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Magnetic Circular Dichroism of Nickel(II) and Copper(II) Complexes with 1,4,8,11-Tetraazacyclotetradecane Derivatives

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The magnetic circular dichroism (MCD) spectra of nickel(II) and copper(II) complexes with 1,4,8,11-tetraazacyclotetradecane derivatives were measured. An anomalous MCD dispersion was observed in a (*d*, *d**) band at 22000 cm^{-1} for the copper(II) complexes and at 22000—23000 cm^{-1} for the nickel(II) complexes. In the ultraviolet region, the nickel(II) complexes show a normal MCD dispersion in the 35500 cm^{-1} band which appears only for the ligands with $\rangle$C=N– double bonds, while the copper(II) complexes show an anomalous dispersion in the 39000 cm^{-1} band which appears even if the ligand lacks $\rangle$C=N– double bonds. The 35500 cm^{-1} band of the nickel(II) complexes is assigned to a "metal to ligand" charge-transfer transition $1e_g \rightarrow \pi^*$ and the 39000 cm^{-1} band of the copper(II) complexes to a "ligand to metal" charge-transfer transition $1e_u \rightarrow 2b_{1g}$. In the nickel(II) complex of a ligand with two isolated and two conjugated double bonds shows a normal MCD dispersion in the 25000 cm^{-1} band. The absorption band is assigned to a "metal to ligand conjugated double bonds" charge-transfer transition rather than a (*d*, *d**) transition.

Macrocyclic coordination compounds formed by condensation of metal-amine complexes with aliphatic carbonyl compounds are of great interest.[1] Recent magnetic circular dichroism (MCD) measurements have furnished various information on the electronic characteristics of the low energy electronic excitations of planar complexes.[2–5] So far, however, the MCD spectra were only briefly discussed with respect to the planar complexes with macrocyclic ligands.[6] In the present work, nickel(II) and copper(II) complexes with different tetraazacyclotetradecane derivatives in various steps of oxidation as well as in different conformations were chosen for the MCD measurements in order to get more general information on the low energy electronic excitations.

Table 1. List of complexes

Complex	Abbreviation	Preparation
5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanecopper(II) diperchlorate (prepared from an isomer ligand of mp 110°C)	IACu	1
5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanecopper(II) diperchlorate (prepared from an isomer ligand of mp 145°C)	IBCu	1
5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) diperchlorate (prepared from an isomer ligand of mp 110°C)	IANi	2
5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienecopper(II) diperchlorate	IICu	1
N-dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienecopper(II) diperchlorate (racemic isomer)	IIICuα	3
C-meso-N-dl-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorate	IVANiα	4
C-meso-N-meso-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorate	IVANiβ	4
C-dl-N-dl-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) diperchlorate	IVBNi	4
meso-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraenenickel(II) diperchlorate	VANi	5
5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,10-tetraenenickel(II) diperchlorate	VINi	6

1. B. Jezowska-Trzebiatowska, R. Kolinski, B. Korybut-Daszkiewicz, J. Mrozinski, and W. Wojciechowski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **17**, 411 (1969).
2. R. A. Kolinski and B. Korybut-Daszkiewicz, *ibid.*, **17**, 13 (1969).
3. N. F. Curtis, Y. M. Curtis, and H. K. Y. Powell, *J. Chem. Soc., A*, **1966**, 1015.
4. R. A. Kolinski and B. Korybut-Daszkiewicz, "Proceedings of the XIII ICCC," September 1970, Poland, I 320.
5. Oxidation of the complex IVANiα by analogy to Curtis' preparative method of the complex VINi.[6]
6. N. F. Curtis, *Chem. Commun.*, **1966**, 882; N. F. Curtis, *Coord. Chem. Rev.*. **3**, 3 (1968).

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1) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

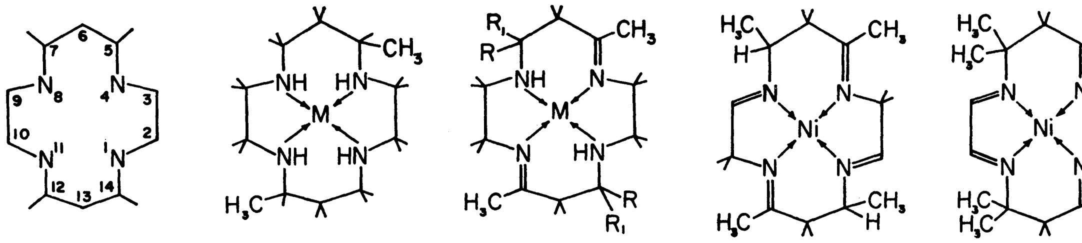
2) D. S. Martin, Jr., J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **5**, 491 (1966).

