Conformational Change of Optically Active [Co(acac)₂(diamine)]⁺ Complexes in Some Organic Solvents

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The circular dichroism(CD) spectra of the optically active [Co(acac)₂(diamine)]⁺ complexes were measured in the several protic and aprotic solvents, where acac = acetylacetonate anion and diamine = ethylenediamine and trimethylenediamine. The degree of the CD variation in protic solvents was enhanced as the dielectric constant decreases except n-butanol and benzylalcohol. And the degree of the CD variation in aprotic solvents was roughly increased as both dipole moment and dielectric constant decrease except aromatic solvents and the solvents having no dipole moment. It was deduced that the CD variations of the complexes have been due to the conformational change of acetylacetonate ligands coordinated to Co(III) ion.

Introduction

It has been known that the solvent dependence of some optically active organic compounds was used for conformational analysis[1]. And it has been also reported that the optical activity of some metal complexes are affected by organic solvents[2-7]. The solvent dependence of the CD spectra was observed in trans-[M(3,2,3-tet)XY]ⁿ⁺ complexes, where 3,2,3-tet is a linear quardridentate amine ligand and M is Co(III), Cr(III), and Rh(III), and it has been assumed that the CD changes were due to conformational instability[8,9].

Recently, Sakaguchi et al.[10] found that the CD spectra of some cis-dianionobis(ethylenediamine)cobalt(III) complexes exhibit a marked solvent dependence. They ascribed the origin of the sign inversion of dominant CD band in the lowest energy spin-allowed transition region to the stereoselective hydrogen bonding of cis-N-H_B with pyridine-like molecules, where cis N-H_B is directed off the two fold axis of the complex. Though there are many literatures which describe solvent dependence for the CD spectra of optically active complexes, the example of systematic studies can be found in only a few examples.

It has been reported that a marked solvent effect was observed in the d-d transition region for the CD spectra of [Co(acac)₂(diamine)]⁺ complexes[4]. However, it has not been explained why the CD spectra of the complexes were varied in solvent, and the used solvent was only ethanol and the origin of the solvent effect was not described.

In this study, in order to investigate further detailed and reliable origin of the dependence of CD spectra on the organic solvents, we have studied the CD spectra of optically active bis(acetylacetonato)(ethylenediamine)cobalt(III) and bis(acetylacetonato)(trimethylenediamine)cobalt(III) complexes in several protic and aprotic solvents which have different dipole moment and dielectric constant.

Experimental

Metal complexes [Co(acac)₂(en)] ClO₄[11,12], [Co(acac)₂(tn)] ClO₄[13], and Na[Co(ox)₂(en)][14] were prepared and resolved by the literature methods, where en = ethylenediamine, tn = trimethylenediamine, and ox = oxalate anion. The purity of the complexes was identified by absorption and/or CD spectra. The organic solvents used for the CD spectra measurement were used as purchased without further purification.

The CD spectra was measured on JASCO J500 automatic spectropolarimeter at room temperature.

Results and Discussion

Figure 1 shows the CD spectra of Δ-[Co(acac)₂(tn)]⁺ in several protic solvents. Though the intensities of the CD spectra of Δ-[Co(acac)₂(en)]⁺ differ from those of Δ-[Co(acac)₂(tn)]⁺ in the d-d transition region, the shapes of the CD variation in the solvents are very similar. The observed CD spectra in Figure 1 are not due to any chemical reactions, since the identical compound is recovered from those solutions by absorption and CD spectra when the solvents are removed.
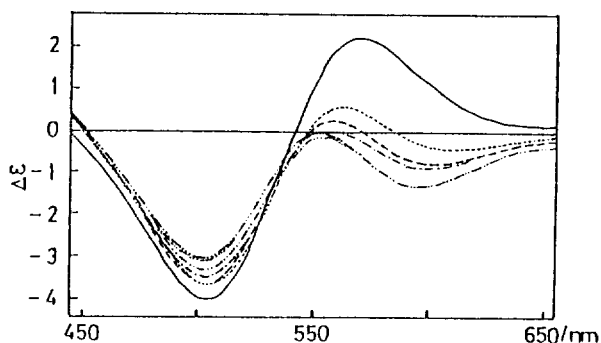
442 *Bull. Korean Chem. Soc., Vol. 8, No. 6, 1987*

