# The Electronic Structure and Electronic Spectrum of Dichlorodipyridinecobalt(II). Charge-Transfer Band Due to Interaction between Halide Ion and Cobalt(II) Cation

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The ultraviolet absorption spectrum of dichlorodipyridinecobalt(II) complex was measured in solution and in the crystal form. The solution spectrum exhibits a strong band at 256 m$\mu$ and a shoulder on the longer wavelength side. The former band was interpreted to be the local excitation band of pyridine. The shoulder band was found to shift to longer wavelengths and to increase in intensity in the order dichloro- < dibromo- < diiododipyridinecobalt(II). Furthermore, the band was found to split into two peaks for the diiodo complex. The separation of 5200 cm$^{-1}$ may correspond to the energy difference between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the free iodine atom. From these experimental facts and the theoretical studies, it was shown that the shoulder band may be regarded as the charge-transfer absorption accompanying the $\pi$-electron migration from the ligand halide ion to the metal cation. The dichroism observed in a single crystal of the dichloro complex supports this interpretation of the weak absorption at 300 m$\mu$. The Davydov splitting was observed with the local excitation band of the ligand pyridine molecule.

## Introduction

Concerning coordination compounds, it is known that the so-called charge-transfer (abbreviated hereafter as CT) interaction exists between metal cations and ligands. Therefore, it may be expected by an analogy with Mulliken's CT interaction[1] between electron donor and acceptor that some metal complexes show new peaks attributable neither to the isolated ligand nor to the metal cation. In actuality, this kind of absorption band which may be called the CT band has been found with several metal complexes.[2] In the present study, we undertook to find the CT band with the $\alpha$-dichlorodipyridinecobalt(II) complex. For this purpose, we have measured the visible and ultraviolet absorption spectra of this complex in the crystal form as well as in solution. Furthermore, theoretical studies have been carried out with the $\pi$-electron structure of the complex in order to certify the existence of the CT absorption.

## Experimental Section

**Materials.**—Dichloro-, dibromo-, and diiododipyridinecobalt-(II) complexes were prepared by a method described in the literature.[3] The chloroform used as a solvent was shaken with sulfuric acid and then with water, dried overnight with calcium chloride, and finally distilled.

**Measurements.**—A Cary recording spectrophotometer, Model 14M, was used for the measurements of visible and ultraviolet spectra in solution. The polarized absorption spectrum of an $\alpha$-dichlorodipyridinecobalt(II) crystal was measured with a microspectrophotometer constructed in our laboratory.[4] The thin crystal used for the measurement was prepared by recrystallization from ethanol.

## Theoretical

We have carried out the theoretical study of the $\pi$-electron structure of dichlorodipyridinecobalt(II) considering the interaction between the Co(II) cation and

the ligand molecules or ions by the aid of the configuration interaction among the ground, CT, and locally excited (LE) configurations. By an analogy with the case of organic unsaturated molecules, we adopted the so-called $\pi$-electron approximation.[5] The calculation procedures adopted by the present authors are very similar to those used for the theoretical consideration of the silver cation complex with an unsaturated hydrocarbon[6] or with pyridine.[7]

The geometrical structure of the $\alpha$-dichlorodipyridinecobalt(II) has been determined by the X-ray crystal analysis technique as is shown in Figure 1.[8] In the actual calculation, we took the part shown in Figure 2 as the unit for the calculation.

