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A Study of Electronic Spectra of Square Planar Copper(II) and Nickel(II) Complexes by Circular Dichroism*1

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Using optically active 1,2-propylenediamine we have synthesized several ligands to form square planar Cu(II) and Ni(II) complexes with optical activity. The CD(circular dichroism) and AB (absorption) spectra of these compounds were measured. The broad absorption bands were resolved in the CD spectra into each component due to a *d-d* transition, to which a specific *d-d* transition was assigned. It was found that in these compounds the change in the central atom from Cu(II) to Ni(II) dose not alter the main feature of CD and AB spectra. This seems to be the general rule for the planar Cu(II) and Ni(II) complexes.

The ligand field theory predicts that three spin-allowed *d–d* transitions may be observed in the electronic spectra of square planar copper(II) and nickel(II) complexes. However, the three d–d bands are usually superposed and are observed as one broad band, sometimes with shoulders. Thus our attempt to assign the absorption bands to each electronic transition was accompanied with considerable difficulty.

Recently, Smith[1,2] has developed an elegant approach for the estimation of energy levels of tetragonal copper(II) complexes, making use of Hathaway and his coworkers' detailed experimental data.[3,4] According to Smith, the order of energy levels of $Cu(NH_3)_4X_2$ and Cu en_2X_2, (X=SCN^-, NO_2^-, $CuCl_2^-$, and other various anions) is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}$, d_{yz}, but in planar $CuCl_4^{2-}$ the order of d_{xy} and d_{z^2} is reversed. This implies that more detailed studies are necessary for the elucidation of the electronic spectra of copper(II) complexes. As for the electronic spectra of square planar nickel(II) complexes, information is still insufficient.[5]

We have prepared numerous square planar copper(II) and nickel(II) complexes of the $[MN_4]$ and $[MN_2O_2]$ types containing optically active ligands, and tried to obtain more information on the energy states of these complexes by taking advantage of CD spectra which give much more resolved spectra than the AB spectra for superposed bands. In addition, we could obtain some information of the configuration and the conformation of the complexes by CD spectra.

Experimental

The absorption and circular dichroism spectra were obtained by a Jasco ORD-UV/5 optical rotatory dispersion recorder with a CD attachment at room temperature. Optically active (−)D-propylenediamine (abbreviated as (−)pn) was obtained by the method of Dwyer *et al.*[6] These complexes may be classified into the following four types.

A. Complexes with optically active propylenediamine. $[Cu(-)pn_2](ClO_4)_2$, and $[Ni(-)pn_2](ClO_4)_2$ were obtained from metal perchlorate and (−)D-propylenediamine in methanol solution.

B. Complexes with optically active Schiff bases resulted from salicylaldehyde or its derivatives and (−)D-propylenediamine, such as sal(−)pnH_2, naphal(−)pnH_2, 7-mesal(−)pnH_2. (For abbreviation, see Table 2). Each of these complexes was obtained from metal acetate and schiff base, which was obtained from the mixture of salicylaldehyde or its derivatives and (−)D-propylenediamine.

C. Complexes with optically active schiff bases from acetylacetone or benzoylacetone and (−)D-propylenediamine, such as acac(−)pnH_2, bzac(−)pnH_2, (see Table 2). These complexes were obtained from a mixture of metal chloride, schiff base and sodium carbonate in water-methanol mixture.

D. Complexes with the mad(−)pnH_2, oxad(−)-pnH_2, sad(−)pnH_4, which were obtained from the condensation reaction between diethylmalonate, diethyloxalate or methyl salicylate and (−)-propylenediamine. Metal complexes were prepared by a method

*1 Presented in part at the 19th Symposium on Coordination Chemistry, Sendai, September, 1969.

1) D. W. Smith, *J. Chem. Soc., A*, **1969**, 1708.

2) D. W. Smith, *ibid., A*, **1969**, 2529.

3) B. J. Hathaway, D. E. Billing, P. Nicholls and I. M. Procter, *ibid., A*, **1969**, 65, 319.

4) I. M. Procter, B. J. Hathaway and P. Nicholls, *ibid., A*, **1968**, 1678.