3) A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Amer. Chem. Soc.*, **90**, 5730 (1968).

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

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

6) Q. Looney and B. E. Douglas, *Inorg. Chem.*, **9**, 1955 (1970).



M=Cu(II) IACu
IBCu
M=Ni(II) IANi

M=Cu(II)
R=R$_1$=H II Cu
R=R$_1$=CH$_3$ III Cuα
M=Ni(II)
R=H, R$_1$=CH$_3$
IVANiα, IVANiβ, IVBNi

VA Ni

VI Ni

Fig. 1. Structures of the complexes studied.

Experimental

Materials. Preparation of the complexes was described elsewhere.[7–9] Samples obtained from the original preparative works were used without further purification. The names, notations, preparation, and structures of the complexes used in the present work are summarized in Table 1 and Fig. 1. Two isomeric 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanes [denoted by IA (mp 110°C) and IB (mp 145°C)] were complexed with copper(II) perchlorate (Table 1). The free ligand 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene was obtained by the condensation of ethylenediamine monohydroperchlorate with methyl propenyl ketone in water-methanol solution and complexed with nickel(II) acetate. Three isomers IVANiα, IVANiβ, and IVBNi (Table 1) were separated by fractional recrystallization. The complexes IVANiα and IVANiβ are an interconvertible pair, while the complex IVBNi is a nonconvertible isomer.

Measurements. The measurement technique of magnetic circular dichroism was given previously.[10] All measurements were carried out with a JASCO ORD/UV-5 spectropolarimeter with its CD attachment and an electromagnet. The magnetic field was set at 10000 Gauss. The visible and ultraviolet absorption spectra were taken on a Shimadzu automatic recording spectrophotometer Model MPS-50 and the infrared spectra of Nujol mull were recorded with a Hitachi spectrophotometer Model EPI-G3. The organic solvents used were nitromethane and pyridine. In the case of aqueous solution, an acidic solution (0.05 N $HClO_4$) was used in order to prevent a possible isomerization of the complexes.

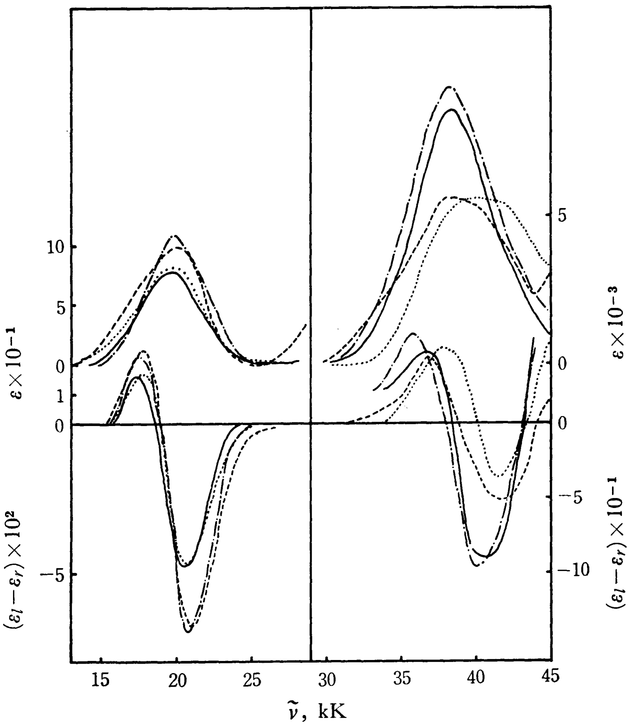


Fig. 2. Absorption and MCD spectra of the copper(II) complexes in acidic water.
——: IACu, —·—: IBCu, ······: IICu, ----: IIICuα

