

to 500 cm^{-1} . If this higher frequency value is chosen, f_{rr} of BrF_4^- becomes more similar to those of BrF_4O^- and BrF_5 . Similarly for the lighter central atoms, the off-diagonal symmetry force constants in the E block become more important, thus increasing the uncertainties in these numbers which were obtained from underdetermined force fields.

General Trends. Inspection of Table IV reveals the following trends. Whereas the values of the XF stretching force constants either are similar (within the XF_4^- series) or increase in the direction $\text{Cl} < \text{Br} < \text{I}$ (for XF_4O^- and XF_5), the XO stretching force constant in ClF_4O^- is much higher than those in both BrF_4O^- and IF_4O^- . Since the values of the XO force constants within the ClO_4^- , BrO_4^- , IO_4^- series (8.24, 6.05, 5.90 $\text{mdyn}/\text{\AA}$)²⁸ exhibit the same trend, this seems to reflect a general characteristic of XO bonds. In the XO_4^- series, the central X atom does not possess any free valence electron pair or fluorine ligands, and therefore no special resonance or bonding effects should be invoked. The bond-weakening effect of a formal negative charge in the anions and the bond-strengthening effect of a positive charge in the cations are as expected. The negative charge increases the $\text{X}^{\delta+}-\text{F}^{\delta-}$ polarity of the XF_4 bonds, thus weakening them. The reverse is true for a positive charge. This effect can also account for most of the observed increase in the force constants when going from an iodine species to the corresponding isoelectronic xenon species which differ by one formal charge.

A comparison of the XF_4^- - XF_4O^- pairs for each halogen shows that for X being chlorine, an oxygen substituent releases electron density to the more electronegative ClF_4 group, thus increasing the polarity of the ClF_4 bonds and decreasing the Cl-F stretching force constant. For X being bromine, there is little change in the X-F stretching force constant indicating comparable electronegativities for oxygen and the BrF_4 group. For X being iodine, oxygen becomes more electronegative than the IF_4 group, thus withdrawing electron density from IF_4 and increasing the covalency of the IF_4 bonds.

The XF_4 deformation constants f_α show the expected trend. With decreasing size of the central atom, the mutual repulsion among the ligands increases and the bonds become more difficult to deform. The FXO angle deformation constant, f_β , does not appear to change significantly when going from chlorine to iodine. However, for a given halogen atom, f_β appears to follow the same trends exhibited by the corre-

sponding XF_4 stretching force constants, f_r .

Acknowledgment. We are grateful to Drs. C. J. Schack and L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support of the work done at Rocketdyne.

Registry No. CsClF_4O , 39018-38-7; CsBrF_4O , 65391-03-9; KIF_4O , 59654-71-6; KF , 7789-23-3; I_2O_5 , 12029-98-0; IF_5 , 7783-66-6; CsBrO_4 , 33259-95-9; BrF_5 , 7789-30-2; F_2 , 7782-41-4; KBrF_4O , 60995-34-8; ClF_3 , 7790-91-2; CsClF_4 , 15321-04-7; ClF_5 , 13637-63-3; BrF_4^- , 19702-38-6; IF_4^- , 19702-40-0; XeF_4 , 13709-61-0; XeF_4O , 13774-85-1; XeF_5^+ , 42879-72-1.

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A Spectroscopic Reexamination of a Series of Bis(β -diketonato)copper(II) Complexes

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Received July 21, 1977

ESR and optical absorption studies of a series of bis(α -substituted β -diketonato)copper(II) complexes (the substituent is the alkyl or trifluoromethyl group) in toluene or cyclohexane have been carried out systematically. ESR spectra have been analyzed by computer simulation. The coordination bondings as well as the energies and intensities of the metal \leftarrow ligand charge-transfer transitions of B_{3u} and $\text{B}_{2u} \leftarrow \text{B}_{1g}$ in D_{2h} and those of d-d transitions have been fully discussed, with special attention to the correlation of them with the pK_a of the ligands, and their mutual relationships have been explained satisfactorily in terms of covalency in the σ bonding.

