Registry No. *trans*-[Pt(pn)₂Cl₂]Cl₂, 54192-98-2; *cis*-[Pt-(pn)₂Cl₂]²⁺, 54192-99-3; Pt(pn)Cl₂, 33727-98-9; Eu²⁺, 16910-54-6; Cr²⁺, 22541-79-3.

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Circular Dichroism of Copper(II) β-Diketonates in Optically Active Bases

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The absorption and circular dichroism (CD) spectra of five copper(II) β-diketonate complexes, dissolved in optically active α-phenylethylamine and nicotine, were measured in the visible and near-ultraviolet regions. The profiles of the absorption spectra in the d–d region suggested the coordination of the bases to the axial position of the copper(II) complexes. The main CD band in the d–d region was observed at the lower wave number side within the d–d absorption band, and it may correspond to the magnetic dipole allowed d–d transition which is directed to the z axis in the complex. A considerably intense CD band was also observed in the π–π* transition region of the β-diketonate ion. The anisotropy factor ($\Delta\epsilon/\epsilon$) of the π–π* band decreased abruptly with increase of the band separation from the lowest energy band of the optically active amine.

In the course of the investigations on the axial coordination in copper(II) complexes, we have studied the circular dichroism of the copper(II) complexes with optically active ligands.[1] In this study, we wish to report on the CD spectra of some copper(II) β-diketonate complexes in optically active bases.

It is well known that the d–d absorption spectra of copper(II) β-diketonates are much influenced by the variation of solvents and that the positions and intensities of the spectra depend primarily upon the solvent basicity.[2,3] The stronger ligation to the copper(II) ion along the tetragonal axis causes an appreciable shift of the d–d absorption band to lower energy and results in an increase of the intensity of the band.

Bosnich has reported that when the complex Na₂[PtCl₄] is dissolved in *l*-2,3-butanediol, a CD band appears at only one magnetic dipole allowed d–d transition which is directed to the z axis and suggested that the dissymmetric influences of the optically active solvent are concentrated and directed to the tetragonal positions of the complex ion.[4]

In the cases of the copper(II) β-diketonates dissolved in optically active bases, it is expected that the dissymmetric influences of the solvent upon the complexes are along the tetragonal axis and that, according to the suggestion of Bosnich,[4] optical activity is observed at only the magnetic dipole allowed d–d transition which is directed to the z axis. In this paper, this expectation was qualitatively supported by the CD measurements.

Experimental Section

Materials. Four copper(II) β-diketonate complexes, *i.e.*, bis-(acetylacetonato)copper(II) (abbreviated to Cu(acac)₂), bis(benzoylacetonato)copper(II) (Cu(bzac)₂), bis(dibenzoylmethanato)-copper(II) (Cu(dbm)₂), and bis(dipivaloylmethanato)copper(II) (Cu(dpm)₂),[5] were prepared according to the method described in the literature.[6] Cu(acac)₂ and Cu(bzac)₂ from methanol, Cu(dbm)₂ from dioxane–water, and Cu(dpm)₂ from ethanol were recrystallized, respectively. Bis(diisobutyroylmethanato)copper(II) (Cu(dibm)₂) was supplied by Dr. Hiroshi Yokoi in this institute.

As optically active bases *d*- or *l*-α-phenylethylamine and 1-methyl-2-(3-pyridyl)pyrrolidine (nicotine) were used. The phenylethylamine was resolved according to the literature method.[7] The values of the specific rotatory power, [α]D, were +36.0° for the *d* antipode of the amine at 25° and −40.8° for the *l* antipode at 20°. The nicotine was obtained commercially and used after the reduced pressure distillation. The value of [α]D was −155° at 25°.

Measurements. The five copper(II) β-diketonate complexes were

Table I. Numerical Data for Absorption and CD Spectra in the Optically Active Bases[a]