Results and Discussion

Magnetic circular dichroism (MCD) and absorption spectra are shown in Figs. 2—6. An apparent single absorption band was observed at about 20000 cm^{-1} (ε=100) for the copper(II) complexes and at 22000—23000 cm^{-1} (ε=80) for the nickel(II) complexes except the complex VINi. The single weak band is composed of an envelope with several overlapping (*d*, *d**) bands. The diamagnetic ground states of the nickel complexes were established by magnetic susceptibility measurements. They are all diamagnetic in the solid state as in nitromethane solution.[1,7,9] Both the nickel(II) and copper(II) complexes show an asymmetric anomalous MCD dispersion in the (*d*, *d**) band. The asymmetric shape of the MCD spectra in the visible region should be interpreted as a superposition of *B* term extremes of the excitations $d_{z^2}\rightarrow d_{x^2-y^2}$ and $d_{xy}\rightarrow d_{x^2-y^2}$ and an *A* term dispersion of a degenerate excitation $d_{zx},d_{yz}\rightarrow d_{x^2-y^2}$ in term of Ste-

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[7] R. A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **17**, 13 (1969).

[8] B. Jezowska-Trzebiatowska, R. Kolinski, B. Korybut-Daszkiewicz, J. Mrozinski, and W. Wojciechowski, *ibid.*, **17**, 411 (1969).

[9] R. A. Kolinski and B. Korybut-Daszkiewicz, "Proceedings of the XIII ICCC," September 1970, Poland, **1** 320.

[10] H. Kobayashi, M. Shimizu, and I. Fujita, This Bulletin, **43**, 2335 (1970).

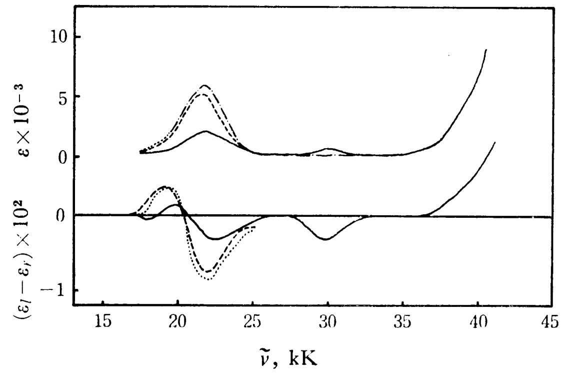

Fig. 3. Absorption and MCD spectra of the nickel(II) complex IANi.
——: in acidic water, —·—: in methanol,
······: in nitromethane, ----: in pyridine

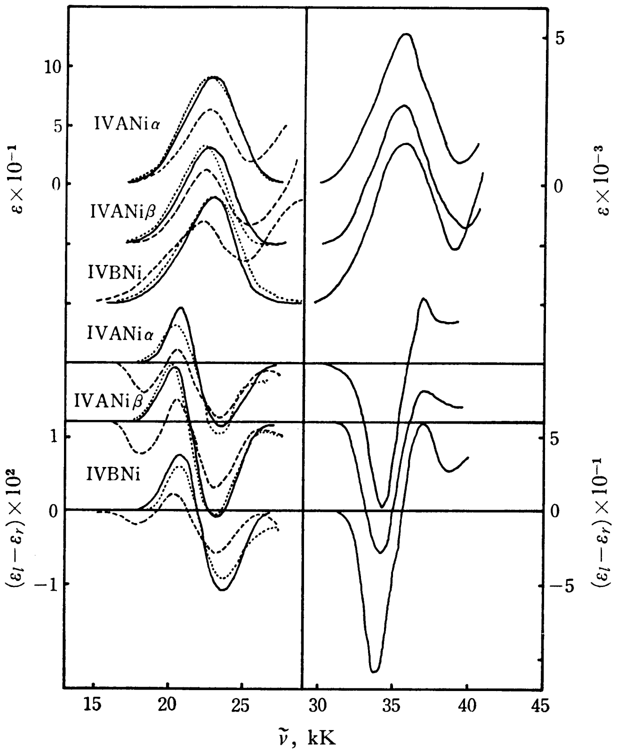

Fig. 4. Absorption and MCD spectra of the nickel(II) complexes IVANiα, IVANiβ, and IVBNi.
——: in acidic water, ······: in nitromethane,
----: in pyridine