Introduction

Many studies on the ultraviolet and visible spectra of bis(β -diketonato)copper(II) complexes have been carried out primarily in order to assign spectral bands.²⁻¹¹ Various ambiguities, however, still remain because conclusive data have not been available. On the other hand, many ESR studies of the complexes also have been done since Maki and McGarvey's excellent work in 1958.¹²⁻¹⁶ The ESR results so far obtained

not only for the complexes but also for many other planar copper(II) complexes, however, do not seem entirely satisfactory. This is because there have not been many cases in which direct comparison among the planar complexes in their ESR results is of significance. Inaccuracies in some data may also be responsible for this situation.

One method for improving the situation is to reinvestigate systematically a series of planar copper(II) complexes of

Table I. ESR Parameters^a and pK_a ^b

Complex	g_{\parallel}	$g_{\perp 1}$	$g_{\perp 2}$	g_0	$ A_{\parallel} $	$ A_{\perp 1} $	$ A_{\perp 2} $	$ A_0 $	pK_a
Cu(dpm) ₂	2.247	2.049	2.047	2.118	185	18	28	77	15.9
Cu(dbm) ₂	2.248	2.050	2.048	2.119	185	17	27	77	13.94
Cu(acac) ₂	2.253	2.052	2.050	2.12	186	17	25	75	12.70
Cu(pta) ₂	2.269	2.055	2.053	2.126	182	16	22	73	9.5
Cu(tfac) ₂	2.268	2.055	2.053	2.126	182	16	22	73	8.83
Cu(hfac) ₂	2.282	2.059	2.057	2.133	178	14	18	69	6.0

^a All values of hyperfine parameters are for ⁶³Cu. All coupling constants are in 10^{-4} cm⁻¹. Estimated errors are ± 0.001 for g values, are $\pm 1 \times 10^{-4}$ cm⁻¹ for hyperfine parameters, but are somewhat larger for g_0 and A_0 , respectively. ^b See ref 20. The pK_a value of ptaH (pivaloyltrifluoroacetone) was estimated from the g_{\parallel} value of its complex using the linear relationship between g_{\parallel} and pK_a in ref 21.

similar kinds from various spectroscopic and chemical points of view and see whether all the results obtained are mutually consistent. In this work, six of the title complexes¹ in inert solvents have been reexamined systematically by ESR and optical absorption, with special attention to the energies and intensities of the metal \leftarrow ligand charge-transfer bands and of d-d bands.

Experimental Section

All of the β -diketone ligands used in this work were available from commercial sources. The copper(II) complexes were prepared and purified according to literature procedures.^{1,17} Reagent grade toluene, which was further purified in the usual way,¹⁸ was used as a solvent for visible and ESR spectral studies. Nakarai's "Spectrograde" cyclohexane was also used as a solvent without further purification for ultraviolet spectral studies. ESR spectra were recorded at room temperature and at the temperature of liquid nitrogen (77 K) on a Hitachi 771 X-band spectrometer. Visible and ultraviolet spectra were recorded at room temperature on a Cary 14 spectrophotometer, using calibrated quartz 40- and 5-mm cells, respectively. The computer simulation of ESR spectra was carried out at the Computer Center of Tohoku University on a NEAC 2200 computer.

