The Magnetic Circular Dichroism of Some Copper(II) β-Diketone Chelate Complexes in Various Media

Hajime KATÔ and Takahide KIMURA

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657

(Received May 15, 1973)

The magnetic circular dichroism (MCD) and absorption spectra of $Cu(acac)_2$, $Cu(bzac)_2$, $Cu(acest)_2$, $Cu(TFacac)_2$, and $Cu(HFacac)_2$ in benzene, chloroform, methylene chloride, 1,4-dioxane, pyridine, and piperidine are observed. The behavior of these spectra can be well explained by proposing this order of energy levels: d_{xz}, $d_{yz} < d_{x^2-y^2} < d_{z^2} < d_{xy}$. The MCD spectra in pyridine do not show any dispersion in the neighbourhood of the absorption peak which seems to correspond to the d_{xz}, $d_{yz} \rightarrow d_{xy}$ transition; this fact suggests that the B-term of the MCD parameters is dominant at room temperature. There is no serious difference between the MCD of $Cu(acac)_2$ and $Cu(bzac)_2$, or between $Cu(HFacac)_2$ and $Cu(TFacac)_2$. It appears that this lowering of symmetry is not important in interpreting the MCD spectra.

The magnetic circular dichroism (MCD) spectra of several Cu(II) complexes have been studied, and the B-term of the MCD parameters has been found to be dominant in the MCD of the Cu(II) complexes at room temperature.[1] The MCD spectrum of bis(acetylacetonato)copper(II), $Cu(acac)_2$, dissolved in chloroform was also studied.[2] The absorption spectra of $Cu(acac)_2$ in various media have been reported, and the positions and intensities have been shown to depend primarily upon the solvent basicity.[3] Therefore, MCD studies of the solvent effects are expected to yield a great deal of information about the assignments of the transitions and the properties of the MCD spectra. Furthermore, we have thought it worth while to investigate the MCD spectra for several substituted β-diketone complexes of copper(II). From this investigation, we expect to ascertain the effect of the lowering of symmetry around copper(II) upon the MCD and to ascertain the effect of various electron-withdrawing abilities of substituted acetylacetonates upon the MCD.

Experimental

Five copper(II) β-diketone chelate complexes, *i.e.*, bis(acetylacetonato)copper(II), bis(benzoylacetonato)copper(II), bis(ethylacetoacetato)copper(II), bis(trifluoroacetylacetonato)copper(II), and bis(hexafluoroacetylacetonato)copper(II) (abbreviated as $Cu(acac)_2$, $Cu(bzac)_2$, $Cu(acest)_2$, $Cu(TFacac)_2$, and $Cu(HFacac)_2$) were prepared and purified according to the methods described in the literature.[4-7] The absorption and MCD spectra of these compounds in the benzene, chloroform, methylene chloride, 1,4-dioxane, pyridine, and piperidine series of solvents were measured by the techniques described in an earlier paper.[1]

Results and Discussion

Figure 1 gives the MCD and absorption spectra of $Cu(acac)_2$ in the chloroform, methylene chloride, 1,4-dioxane, pyridine, and piperidine series of solvents. The MCD datum of $Cu(acac)_2$ in benzene was not available because of its poor solubility. Belford and his co-workers[3] have studied the absorption spectra, in the visible and near infrared region, of $Cu(acac)_2$ and bis(3-ethylacetylacetonato)copper(II) in various

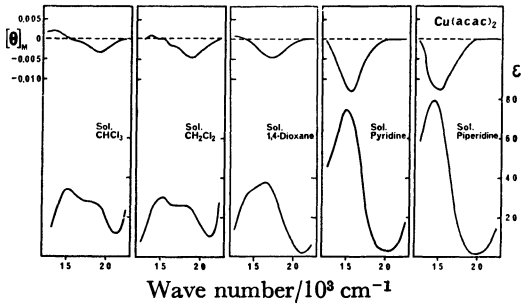

Fig. 1. The MCD (upper) and absorption (lower) spectra of $Cu(acac)_2$ dissolved in various solvents at room temperature.

