Magnetic Circular Dichroism of Dicyanobis(2,2′-bipyridine)iron(II)

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Magnetic circular dichroism (MCD) of *cis*-dicyanobis(2,2′-bipyridine) iron(II) was measured for a variety of solvents. The visible absorption band is assigned to the lowest "iron(II) to bipyridine" charge-transfer transition. The complex exhibits a significant MCD in its lowest charge-transfer absorption band. The transition shows a shift to higher wave number with an increase in the proton-donating power of solvent. This spectral shift is attributed to hydrogen-bonding interactions of protolytic solvent molecules. In H_2SO_4 this dibasic complex is subjected to stepwise protonations. The complex is diamagnetic in protolytic solvents, and even in conc H_2SO_4 the diprotonated complex formed is mostly present in the diamagnetic state.

Schilt has described the mixed-ligand complex of iron(II) with cyanide and 2,2′-bipyridine.[1] The neutral complex $[Fe(CN)_2(2,2'\text{-bipyridine})_2]$ was found to be especially interesting because of its unique property. It gives violet, blue, red, orange and yellow colors depending upon the nature of the solvent. Concentrated sulfuric acid dissolves large amounts without decomposition. The compound shows dibasic character and reacts reversibly with acids to form stable protonated species.[2] $[Fe(2,2'\text{-bipyridine})_3]^{2+}$ is stable against oxidation, but $[Fe(CN)_2(2,2'\text{-bipyridine})_2]$ is rather readily oxidized. It has been employed as nonaqueous acid-base and aqueous oxidation-reduction indicators.[3]

A change between high-spin $^5T_2$ and low-spin $^1A_1$ ground states has been established within the series of *cis*-$[FeX_2(2,2'\text{-bipyridine})_2]$ complexes. Considerable efforts have been achieved in the synthesis and physical measurements of the complexes with ligands X covering a wide range of ligand field strengths.[4] Only when X=CN, a stable diamagnetic complex is obtained. In the present work, the magnetic circular dichroism (MCD) spectra of *cis*-$[Fe(CN)_2(2,2'\text{-bipyridine})_2]$ (abbreviated to $[Fe(CN)_2(bipy)_2]$) in a variety of solvents were measured for understanding of the lowest electronic excitations.

Experimental

Materials. *cis*-Dicyanobis(2,2′-bipyridine)iron(II) trihydrate was prepared by the method of Schilt[1] and identified by elemental analysis.

Found: C, 55.66; H, 4.44; N, 17.37%. Calcd for $C_{22}H_{16}N_6Fe\cdot 3H_2O$: C, 55.70; H, 4.68; N, 17.72%. By means of Sasse's method, 4,4′-dimethyl- and 5,5′-dimethyl-2,2′-bipyridine (abbreviated to 4 dmbip and 5 dmbip, respectively) were prepared.[5,6] The dimethyl bipyridine analogs of dicyanobis(2,2′-bipyridine)iron(II) were also prepared by the method of Schilt:[1]

Found: C, 63.30, H, 5.24, N, 16.96%. Calcd for $C_{26}H_{24}N_6$ (4 dmbip) $Fe\cdot H_2O$: C, 63.17; H, 5.30; N, 17.00%.

Found: C, 59.12; H, 5.28; N, 15.93%. Calcd for $C_{26}H_{24}N_6$ (5 dmbip) $Fe\cdot 3H_2O$: C, 58.88; H, 5.70; N, 15.85%. The 4 dmbip complex was dried over silicagel prior to the elemental analysis.

All solvents including C_2H_5OH and $CHCl_3$ were commercially available and purified by distillation except H_2SO_4.

Measurements. MCD spectra were recorded on a JASCO ORD/UV-5 spectropolarimeter with its CD attachment and electromagnet. The measurement technique had been described earlier.[7] The magnetic field was set at 10,000 G. The visible and ultraviolet absorption spectra were taken on a Shimadzu automatic recording spectrophotometer Model MPS-50. The NMR spectra were taken on a 60 MHz Varian T-60 NMR spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard.