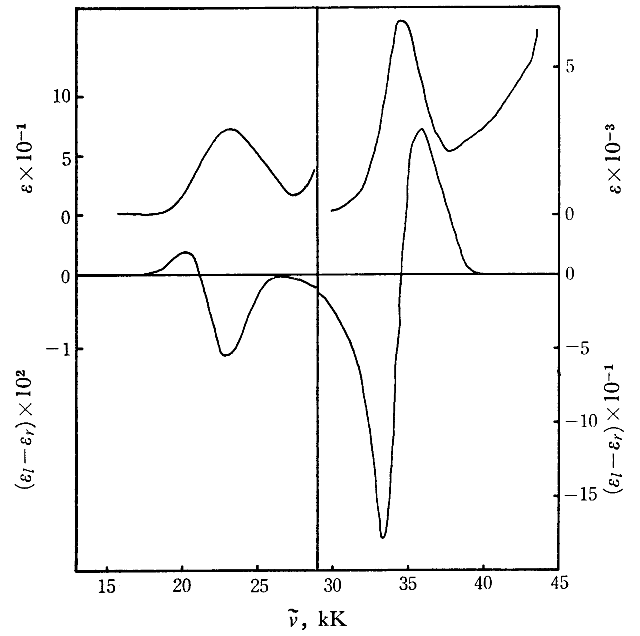

Fig. 5. Absorption and MCD spectra of the nickel(II) complex VANi in H_2O.

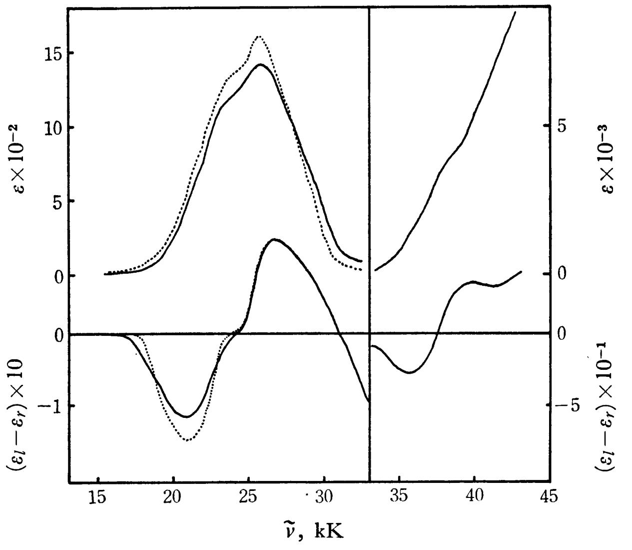

Fig. 6. Absorption and MCD spectra of the nickel(II) complex VINi.
——: in acidic water, ······: in nitromethane

phens' theory of MCD.[11-13] Such a superposition of (d, d^*) bands can also be confirmed by the measurements of optical rotatory dispersion (ORD) or circular dichroism (CD) of the optically active isomers of the complex IVBNi. The CD curve extremes, in fact, were not coincident with the observed absorption maximum. Similar phenomena have been observed.[14,15] An MCD dispersion observed in the (d, d^*) bands of the nickel(II) and copper(II) complexes evidently reveals the location of a degenerate excitation $d_{zx}, d_{yz} \rightarrow d_{x^2-y^2}$.

When the solvent was changed, a red-shift and intensity enhancement of the absorption band of the copper(II) complexes were observed in the ordering nitromethane<water<pyridine. The solvent effect is shown in Fig. 7. In the case of the nickel(II) complexes, however, no such red-shift and intensity enhancement were observed. In pyridine solution a remarkable splitting and intensity reduction were found in the visible band of the nickel(II) complexes IVANiα, IVANiβ, and IVBNi and an appreciable enhancement of the absorption intensity was observed in near-ultraviolet region. As evidenced by magnetic

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11) P. J. Stephens, "Theoretical Studies of Magneto-Optics Phenomena," Thesis, Oxford University, 1964.

12) A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

13) P. J. Stephens, *J. Chem. Phys.*, **52**, 3489 (1970).

14) H. Ito and J. Fujita, This Bulletin, **44**, 741 (1971).

15) Y. Nishida and S. Kida, *ibid.*, **43**, 3814 (1970).