Results

ESR Spectra and Computer Simulation. Representative ESR spectra observed in toluene at 77 K are shown by Figure 1 to be axial or nearly axial in nature. All of these spectra were analyzed by computer simulation. The simulation procedure was essentially similar to that of Pilbrow and co-workers.¹⁹ The ESR spectra due to the present complexes are accounted for by a nearly axial spin Hamiltonian with the parameters g_{\parallel} , $g_{\perp 1}$, $g_{\perp 2}$, A_{\parallel} , $A_{\perp 1}$, and $A_{\perp 2}$. The spin Hamiltonian was solved to second order in A_i . Line intensities were weighted for the anisotropic g . Anisotropy in the line width ΔH was included. A linear combination of the Gaussian and Lorentzian line shapes G and L , respectively, with the same line width was used as $\omega G + (1 - \omega)L$, where $0 \leq \omega \leq 1$. In our calculations, we took 90 or 120 orientations for the so-called θ and 7 or 10 orientations for the ϕ . Isotope effects on hyperfine structures due to the natural occurrence of ⁶³Cu and ⁶⁵Cu were taken into consideration for every case. Examples of simulated spectra are shown as dotted lines in Figure 1. As seen in this figure, simulated spectra agreed satisfactorily with observed ones. Solution ESR spectra of the present complexes in toluene at room temperature consisted of four lines with different line widths. The g_0 and A_0 values were approximately derived from these spectra with the consideration of the second-order correction. All of the g and A values determined are summarized in Table I, together with the pK_a values of the ligands.²⁰

An inspection of Table I indicates that all parameter values change regularly with the pK_a ²¹ and that all of the complexes are of nearly axial symmetry in nature. It is also shown in this table that the relations of $g_0 = (g_{\parallel} + g_{\perp 1} + g_{\perp 2})/3$ and $A_0 = (A_{\parallel} + A_{\perp 1} + A_{\perp 2})/3$ hold fairly well, so that the complexes in both the frozen and fluid solutions are the same. A test for the relations is of significance, since there have been many cases in which copper(II) complexes in both of the states may be different.²²

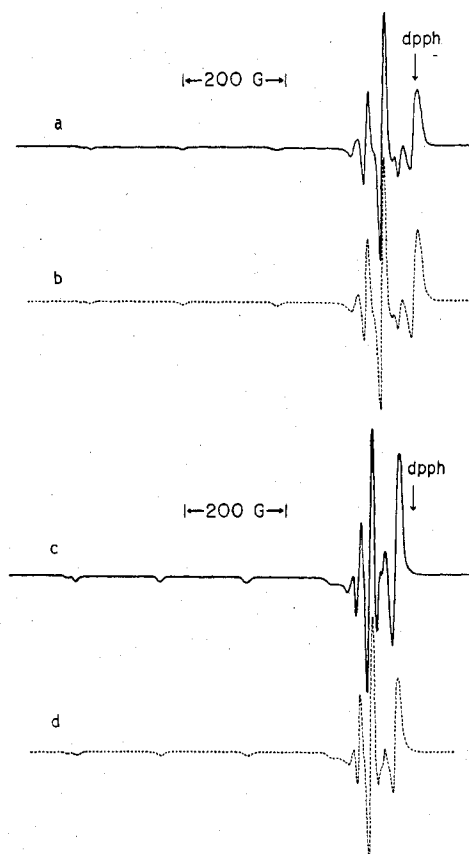


Figure 1. X-Band first-derivative ESR spectra: a, observed for Cu(dpm)₂ in toluene at 77 K; b, simulated for a with the parameters listed in Table I and with $\omega = 0.25$, $\Delta H_{\parallel} = 12.0$ G, $\Delta H_{\perp 1} = 5.0$ G, and $\Delta H_{\perp 2} = 7.0$ G; c, observed for Cu(hfac)₂ in toluene at 77 K; d, simulated for c with the parameters listed in Table I and with $\omega = 0.25$, $\Delta H_{\parallel} = 12.0$ G, $\Delta H_{\perp 1} = 5.0$ G, and $\Delta H_{\perp 2} = 7.0$ G.

Visible and Ultraviolet Spectra. Representative visible and ultraviolet spectra observed in toluene and in cyclohexane, respectively, are shown in Figures 2 and 3. These spectral features are almost the same as those previously reported for similar systems by Fackler et al.³ For purposes of discussion, the observed bands in these spectra in order of decreasing energy were labeled I, II, III, IV, and V in the same way as previously.³ The energy and intensity of band N ($N = I, II, \dots, V$) will be hereafter referred to as E_N and f_N , respectively, where f is expressed by oscillator strength. In every visible spectrum, two peaks labeled as bands IV and V were clearly discernible, as seen in Figure 2. The spectral envelope could be cleanly resolved into just two Gaussian components, as has been done for those of Cu(acac)₂ and bis(ethyl acetoaceto)copper(II) by Graddon²³ and by Belford et al.,²⁴ respectively. Both E_{IV} and E_V decrease regularly in the complex order listed in the tables.

