November, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 3411—3412 (1985)* 3411

Induced Circular Dichroism of Bis(tropolonato)copper(II) with Optically Active Amines

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(Received June 18, 1985)

Synopsis. Bis(tropolonato)copper(II) forms adducts with chiral aromatic amines and exhibits circular dichroism(CD) induced for d-d and intra-ligand transitions. The applicability of the dispersion-induced CD theory to this complex system is discussed.

In a previous paper, we reported the CD spectra of some copper(II) β-diketonates in optically active bases such as (+)-1-phenylethylamine.[1] The chiral base coordinates at the axial position of the complexes to form mono base-adducts, gives a dissymmetric influence to the parent achiral complexes, and induces optical activities to their electronic transitions.

Dispersion-induced circular dichroism(DICD) treatment has been developed by Schipper for the interaction between achiral and chiral species with no specific orientation; for example, an achiral solute/chiral solvent system.[2,3] He applied this theory to the above system of copper(II) β-diketonates with optically active amines and his results supported most of our discussion.[2]

However, the examined achiral complex/chiral amine couples were so limited that the observations and theoretical applications could not be generalized. Thus, we have studied more systems including a tropolonate complex and (+)-1-(1-naphthyl)ethyl- and (+)-1-(2-naphthyl)ethylamine.

Experimental

Bis(tropolonato)copper(II), Cu(trop)$_2$, was prepared according to the literature.[4] (+)-1-(1-Naphthyl)ethylamine was commercially available and distilled before use. $[\alpha]_D^{20}$=+58.2° (*c*=2, methanol). 1-(2-Naphthyl)ethylamine was prepared from 2′-acetonaphthone according to literature[5] and resolved by the use of (+)-tartric acid. For its (+)-antipode, $[\alpha]_D^{20}$=+19.6° (*c*=3.5, methanol). Chloroform of spectro-grade was used as solvent without further purification.

TABLE 1. THE VALUES OF $\Delta\varepsilon$ AND STABILITY CONSTANT(K_b) FOR THE 1:1 BASE-ADDUCTS OF Cu(trop)$_2$ IN CHLOROFORM

(+)-Amine	K_b, M^{-1} (25 °C)	$\Delta\varepsilon$, cm^{-1} M^{-1} ($\tilde{\nu}$/10^3 cm^{-1})
1-Phenylethylamine	2.3	+0.009(12.7), −0.002(16.7) −0.32(25.6), +0.55(30.0)
1-(1-Naphthyl)-ethylamine	3.1	+0.027(12.4) −1.01(24.8), +0.64(30.4)
1-(2-Naphthyl)-ethylamine	2.6	−0.65(25.6), +0.66(29.8)

Upon the addition of bases, the visible absorption band shifts to a longer wavelength with a much-increased intensity (Fig. 1). From this spectral change, the formation of mono base-adducts is obvious.[6] The formation constant (K_b) of the adducts was determined by the ordinary spectrophotometric method.[7] The values of K_b are listed in Table 1.

The spectra of the chiral amine-adducts were obtained for the chloroform solutions containing 5×10^{-3} M of complex and 1—1.5 M of amines(1 M=1 mol dm^{-3}). Under this condition, approximately 70% of the parent complex transforms to the adduct, in spite of the low K_b values. The values of $\Delta\varepsilon$ summarized in Table 1 are based on the adduct concentration, whereas the vertical scales of Fig. 1 refer to 1 mol of the copper ion. Since tropolone seems to undergo no corbonyl reactions,[4] the chelated tropolonate appeared stable even in the presence of primary amines.