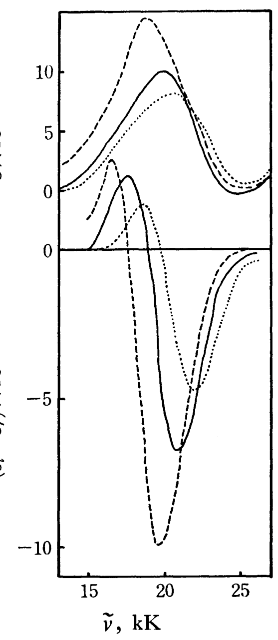

Fig. 7. Absorption and MCD spectra of the copper(II) complex IIICuα.
——: in acidic water, ⋯⋯: in nitromethane,
----: in pyridine

susceptibility and NMR measurements, these complexes in pyridine solution exist partially in a paramagnetic state. An axial coordination of pyridine sufficiently reduces an energy gap between the diamagnetic and triplet ground states, thus giving rise to a thermal equilibrium between the states. The MCD minima at 18000—19000 cm^{-1} are assigned to the second (d, d^*) transition $^3A_2\rightarrow a^3T_1$ in the paramagnetic octahedral nickel(II) complexes. Enhancement of absorption intensity in near-ultraviolet is also interpreted as arising from the third (d, d^*) transition $^3A_2\rightarrow b^3T_1$ of the paramagnetic species. This is in good agreement with the recent observations by Harding *et al.* on paramagnetic trisethylenediamine nickel(II) and tris-2,2′-bipyridine nickel(II) complexes.[16] The complex IANi shows this type of spectral behavior even in aqueous solution as shown in Fig. 3, whereas in pyridine, alcohol and nitromethane it shows a single absorption band at 22000 cm^{-1} characteristic of the diamagnetic square-planar nickel complexes. In organic solvents, the counter perchlorate ion tends to disturb the coordination of solvent donors. Furthermore a steric hindrance against axial coordination arising from a conformation of two methyl groups in one side of the macrocyclic ligand of the complex IANi should be noted. On the contrary, a similar complex prepared by reduction of 2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-dienenickel(II) perchlorate shows a coexistence of the triplet and singlet ground states in such donor solvents as dimethylsulfoxide, dimethylformamide and methyl cyanide, whereas in aqueous solution it gives rise to only a single absorption band at 22500 cm^{-1} of the diamagnetic species.[17]

In the ultraviolet region the nickel(II) complex with isolated ⟩C=N– double bonds shows an absorption band of intermediate intensity (ε=5000) at 35500 cm^{-1}, which increases with the number of isolated double bonds. The other bands appear around 44000 cm^{-1} and 47500 cm^{-1} (ε=12000). The copper(II) complexes, even if the ligand lacks the ⟩C=N– double bonds, show an absorption band around 39000 cm^{-1} (ε=5000—10000) with a similar shape as observed in the nickel(II) complexes. The nickel(II) complexes of the ligands with no ⟩C=N– double bands show no absorption band up to the 44000 cm^{-1} band. Non-existence of the ⟩C=N– double bonds in the complexes IACu, IBCu and IANi was confirmed by IR spectrum. The A term dispersion of MCD is observed in the ultraviolet region as shown in Figs. 2, 4, and 5. However, the A term dispersion in ultraviolet region of the nickel(II) complexes has a sign opposite to that of the A term dispersion in visible region observed for both nickel(II) and copper(II) complexes and also to that of the A term dispersion in ultraviolet region of the copper(II) complexes.

The ultraviolet band at 39000 cm^{-1} of the copper(II) complexes observed even when the ligand lacks ⟩C=N– double bonds is assigned to a degenerate charge-transfer transition from a degenerate molecular orbital pair σ_x and σ_y, predominantly localized on nitrogen lone-pair orbitals, a vacant copper(II) antibonding orbital x^2—y^2. In the case of the nickel(II) complexes, the ultraviolet band at 35500 cm^{-1} is assigned to a degenerate charge-transfer transition from a degenerate non-bonding $d\pi$ orbital pair zx and yz to the lowest antibonding molecular orbital π^*. When the number of isolated ⟩C=N– double bonds in the ligand is increased, the ultraviolet charge-transfer band makes no shift but the intensity is enhanced. However, a complex of the ligand with two isolated double bonds and two conjugated ones gives rise to an intense absorption band around 25000 cm^{-1} (ε=1400) with a shoulder on the lower wave number side around 24100 cm^{-1} as shown in Fig. 6. The sign of term dispersion in the 25000 cm^{-1} band is opposite to that in (d, d^*) bands, which are usually observed in the same region, and the same as the sign observed at the 35500 cm^{-1} band of the nickel(II) complexes with isolated double bonds. The shoulder at 24100 cm^{-1} might be due to a (d, d^*) transition. The absorption band at 25000 cm^{-1} should be assigned to a degenerate charge-transfer transition from a degenerate non-bonding $d\pi$ orbital pair to the antibonding molecular orbital π^* predominantly delocalized over the conjugated double bonds.