Yang Kim and Chang Eon Oh

Figure 1. The CD spectra of Δ-[Co(acac)$_2$(tn)]ClO$_4$ in water(—), benzylalcohol(·····), n-BuOH(——), MeOH(----), EtOH(·····-), n-PrOH (············), and *iso*-PrOH(·········).
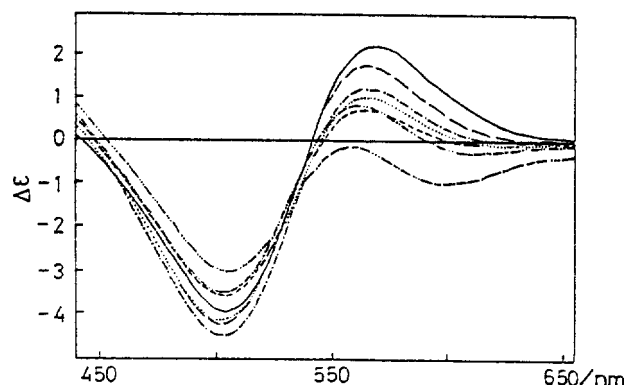
Figure 2. The CD spectra of Δ-[Co(acac)$_2$(tn)]ClO$_4$ in water(—), DMSO(- - -), DMF(----), CCl$_4$(·····), acetonitrile(——), benzonitrile (········), and dichloromethane(·········).

Figure 3. The CD spectra of Δ-[Co(acac)$_2$(tn)]ClO$_4$ in 1,4-dioxane (····), acetone(——), THF(----), CHCl$_3$(- - -), pyridine(······), and nitrobenzene(············).

Figure 4. The CD variation of Δ-[Co(acac)$_2$(tn)]ClO$_4$ as a ratio of EtOH content in DMSO/EtOH mixed solvents.

Therefore, it can be deduced that the variations of these CD spectra are not due to the configurational change of complex.

In a complex of C_2 symmetry, the octahedral T_{1g} transition ($A_{1g} \leftarrow T_{1g}$) breaks down into one component with A symmetry and two components with B symmetry ($A_2 + B_1 + B_2 \leftarrow A$)[15]. The lowest energy CD peak, which is assigned to the B_1 transition, has a plus sign in water. And the higher energy CD peak, which is assigned to the $A_2 + B_2$ transition, is minus. As seen in Figure 1, the sign of the CD spectrum of the complex in aqueous solution has a plus sign in B_1 component. However, the spectra yield minus-plus couplets in n-butanol (n-BuOH) and benzylalcohol. And in other protic solvents such as methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH), and isopropanol (*iso*-PrOH) *etc.*, the sign is changed from plus to minus, while the major CD bands which are corresponded to $A_2 + B_2$ component in C_2 symmetry are relatively unaffected to B_1 component.