5) H. B. Gray, "Transition Metal Chemistry," Vol. 1, ed. by R. L. Carlin, Marcel Dekker, New York (1965), p. 239.

6) F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959).

Table 1. Elementary analyses of the complexes

Complex	Formula	Found (%)			Calcd (%)		
		C	H	N	C	H	N
[Cu(−)pn$_2$](ClO$_4$)$_2$H$_2$O	$CuC_6H_{22}O_9N_4Cl_2$	17.35	4.89	13.43	17.14	4.76	13.33
[Ni(−)pn$_2$](ClO$_4$)$_2$	$NiC_6H_{20}O_8N_4Cl_2$	17.88	5.11	13.71	17.73	4.92	13.79
[Cu sal(−)pn]	$CuC_{17}H_{18}O_3N_2$	56.64	5.14	7.70	56.35	4.97	7.71
[Cu 7-mesal(−)pn]	$CuC_{19}H_{20}O_2N_2$	60.81	5.50	7.52	61.20	5.37	7.52
[Ni sal(−)pn]	$NiC_{17}H_{20}O_2N_2$	60.18	4.79	8.21	60.17	4.72	8.26
[Ni naphal(−)pn]*	$NiC_{25}H_{20}O_2N_2$	68.05	4.71	6.25	68.33	4.56	6.37
[Ni 7-mesal(−)pn]*	$NiC_{19}H_{20}O_2N_2$	61.85	5.38	7.82	62.12	5.45	7.63
[Cu acac(−)pn]	$CuC_{13}H_{19}O_2N_2$	52.61	6.89	9.41	52.10	6.68	9.32
[Ni acac(−)pn]	$NiC_{13}H_{19}O_2N_2$	52.77	6.83	9.52	52.88	6.77	9.49
[Ni bzac(−)pn]*	$NiC_{23}H_{24}O_2N_2$	66.02	5.83	6.87	65.60	6.17	6.65
[Cu mad(−)pn]·9H$_2$O*[a]	$CuC_9H_{38}O_{11}N_4$	24.93	7.86	12.98	24.55	8.18	12.98
[Cu mad(−)pn]·3/2H$_2$O*	$CuC_9H_{23}O_{3.5}N_4$	35.24	6.97	18.34	35.61	6.59	18.45
[Cu oxad(−)pn]·3/2H$_2$O*	$CuC_8H_{21}O_{3.5}N_4$	32.90	6.70	18.27	33.02	6.53	18.55
[Ni mad(−)pn]·H$_2$O*	$NiC_9H_{22}O_3N_4$	37.31	6.80	19.14	37.24	6.52	19.31
[Ni oxad(−)pn]·H$_2$O*	$NiC_8H_{20}O_3N_4$	34.46	7.03	19.74	34.77	6.52	19.74
Na$_2$[Cu sad(−)pn]·5.5H$_2$O*[b]	$CuC_{17}H_{25}O_{9.5}N_2Na_2$	39.32	4.22	5.22	39.15	4.70	5.37

* New complex

a) This complex, which is orange, gradually turns violet losing water in the atmosphere.

b) This complex is hygroscopic.

similar to the Ojima's method.[7,8] Since the nickel complex of sad(−)pnH$_4$ did not crystallize, the solution was purified by eluting on alumina and the ion-exchange resin, Amberlite CG 120. The solution thus obtained was immediately used for optical measurements. The obtained spectrum agreed well with that of the ethylenediamine homologue, indicating that [Ni sad(−)pn]$^{2-}$ was formed in the solution.