**The Component Orbitals.**—The dichlorodipyridinecobalt(II) was separated into the components, namely, the metal cation and the ligand molecules or ions, and the $\pi$-electron orbitals of each component were determined. As the SCFMO's of the pyridine, we used those calculated by Mataga and Nishimoto.[9] The estimation of the overlap integrals between the ligand and the cobalt cation was made by the aid of the SCFAO's of nitrogen and chlorine determined by Clementi[10] and the SCFAO of cobalt determined by Richardson, *et al.*[11] The formal charges of cobalt cation and chloride anion were assumed to be +2 and −1, respectively. Hereafter we represent the component $\pi$ orbitals by the following symbols: occupied $\pi$ orbitals of pyridine: 1 (−14.32 eV), 2 (−11.44 eV), 3 (−10.76 eV); vacant $\pi$ orbitals of pyridine: 4 (−1.58 eV), 5 (−1.29 eV); orbitals of chlorine taken in the present calculation: $p_z$, p orbital parallel to the z axis; $p_\perp$, p orbital perpendicular to the z axis

(1) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(2) E. König and H. L. Shläfer, *Z. Physik. Chem.* (Frankfurt), **26**, 371 (1960); C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959); H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

(3) E. G. Cox, A. J. Shorter, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937).

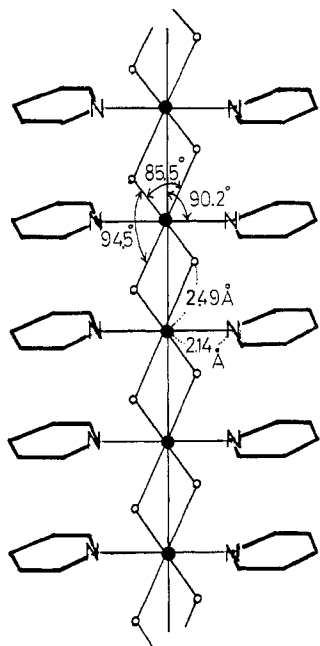(4) J. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 833 (1963).

(5) The detailed discussion on the application of the $\pi$-electron approximation to metal complexes has been made by I. Hanazaki and S. Nagakura, submitted for publication.

(6) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 249 (1964).

(7) Y. Bando and S. Nagakura, *Theor. Chim. Acta*, **9**, 210 (1968).

(8) J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

(9) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957).

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

(11) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *ibid.*, **36**, 1057 (1962).

Figure 1.—The geometrical structure of α-dichlorodipyridine-cobalt(II): ●, the cobalt(II) cation; O, the chloride anion.
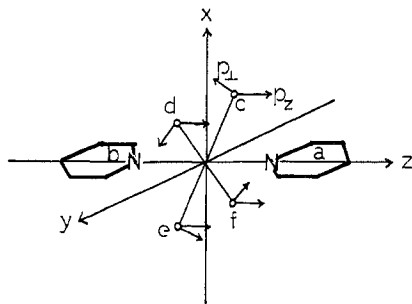


Figure 2.—The structural unit taken in the present theoretical study.

and the bonding axis connecting the cobalt cation and the chloride anion; orbitals of cobalt taken in the present calculation: $d_{zx}$, $d_{yz}$, $d_{x^2-y^2}$.

**The Configurations and Their Energies.**—By putting the $\pi$ electrons in the above orbitals, a number of electron configurations can be obtained. The wave function of the ground configuration can be represented by the expression: $|(1\bar{1}2\bar{2}3\bar{3})^a(1\bar{1}2\bar{2}3\bar{3})^b(p_z\bar{p}_z p_\perp \bar{p}_\perp)^c(p_z-\bar{p}_z p_\perp \bar{p}_\perp)^d(p_z\bar{p}_z p_\perp \bar{p}_\perp)^e(p_z\bar{p}_z p_\perp \bar{p}_\perp)^f d_{zx}\bar{d}_{zx}d_{yz}\bar{d}_{yz}d_{x^2-y^2}|$.

The superscripts a and b denote the two pyridine molecules on the different positions in Figure 2, and c, d, e, and f show the chloride anions. In addition to the ground configuration, the LE configurations corresponding to the $2 \to 4$, $2 \to 5$, $3 \to 4$, and $3 \to 5$ transitions of pyridine and the CT configurations corresponding to the $p_z \to d_{x^2-y^2}$, $p_\perp \to d_{x^2-y^2}$, $2 \to d_{x^2-y^2}$, $3 \to d_{x^2-y^2}$, and $d_{x^2-y^2} \to 4$ transitions were taken into account. The above-mentioned configurations are classified into the irreducible representations of the $D_{2h}$ symmetry as is shown in Table I.