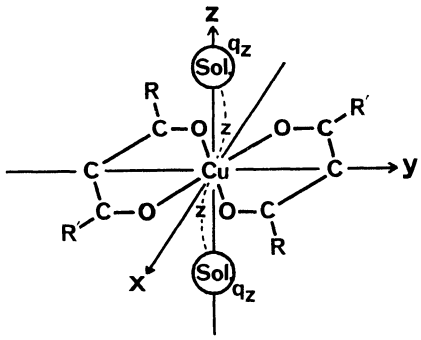

Fig. 2. The coordinate system and geometrical model for the calculation of solvent effects.

media. The behavior of these absorption bands upon the alternation of the solvent have been quite successfully explained in terms of the crystal field theory. Let us adopt the same model. The effect of the solvent is considered as two axial ligands (two charges, q_z, at (0, 0, z) and (0, 0, −z), as is shown in Fig. 2) are added to a square planar complex. $Cu(acac)_2$ molecule in a noninteracting solvent, chloroform, may be considered as an isolated square-planar complex. If we assign the bands at 18810 and 15190 cm^{-1} observed for $Cu(acac)_2$ in chloroform to the d_{yz}, $d_{yz} \rightarrow d_{yz}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transitions respectively,[3] the transition energies in the presence of an interacting solvent are given by:

$$\delta E_1(|xz\rangle, |yz\rangle \rightarrow |xy\rangle) = 18810 + (-9\langle r^2\rangle/z^2 + 5\langle r^4\rangle/z^4)2q_z e^2/21z,$$
$$\delta E_2(|x^2-y^2\rangle \rightarrow |xy\rangle) = 15190,$$
$$\delta E_3(|z^2\rangle \rightarrow |xy\rangle) = 14950 + (-12\langle r^2\rangle/z^2 - 5\langle r^4\rangle/z^4)2q_z e^2/21z \quad (1)$$

in units of cm^{-1}. The values of $\langle r^2\rangle$ and $\langle r^4\rangle$ are evaluated by using the analytical SCF function for Cu obtained by Clementi:[8] $\langle r^2\rangle_{Cu}=1.106\ a_0^2$, $\langle r^4\rangle_{Cu}=3.301\ a_0^4$. If we assume the distance, z, between the metal and the solvent charge, q_z, to be 2 A, then the excitation energies given by Eq. (1) are reduced to functions of q_z only. The results are shwon schematically in Fig. 3. $\delta E_2(|^2x-y^2\rangle \rightarrow |xy\rangle)$ displays little variation from solvent to solvent. $\delta E_1(|xz\rangle, |yz\rangle \rightarrow |xy\rangle)$ approaches $\delta E_2(|x^2-y^2\rangle \rightarrow |xy\rangle)$ as the solvent basicity is increased. The variation in the absorption bands upon the alternation of the solvent can be well explained by assuming the q_z values to be about 0.0, 0.1, 0.3, 0.7, and 0.9 for the spectra of $Cu(acac)_2$ in chloroform, methylene chloride, 1,4-dioxane, pyridine, and piperidine respectively. These values seem to be of a plausible order of magnitude.

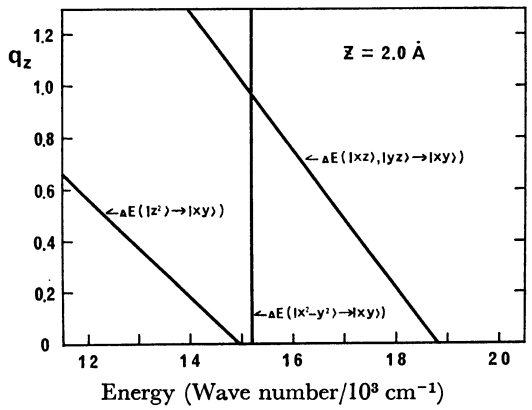

Fig. 3. Excitation energy diagram as a function of solvent charges q_z, which are assumed to be located axially to a square-planar complex at (0, 0, 2A) and (0, 0, −2A).

The interpretation of the polarized visible absorption spectrum of $Cu(acac)_2$ has been the subject of speculation and controversy as attempts have been made to remove the ambiguity of the assignment.[9-12] Unfortunately, however, the type of packing of molecules in the crystal was inadequate for the attempt.[13] Hitchman and Belford[13] studied the temperature-dependent polarized spectra of $Cu(bzac)_2$; they assigned the band at 18.1 kK to d_{xz}, $d_{yz} \rightarrow d_{xy}$, the band at 15.6 kK to $d_{x^2-y^2} \rightarrow d_{xy}$ and the band at 14.2 kK to $d_{z^2} \rightarrow d_{xy}$ on the basis of the temperature dependence and the relative polarization. This ordering of the d levels is the same as that suggested for bis(3-phenyl acethylacetonato)copper.[14] The positions of the d-d bands in $Cu(bzac)_2$ at 14.2, 15.6, and 18.1 kK, are very similar to those of the bands in $Cu(acac)_2$, at 14.5, 16.3, and 18.0 kK;[13] this suggests the same ordering of the d levels. Katô and Gohda[2] proposed the same order of energy levels (d_{xz}, $d_{yz} < d_{x^2-y^2} < d_{z^2} < d_{xy}$) for $Cu(acac)_2$ in chloroform on the basis of the MCD analysis.