Results and Discussion

Copper Complexes. It is believed that bis(propylenediamine)copper(II) ion has a nearly tatragonal configuration in methanol solution as in the case of bis(ethylenediamine)copper(II) ion. As is seen in Fig. 3, CD spectrum of Cu(−)pn$_2$(ClO$_4$)$_2$ shows a small band at 15.2 kK. besides the main broad band at 19.7 kK. Gillard[9] assigned the main band to the $d_{xz},d_{yz}\rightarrow d_{x^2-y^2}$ transition and the small bond at 15.2 kK to the $d_{xy}\rightarrow d_{x^2-y^2}$ transition. The band due to the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition was assumed to be located at the region of much lower wave-number (*cf.* Fig. 2). However, from the Gaussian analysis of electronic spectra, measured at room temperature and at the temperature of liquid nitrogen, of the crystals of bis(ethylenediamine)copper(II) salts with different anion, Hathaway *et al.* found three bands in the visible region. They assigned the bands which were found at 20.3—17.9 kK, 18.0—16.2 kK and 16.8—12.2 kK to the transitions $d_{xz},d_{yz}\rightarrow d_{x^2-y^2}$, $d_{xy}\rightarrow d_{x^2-y^2}$, and $d_{z^2}\rightarrow d_{x^2-y^2}$, respectively. The result of Smith's calculation agreed satisfactorily with the experimental values on the same assignment. The band at 15.2 kK of Cu(−)pn$_2^{2+}$ was clearly resolved in our CD measurement, which should correspond to the band of the lowest wave-number in Cu en$_2^{2+}$, and is assigned to the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition. Further support for this assignment will be seen in the following discussion.

In the solvent of stronger donating ability, such as pyridine, the coordination or semi-coordination of the solvent molecule to the copper ion along the

Table 2. Legend for abbreviations of ligands

	Ligand	Abbreviation
I	(−)$_D$-propylenediamine	(−)pn
II	bis(salicylaldehyde)-(−)$_D$-propylenediamine	sal(−)pnH$_2$
III	bis(acetophenone)-(−)$_D$-propylenediamine	7-mesal(−)pnH$_2$
IV	bis(α-naphthol-β-aldehyde)-(−)$_D$-propylenediamine	naphal(−)pnH$_2$
V	bis(acetylacetone)-(−)$_D$-propylenediamine	acac(−)pnH$_2$
VI	bis(benzoylacetone)-(−)$_D$-propylenediamine	bzac(−)pnH$_2$
VII	*N,N'*-bis(2-aminopropyl)-malonamide	mad(−)pnH$_2$
VIII	*N,N'*-bis(2-aminopropyl)-oxalamine	oxad(−)pnH$_2$
IX	*N,N'*-propylene-bis(salicylamide)	sad(−)pnH$_4$

7) H. Ojima and K. Yamada, *Nippon Kagaku Zasshi*, **89**, 490 (1968).

8) H. Ojima, *ibid.*, **88**, 329 (1967).

9) R. D. Gillard, *J. Inorg. Nucl. Chem.*, **26**, 1455 (1964).

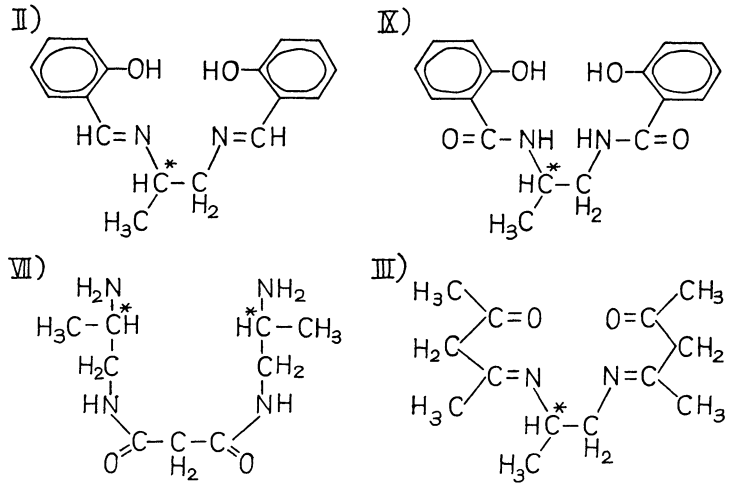

Fig. 1. Structure of ligands (see Table 2).

tetragonal axis would become stronger, and d_{z^2} orbital of the copper ion suffers the most profound effect among the *d*-orbitals (Fig. 2). As a result of this effect, the band due to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition will show the largest red shift among the *d–d* bands. In fact, as seen in Fig. 3, in the CD and absorption spectra of $Cu(-)pn_2(ClO_4)_2$ in pyridine solution, the red shift of the main peak is only about 1 kK in either AB or CD spectrum compared with that in methanol solution. On the other hand, the CD band, which was observed at 15.2 kK in methanol solution and was assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, disappeared in pyridine solution, and a shoulder appeared at 12 kK in the absorption spectrum, suggesting that this band shifted from 15.2 kK to 12 kK.