The energies of the CT configurations were evaluated by the relation of $I - A + \Delta$, where $I$ and $A$ are the ionization potential of donor and the electron affinity

TABLE I

SYMMETRIES AND ENERGIES OF ELECTRON CONFIGURATIONS

| Irreducible representation | Configuration | Energy, eV | | |
|---|---|---|---|---|
| $A_g$ | Ground | 0.00 | | |
| | CT $(p_\perp \to d_{x^2-y^2})$ | 4.00 | | |
| | LE $(3 \to 5)$ | 6.64 (LE$(3 \to 5)^+$), | 3.56 (LE$(3 \to 5)^+)'$ | |
| | LE $(2 \to 4)$ | 7.16 (LE$(2 \to 4)^+$), | 3.99 (LE$(2 \to 4)^+)'$ | |
| $B_{1u}$ | CT $(p_z \to d_{x^2-y^2})$ | 4.00 | | |
| | LE$(3 \to 5)$ | 6.47 (LE$(3 \to 5)^-$), | 3.56 (LE$(3 \to 5)^-)'$ | |
| | LE$(2 \to 4)$ | 7.03 (LE$(2 \to 4)^-$), | 4.04 (LE$(2 \to 4)^-)'$ | |
| $B_{2u}$ | CT $(p_\perp \to d_{x^2-y^2})$ | 4.00 | | |
| | LE$(3 \to 4)$ | 5.15 (LE$(3 \to 4)^-$), | 3.55 (LE$(3 \to 4)^-)'$ | |
| | LE$(2 \to 5)$ | 7.20 (LE$(2 \to 5)^-$), | 5.60 (LE$(2 \to 5)^-)'$ | |
| $B_{3u}$ | CT$(2 \to d_{x^2-y^2})$ | 8.43 | | |
| | CT$(p_\perp \to d_{x^2-y^2})$ | 4.00 | | |
| | CT$(d_{x^2-y^2} \to 4)$ | 10.48 | | |

of acceptor, respectively, and $\Delta$ is the electrostatic energy between electron donor and acceptor. The energies of LE configurations were taken to be $E(i \to j) + \Delta'$, where $E(i \to j)$ is the transition energy calculated for the excitation from orbital $i$ to orbital $j$ of the free pyridine molecule and $\Delta'$ is the change in the transition energy $E(i \to j)$ due to perturbation of the Co(II) cation and the Cl anion.

In the present study, the system belongs to the open shell. Therefore, two locally excited configurations corresponding to the singlet and triplet local excitations from orbital $i$ to orbital $j$ in each pyridine molecule can interact with the ground configuration. Furthermore, under the $D_{2h}$ symmetry the two locally excited configurations corresponding to the singlet excitations of the ligand pyridine molecules "a" and "b" can mix with each other giving LE$(i \to j)^+$ = [LE$(i \to j)_a$ + LE$(i \to j)_b$]$/\sqrt{2}$ and LE$(i \to j)^-$ = [LE$(i \to j)_a$ − LE$(i \to j)_b$]$/\sqrt{2}$. In the similar way, we can construct (LE$(i \to j)^+)'$ and (LE$(i \to j)^-)'$ for the triplet local excitation $(i \to j)$.

**Configuration Interaction.**—The above-mentioned configurations belonging to the same representation interact with one another.[6,7] In the calculation of the configuration interaction, the zero-differential overlap approximation was applied to the evaluation of Coulomb repulsion integrals.[12] The two-center Coulomb repulsion integrals of the type $(pp|qq)$ between the atoms within a pyridine molecule were calculated by the Nishimoto and Mataga[9] approximation, and those for the other cases, by the point charge approximation. The one-center Coulomb repulsion integrals of the type $(pp|pp)$ were evaluated by the Pariser–Parr approximation and were set equal to $I - A$, the difference between the valence state ionization potential and electron affinity.[12] Consequently, the off-diagonal matrix elements of the total electron Hamiltonian, each of which represents the interaction between the two configurations, can be obtained as is shown in Table II.