Complex	Solvent base	Absorption ν_{max} (ϵ)	CD ν_{max} ($\Delta\epsilon$)
Cu(acac)₂	*d*-α-Phenyl-ethylamine	14.6 (78)	12.9 (+0.04₂)
		26 sh (260)	25.3 (−0.06₅)
		32.6 (25,000)	32.5 (−21)
	Nicotine	15.3 (75)	13.5 (−0.02₃)
		26 sh (400)	26.3 (−0.02)
Cu(bzac)₂	*d*-α-Phenyl-ethylamine	14.4 (92)	13.1 (+0.05₄)
		30.3 (28,500)	30.3 (−3.1)
	Nicotine	15.2 (90)	13.1 (−0.00₇)
			15.8 (+0.00₃)
Cu(dbm)₂	*d*-α-Phenyl-ethylamine	14.4 (103)	13.2 (+0.05₈)
		28.0 (41,000)	27.7 (−2.0)
	Nicotine	15.0 (92)	14.2 (+0.01₄)
Cu(dpm)₂	*d*-α-Phenyl-ethylamine	14.6 (106)	13.6 (−0.09)
			17.8 (+0.01₄)
		25.5 sh (160)	22.8 (+0.01)
			25.7 (−0.05₅)
		33 sh (10,000)	34.0 (+1.0)
Cu(dibm)₂	*l*-α-Phenyl-ethylamine	14.4 (96)	12.8 (−0.02₄)
			16.5 (−0.01₁)
		25 sh (180)	25.6 (+0.10)
			28.5 (+0.14)
		33.5 sh (20,000)	34.5 (−2.0)

[a] In 10³ cm⁻¹; sh = shoulder.

dissolved in the optically active bases, and the absorption and CD spectra were measured at room temperature. The absorption spectra were obtained by means of a Hitachi EPS-3T spectrophotometer, and the CD measurements in the region from 270 to 1000 nm were made on a JASCO J-20A spectropolarimeter. All molar absorptivities, ϵ, and differential molar absorptivities, $\Delta\epsilon$, between left and right circularly polarized lights refer to 1 mol of copper(II) ion.

The CD spectra in the ligand-field region of Cu(acac)₂ and Cu(bzac)₂ in *d*-α-phenylethylamine exhibited remarkable change with time, while the absorption spectra were little affected. All spectra were measured immediately after the dissolution of the complexes into the amine. The spectral change was so slow that the time taken for the spectral measurement was negligible. The details of the reaction responsible for this CD spectral change will be reported in the near future.

Results and Discussion

Figures 1–4 show the absorption and CD spectra of the five complexes dissolved in *d*-(or *l*-)α-phenylethylamine or nicotine. In addition, these figures involve the absorption curves in noncoordinating solvents. Numerical data for the absorption
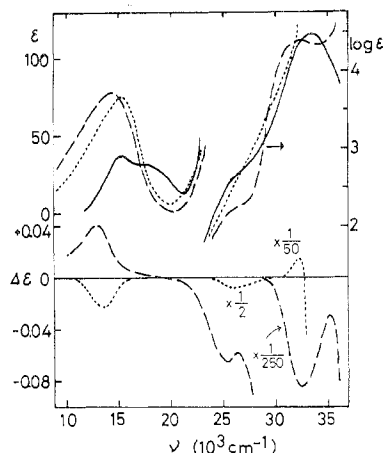
Figure 1. Absorption and CD spectra of Cu(acac)₂: ———, in chloroform; — — — —, in *d*-α-phenylethylamine; · · · · ·, in nicotine.
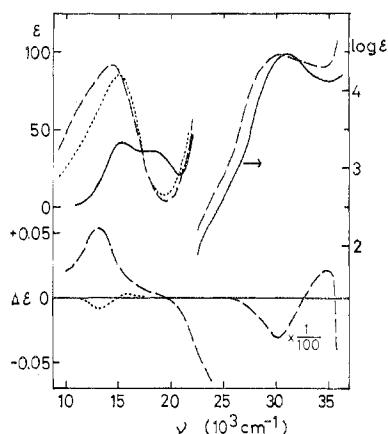
Figure 2. Absorption and CD spectra of Cu(bzac)₂: ———, in chloroform; — — — —, in *d*-α-phenylethylamine; · · · · ·, in nicotine.
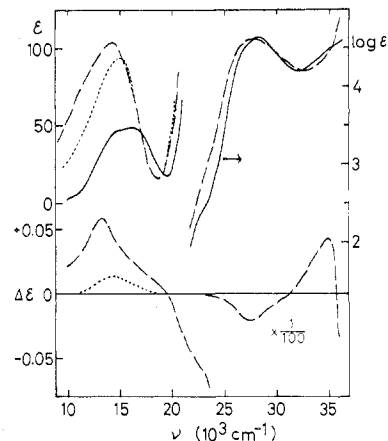
Figure 3. Absorption and CD spectra of Cu(dbm)₂: ———, in dioxane; — — —, in *d*-α-phenylethylamine; · · · · ·, in nicotine.

Figure 4. Absorption and CD spectra of Cu(dpm)₂ and Cu-(dibm)₂: ———, Cu(dpm)₂ in cyclohexane; — — —, Cu(dpm)₂ in *d*-α-phenylethylamine; · · · · ·, Cu(dibm)₂ in *l*-α-phenylethylamine.

and CD bands in the optically active bases are summarized in Table I. These spectra may be divided for convenience into three kinds of the band regions as follows.