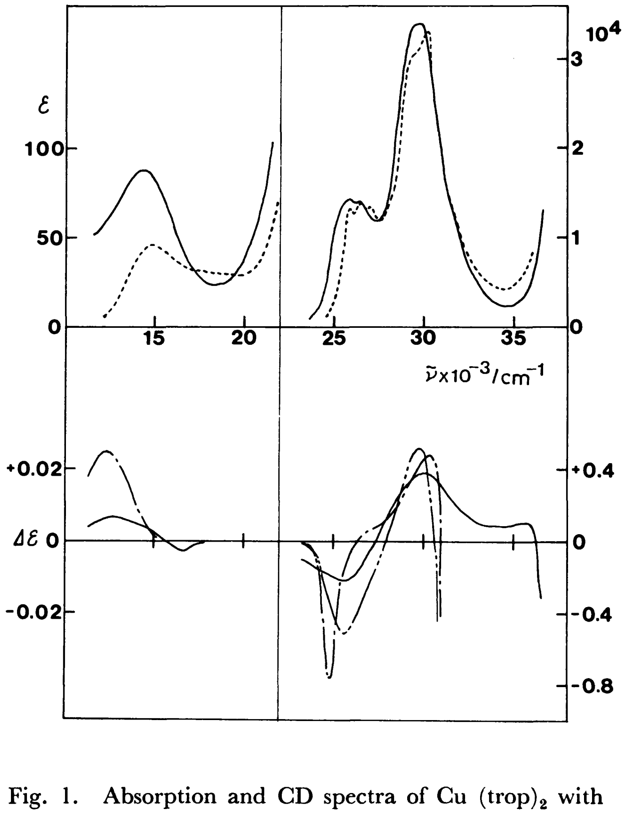

Fig. 1. Absorption and CD spectra of Cu (trop)$_2$ with the addition of (+)-amines in chloroform; the concentration of complex is about 5×10^{-3} M and the numbers in parentheses represent mole ratios in amine/complex. ----, no amine added; ——, (+)-1-phenylethylamine (200); —-—, (+)-1-(1-naphthyl)ethylamine (190); ——-—, (+)-1-(2-naphthyl)ethylamine (240).

Results and Discussion

Figure 1 shows the absorption and CD spectra of Cu(trop)$_2$ in chloroform containing (+)-amines. The main CD band in the visible region appears at the lower wavenumber side of the broad d-d absorption band. This is the same result as those for the β-diketonate complexes as previously reported.[1] Therefore, this CD band originates from the two low-energy transitions, $d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$. As suggested by Schipper,[2] only the latter, which is z-polarized magnetic dipole-allowed in a parent molecular symmetry D_{4h}, mainly contributes the optical activity.

Two intense absorption bands are observed at around 26000 and 30000 cm^{-1} as shown in Fig. 1, and at a higher wavenumber another more intense band is expected to appear.[4] Free tropolone also exhibits three bands, each located at a slightly higher wavenumber compared with the corresponding three bands of Cu(trop)$_2$.[4,8,9] Such a red shift of the intraligand band due to the complex formation has been also observed for other ligands, acetylacetone, salicylaldehyde, and so on.[10,11] Thus, from the positions and intensities, the two bands at 26000 and 30000 cm^{-1} are supposedly associated with the intraligand transitions, although their more detailed nature is not clear so far.

Upon the addition of amine, the tropolone bands shift slightly to lower wavenumbers. Any of three (+)-amines used induces similar optical activities; a negative band at 26000 and a positive one at 30000 cm^{-1}. These (+)-amines show an intrinsic negative CD band at the lowest energy transition which corresponds to the L_b band of phenyl or naphthyl ring.[12,13] On the basis of these findings, the induced CD of this region is discussed as follows.

(1) Schipper has suggested that DICD bands for the electric dipole-allowed transitions of achiral species have the same sign as that of the intrinsic CD of the inducing transition of chiral species.[2] However, the induced optical activity observed possesses different signs as mentioned above. This discrepancy between the DICD theory and the observation would be caused by the assumption that the achiral and chiral species have no orientational correlation. In the amine-adducts, the amine molecule acts as ligand rather than as mere solvent and coordinates to the copper ion. Therefore, the chiral amine and the achiral tropolonate will have a fairly fixed orientation, although the aromatic chromophore of the amine will rotate, to some extent, around the tetragonal axis in the solution. The two tropolone transitions in question possess different polarizations along the tropolone plane,[9] which may be responsible for their opposite-signed CD bands.

(2) The exciton coupling between the transitions of the tropolonate rings cannot constitute the inducing mechanism, since only one CD component appears under the lobe of each absorption band, as previously mentioned.[1]

(3) The inherent CD intensity associated with the L_b band of (+)-1-(1-naphthyl)ethylamine is much different from that of (+)-1-(2-naphthyl)ethylamine; the value of $\Delta\varepsilon$ at 320 nm is -0.03 for the former and -0.27 for the latter in chloroform.[14] This comes from the polarization of the L_b transition which is along the long axis of the naphthalene plane. In spite of such a different electric inducing power,[2] these two (+)-amines induce comparable optical activities for each of the two tropolonate transitions. This also suggests that the orientation between the chromophores of the chiral amine and the achiral tropolonate ring is significant as mentioned above.

The author thanks Prof. Masahiro Hatano for his permission of use of Jasco J-500c spectropolarimeter.

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