In the present calculation, the system containing four Cl⁻, one Co²⁺, and two pyridines is taken into account. However, the α-dichlorodipyridinecobalt(II) crystal forms the chain polymer as is shown in Figure 1. Therefore we tried to consider the perturbation due to chain formation, especially due to the neighboring

(12) R. Pariser and R. G. Parr, J. *Chem. Phys.*, **21**, 466, 767 (1953).

TABLE II

OFF-DIAGONAL MATRIX ELEMENTS OF THE
TOTAL ELECTRON HAMILTONIAN

| | Value, eV 3618 |
|---|---|
| $H(G, CT) = 2\beta(Cl, Co)$ | −0.40 |
| $H(G, LE(3 \rightarrow 5)^+) = 4[2(3^a5^a\|pp) - (3^a5^a\|dd)]$ | 0.91 |
| $H(G, LE(2 \rightarrow 4)^+) = 4[2(2^a4^a\|pp) - (2^a4^a\|dd)]$ | −0.26 |
| $H(LE(3 \rightarrow 5)^+, LE(2 \rightarrow 4)^+) = 2(2^a4^a\|3^a5^a) -$ $(2^a3^a\|4^a5^a) + 2(3^a5^a\|2^b4^b)$ | 0.51 |
| $H(LE(3 \rightarrow 5)^{+\prime}, LE(2 \rightarrow 4)^{+\prime}) = -(2^a3^a\|4^a5^a)$ | −0.39 |
| $H(LE(3 \rightarrow 5)^-, LE(2 \rightarrow 4)^-) = 2(2^a4^a\|3^a5^a) -$ $(2^a3^a\|4^a5^a) - 2(3^a5^a\|2^b4^b)$ | −0.09 |
| $H(LE(3 \rightarrow 5)^{-\prime}, LE(2 \rightarrow 4)^{-\prime}) = -(2^a3^a\|4^a5^a)$ | −0.39 |
| $H(LE(3 \rightarrow 4)^-, LE(2 \rightarrow 5)^-) = 2(3^a4^a\|2^a5^a) -$ $(2^a3^a\|4^a5^a) - 2(3^a4^a\|2^b5^b)$ | 1.04 |
| $H(LE(3 \rightarrow 4)^{-\prime}, LE(2 \rightarrow 5)^{-\prime}) = -(2^a3^a\|4^a5^a)$ | −0.39 |

$Co^{2+}$ ions, by decreasing the contribution of the electrostatic energy to the configuration energy by 30%. This correction is less than 10% of the configuration energy.[13] The core resonance integral between the $3p\pi$ orbital of chlorine and $3d\pi$ orbital of cobalt(II) $\beta(Cl, Co)$ was determined by the usual equation $\beta = -kS$,[14] $S$ being the overlap integral between the corresponding orbitals and $k$ being constant, 10 eV. $S$ is calculated to be 0.02 by the aid of the SCFAO's and therefore $\beta(Cl, Co)$ amounts to −0.20 eV.

The calculated transition energies and oscillator strengths are shown in Table III, together with the observed values.

This complex shows weak absorption bands in the visible region in addition to the bands given in Table III. The former bands are due to the d–d transition of the metal cation. In the present paper, we are only concerned with the near-ultraviolet absorption bands.