A schematic molecular orbital diagram of the diamagnetic d^8 planar complex is given in Fig. 8. There are three spin-allowed (d, d^*) transitions corresponding to the one-electron transitions $1b_{2g}\rightarrow2b_{1g}$ ($^1A_{1g}\rightarrow{}^1A_{2g}$), $2a_{1g}\rightarrow2b_{1g}$ ($^1A_{1g}\rightarrow{}^1B_{1g}$), and $1e_g\rightarrow2b_{1g}$ ($^1A_{1g}\rightarrow{}^1E_g$). An A term dispersion is anticipated for the (d, d^*) transition $1e_g\rightarrow2b_{1g}$ ($^1A_{1g}\rightarrow{}^1E_g$). Because of

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[16] M. J. Harding, S. F. Mason, D. J. Robbins, and A. J. Thomson, *J. Chem. Soc.*, *A*, **1971**, 3058.

[17] L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969), and also E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 1216 (1971).

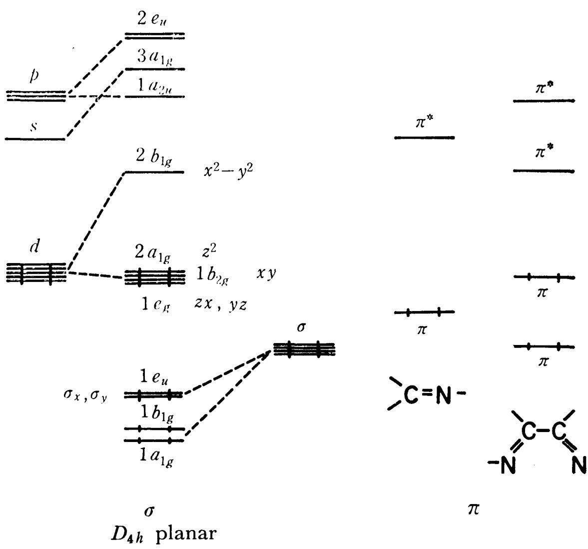

Fig. 8. Molecular orbital diagrams (schematic).

the Laporte forbidden character, the transition should borrow a spectral intensity by vibronic coupling from the allowed charge-transfer transition $1e_u \rightarrow 2b_{1g}$ ($^1A_{1g} \rightarrow {}^1E_u$ x, y polarized), $1e_g \rightarrow 1a_{2u}$ ($^1A_{1g} \rightarrow {}^1E_u$ x, y polarized) and/or $1e_g \rightarrow 1e_u$ ($^1A_{1g} \rightarrow {}^1A_{2u}$ z polarized). Since the transition $1e_g \rightarrow 1e_u$ is z polarized, it can not participate in the MCD observed in (d, d^*) band. As shown in the Appendix, A/D of the transition $1e_u \rightarrow 2b_{1g}$ is negative, while A/D of the transition $1e_g \rightarrow 1a_{2u}$ is positive. Since the MCD dispersion observed in (d, d^*) band is an anomalous one, the allowed transition granting spectral intensity to the (d, d^*) transition is a charge-transfer transition with negative A/D, namely $1e_u \rightarrow 2b_{1g}$. The same theory can also be applied to the (d, d^*) transition of the copper(II) complexes. Molecular vibrations which can mix the Laporte forbidden transition $1e_g \rightarrow 2b_{1g}$ with the allowed transition $1e_u \rightarrow 2b_{1g}$ are out of plane deformation vibrations ν_3 (a_{2u}) and ν_5 (b_{2u}) rather than any other stretching vibrations. These vibrations give rise to a temporary overlapping between zx, yz and nitrogen lone-pair orbitals and thus a non-zero off-diagonal term $(1e_g|\hat{h}'|1e_u)$.