Results and Discussion

The MCD and absorption spectra of $[Fe(CN)_2(bipy)_2]$ in $CHCl_3$, C_2H_5OH, H_2O and H_2SO_4 are shown in Figs. 1 and 2. The prominent maxima are summarized in Table 1. The electronic transitions which give rise to the MCD extrema and absorption maxima in 15000—30000 cm^{-1} are assigned to the lowest "iron to bipyridine" charge-transfer excitations. The lowest wave number absorption peak exhibits a blue shift in the order bipy<4 dmbip<5 dmbip and the second peak shows a blue shift in the order 4 dmbip<5 dmbip≤bipy. Such spectral shifts for the dimethyl substitutions in coordinated bipyridine have been observed in the lowest and the second "metal to

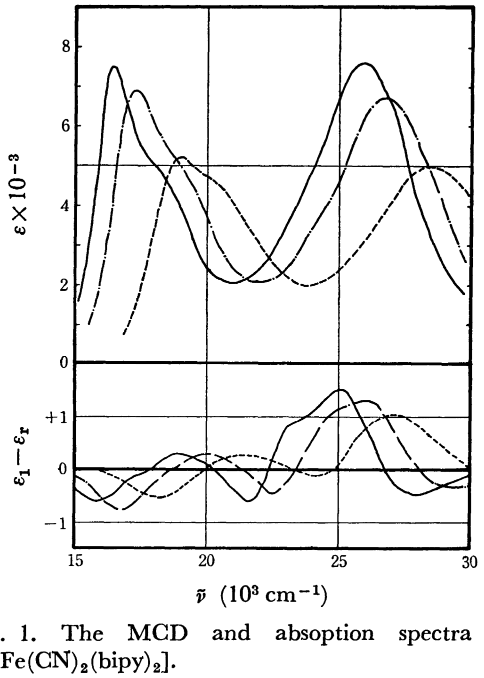

Fig. 1. The MCD and absoption spectra of $[Fe(CN)_2(bipy)_2]$.
——; in $CHCl_3$, —·—·; in C_2H_5OH, ----; in H_2O,

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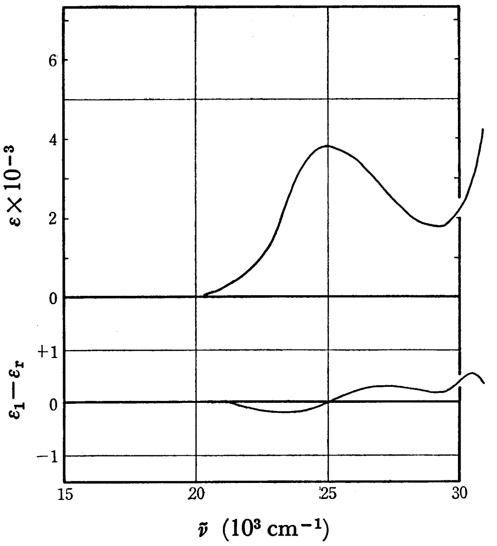

Fig. 2. The MCD and absorption spectra of $[Fe(CN)_2(bipy)_2]$ in 18 M H_2SO_4.

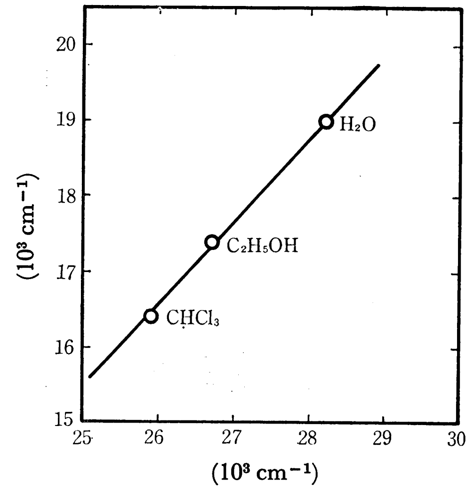

Fig. 3. A linear relationship between the first and second charge-transfer bands.

bipyridine" charge-transfer excitations in 2,2′-bipyridine tetracarbonylchromium, -molybdenum, and -wolfram.[8] The ultraviolet peak shows a shift for dimethyl substitutions in the order 5 dmbip<bipy≤4 dmbip. This indicates that the ultraviolet peak arises from the lowest (π, π^*) excitation in coordinated bipyridine.[8]

