] which means that methanol will coordinate to the [Ni((+)-stien)$_2$]$^{2+}$ much more strongly than will acetone.

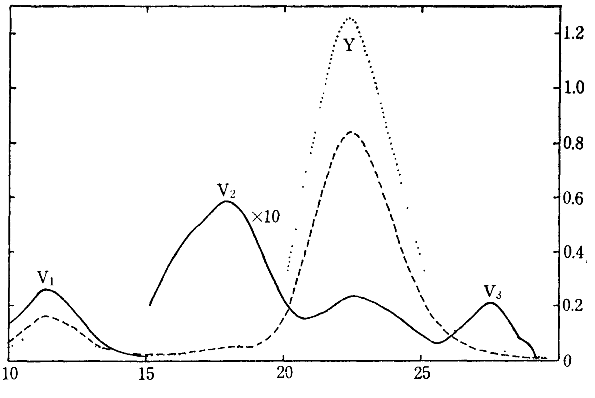

Fig. 2. CD spectra for [Ni((+)-stien)$_2$](ClO$_4$)$_2$ in an acetone solution at +21 (······), +0.8 (-----), and −75 °C (——). Y and V denote the CD bands ascribed to the yellow and violet complexes, respectively.

The occurrence of the equilibrium discussed above was also confirmed by means of the CD spectra. In Fig. 2 the CD bands at 22500, 11400, 18000, and 27500 cm^{-1} are denoted as the Y, V$_1$, V$_2$, and V$_3$ CD bands respectively, corresponding to the AB bands.

First, it should be noted that the shape of the V$_1$, V$_2$, and V$_3$ CD bands are not symmetric, which suggests that they contain more than one transition. On the assumption of the octahedral (O$_h$) local symmetry of the complex, the V$_1$, V$_2$, and V$_3$ CD bands can be assigned to three spin-allowed d-d transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) respectively. However, in view of the facts that the violet complex [Ni((+)-stien)$_2$·2S]$^{2+}$ is presumably six-coordinated with the environment of *trans*-NiN$_4$O$_2$ with the two oxygen atoms furnished by acetone, and that these CD bands seem to contain more than one transition, the symmetry of the ligand field may be anticipated to be an octahedron elongated along the *z*-axis—namely, tetragonal (D$_{4h}$). The assignment of the CD bands can thus be examined as follows, assuming the D$_{4h}$ symmetry. In this symmetry, the $^3T_{2g}$ and $^3T_{1g}$ levels of an octahedral complex split into $^3B_{2g}+{}^3E_g$ and $^3A_{2g}+{}^3E_g$ levels, respectively (see Fig. 3). According to Fig. 3, three CD bands, V$_1$, V$_2$, and V$_3$, can thus be assigned to spin-allowed transitions—$^3B_{1g} \rightarrow ({}^3E_g, {}^3B_{2g})$, $^3B_{1g} \rightarrow ({}^3A_{2g}, {}^3E_g)$, and $^3B_{1g} \rightarrow ({}^3E_g, {}^3A_{2g})$ respectively. The magnetic dipole forbidden transition, $^3B_{1g} \rightarrow {}^3A_{2g}$, in D$_{4h}$ seems to appear as a shoulder in the V$_2$ and V$_3$ CD bands. This possibly implies that [Ni((+)-stien)$_2$·2S]$^{2+}$ contains lower symmetry components than does D$_{4h}$.

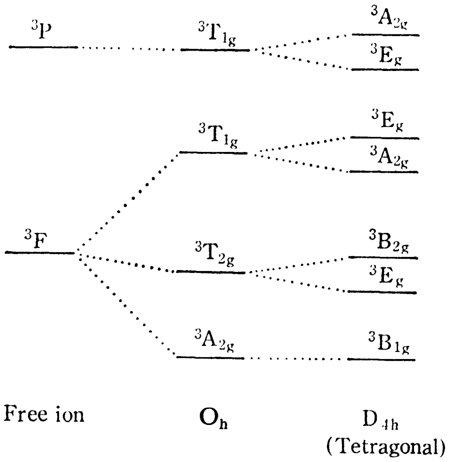

Fig. 3. Correlation diagram (Spin triplet only) for a d^8 ion in an octahedral (O$_h$) and tetragonal (D$_{4h}$) field.