The CD and AB spectra of [Cu mag(−)pn] are shown in Fig. 4. In this complex two of four coordinated nitrogen atoms are anions of amide nitrogen which has lost a proton. It is accepted that in such a $[CuN_4]$ type complex as involving anion nitrogen in coordination, the coordination bonds in the tetragonal plane is much stronger than those of the complex coordinated by four neutral nitrogen atoms, and the axial coordination becomes very weak.[7,8] As a result of this effect, the d_{z^2} orbital will be stabilized and the $d_{z^2} \rightarrow d_{x^2-y^2}$ band will shift to the higher wave-number. This is the reversal of the spectral change from a methanol solution to a pyridine solution. In fact, only one broad band was observed in either AB or CD spectrum of [Cu mad(−)pn] in the visible region. This is understandable in view of the blue shift of the $d_{z^2} \rightarrow d_{x^2-y^2}$ band to the region of the main band.

The Resemblance of CD Spectra of Planar Cu(II) and Ni(II) complexes. It is readily ob-

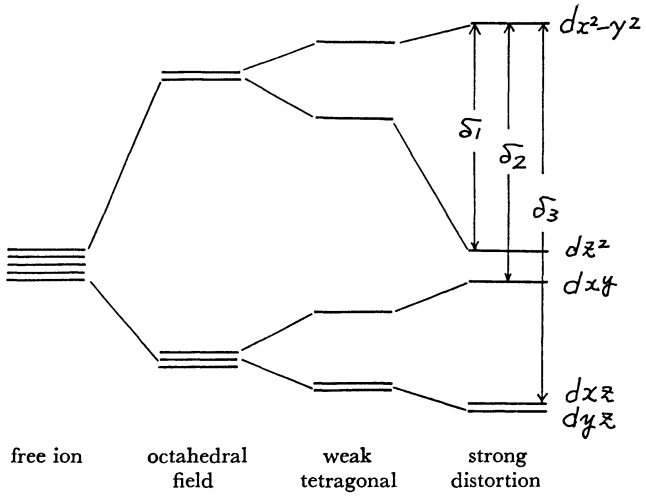

Fig. 2. Assumed scheme of *d*-orbital splitting.

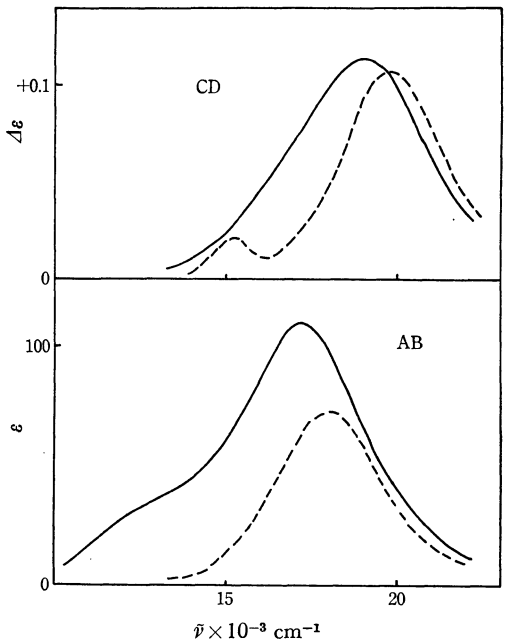

Fig. 3. AB and CD spectra of $[Cu(-)pn_2](ClO_4)_2$.
------ in methanol —— in pyridine

served that the CD and AB spectra of [Cu mad(−)-pn] resemble those of the nickel(II) complex of the same ligand as seen in Fig. 4. In the Cu(II) and Ni(II) complexes of sad(−)pn, which are shown in Fig. 5, the three components of the *d–d* bands are clearly resolved in CD spectra of both complexes. Resemblance of the two spectra is rather surprising, and the three bands may be assigned from the lower wave-number side to $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ in each complex.