Band III has shoulders in every spectrum, but its position and intensity do not largely change from one complex to

Table II. Visible and Ultraviolet Spectral Data^a

Complex	Obsd			Obsd			Calcd ^c
	E_V	E_{IV} ($=\Delta E_{xz}$ ^b)	ΔE_{xy} ^b	f_{III}	E_{II}	f_{II}	f_{II}
Cu(dpm) ₂	15.0	18.9	15.7	0.42	40.05	0.33	0.40
Cu(dbm) ₂	14.9	18.9	15.6	0.43	40.30	0.32	0.40
Cu(acac) ₂	14.9	18.6	15.5	0.42	40.80	0.31	0.38
Cu(pta) ₂	14.8	18.3	15.3	0.41	41.25	0.29	0.36
Cu(tfac) ₂	14.8	18.2	15.2	0.41	41.50	0.29	0.36
Cu(hfac) ₂	14.5	17.6	14.7	0.39	41.65	0.27	0.34

^a All energy values are in 10^3 cm^{-1} . ^b Estimated values (see text). ^c See text.

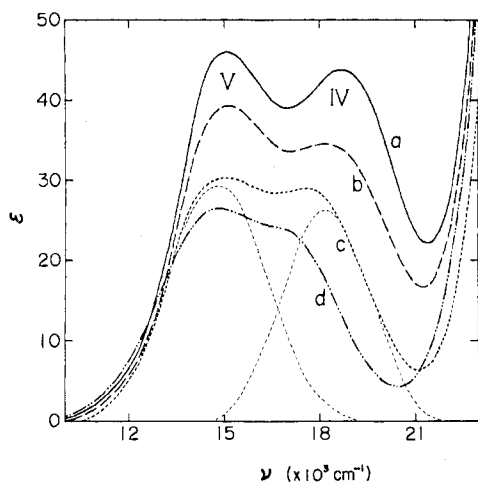


Figure 2. Visible spectra in toluene at room temperature: a, Cu(dpm)₂; b, Cu(acac)₂; c, Cu(tfac)₂; d, Cu(hfac)₂. Resolution into two Gaussian components is shown only in the case of c as an example.

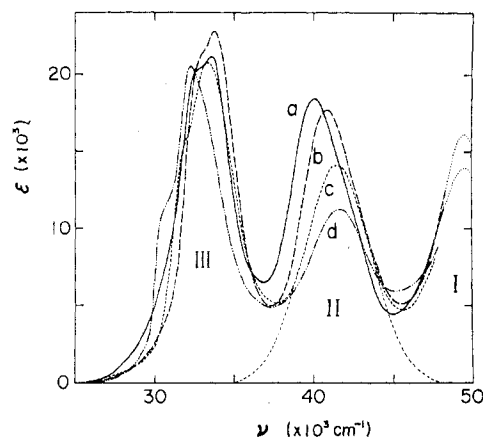


Figure 3. Ultraviolet spectra in cyclohexane at room temperature: a, Cu(dpm)₂; b, Cu(acac)₂; c, Cu(tfac)₂; d, Cu(hfac)₂. A Gaussian analysis of band II is shown only in the case of c as an example.

another. On the other hand, it is characteristic of band II that E_{II} decreases and f_{II} increases in the same complex order, as seen in Figure 3. The spectral envelopes of band II for the latter three complexes in the tables were almost symmetrical, but those for Cu(acac)₂, Cu(dbm)₂, and Cu(dpm)₂ became increasingly unsymmetrical in this order; this indicates that a shoulder on the higher energy side of the band appears for these complexes. In this study, we assigned a Gaussian curve to every band II spectrum so the peaks would coincide with each other. All of the spectral data obtained are summarized in Table II.