The ultraviolet spectra of the complex were measured in chloroform solution. The results are shown in Figure 3. As is seen in this figure, the spectrum of the chloroform solution exhibits a strong peak at 256 m$\mu$ and a shoulder on its longer wavelength side.[15]

First let us clarify the nature of this weak shoulder. For this purpose, we prepared $\beta$-dibromo- and $\beta$-diiododipyridinecobalt(II) complexes and measured their absorption spectra in the chloroform solution. The results for these complexes are also shown in Figure 3. As is seen in this figure, the weak band shifts to longer wavelengths and increases its intensity in the order dichloro < dibromo < diiodo complexes. The above-mentioned experimental results show the possibility that this weak band may be regarded as the CT band accompanying an electron transfer from the halide anion to the cobalt cation.

As mentioned above, the energies of the CT configuration can approximately be represented by $I - A + \Delta$. The ionization potentials, $I$, of $I^-$, $Br^-$, and $Cl^-$ are determined to be 3.22, 3.54, and 3.75 eV, respectively.[16] Therefore, the energy of the CT state may be expected to decrease in the order dichloro > dibromo > diiodo complexes. This tendency is co-

TABLE III

CALCULATED WAVE FUNCTIONS OF EXCITED STATES AND EXCITATION ENERGIES

| | Wave function | Excitation energy, eV | |
|---|---|---|---|
| | | Calcd[a] | Obsd[a,b] |
| $W_1$ | $0.87LE(3 \rightarrow 5)^{-\prime} + 0.49LE(2 \rightarrow 4)^{-\prime}$ | 3.54 | Forbidden |
| $W_2$ | $0.98LE(3 \rightarrow 4)^{-\prime} + 0.18LE(2 \rightarrow 5)^{-\prime}$ | 3.68 | Forbidden |
| $W_3$ | $CT(p_z \rightarrow d_{x^2-y^2})$ | 4.20 | Forbidden |
| $W_4$ | $CT(p_\perp \rightarrow d_{x^2-y^2})$ | 4.20 (0.01) | 4.13 $(c_{\|})$ (0.008) |
| $W_5$ | $-0.49LE(3 \rightarrow 5)^{-\prime} + 0.87LE(2 \rightarrow 4)^{-\prime}$ | 4.46 | Forbidden |
| $W_6$ | $0.92LE(3 \rightarrow 4)^- - 0.39LE(2 \rightarrow 5)^-$ | 4.91 (0.22) | 4.84 $(c_{\|})$ 4.65 $(b_{\|})$ (0.14) |
| $W_7$ | $-0.18LE(3 \rightarrow 4)^{-\prime} + 0.98LE(2 \rightarrow 5)^{-\prime}$ | 5.87 | Forbidden |
| $W_8$ | $0.99LE(3 \rightarrow 5)^- + 0.16LE(2 \rightarrow 4)^-$ | 6.65 | Not obsd |
| $W_9$ | $-0.16LE(3 \rightarrow 5)^- + 0.99LE(2 \rightarrow 4)^-$ | 7.25 | Not obsd |
| $W_{10}$ | $0.39LE(3 \rightarrow 4)^- + 0.92LE(2 \rightarrow 5)^-$ | 7.84 | Not obsd |
| $W_{11}$ | $CT(2 \rightarrow d_{x^2-y^2})$ | 8.63 | Forbidden |

[a] The values in parentheses of these columns are observed and calculated oscillator strengths. [b] The observed excitation energies and oscillator strengths are, respectively, taken from the data on $\alpha$-form crystal and on the chloroform solution. Since we could not measure the thickness of the crystal, we were unable to obtain the molar extinction coefficient. Therefore, we list the observed oscillator strengths of the corresponding spectra in solution.

## Results and Discussion

The dichlorodipyridinecobalt(II) complex has the two crystal forms $\alpha$ and $\beta$. The $\alpha$ form, the octahedrally coordinated chain polymer, is a stable form at room temperature (see Figure 1), and the $\beta$ form, the tetrahedrally coordinated monomer, is the stable one in the crystal above 110° and in solution.

incident with the maximum absorption shift observed with the weak band of these complexes.