The Ligand-Field Region. Belford and his coworkers have reported that the visible absorption band of copper(II) β-diketonates is more intense and locates at lower energy in coordinating solvents such as pyridine or piperidine than in noncoordinating solvents such as chloroform.[2] Moreover, Funck and Ortolano have concluded on the basis of an absorption spectral study that the behavior of the absorption band in pyridine solution results from the formation of a mono-pyridine adduct, in which the pyridine coordinates to an axial
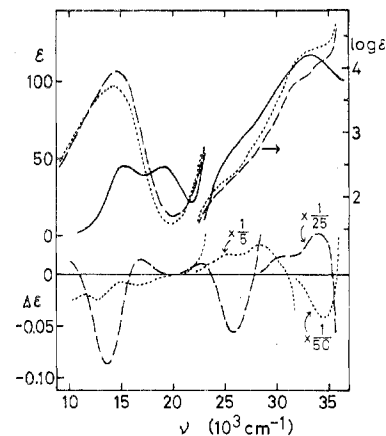
position of the copper(II) ion.[8]

In this study, the present five copper(II) β-diketonates exhibited the same spectral behavior in α-phenylethylamine or nicotine as that in pyridine, as shown in the figures. Therefore, it seems reasonable to expect that the similar monoadducts are formed in the present bases. In nicotine the absorption band appeared at slightly low wave number in comparison with those in pyridine or α-phenylethylamine. Since nicotine is one of the β-substituted pyridines, the effect upon the spectral feature may be smaller than that of pyridine because of its steric factor.

The three complexes Cu(acac)₂, Cu(bzac)₂, and Cu(dbm)₂, in *d*-phenylethylamine exhibited similar CD spectra which have one CD peak at the lower wave number side in the d–d band region, while the other two complexes Cu(dpm)₂ and Cu-(dibm)₂ exhibited different CD curves from those of the above three complexes. Especially, the main CD component of Cu(dpm)₂ was opposite in sign to those of the other four complexes; the main CD band observed for Cu(dibm)₂ was negative in sign, since it was dissolved in the *l* antipode of the amine.

The facts that different CD spectra were observed for these β-diketonate complexes, in spite of the similarity of their absorption spectra, are worthy of a further discussion. In general, the optical activity in the d–d transition of dissymmetric metal complexes has been interpreted in terms of the mixing of the d orbitals with some ungerade orbitals of the central metal ion and/or ligand molecules.[9] Then, the different CD spectra may be ascribed to the assumption that the mixing of the d orbitals with ungerade orbitals in Cu(dpm)₂ is different from those in the other complexes. From a different point of view, the differences in the CD spectra are also likely due to preferred dissymmetric conformations of the substituents on the β-diketonate rings. However, there is no further explicit decision as to whether this is due to a steric factor or an electronic effect of the *tert*-butyl group in the dipivaloyl-methanate ion.

It has been proposed that the order of d orbitals of copper(II) β-diketonates in coordinating solvents is $d_{xy} \gg d_{z^2} > d_{x^2-y^2} > d_{xz} \approx d_{yz}$, if the molecular symmetry is taken as D_{2h}.[2,3] The application of this order to our five complexes leads to the fact that the main CD band corresponds to $d_{z^2} \rightarrow d_{xy}$ and/or $d_{x^2-y^2} \rightarrow d_{xy}$, since the optical activity appeared mainly at the lower wave number side within the d–d absorption band, as shown in the figures. If the molecular symmetry of the β-diketonate complexes is approximated to D_{4h}, only the transition $d_{x^2-y^2} \rightarrow d_{xy}$ is the z axis directed magnetic dipole allowed transition. However, the effective symmetry in these complexes is closer to D_{2h}, and then both of the two transitions, $d_{x^2-y^2} \rightarrow d_{xy}$ and

$d_{z^2} \rightarrow d_{xy}$, lead to the magnetic dipole allowed transition having z axis polarization. In any of the two cases, the main CD band observed for these β-diketonate complexes in the optically active bases seems to be the magnetic dipole allowed transitions which are directed to the z axis. This is in accordance with the observation of Bosnich for $[PtCl_4]^{2-}$ dissolved in *l*-2,3-butanediol as described above.[4]

The Region near 25,000 cm⁻¹. The three complexes Cu-(acac)₂, Cu(dpm)₂, and Cu(dibm)₂ in the optically active amine exhibited one or two CD peaks in the vicinity of the absorption shoulder at about 25,000 cm⁻¹. In the spectra of Cu(dbm)₂ and Cu(bzac)₂, this band was almost overlapped with another higher energy transition. Recently, the shoulder band has been assigned to the charge-transfer transition between the metal d orbital and the ligand π orbital.[10-12] However, the position of the shoulder band cannot be determined exactly by means of absorption measurements. By the CD measurements it was found that the position of the shoulder band of Cu(acac)₂ in *d*-phenylethylamine is at 25,000 cm⁻¹ and that this band in Cu(dpm)₂ and Cu(dibm)₂ is composed of two components at least.