Discussion

Calculation of Bonding Parameters. The effective ligand field symmetry in the title complexes is considered to be D_{2h}

from their molecular symmetry but, actually, is very close to D_{4h} from Table I. The following antibonding molecular orbitals can be formed from the central atom 3d and the ligand 2s and 2p orbitals:

$$\psi(b_{1g}) = \alpha d_{x^2-y^2} - \alpha'(-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)})/2 \quad (1a)$$

$$\psi(b_{2g}) = \beta_1 d_{xy} - \beta_1'(p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)})/2 \quad (1b)$$

$$\psi(a_{1g}) = \alpha_1 d_z^2 - \alpha_1'(\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)})/2 \quad (1c)$$

$$\psi(e_g) = \begin{cases} \beta d_{xz} - \beta'(p_z^{(1)} - p_z^{(3)})/\sqrt{2} \\ \beta d_{yz} - \beta'(p_z^{(2)} - p_z^{(4)})/\sqrt{2} \end{cases} \quad (1d)$$

All terminologies and equations and the coordinate system used here are the same as those previously defined by Kivelson and Neiman.¹³ The ligand σ orbitals are viewed as sp^2 -hybrid orbitals. Overlap is included only for the in-plane σ bonding, $\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1$.

The magnetic parameters are shown to be

$$g_{\parallel} = 2.0023 - (8\lambda/\Delta E_{xy})[\alpha^2\beta_1^2 - f(\beta_1)] \quad (2a)$$

$$g_{\perp} = 2.0023 - (2\lambda/\Delta E_{xz})[\alpha^2\beta^2 - f(\beta)] \quad (2b)$$

$$A_{\parallel} = P[-\kappa - 4/\tau\alpha^2 - 2\lambda\alpha^2(4\beta_1^2/\Delta E_{xy} + 3\beta^2/7\Delta E_{xz})] \quad (2c)$$

$$A_{\perp} = P[-\kappa + 2/\tau\alpha^2 - 11\lambda\alpha^2\beta^2/7\Delta E_{xz}] \quad (2d)$$

where

$$f(\beta_1) = \alpha\alpha'\beta_1^2S + \alpha\alpha'\beta_1(1 - \beta_1^2)^{1/2}T(n)/2$$

$$f(\beta) = \alpha\alpha'\beta^2S + \alpha\alpha'\beta(1 - \beta^2)^{1/2}T(n)/\sqrt{2}$$

with the spin-orbit coupling constant for the copper(II) ion $\lambda = -828 \text{ cm}^{-1}$, the free-ion dipole term $P = 0.036 \text{ cm}^{-1}$, and $T(n) = 0.220$ for ordinary ligand oxygen atoms.

The overlap integral S for $R = 1.9 \text{ \AA}$ has been given the values 0.076 for the Cu-O bonds and 0.093 for the Cu-N bonds by Kivelson and Neiman,¹³ whereas the average has been customarily adopted for the N-Cu-O bonds.^{25,27} This aspect of S suggests that the assignment of a constant S value to all of the present complexes may not be practical, because considerable differences in coordination bonding among the complexes are expected from the wide ranges of values, especially in pK_a and g_{\parallel} (Table I). The parameter of g_{\parallel} for copper(II) complexes has been often used as a good index to many other properties of them,^{21,22,27,28} and the g_{\parallel} values of ordinary planar CuN_4 , CuN_2O_2 , and CuO_4 ($\text{Cu}(\text{acac})_2$) chromophores are ~ 2.19 ,²⁷ ~ 2.22 ,^{13,25,29} and 2.25, respectively. We assigned such S values as listed in Table III to the present complexes in proportion to their g_{\parallel} values, setting $\text{Cu}(\text{acac})_2$ as a standard. The main effect of this assignment was a slight reduction of the α'^2 value for $\text{Cu}(\text{hfac})_2$.