The degree of the CD variation of Δ-[Co(acac)$_2$(tn)]$^+$ and Δ-[Co(acac)$_2$(en)]$^+$ complexes in B_1 component by some protic solvents are follows; *iso*-PrOH $\approx$ n-PrOH $\approx$ EtOH > MeOH > n-BuOH > benzylalcohol. The dielectric constants[16] of *iso*-PrOH, n-PrOH, EtOH, MeOH, n-BuOH, and benzylalcohol are about 18.3, 20.1, 24.3, 32.6, 17.6, and 13.1, respectively. The degree of the CD variation in these solvents is enhanced as the dielectric constants decrease except n-BuOH and benzylalcohol. Though n-BuOH and benzylalcohol have lower dielectric constants than MeOH, the degree of the CD variations is smaller than MeOH. This reason is not clear as yet. And the dipole moments[16] of *iso*-PrOH,
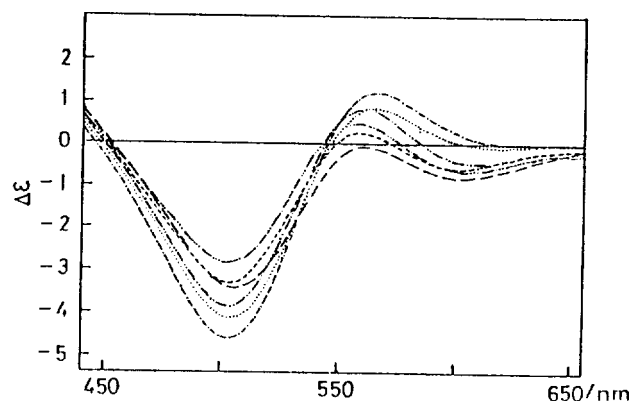
n-PrOH, EtOH, MeOH, n-BuOH, and benzylalcohol are about 1.66, 1.68, 1.69, 1.70, 1.66, and 1.77 Debye, respectively. The degree of the CD variation of [Co(acac)$_2$(tn)]$^+$ and [Co(acac)$_2$(en)]$^+$ complexes can not be simply correlated with the dipole moments, since those values of above solvents are nearly similar. Thus, the CD variations in protic solvents seem to be due to the dielectric constant rather than the dipole moment.

Figure 2 and 3 show the miscellaneous CD spectra of Δ-[Co(acac)$_2$(tn)]$^+$ complex which is affected by several aprotic solvents in d-d transition region. In aprotic solvents, the degree of the CD variation in B_1 component has close correlations with both magnitudes of the dipole moment and the dielectric constant except for aromatic solvents (nitrobenzene, pyridine, and benzonitrile *etc.*) and the solvents having no dipole moment (CCl$_4$ and 1,4-dioxane). The degree of the CD variation is roughly increased as both physical values are decreased. Since acetonitrile ($\varepsilon = 36.2$) has a smaller dielectric constant than DMSO ($\varepsilon = 49$), the CD variation in the former is greater than the latter. On the other hand, the dipole moments of DMSO (3.96D) and acetonitrile (3.92D) are similar, but the CD variation in the latter is much greater than the former. And since 1,4-dioxane and CCl$_4$ having no dipole moment also have affected to the CD change, the solvent effect for the CD variation indicates that the dielectric constant effect is greater than the dipole moment effect. These results show that there are a certain interaction between the complex cations and solvent molecules. In aromatic
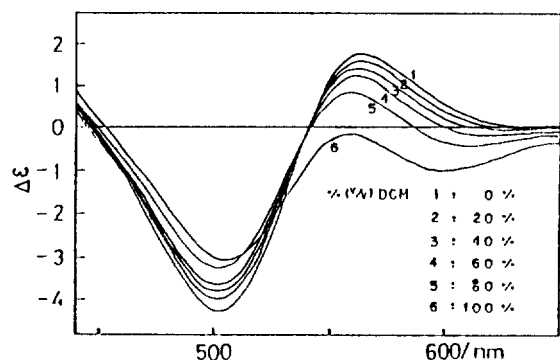
Figure 5. The CD variation of Δ-[Co(acac)₂(tn)]ClO₄ as a ratio of dichloromethane(DCM) content in DMSO/DCM mixed solvents.
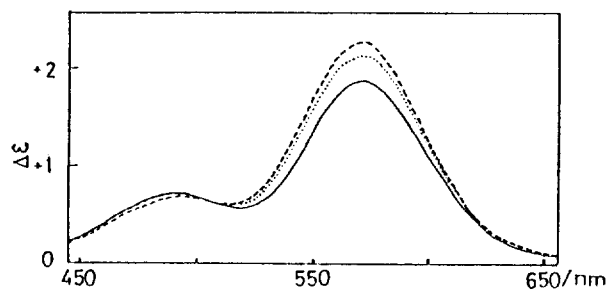
Figure 6. The CD spectra of Λ-Na[Co(ox)₂(en)] in water(—), 80% (v/v) EtOH(·····), and 80%(v/v) acetone(-----).