The spectra of [Cu acac(−)pn], [Cu sal(−)pn] and [Cu 7-mesal(−)pn] in chloroform are shown in Fig. 6. Judging from the absorption intensity, the bands above 23 kK would not be due to the d–d transition but could be attributed to the origin in the ligand electron. Though the three complexes all belong to the square planar *cis*-$[CuN_2O_2]$ type, the CD spectrum of [Cu sal(−)pn] associated with d–d transision entirely differs from those of the other two complexes, as is obvious from Fig. 6. Downing and Urbach,[10] and the present authors[11] independently reached the same conclusion that this fact may be rationalized in terms of the conformational preference of the central chelate ring resulting from the steric requirements of the ligands.

The nickel(II) complexes of acac(−)pnH_2, sal-(−)pnH_2 and 7-mesal(−)pnH_2 are expected to have a square planar configuration from the electronic spectra and a structure of homologous ethylenediamine derivatives. Each of the CD spectra of the nickel complexes bears a close resemblance to that of the corresponding copper complex, suggesting that the conformations of the bridging propane-1,2 diamine group are similar to each other in the nickel

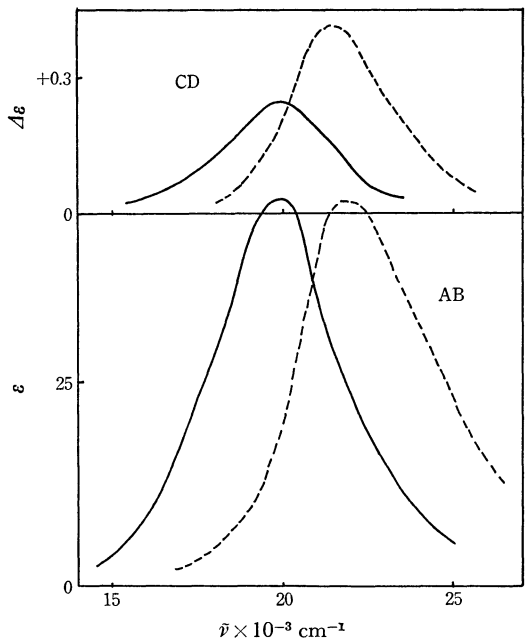

Fig. 4. AB and CD spectra of —— [Cu mad-(−)pn] in methanol ------ [Ni mad(−)pn] in methanol.

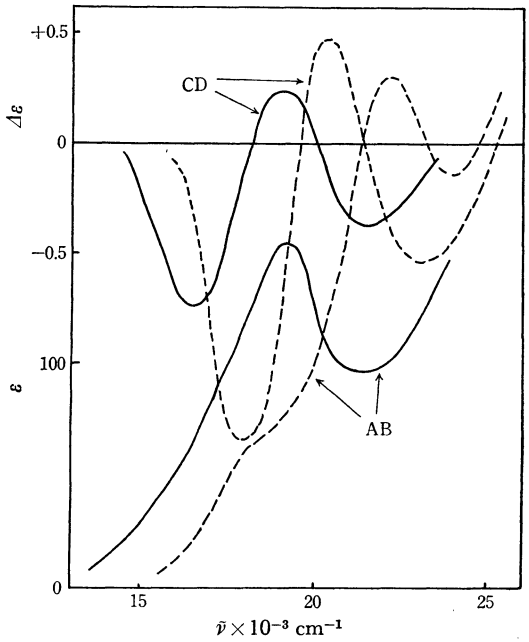

Fig. 5. AB and CD spectra of —— [Cu sad-(−)pn]$^{2-}$ in methanol ------ [Ni sad(−)pn]$^{2-}$ in methanol.

10) R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, **91**, 5977 (1969).

11) 19th Symposium on Coordination Chemistry, at Tohoku University, September, 1969.