Secondly, it should be noted that the shape of the Y CD band, which is characteristic of the yellow diamagnetic square planar complexes, is not symmetric. Although the Y CD band has already been assigned by Bosnich *et al.* for complexes of Ni(II) with (+)-propylenediamine,[9] we reassigned this CD band using the same line of reasoning as was employed. For the spin-paired Ni(II) complexes in a ligand field of approximately D$_{4h}$ symmetry, three bands resulting from the $d_{xy} \rightarrow d_{x^2-y^2}$ ($^1A_{1g} \rightarrow {}^1A_{2g}$), $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ ($^1A_{1g} \rightarrow {}^1E_g$), and $d_{z^2} \rightarrow d_{x^2-y^2}$ ($^1A_{1g} \rightarrow {}^1B_{1g}$) transitions, may be expected in almost the same wave number region (Fig. 6). Only the first two transitions are magnetic-dipole allowed transitions. The Y CD band, centered around 22500 cm^{-1}, is situated on the higher-frequency side of the AB band (ν_{max}=22200 cm^{-1}). On the higher-frequency side of the Y CD band, its anisotropy factor ($\Delta\varepsilon/\varepsilon$) is about 0.03, while on the lower-frequency side, below 22200 cm^{-1}, it decreases below 0.03. This trend was also observed in other solvents such as nitromethane and ethylacetate.[15] This suggests that the apparently single Y CD band contains two transitions. The magnetic dipole-allowed transitions, $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$, are well-separated and give strongly negative and moderately negative CD bands respectively in the case of *trans*-[Co((−)-stien)$_2$Cl$_2$]ClO$_4$.[16] If we can assume that the similarity concerning the relative CD magnitudes with opposite signs will also be observed in the corresponding transitions for the square planar [Ni((+)-stien)$_2$](ClO$_4$)$_2$, it can be expected that the strongly positive and moderately positive CD bands are to be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ respectively in the [Ni((+)-stien)$_2$]$^{2+}$ complex. The large amount of overlap between these transitions is believed to account for the apparently single band with a dissymmetric shape. This assignment suggests that the d_{xy} orbital lies below the degenerate d_{xz}, d_{yz} orbitals in the yellow diamagnetic species of [Ni((+)-stien)$_2$](ClO$_4$)$_2$.

MCD Spectra of Bis(stien)nickel(II) Complexes. Figure 4 shows the MCD spectra for the [Ni((+)-stien)$_2$](ClO$_4$)$_2$, along with its AB spectra. As was discussed in the previous section, both the yellow dia-

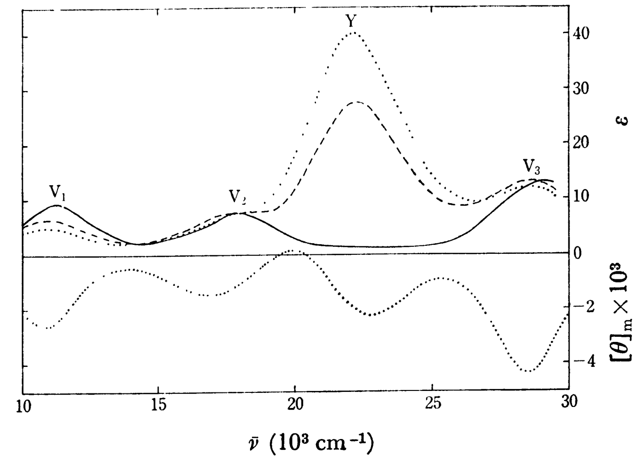

Fig. 4. AB and MCD spectra for $[Ni((+)\text{-stien})_2](ClO_4)_2$ in an acetone solution at +21 (······), +0.8 (------), and −75 °C (——). Y and V denote the AB bands ascribed to the yellow and violet complexes, respectively.

magnetic and violet paramagnetic species are present in an acetone solution at 21 °C. The temperature-variation studies of the AB and CD spectra in Figs. 1 and 2 indicate that the violet paramagnetic species is predominant in an acetone solution at −75 °C. The CD magnitude ($\Delta\varepsilon$) for the V_1 band, then, gives the approximate percentage of the violet paramagnetic species present. The calculation shows that the molar ratio of the violet paramagnetic species to that of the yellow diamagnetic species is 1 : 2 at 21 °C in an acetone solution. Hence, the MCD spectra in an acetone solution at 21 °C (Fig. 4) reveal that the MCD intensity of the V_3 band is about four times stronger than that of the negative band, Y.

Figure 5 shows the MCD spectrum for the $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ in a methanol solution. Though methanol is a solvent which gives the violet species more preferably than acetone, the $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ in a methanol solution does not show any MCD due to the main violet species band (V_3) at around 27000 cm^{-1}. The most plausible reason why $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ tends to give the yellow species more easily than $[Ni((+)\text{-stien})_2](ClO_4)_2$ seems to be a steric effect; that is, the axial phenyl group in the complexes will exert more steric hindrance toward the axial ligands than will the equatorial one. The molecular model and the X-ray analysis indicate that one of the phenyl groups in a *meso*-stien of the Ni(II) complex will be in an axial position, and the other in an equatorial position, relative to the NiN_4 plane in the $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$, while both phenyl groups of (+)-stien in the $[Ni((+)\text{-stien})_2](ClO_4)_2$ will be in equatorial positions in an energetically-favored form.[17]