Table III. Bonding Parameters

Complex	α^2	α'^2	β_1^2	β^2	κ	S
Cu(dpm) ₂	0.814	0.257	0.774	0.721	0.337	0.078
Cu(dbm) ₂	0.817	0.254	0.768	0.722	0.335	0.077
Cu(acac) ₂	0.827	0.241	0.767	0.732	0.338	0.076
Cu(pta) ₂	0.838	0.224	0.791	0.753	0.337	0.072
Cu(tfac) ₂	0.837	0.225	0.784	0.753	0.337	0.072
Cu(hfac) ₂	0.848	0.209	0.783	0.760	0.334	0.067

Finally, ΔE_{xy} and ΔE_{xz} must be estimated in order to solve eq 2. The d-d bands of such β -diketonate-copper(II) complexes as Cu(acac)₂ are observed in the range 1.4–2.1 μm^{-1} and the d-orbital energies are given as $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \geq d_{yz}$. This assignment, which now seems to be a conclusive one, has been made by Belford et al. through studies on polarized crystal spectra.^{6,7} Similarly, the polarized crystal spectrum of Cu(dpm)₂ reported by Cotton and Wise is informative.^{10,30} It is now obvious that the four d-d bands of the present complexes in toluene are included in bands IV and V and that, by reference to the results of the polarized crystal spectra, band IV consists of ΔE_{xz} and ΔE_{yz} , and band V, of ΔE_{z^2} and ΔE_{xy} . Judging from the fact that $\Delta E_{xz} \approx \Delta E_{yz}$ was experimentally determined for crystals of bis(benzoylacetonato)copper(II)⁷ and that the effective ligand field symmetry of the present complexes in toluene is actually close to D_{4h} , $E_{IV} \approx \Delta E_{xz} \approx \Delta E_{yz}$ is reasonably assigned. On the other hand, an estimation of ΔE_{xy} is not facile. The results of the polarized crystal spectra mentioned above indicate that the difference between ΔE_{xy} and ΔE_{z^2} is on the order of 0.12 μm^{-1} . Since both E_V and E_{IV} change regularly among the present complexes (Table II) and since the same kind of complexes are probably similar in ligand field splittings, we estimated ΔE_{xy} by assuming a constant ratio of ΔE_{xy} to ΔE_{xz} for all of the complexes, adopting Cu(acac)₂ as a standard. The ΔE_{xz} and ΔE_{xy} values thus estimated are listed in Table II.

Now, all sets of data necessary for solving eq 2 have been supplied for the present complexes in toluene. Here, $g_{\perp} = (g_{\perp 1} + g_{\perp 2})/2$ and $A_{\perp} = (A_{\perp 1} + A_{\perp 2})/2$ are used as a matter of course. All of the bonding parameters and the κ values calculated are summarized in Table III. A closer inspection of this table indicates that the α^2 value increases regularly in the complex order listed; namely, the σ bonding becomes less covalent in the same order. This trend is consistent with that in the ligand pK_a , since the pK_a of acidic molecules with similar structures is considered as a measure of the σ -bond strength between the molecular anions and proton;³¹ as far as the σ bonding is concerned, a parallelism between Cu²⁺ and H⁺ seems reasonable. The β_1^2 values calculated are almost constant, but the β^2 value increases in the same order as mentioned above. It is a surprise to us that $\beta^2 \leq \beta_1^2 < \alpha^2$ holds for all of the β -diketonate complexes. This fact suggests that, contrary to expectation, there are considerably strong π bondings in these complexes. Another interest is in the fact that all the κ values listed in the table are about 0.335.

Ultraviolet Spectral Bands. According to a conventional discussion on absorption spectra for the present complex molecules, the x and y axes chosen in the preceding paragraph are rotated around the z axis by 45° so that the y axis passes through the origin and the midpoint of the internal copper-oxygen angle. Hence, discussion will be hereafter given under the molecular symmetry of D_{2h} .