Figure 7. The CD spectra of Δ-[Co(acac)₂(tn)]ClO₄ in water(---), dichloromethane(·····), and KBr disc(—)(arbitrary scale).

solvents such as pyridine, the interaction between complexes and solvents seems to be due to the π-π interaction between solvent molecules and coordinated acetylacetonate ligands with the pseudo aromaticity[17].

In order to see what types of the spectra are obtained in mixed solvents, the CD spectra of Δ-[Co(acac)₂(tn)]⁺ were measured as a ratio of solvent composition. For the combinations of DMSO/EtOH systems (Figure 4), the spectra are varying smoothly as the solvent composition is changed. On the other hand, the patterns of varying CD spectra in DMSO/DCM systems (Figure 5) are slightly different from above system, where DCM is dichloromethane. For example, the spectrum of 80% (v/v) DCM solution in DMSO/ DCM system is shown in the nearly middle position between 100% DMSO and 100% DCM solutions. And the shape of the CD spectrum of 80% (v/v) EtOH solution in DMSO/EtOH systems bears a resemblance to that of 100% EtOH solution.

The dipole moments of DMSO, EtOH, and DCM are about 3.96, 1.69, and 1.60 Debye, respectively. And the dielectric constants of those solvents are about 49, 24.3, and 8.9, respectively. For the DMSO/EtOH and DMSO/DCM systems, the differences of the dipole moments are 2.27 and 2.36 Debye, respectively, and the differences of those values are similar. For those systems, however, the differences of the dielectric constants are 24.7 and 40.1, respectively. Thus, these results indicate that the factor which influence the CD variations of bis(acetylacetonato) complexes in mixed solvents is the dielectric constant rather than the dipole moment, and that the complexes are preferentially solvated by the solvent having greater dielectric constant.

In order to ascertain the site of actural interaction between the organic solvents and complexes, we have investigated the CD spectrum of Λ-[Co(ox)₂(en)]⁻ complex having a

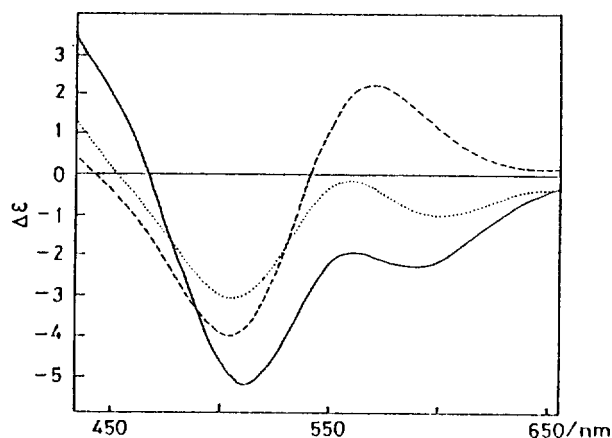N₂O₄ type ligand (Figure 6). The intensities of the CD spectra of Λ-[Co(ox)₂(en)]⁻ in EtOH and acetone solutions are increased somewhat more than aqueous solution, but the sign inversion such as bis(acetylacetonato)(diamine)cobalt(III) complexes is not found in B₁ component. In conductance study of [Co(acac)₂(diamine)]⁺ complexes, Ito et al.,[17-19] have proposed a hydrogen bonding interaction between the NH proton of diamine in complex and oxygen atom of n-PrOH. They have proposed that [Co(acac)₂(diamine)]⁺ is solvated through a six-membered ring between alcohol and complex. However, this hydrogen bonding can not act as a source of the CD variation of the optically active [Co(acac)₂(diamine)]⁺ complexes, since a similar solvent effect like protic solvents is shown by the aprotic solvents such as DCM, acetone, and CHCl₃ etc., which can not form six-membered rings with the complexes (see Figure 2 and 3). Furthermore, the CD spectra of the optically active [Co(acac)₂(phen)]⁺ and [Co(acac)₂(bpy)]⁺ complexes which have no NH protons, and which can not form a hydrogen bonding of six-membered ring, have also exhibited a notable solvent effect in EtOH solution[4]. And the ring formation of [Co(ox)₂(en)]⁻ complex which are formed the six-membered rings by hydrogen bonding with EtOH do not exhibit a remarkable CD change as the CD spectra of acetylacetonate complexes have been notably changed in EtOH solution (Figure 6).