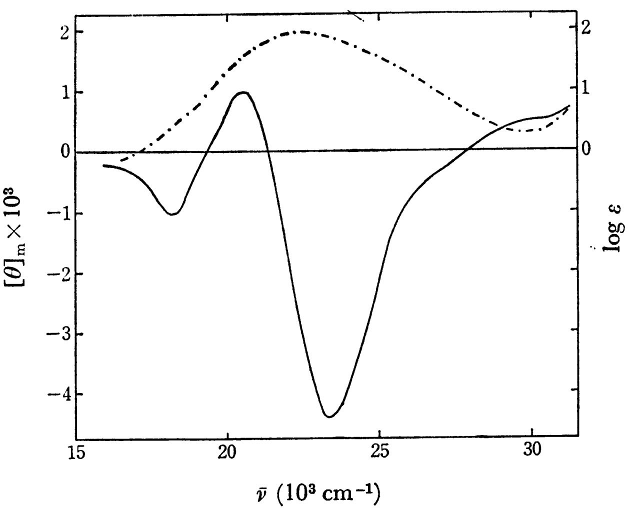

Fig. 5. AB (-·-·-) and MCD (——) spectra for $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ in a methanol solution at room temperature.

It has been reported by Kobayashi[4] that the A term MCD in the diamagnetic yellow Ni(II) complex shows a normal A-term dispersion. If this is also the case for the yellow diamagnetic $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$, the positive part for a normal A term will be nearly the positive peak at around 21500 cm^{-1}. Hence, three possibly B terms above, at and below the transition for the A term, are necessary to explain the experimental MCD curve for the $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ in Fig. 5. Thus, the MCD for $[Ni(\textit{meso}\text{-stien})_2](ClO_4)_2$ may be considered to consist of a normal A term with three possibly B terms with lower, the same, and higher transition energies. These MCD results suggest that the degenerate transition may be in the middle of the two nondegenerate transitions. This MCD assignment with the CD assignment for the yellow diamagnetic $[Ni((+)\text{-stien})_2](ClO_4)_2$, as described in the previous

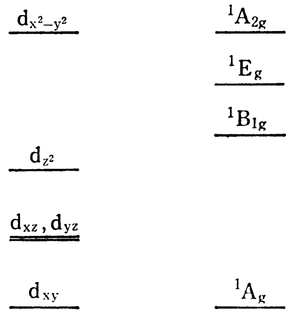

Fig. 6. Ordering of the d-orbital energy levels and the energy level diagram for a d^8 ion in a square-planar (D_{4h}) field.

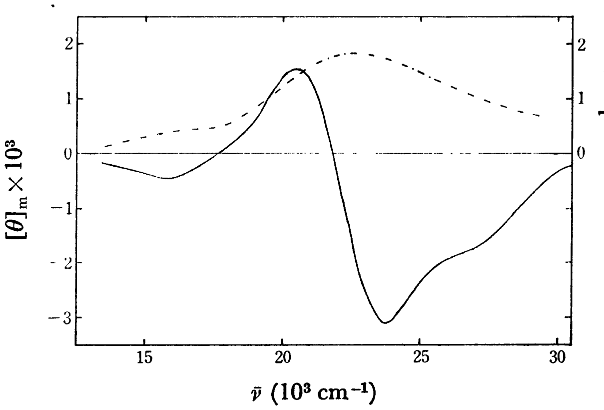

Fig. 7. AB (-·-·-) and MCD (——) spectra for $[Ni(\textit{meso}\text{-stien})_2]Cl_2$ in a methanol-water (4: 1) solution at room temperature.

section, implies an energy order of the d-orbital of $d_{z^2} > d_{xz}, d_{yz} > d_{xy}$. (Fig. 6)

The effect of counter anions on the equilibrium between the yellow diamagnetic and violet paramagnetic species was examined using [Ni(*meso*-stien)$_2$]Cl$_2$, the MCD and AB spectra of which are shown in Fig. 7. Figure 7 indicates that the [Ni(*meso*-stien)$_2$]Cl$_2$ in a methanol–water solution has the violet paramagnetic species besides the yellow diamagnetic species, and that the ratio of the former to the latter is about 1 : 8. The existence of the violet paramagnetic species in the case of [Ni(*meso*-stien)$_2$]Cl$_2$ in a methanol–water solution at room temperature should be compared with the finding that [Ni(*meso*-stien)$_2$](ClO$_4$)$_2$ has no violet paramagnetic species under the same conditions. This might be attributed to the greater bulkiness of ClO_4^- in comparison with that of Cl^-.

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