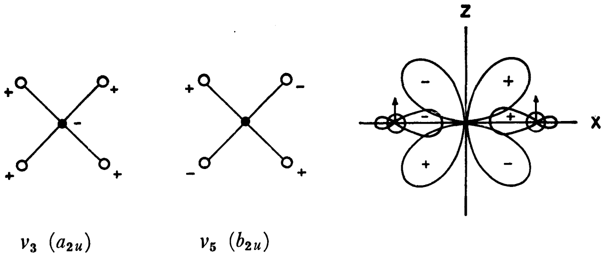

Fig. 9. Out of plane deformation vibrations which mix a Laporte forbidden transition $1e_g \rightarrow 2b_{1g}$ with the allowed transition $1e_u \rightarrow 2b_{1g}$.

The copper(II) complexes, even when the ligand lacks >C=N– double bonds, show an ultraviolet band of intermediate intensity at 39000 cm^{-1} and an anomalous MCD dispersion in the band. Thus the band is assigned to a symmetry allowed transition with a character of charge-transfer from the degenerate molecular orbital pair $1e_u$ to the vacant copper(II) antibonding orbital $2b_{1g}$. The transition $1e_u \rightarrow 2b_{1g}$ gives negative A/D and thus an anomalous MCD dispersion. In the case of the nickel(II) complexes, however, the ultraviolet band of intermediate intensity at 35500 cm^{-1} is observed only when the ligand has isolated >C=N– double bonds and shows a normal MCD dispersion. The band is assigned to a "metal to ligand" charge-transfer transition from the degenerate nickel(II) $d\pi$ orbitals zx, yz to a vacant antibonding molecular orbital of exciton-coupling >C=N– double bonds π^*. The charge-transfer transition should borrow spectral intensity from a strongly allowed coupling (π, π^*) transition in the isolated >C=N– double bonds or the Laporte allowed transition $1e_g \rightarrow 1a_{2u}$.

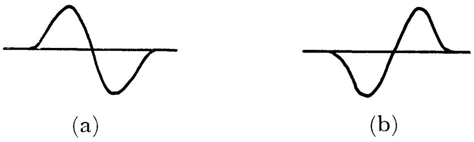

Fig. 10. Normal and anomalous dispersions.
(a) normal dispersion
(b) anomalous dispersion

An exciton coupling between isolated π systems in the coordinating ligand is possible and thus the resultant allowed (π, π^*) oscillator can be a planar oscillator in the case of the complexes VANi and VINi, whereas it gives only a linear oscillator in the case of the complexes with two *trans* >C=N– double bonds such as IVANiα, IVANiβ, and IVBNi. Thus the allowed (π, π^*) transitions in the double bond systems in the coordinating ligand could grant an MCD dispersion intensity to the "metal to ligand" charge-transfer transition only in the cases of the complexes VANi and VINi. In such a planar molecular environment, the allowed degenerate excitation $1e_g \rightarrow 1a_{2u}$ principally localized on the central metal ion is a planar oscillator rather energetically low. Since the molecular orbital $1a_{2u}$ can conjugate with two *trans* >C=N– double bonds in the complexes IVANiα, IVANiβ and IVBNi, the transition $1e_g \rightarrow 1a_{2u}$ can grant a spectral intensity and also an MCD dispersion intensity to the charge-transfer transition $1e_g \rightarrow \pi^*$. Although the possibility of spectral intensity borrowing in the "metal to ligand" charge-transfer transition from the allowed (π, π^*) transitions can not be eliminated, some spectral intensity should surely be stolen from the intrametal allowed transition $1e_g \rightarrow 1a_{2u}$. As shown in the Appendix, the excitation $1e_g \rightarrow 1a_{2u}$ gives rise to a normal MCD dispersion. In fact, the "metal to ligand" charge-transfer transition in the nickel complexes IVANiα, IVANiβ, IANi, and VINi constantly shows a normal MCD dispersion which indicates a borrowing of spectral intensity from the planar oscillator $1e_g \rightarrow 1a_{2u}$.