The nature of MCD and absorption spectra does not change in different solvents. However a shift observed in different solvents should be noted. With an increase in the proton-donating power of solvent, the absorption band shifts to higher wave number : chloroform<ethanol<water. Figure 3 shows a linear relationship obtained between the first and second absorption peaks for a variety of proton-donating power of solvents. In a protolytic solvent, a hydrogen-bonding interaction of the solvent molecules arises on coordinated cyano groups. The coordinated cyano group is a σ-donor but a π-acceptor. The iron dπ electrons even in the ground state migrate into the lowest vacant π^* molecular orbitals which delocalize not only over coordinated bipyridines but also over coordinated cyano groups. Thus the hydrogen-bonding interaction of protolytic solvent molecules with coordinated cyano groups encourages the migration of iron dπ electrons into the coordinated cyano groups. This gives rise to a blue-shift of the "iron to bipyridine" charge-transfer excitations in protolytic solvents. In conc H_2SO_4, the lowest wave number absorption peak appears at 25000 cm^{-1}. This blue-shift, however, should be attributed to the protonations in conc H_2SO_4 since the effect is greater than expected for the hy-

TABLE 1. THE MCD AND ABSORPTION DATA

Solvent		Absorption peaks (10^3 cm^{-1})		MCD extrema (10^3 cm^{-1})
	I	16.5	Ia	15.8
$CHCl_3$	II	25.9	Ib	19.0
	III	33.0	IIa	21.5
	IV	40.0	IIb	25.0
			IIIa	28.0
	I	17.4		16.9
C_2H_5OH	II	26.7		20.0
	III	33.2		22.5
	IV	40.2		26.0
				30.0
	I	19.1		18.3
H_2O	II	28.4		21.5
	III	33.5		24.3
	IV	40.6		27.2
				31.5
	I	25.1		23.3
18 M H_2SO_4	II	35.0		27.2
	IV	41.0		30.4

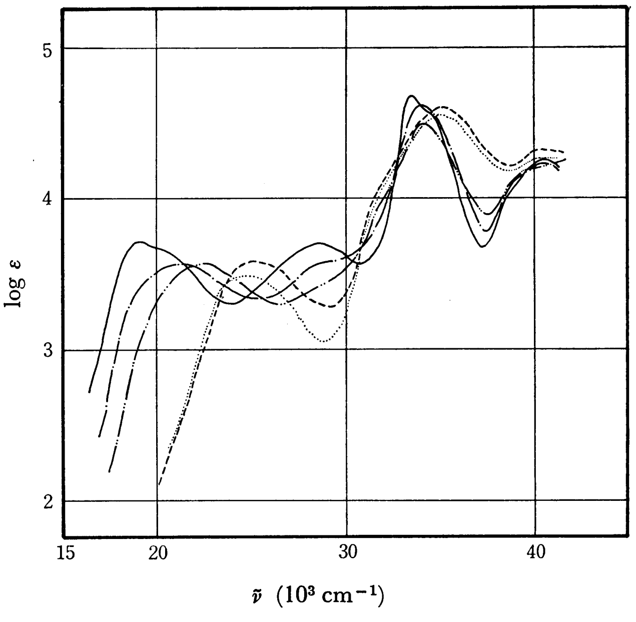

Fig. 4. The absorption spectra of $[Fe(CN)_2(bipy)_2]$ as a function of the concentration of H_2SO_4.
——: H_2O, —·—·: 1.8 M H_2SO_4, —··—··: 3.6 M H_2SO_4, ······: 9 M H_2SO_4, ----: 18 M H_2SO_4.

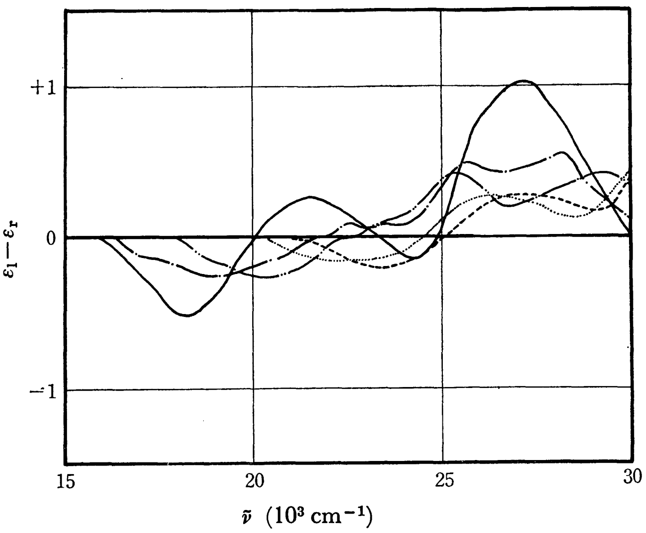

Fig. 5. The MCD spectra of $[Fe(CN)_2(bipy)_2]$ as a function of the concentration of H_2SO_4. ——: H_2O, —·—·: 1.8 M H_2SO_4, —··—··: 3.6 M H_2SO_4, ······: 9 M H_2SO_4, ----: 18 M H_2SO_4.