The conformational changes of the diamine ligand (en or tn) can also affect the change of the CD spectra. However, we can verify that the variation of the CD spectra in solvents is not greatly influenced by the conformational change of diamine, since the CD spectra[4] of the optically active [Co(acac)₂(phen)]³⁺ complex that the rigid phenanthroline ligand having no conformational change was coordinated to Co (III) ion have been also varied by EtOH and the shape of its spectrum was similar to that of [Co(acac)₂(tn)]³⁺ complex. Therefore, we can ascertain that the actual site which can affect the CD variation is not a diamine but two acetylacetonate ligands coordinated to the central metal ion.

Palmer et al.,[20] reported that the dipole moment of C-CH₃ group in M(tfac)ₙ(acac)₃₋ₙ complexes is 0.37 Debye, where tfac is 1,1,1-trifluoro-2,4-pentanedionato anion. From this report, we can presuppose that an interaction between acetylacetonate ligand and solvents is present. The conformation of coordinated acac ligand has the planarity due to its pseudo aromaticity, and the conformational form of the

444 *Bull. Korean Chem. Soc., Vol. 8, No. 6, 1987*

Ikchoon Lee et al.

ligand in organic solvent is not clear as yet. From our results, however, we can deduce that the planarity of the acac ligand having dipole moment is influenced by the solvent molecules, and that the distortion of its planarity due to an interaction such as polar linkage between solvent and C-CH$_3$ group of acac is induced.

As seen in Figure 7, the CD spectrum of Λ-[Co(acac)$_2$(tn)] ClO$_4$ complex in solid state bears some resemblance to the spectra in organic solvents which have low dipole moment and dielectric constant with the exception of some solvents. Thus, because of the interaction between solvents and C-CH$_3$ groups of acetylacetonate ligands, it is deduced that the conformation of coordinated acac ligands can be changed in solvents, and that the conformational changes influence on the CD spectra. The similarity of the CD spectra measured in the solvents of low polarity and that in solid indicate that the ligand conformation of the complex is similar in both states. Since a series of solvents interact with C-CH$_3$ groups of acac ligand more weakly than water, does the acac ring of complex can be less flexible, and it is deduced that the CD spectra in both states resemble each other.

In conclusion, from CD spectra analyses, it is apparent that the solvent plays an important role in the conformational change of acetylacetonate rings in [Co(acac)$_2$(diamine)]$^+$ complexes, and that the degree of flexibility of acac rings is more affected by the dielectric constant than by the dipole moment.

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Theoretical Studies of Solvent Effects on Gas Phase Reactions of Methoxide Ion with Substituted Ethylenes[†]

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Solvent effects on gas phase reactions of methoxide ion with substituted ethylenes, CH$_2$=CHR where R=CN,CHO and NO$_2$, are investigated theoretically using the AM1 method. Results show that the methoxide approaches in-plane in all reactions, but subsequently rotate out-of-plane to form tetrahedral complexes in additon reactions. All reactions of a bare methoxide are found to be exothermic, the exothermicity being the greatest in the β-addition, in which the excess energy is forced to be contained within the β-adduct rendering extreme instability. However a part of the excess energy can be removed by a solvate molecule giving a stable complex prior to the product formation. The hydride transfer processes were found to be unfavorable due to the high activation barriers. The α-H$^+$ abstraction process from acrylonitrile becomes endothermic as a result of monosolvation of the methoxide, in agreement with experimental results.

Introduction

Gas phase ion-molecule reactions have played an impor-

tant role in the elucidation of mechanisms in organic chemistry. Recently it has been shown both experimentally[1] and theoretically[2] that the removal of all solvation from reactants in ion-molecule reactions can drastically alter not only

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[†] Determination of Reactivity by MO Theory (Part 51).