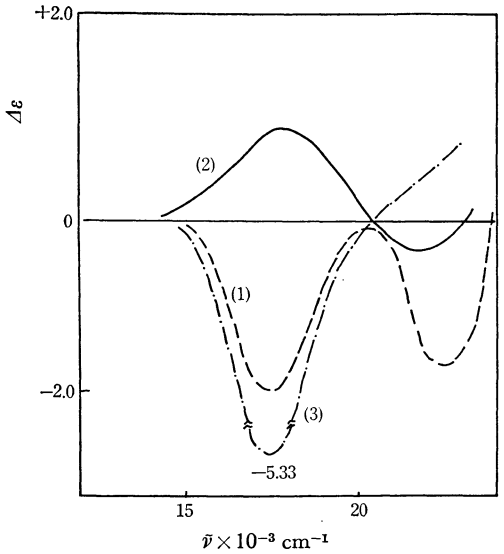

Fig. 6. CD spectra of (1) -------- [Cu acac(−)pn] (2) ——— [Cu sal(−)pn] (3) ------ [Cu 7-mesal(−)pn] in chloroform.

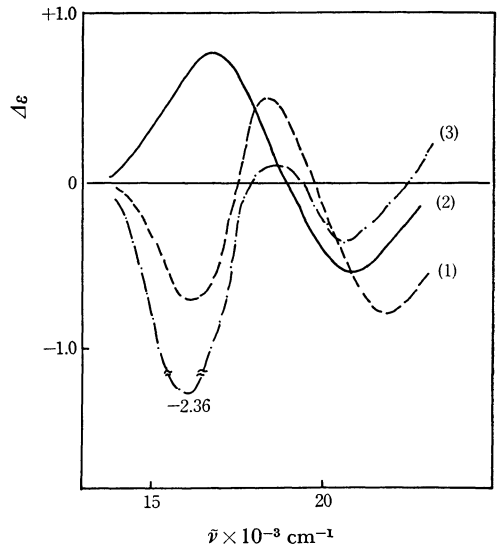

Fig. 7. CD spectra of (1) -------- [Ni acac(−)pn] (2) ——— [Ni sal(−)pn] (3) ------ [Ni 7-mesal(−)pn] in chloroform.

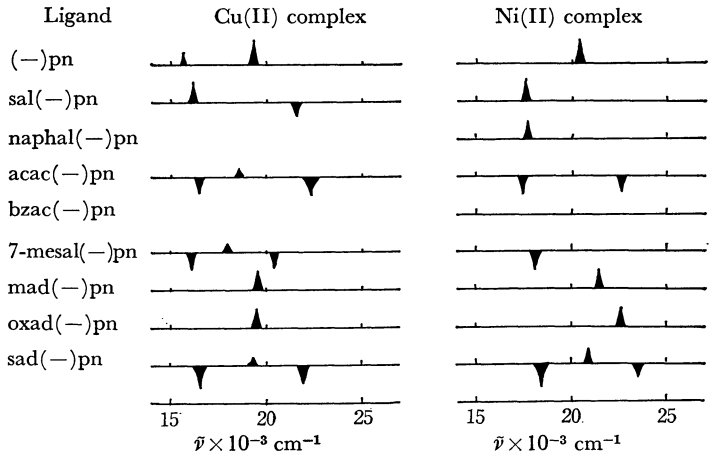

Fig. 8. Simple representation of CD spectra.

and copper complexes of the same ligand (Figs. 6 and 7).

The close resemblance of CD spectra of the planar copper(II) and nickel(II) complexes of the same ligand is too obvious to be considered accidental. In fact, this tendency was observed not only in the above complexes but in the spectra of Ni(II) and Cu(II) complexes of every ligand studied in the present work (Fig. 8). Further, from literature we investigated we have always found such resemblance in CD spectra for each pair of nickel and copper complexes of the same ligand.[12–14] Thus, this appears to be the general rule.