drogen-bonding interactions in protolytic solvents. Hamer and Orgel have suggested the protonation of the complex in conc H_2SO_4.[9] The MCD and absorption spectra measured for a variety of concentrations of H_2SO_4 in solution are presented in Figs. 4 and 5. These stepwise spectral changes for an increase in the concentration of H_2SO_4 indicate the stepwise protonation toward two coordinated cyano groups. The straight line with a slope of 1.00 in Fig. 3 predicts the second peak in conc H_2SO_4 at 34200 cm^{-1} for the first peak at 25000 cm^{-1}. Since the second band as well as the first band is not so intense as the bipyridine (π, π^*) band, the second band of the complex in conc H_2SO_4 must be present beneath the ligand (π,π^*) band.

The energy of the ground state of *cis*-$[FeA_4B_2]$ complex is given as follows:

$^5\Gamma(^5T_2$ in Oh symmetry: $(xy)^2(yz)(zx)(z^2)(x^2-y^2))$
$2\{\Delta-(X_A-X_B)\}+15\Delta-35B+7C$
$^1\Gamma_1(^1A_1$ in Oh symmetry: $(xy)^2(yz)^2(zx)^2)$
$15\Delta-30B+15C$,

where Δ is the cubic ligand field parameter of $[FeA_6]$, (X_A-X_B) is a correction for the ligand field of ligand B at *cis*-positions (X_B is defined as a one third of the cubic ligand field parameter of $[FeB_6]$ as well as $X_A=\Delta/3$), and A, B, and C are Racah's interelectronic electrostatic energy parameters. Provided that $3(X_A-X_B)=x\Delta$ and $4B=C$, an energy difference between the quintet and singlet ground states is given by $2(1-x/3)\Delta-37B$. Since the ground state of $[Fe(bipy)_3]^{2+}$ $(x=0)$ is singlet, $\Delta>(37/2)B$. In fact, the d-d transition $^3T_1\leftarrow{}^1A_1(\Delta-12B)$ in $[Fe(bipy)_3]^{2+}$ is observed at 12000 cm^{-1},[10] which indicates that $\Delta=24B$ if $B=1000$ cm^{-1}. The energy diagram of the ground state of $[FeA_4B_2]$ is shown in Fig. 6. When the value of x increases, the ligand field of B decreases. For high values of x, the ground state of $[FeA_4B_2]$ should be quintet even for a fairly high value of Δ which gives the singlet ground state for $[FeA_6]$. In fact, the ground states of $[FeX_2(bipy)_2]$ are mostly quintet, whereas the ground state of $[Fe(bipy)_3]^{2+}$ is singlet.[4] A decrease in x, which is revealed by a greater value of Δ in $[Fe(CN)_6]^{4-}$, gives rise to diamagnetic $[Fe(CN)_2(bipy)_2]$. The vacant antibonding π^* orbitals of coordinated bipyridines and cyano groups accept iron dπ electrons, and thus an enhancement of the ligand field splitting in diamagnetic $[Fe(CN)_2(bipy)_2]$ should be attributed partly to the back-donation effect. The back donation also gives rise to a splitting in dπ orbitals: d_{xy} is a little more stabilized than d_{yz} and d_{zx} orbitals in $[Fe(CN)_2(bipy)_2]$ (Fig. 7).

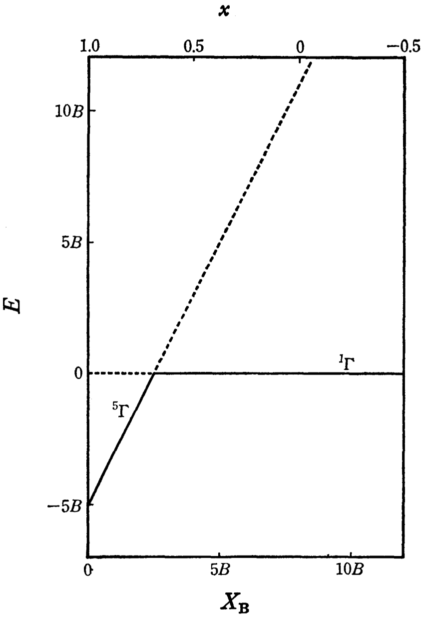

Fig. 6. The energy diagram of the ground state of $[FeX_2(bipy)_2]$.
$X_B=X_A-x\Delta/3=(1-x)X_A$ $\quad X_A=8B$

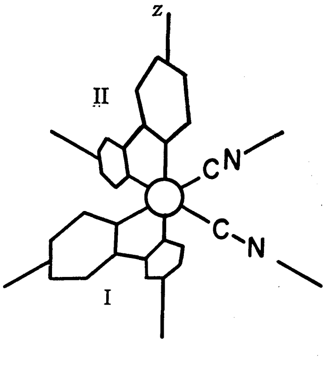

Fig. 7. Molecular coordinate.