The variation in the absorption bands upon the alternation of the solvent can be well explained by proposing this order of energy levels, as we have seen above. On the other hand, if we assign the bands at 18810 and 15190 cm^{-1} observed for $Cu(acac)_2$ in chloroform to the $d_{x^2-y^2} \rightarrow d_{xy}$ and d_{xz}, $d_{yz} \rightarrow d_{xy}$ transitions respectively, we can not explain the observed red shift of the bands as the basicity of the solvent increases. The energy for the $d_{x^2-y^2} \rightarrow d_{xy}$ transition should undergo little change from the variation in the basicity of solvent which coordinates axially to a square-planar complex. This property is due to the geometrical structure of the d_{xy} and $d_{x^2-y^2}$ orbitals and does not depend greatly on the model of the calculation.

The MCD spectra of $Cu(acac)_2$ display a remarkable change on going to a more basic solvent. This change can be explained on the basis of the above discussion about the transition energies and the previous analysis about the MCD of the Cu(II) complexes.[1] The d_{xz}, $d_{yz} \rightarrow d_{xy}$ transition, which shows an MCD with a positive B-term, approaches the $d_{x^2-y^2} \rightarrow d_{xy}$ transition band, which shows an MCD with a small positive B-term, as the solvent basicity is increased. The $d_{z^2} \rightarrow d_{xy}$ transition, which shows an MCD with a negative B-term, shifts to the lower frequency region, in which we can not measure the MCD spectra because of our instrumental restriction. Therefore, $Cu(acac)_2$ values in pyridine and piperidine display only a negative MCD in the region of 12.5—20.0 kK.

The MCD spectra of $Cu(acac)_2$ in 1,4-dioxane and pyridine do not show any dispersion in the neighbourhood of the absorption peak which seems to correspond to the d_{xz}, $d_{yz} \rightarrow d_{xy}$ transition. This fact strongly suggests that the B-term of the MCD parameters is dominant in the MCD of $Cu(acac)_2$ at room temperature. This conclusion is consistent with the theoretical prediction previously proposed by one of the present authors.[1]

The MCD and absorption spectra of $Cu(bzac)_2$, $Cu(acest)_2$, $Cu(TFacac)_2$, and $Cu(HFacac)_2$ in the benzene, chloroform, methylene chloride, 1,4-dioxane, pyridine, and piperidine series of solvents are shown in Figs. 4—7. In these spectra, the effect of changing the substituents is smaller than the effect of changing the solvent. However, the MCD and absorption spectra in the solvent with a weak basicity suggest a correla-

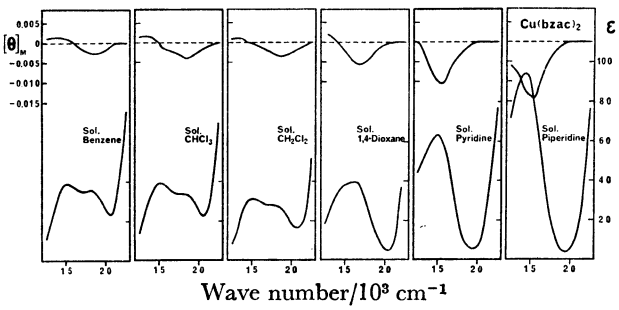

Fig. 4. The MCD and absorption spectra of $Cu(bzac)_2$ dissolved in various solvents at room temperature.

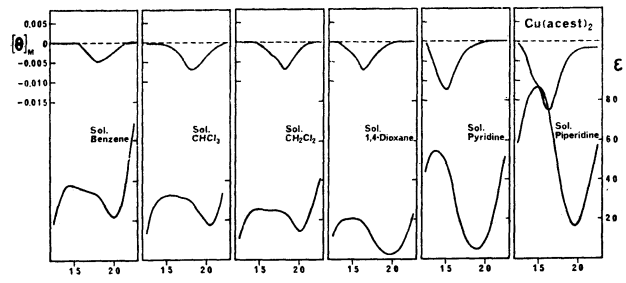

Fig. 5. The MCD and absorption spectra of $Cu(acest)_2$ dissolved in various solvents at room temperature.