It is clear from Figure 3 that the diiodo complex exhibits two bands on the longer wavelength side of the peak at 256 m$\mu$. They appear at 325 and 390 m$\mu$ with the wave number separation of $\sim$5200 cm$^{-1}$. The CT band from $I^-$ to $Co^{2+}$ may be expected to split into two bands corresponding to the $^2P_{1/2}$ and $^2P_{3/2}$ states

(13) Since we adopted the $\pi$-electron approximation, the $\sigma$ electrons were not considered explicitly, although their effects were included in the core potential of the system. In the present calculation, the core potential was evaluated on the assumption that $\sigma$-electron migration did not occur between the central metal ion and the ligand molecules or ions.

(14) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

(15) The spectrum of the ethanol solution exhibits no shoulder. This may be due to the fact that the substitution of the ethanol molecule for the chloride ion occurs in the ethanol solution.

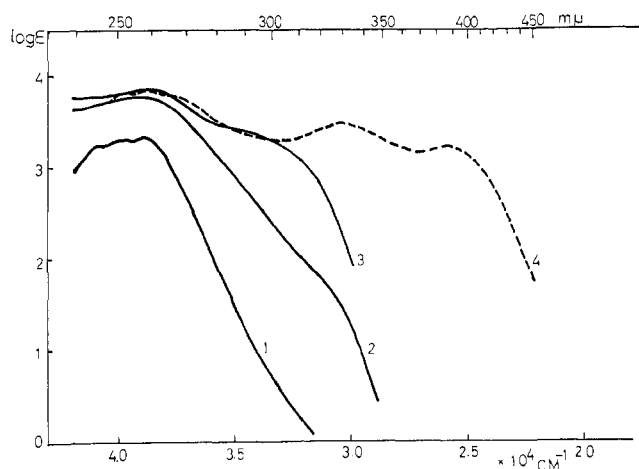(16) E. Kodes, *Z. Elektrochem.*, **65**, 908 (1961).

Figure 3.—The spectra of dihalogenodipyridinecobalt(II) in CHCl₃: (1) free pyridine in CHCl₃, (2) dichlorodipyridine-cobalt(II), (3) dibromodipyridinecobalt(II), (4) diiododipyri-dinecobalt(II).

of the iodine atom. Therefore, the appearance of the two bands seems to support the interpretation that they are due to the charge transfer from the iodine anion to the cobalt cation. The observed splitting of ∼5200 cm⁻¹ is smaller than that of the free iodine atom (7603 cm⁻¹).[17] In general, it is known that the spin–orbit coupling constant is smaller in the complex than in the free state.[18]

The interaction between the ground and $CT(p_{\perp} \rightarrow d_{x^2-y^2})$ configurations was concluded by the present calculation to be rather small for the dichlorodipyri-dinecobalt(II) complex. This is clear from the fact that the off-diagonal matrix element between them is small, −0.40 eV (see Table II). The fact that the observed intensity of the CT band is very weak also supports the above consideration. This means that the contribution of the $CT(p_{\perp} \rightarrow d_{x^2-y^2})$ configuration to the ground state is small[19] and the transition energy corresponding to the CT absorption band may be very close to the energy of the CT configuration, $I - A + \Delta$.

As is seen from Table III, some LE states with low excitation energy exist. However, the transitions from the ground state to them are completely forbidden. The strong peak at 256 mμ may safely be assigned to the excitation to the W₆ state of Table III and to the local excitation within the pyridine molecule.