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Appendix

A degenerate transition from the ground state $|o>$ to a degenerate excited state pair $|\pm j>$ is accompanied by an A term dispersion of MCD. The molecular constant A in the transition $|o> \rightarrow |\pm j>$ is defined as follows:[11-13)]

$$A = 6<+j|\mu_z|+j>\mathrm{Im}\{<o|\hat{m}_x|+j><+j|\hat{m}_y|o>\}$$

where $\hat{\mu}$ and $\hat{m}$ are magnetic and electric dipole operators, respectively, and

$$<\pm j|\hat{\mu}_z|\pm j> = -\beta/\hbar<\pm j|\hat{l}_z|\pm j> .$$

MCD spectrum shows a normal dispersion when $A/D>0$, where

$$D = 6\{|<o|\hat{m}_x|+j>|^2+|<o|\hat{m}_y|+j>|^2\} .$$

It shows an anomalous dispersion when $A/D<0$.

The state wave functions $|o>$ and $|\pm j>$ are given in terms of a degenerate molecular orbital pair $|\pm j)$ and a non-degenerate molecular orbital $|a)$ as follows:

$$\begin{array}{ll} |o> & |+j)|\overline{+j})|-j)|\overline{-j}) \\ |+j> & |+j)|\overline{+j})[|-j)|\overline{a})-|\overline{-j})|a)]/\sqrt{2} \\ |-j> & |-j)|\overline{-j})[|+j)|\overline{a})-|\overline{+j})|a)]/\sqrt{2} \end{array}$$

where no bar implies spin α, a bar implies spin β and

$$(\pm j|\hat{\mu}_z|\pm j) = -\beta/\hbar(\pm j|\hat{l}_z|\pm j) = \mp j'\beta.$$

Since

$$<\pm j|\hat{\mu}_z|\pm j> = (\pm j|\hat{\mu}_z|\pm j) = \mp j'\beta,$$

it follows that

$$A = 6(-j'\beta)\mathrm{Im}\{2(-j|\hat{m}_x|a)(a|\hat{m}_y|-j)\}$$

and

$$D = 6\{2|(-j|\hat{m}_x|a)|^2+2|(-j|\hat{m}_y|a)|^2\}.$$

The degenerate transition $1e_g \rightarrow 1a_{2u}$, for example, is rewritten $|\pm j) \rightarrow |a)$, in terms of $|\pm j) = \{|xz) \pm i|yz)\}/\sqrt{2}$ and $|a) = |z)$. Since

$$(-j|\hat{m}_x|a) = \frac{1}{\sqrt{2}}(zx+iyz|\hat{m}_x|z)$$

$$= \frac{1}{\sqrt{2}}(zx|\hat{m}_x|z) \equiv \frac{1}{\sqrt{2}}m$$

and

$$(a|\hat{m}_y|-j) = \frac{1}{\sqrt{2}}(z|\hat{m}_y|zx-\mathrm{i}yz)$$

$$= -\frac{i}{\sqrt{2}}(z|\hat{m}_y|yz) \equiv -\frac{i}{\sqrt{2}}m$$

it follows that

$$A/D = (1/2)j'\beta.$$

This gives a normal dispersion. For the degenerate transition $1e_u \rightarrow 2b_{1g}$ given in terms of $|\pm j) = \{|\sigma_x) \pm i|\sigma_y)\}/\sqrt{2}$ and $|a) = |x^2-y^2)$, we have

$$(-j|\hat{m}_x|a) = \frac{1}{\sqrt{2}}(\sigma_x+i\sigma_y|\hat{m}_x|x^2-y^2)$$

$$= \frac{1}{\sqrt{2}}(\sigma_x|\hat{m}_x|x^2-y^2) \equiv \frac{1}{\sqrt{2}}m'$$

$$(a|\hat{m}_y|-j) = \frac{1}{\sqrt{2}}(x^2-y^2|\hat{m}_y|\sigma_x-\mathrm{i}\sigma_y)$$

$$= \frac{-i}{\sqrt{2}}(x^2-y^2|\hat{m}_y|\sigma_y) \equiv \frac{i}{\sqrt{2}}m'$$

and thus $A/D = -(1/2)j'\beta$. The gives an anomalous dispersion.