The *d*-orbitals split under the ligand field of square planar coordination as shown in Fig. 2. If interelectronic interaction is neglected, there is no significant difference between planar Cu(II) and Ni(II) complexes. Actually, however, the energy states of nickel(II) complexes are largely dependent on interelectronic repulsion, even if the spin-orbit-coupling is neglected. Accordingly, the energies for some lower singlet states of a planar nickel(II) complex are expressed as

$$^1A_{1g}: E_0 = F_0 + 4F_2 + 36F_4$$
$$^1B_{1g}: E_1 = \delta_1 + F_0 + 21F_4$$
$$^1A_{2g}: E_2 = \delta_2 + F_0 + 4F_2 + F_4$$
$$^1E_g: E_3 = \delta_3 + F_0 + F_2 + 16F_4$$

Following Ballhausen and Liehr,[15] we assume $F_2 = 10F_4 = 1$ kK,

12) T. Komorita, J. Hidaka and Y. Shimura, This Bulletin, **42**, 168 (1969).

13) G. K. Bryce and F. R. N. Gurd, *J. Boil. Chem.*, **241**, 1439 (1969).

14) K. M. Wellman, S. Bogdansky, C. R. Hare and M. Mathiesm, *Inorg. Chem.*, **8**, 1025 (1969).

$$\Delta E_1 = \delta_1 - 4F_2 - 15F_4 = \delta_1 - 5.5\,\text{kK}$$

$$\Delta E_2 = E_2 - E_0 = \delta_2 - 35F_4 = \delta_2 - 3.5\,\text{kK}$$

$$\Delta E_3 = E_3 - E_0 = \delta_3 - 3F_2 - 20F_4 = \delta_3 - 5.0\,\text{kK}$$

and

$$\Delta E_{12} = E_2 - E_1 = \delta_2 - \delta_1 + 4F_2 - 20F_4 = \delta_2 - \delta_1 + 2.0\,\text{kK}$$

$$\Delta E_{23} = E_3 - E_2 = \delta_3 - \delta_2 + 3F_2 + 15F_4 = \delta_3 - \delta_2 - 0.5\,\text{kK}$$

From the above result, the effect due to the interelectronic repulsion is comparable to the observed band separations 2.5—3.0 kK, but is not large enough to change the order of energy levels $E_1 < E_2 < E_3$. Therefore, the same pattern can be expected with the same ligands. However, it is to be noted that the resemblance is close, at least in the examples cited above, and is considered to be more than that expected from the above discussion. An explanation for this tendency is still in question at present.[16]

The reason for the planar Ni(II) and Cu(II) complexes giving similar CD spectra for bands whose origins are the transitions between the same combination of *d*-orbitals is given as follows. According to Condon,[17] the rotational strength R_{ab} associated with the electronic transition from the state, a, to the state, b, is determined by

$$R_{ab} = \text{Im}\langle(a)|\mathbf{P}|(b)\rangle\langle(b)|\mathbf{M}|(a)\rangle$$

where Im denotes the imaginary part of the scalar product of these moments; (a) and (b) stand for the wave functions of the ground and the excited states, and **P** and **M** are the electric and magnetic dipole moment-oparators. In the case of a multi-electron system, (a) and (b) are to be expressed by the Slater determinants. However, since **P** and **M** are one-electron operators, $\langle(a)|\mathbf{P}|(b)\rangle$ and $\langle(b)|\mathbf{M}|(a)\rangle$ are reduced to the simple formulas, $\langle a'|\mathbf{P}|b'\rangle$ and $\langle b'|\mathbf{M}|a'\rangle$, where a' and b' represent the wave functions of simple orbitals between which an electron transfers. Thus, it has been verified that rotational strengths of Ni(II) and Cu(II) complexes of the same ligand may be expressed by the same formula for the transitions between the same combination of *d*-orbitals.

The authors would like to express their thanks to Mr. Masaaki Narimatsu for help in the experiment.

15) C. J. Ballhausen and A. D. Liehr, *J. Amer. Chem. Soc.*, **81**, 538 (1958).

16) The energies due to the interaction with upper $^1A'_{1g}$ and $^1B'_{1g}$ states were found to be less than 0.2 kK which is negligible in the present discussion.

17) E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1932).