We measured the polarized spectrum of the α-dichlorodipyridinecobalt(II) crystal for the purpose of determining the directions of transition moments and of checking the above-mentioned assignment of the absorption bands. This crystal is monoclinic and is a poorly developed needle extending parallel to the c axis (the c axis coincides with the x axis in Figure 2). The determination of the crystal axes was made by the

(17) C. E. Moore, "Atomic Energy Levels," Vol. III, National Bureau of Standard Circular 467, U. S. Government Printing Office, Washington, D. C., 1958.
(18) J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.* (London), **A213**, 459 (1952).
(19) The calculated wave function shows that the contribution of the CT configuration in the ground state is only 1%.

aid of an X-ray diffraction technique. The absorption measurement was made with the (100) plane by polarized light parallel or perpendicular to the c axis. The results are shown in Figure 4.
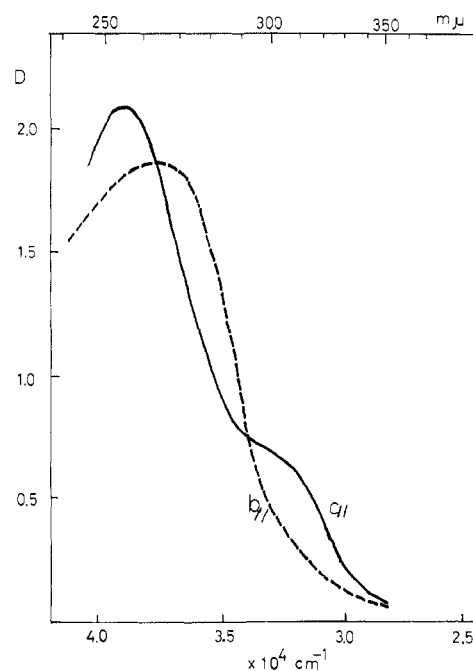


Figure 4.— The polarized absorption spectrum of the α-dichloro-dipyridinecobalt(II) crystal.

Under the above-mentioned conditions, we expected that the absorption corresponding to the local excitation within the pyridine occurs only for the direction parallel to the b axis. With regard to the CT band corresponding to the excitation to the W₄ state, the absorption intensity ratio ought to be 2:1 for the light polarized parallel and perpendicular to the c axis. Figure 4 shows that a weak band appears at 300 mμ with the stronger intensity in the c-parallel direction. Therefore, the results of the crystal spectrum also imply that the CT band appears at about 300 mμ.

According to our experimental results shown in Figure 4, the absorption near 260 mμ has the transition moments in directions both parallel and perpendicular to the c axis and the positions of the absorption maxima of the bands split off by the magnitude of ∼1000 cm⁻¹. Dunitz showed two possibilities for the orientation of the pyridine molecule in the complex from the X-ray crystal analysis experiment:[8] one with the planes of pyridine molecules lying in the yz plane and the other with the plane tilted about 10° from the yz plane. Therefore, if we take the latter case, the LE band can gain to some extent the absorption intensity in the direction parallel to the c axis. However, this intensity gain is only 3% of the actually observed absorption intensity in that direction; furthermore we cannot expect the splitting of the band from this model. Therefore we consider the effect of Davy-dov splitting.[20]

(20) A. S. Davydov, *Soviet Phys. Usp.*, **82**, 145 (1964).

In order to estimate theoretically the magnitude of the Davydov splitting and the intensity enhancement for the direction parallel to the $c$ axis, we carried out the calculation of the exciton–exciton type of interaction for the pyridine molecules in the crystal form. The actual calculation was made by the SCFMO method which was adopted by Tanaka and Tanaka[21] for the calculation of anthracene, long-range interaction (50 Å–∞) being taken into account following the approximate method developed by Rice, *et al.*[22] The result shows that the splitting is larger for the direction parallel to the $b$ axis than for the direction parallel to the $c$ axis. Further, in consistency with the theoretical consideration, the absorption band appears at lower frequencies for the former direction than for the latter. The calculated oscillator strengths depend strongly on the model used for the estimation of the intermolecular Coulomb integral.[23] This prevents us from discussing quantitatively the intensity change due to the exciton–exciton type of interaction. However, from the qual-

itative point of view, the calculation shows that the intensity of the $b$-parallel band considerably decreases as the result of exciton–exciton type of interaction and that this absorption has comparable intensity with the weak $c$-parallel band.[24] From the above discussion, we consider that the two bands at 4.84 eV ($c_{||}$) and 4.65 eV ($b_{||}$) may both be attributed to the local excitation within pyridine.