The lowest "metal to bipyridine" charge-transfer transitions borrow their intensity from the allowed (π, π^*) transitions localized in coordinated bipyridines I and II, $1/\sqrt{2}\{(j\rightarrow k)_I\pm(j\rightarrow k)_{II}\}$.[11] Among possible six charge-transfer excitations d$\pi\rightarrow k_I$, k_{II}, $1/\sqrt{2}\{(xy\rightarrow k_I)\pm(xy\rightarrow k_{II})\}$ and $1/\sqrt{2}\{(yz\rightarrow k_I)\pm(zx\rightarrow k_{II})\}$ can borrow the intensity. Since d_{xy} orbital is lower than d_{yz} and d_{zx} orbitals, the charge-transfer transitions arising from the d_{xy} orbital must be in a wave number higher than those from the d_{yz} and d_{zx} orbitals. The MCD spectra indicate separate four B peaks with alternating sign corresponding to two components of the charge-transfer transitions to the lowest and the second lowest vacant π^* orbitals. Since the plus and minus combinations in $1/\sqrt{2}\{(xy \rightarrow k_I) \pm (xy \rightarrow k_{II})\}$ and $1/\sqrt{2}\{(yz \rightarrow k_I) \pm (zx \rightarrow k_{II})\}$ form a degenerate pair, an A-term dispersion is expected in the corresponding absorption peak. However the expectation value of angular momentum between the wave functions within the degenerate pair is vanished and thus the A-term dispersion does not appear. On the other hand, a non-zero value of angular momentum comes out between the wave functions of different degenerate pairs and gives rise to a magnetic-field induced mixing between different degenerate excited states.[12,13] The MCD spectra thus exhibit B-term extrema with alternating sign.

The blue shift of the lowest charge-transfer transitions in conc H_2SO_4 is as great as 5000 cm^{-1}. This spectral blue shift is attributed to protonation rather than hydrogen-bonding. Since the character of the lowest charge-transfer transition is still conserved even in conc H_2SO_4, the complex is mostly in the diamagnetic state. The ionization potential of dπ orbitals is dependent upon the spin state of iron(II) in complex. The values given in Table 2 were obtained by the procedure described in Griffith's book.[14] In the high spin state, only an electron pair in d_{xy} orbital shows a higher tendency of back donation. In the diamagnetic state, all dπ electrons equally show an enhanced tendency of back donation. If a change of the spin state of the complex comes out upon protonation, the charge-transfer transition should exhibit a more drastic red shift or blue shift since the ionization potential of dπ electrons in the high spin state is very different (more than 10000 cm^{-1}) from the corresponding ionization potential of diamagnetic iron(II) as shown in Table 2. The spectral intensity of the complex in conc H_2SO_4 is almost reproducible within experimental error, however, the spectral intensity depends on somewhat how to prepare the solution. The high spin complex must be labile, and thus the high spin species, if it is formed upon protonation, suddenly dissociates ligands and/or is oxidized. The NMR spectrum of the complex in conc H_2SO_4 shows, in fact, a significant line broadening which indicates the presence of some high spin species. One of the authors (B.V.A.) wishes to express his gratitude to the Japanese Government for a UNESCO fellowship.

Table 2. The dπ ionization potentials

$^1A_1$	
$(xy)^2(yz)^2(zx)^2 \rightarrow (xy)(yz)^2(zx)^2$	$\Phi - 10B$
$^5T_2$	
$(xy)^2(yz)(zx)(z^2)(x^2-y^2) \rightarrow (xy)(yz)(zx)(z^2)(x^2-y^2)$	$\Phi - 28B$
$(xy)^2(yz)(zx)(z^2)(x^2-y^2) \rightarrow (xy)^2(yz)(z^2)(x^2-y^2)$	$\Phi + 12B$

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