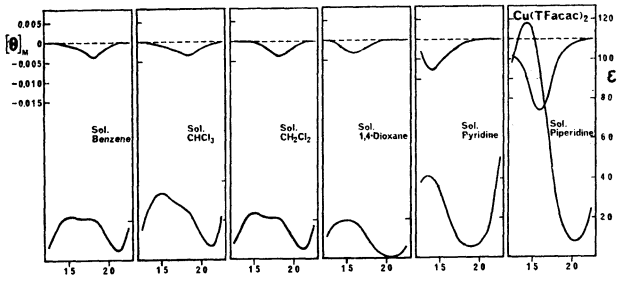

Fig. 6. The MCD and absorption spectra of $Cu(TFacac)_2$ dissolved in various solvents at room temperature.

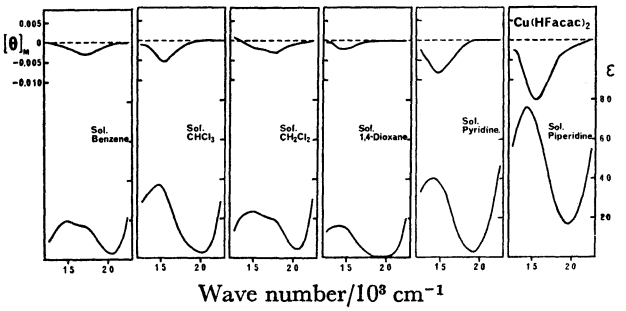

Fig. 7. The MCD and absorption spectra of $Cu(HFacac)_2$ dissolved in various solvents at room temperature.

tion between the relative electron-withdrawing ability of substituents and the energy levels of copper d electrons; the more electronegative the substituent, the smaller the energy separation. The order of electronegativity must be $CF_3 > OC_2H_5 > Ph > H > CH_3$. The MCD of the positive B-term of the $d_{xz}, d_{yz} \rightarrow d_{xy}$ transition would overcome the MCD of the negative B-term of the $d_{z^2} \rightarrow d_{xy}$ transition in $Cu(acest)_2$, $Cu(TFacac)_2$, and $Cu(HFacac)_2$.

Of course, the coordinating form and the steric effect of the solvent in each case is important. Kuska and Rogers[15] have reported that increasing the basicity of the solvent has the same effect on the d electron energy levels and on the unpaired electron density of copper as increasing the electronegativity of the substituents. To be sure, there are also similarities in the ESR parameters for $Cu(HFacac)_2$ in a chloroform solution and for $Cu(acac)_2$ in a pyridine solution, and the same similarity in the absorption and MCD spectra. However, the spectrum of $Cu(HFacac)_2$ in chloroform is rather a special case; the spectrum of $Cu(HFacac)_2$ in solvents of a weak basicity, benzene or methylene chloride, is similar to that of $Cu(acac)_2$ in chloroform. Chloroform would be an interacting solvent for $Cu(HFacac)_2$.

The symmetry of $Cu(bzac)_2$ or $Cu(TFacac)_2$ is lower than that of $Cu(acac)_2$ or $Cu(HFacac)_2$, but there is no serious difference between the MCD spectra of $Cu(acac)_2$ and $Cu(bzac)_2$ or between those of $Cu(HFacac)_2$ and $Cu(TFacac)_2$. It appears that this lowering of the symmetry is not important in interpreting the MCD spectra.

This work was partially supported by a Scientific Research Grant from the Ministry of Education of Japan.

References

1) H. Katô, *Mol. Phys.*, **24**, 81 (1972).
2) H. Katô and J. Gohda, This Bulletin, **46**, 636 (1973).
3) R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).
4) W. C. Fernelius and B. E. Bryant, *Inorg. Synthesis*, **5**, 105 (1957).
5) Ping-Kay Hon, C. E. Peluger, and R. L. Belford, *Inorg. Chem.*, **5**, 516 (1966).
6) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).
7) R. L. Belford, A. E. Martell, and M. Calvin, *ibid.*, **2**, 11 (1956).
8) E. Clementi, *J. Chem. Phys.*, **41**, 295 (1964).
9) J. Ferguson, *ibid.*, **34**, 1609 (1961).
10) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).
11) J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1569 (1962).
12) H. C. Allen, Jr., *ibid.*, **45**, 553 (1966).
13) M. A. Hitchman and R. L. Belford, *Inorg. Chem.*, **10**, 984 (1971).
14) R. L. Belford and J. W. Carmichael, Jr., *J. Chem. Phys.*, **5**, 516 (1966).
15) H. A. Kuska and M. T. Rogers, *ibid.*, **43**, 1744 (1965).