The Near-Ultraviolet Region. The intense band at about 30,000 cm⁻¹ is the π–π* transition of β-diketonate ions, which is polarized along the long axis of the ligand ion.[13,14] This π-conjugated system is long in the order acac⁻, bzac⁻, and dbm⁻, so that the transition shifts to lower wave number in this order.[15] In this region, considerably intense CD bands were also observed for the complexes in the optically active amine, and these bands may be assigned to the π–π* transition in the ligand anions.

Since the β-diketonate molecules are originally inactive, it is of interest to analyze the mechanism of the optical activity induced for the π–π* internal-ligand transition. The following three mechanisms may be considered as the origins for the induced optical activity. The first mechanism is connected with the dissymmetric distortion of the β-diketonate ion itself by the coordination of the optically active amine to the copper(II) ion. This effect is negligible, because the shift to a higher energy of the π–π* bands was not observed. The second mechanism is related to the coupling between the transition dipole moments of the π–π* transition of the two β-diketonate ions in one complex molecule. The presence of the exciton coupling should lead to a split of the π–π* band and show one positive CD band and one negative CD band, which have nearly equal CD magnitude.[14,16] Contrary to the expectations, such phenomena were not observed in the present cases.[17]

The third is the mechanism that the π–π* transition mixes with the transition of the chromophore in the optically active amine. According to this mechanism, the induced optical activity in the π–π* band is expected to decrease with the increase of the energy difference between the transition of the amine to be mixed with the π–π* band and the π–π* transition itself.[18] The absorption and CD spectra of the π–π* band region of Cu(acac)₂, Cu(bzac)₂, and Cu(dbm)₂ in *d*-phenylethylamine are again given in Figure 5. The band in the wave number region higher than 36,000 cm⁻¹ is the transition of the phenyl ring chromophore of the solvent amine.[19] The π–π* band of Cu(dpm)₂ and Cu(dibm)₂ in the amine is partly concealed by the band of the amine as shown in Figure 4. It can be seen from Figure 5 that the most intense CD band is observed in the π–π* band of Cu(acac)₂ which locates at the nearest neighbor to the CD band of the amine itself and that the anisotropy factor ($\Delta\epsilon/\epsilon$) of the π–π* band decreases abruptly with increase of the energy separation from the band of the amine. Thus, the CD measurements support qualitatively the mixing mechanism, *i.e.*, the third mechanism.
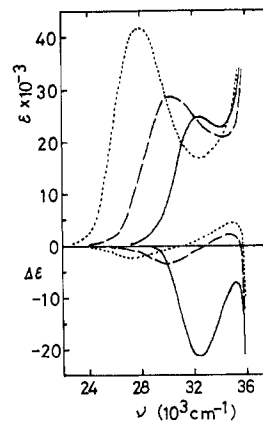
When the inert complex Co(acac)₃ was dissolved in the

Figure 5. Absorption and CD spectra of the π–π* band in *d*-α-phenylethylamine: ——, Cu(acac)₂; –––, Cu(bzac)₂; · · · · ·, Cu(dbm)₂.

optically active amine or when the optically active amine was added to an acac⁻–methanol solution, no optical activity in the π–π* region was detected.[20] From the facts, the coordination of the active amine to the axial position of the copper(II) complex is expected to play an important role in the position fixing or bridging between the β-diketonate ion and the amine.

Registry No. Cu(acac)₂, 13395-16-9; Cu(acac)₂(*d*-α-phenylethylamine), 54229-85-5; Cu(acac)₂(nicotine), 54229-82-2; Cu(bzac)₂, 36799-65-2; Cu(bzac)₂(*d*-α-phenylethylamine), 54229-86-6; Cu-(bzac)₂(nicotine), 54229-81-1; Cu(dbm)₂, 14405-48-2; Cu(dbm)₂-(*d*-α-phenylethylamine), 54229-87-7; Cu(dbm)₂(nicotine), 54229-80-0; Cu(dpm)₂, 14040-05-2; Cu(dpm)₂(*d*-α-phenylethylamine), 54229-83-3; Cu(dibm)₂(*l*-α-phenylethylamine), 54229-84-4.

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