(21) M. Tanaka and J. Tanaka, private communication.
(22) R. Silbey, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, **42**, 1515 (1965).

(23) In the present calculation, interatomic Coulomb integrals for distances within 50 Å were estimated by use of two models. In one of them, the point charge approximation was adopted, and in the other, interatomic Coulomb integrals were represented by $e^2 e^{-R/20}/R$ ($R$ is the interatomic distance). In the latter, the screening effect of the other electrons was considered. The calculated oscillator strengths sometimes differ by the order of 10 by changing the model from one to the other. Moreover, it was found that the long-range interaction over 50 Å of interatomic distances gives great effect on the oscillator strengths. Taking the latter model and considering the long-range effect, the band under consideration turns out to have comparable intensities in the directions parallel to the $b$ and $c$ axes.
(24) As already mentioned above, as far as the plane of pyridine molecule tilts from the $yz$ plane by only ~10°, the intensity of the $c$-parallel band is small.

# The Solvent Isotope Effect on the Dissociation of the Aquopentaamminecobalt(III) Ion[1]

BY ROGER C. SPLINTER,[2] SIMON J. HARRIS,[3] AND R. STUART TOBIAS

Potentiometric and spectrophotometric techniques were used to determine the equilibrium constants for three reactions: (1) $Co(NH_3)_5OH_2{}^{3+} + H_2O = Co(NH_3)_5OH^{2+} + H_3O^+$; (2) $Co(NH_3)_5OD_2{}^{3+} + D_2O = Co(NH_3)_5OD^{2+} + D_3O^+$; (3) $Co(ND_3)_5OD_2{}^{3+} + D_2O = Co(ND_3)_5OD^{2+} + D_3O^+$ at 25° in a medium with $[ClO_4{}^-] = 0.3000\ M$. Values of log $^*K_1 = -6.22$, $-6.75$ (89% D₂O), and $-6.70$ (99% D₂O), respectively, were obtained. Each value of the equilibrium constant was refined by least squares. The partially exchanged species $Co(NH_3)_5OD_2{}^{3+}$ was studied using a flow system. Contrary to an earlier report, the aquopentaamminecobalt(III) ion exhibits a rather normal isotope effect, log $(K_H/K_D) = 0.48 \pm 0.01$ (error at the 99% confidence limit). A comparison of the dissociation constant of $Co(NH_3)_5OD_2{}^{3+}$ with that of $Co(ND_3)_5-OD_2{}^{3+}$, log $K_1 = -6.81$ and $-6.70$ (valid for 100 mol % D₂O), respectively, indicates the size of any secondary isotope effect which arises from the exchange of the 15 ammine hydrogens.

## Introduction

Both theory and measurement of acid dissociation constants in protium and deuterium oxides have indicated a correlation between the magnitude of the dissociation constant and the magnitude of the solvent isotope effect. This equilibrium isotope effect is conveniently described in terms of log $(K_H/K_D)$ where $K_H$ and $K_D$ are the acid dissociation constants in H₂O and

D₂O solution, respectively.[4] In general, this quantity increases as the acid strength decreases.

Early measurements suggested an approximately linear relation between log $(K_H/K_D)$ and p$K_H$. The same conclusion was anticipated[4] on the basis of a very simple model; however, more recent studies[5,6] have shown that this result is not necessarily true if the acids are of different structural types.

One class of acid which has appeared to behave very

(4) See R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter 11, and R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p 150, for discussions of this effect.
(5) R. P. Bell and A. T. Kuhn, *Trans. Faraday Soc.*, **59**, 1789 (1963).
(6) A. O. McDougall and F. H. Long, *J. Phys. Chem.*, **66**, 429 (1962).