Table II indicates that E_{II} increases regularly in the complex order listed there. On the basis of the fact that a reduction in E_{II} occurs on increasing electron density at the oxygen atoms by increasing the inductive effect of the α substituents, Fackler et al. assigned band II to a charge-transfer band involving the jump of an oxygen lone-pair electron to a metal orbital.³ This assignment is further supported by the fact that there is a favorable correlation between E_{II} and the pK_a of the ligands,

since the pK_a is a good measure of electron density at protonated atoms in a series of acidic molecules of the same kind.³¹ Recently, Johnson and Thornton have also agreed with Fackler et al. on the assignments of ultraviolet spectral bands for the present complexes.¹¹ Cotton et al. have assigned band II to the metal-ligand charge-transfer transition of $B_{2u} \leftarrow B_{1g}$ on the basis of extended Hückel MO calculations.^{9,10}

It is especially characteristic of band II that its intensity increases almost linearly with the pK_a . We calculated the intensity of the above-mentioned charge-transfer transition of $B_{2u} \leftarrow B_{1g}$. The molecular orbitals concerned are written as

$$\psi_M(b_{1g}) = \alpha d_{xy} - \alpha'(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2 \quad (3a)$$

$$\psi_{\sigma}(b_{2u}) = (\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)/2 \quad (3b)$$

where σ_i expresses the i th oxygen lone-pair orbital. Equation 3b is just an approximate one but is almost consistent with the result of extended Hückel MO calculations.⁹ The oscillator strength of this allowed transition is expressed as³²

$$f = (8\pi^2 mc/3h)\nu |\langle \psi_{\sigma}(b_{2u}) | r | \psi_M(b_{1g}) \rangle|^2 \\ = 1.085 \times 10^{-5} \nu_0 R^2 (\alpha^2 S^2 + \alpha'^2)/2 \quad (4a)$$

where ν_0 is the average energy of this transition in cm^{-1} and where R is the copper-oxygen bond length in Å. $\langle \sigma_i | \sigma_j \rangle = 0$ ($i \neq j$) was assumed in the derivation of eq 4a. The same is said of the charge-transfer transition of $B_{3u} \leftarrow B_{1g}$ using $\psi_{\sigma}(b_{3u}) = (\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4)/2$.

In the present case where the effective ligand field symmetry is close to an axial one, it seems unlikely that the transition energies of B_{2u} and $B_{3u} \leftarrow B_{1g}$ are vastly different. Cotton et al. have predicted that $B_{3u} \leftarrow B_{1g}$ is at $\sim 2.8 \mu\text{m}^{-1}$ in the region of band III and $B_{2u} \leftarrow B_{1g}$, at $\sim 4.0 \mu\text{m}^{-1}$ with almost equal intensities, but this is untrustworthy. Fackler et al. and Johnson and Thornton also assigned band III as ligand $\pi-\pi^*$ transitions only. Now, band II is assigned as the two charge-transfer transitions, and f_{II} can be written as

$$f_{II} = 1.085 \times 10^{-5} E_{II} R^2 \alpha'^2 \quad (4b)$$

In eq 4b, $\alpha^2 S^2$ was eliminated as a negligibly small term because $S^2 = 0.006$.

We calculated the f_{II} values from eq 4b using the α'^2 values already determined (Table III) and $R = 1.9$ Å. The results, which are also summarized in Table III, are most satisfactory, since the observed and calculated f_{II} values for the complexes vary in almost the same manner. It is of small significance that every calculated value is somewhat larger than the observed one, because this is a general tendency in most intensity studies which have been done with simple LCAO functions.³² Anyhow, it should be noted that f_{II} depends primarily on the covalency of the σ bonding.

Visible Spectral Bands. The d-d spectral intensity f_D was also found to have a linear relationship to the pK_a of the ligands, as shown in Figure 4. This seems to give us a clue to studies on d-d spectral intensity from the chemical points of view. It is of great interest that the pK_a of the β -diketonate ligands can be a good index to many properties of the complexes, as shown in many places in this article.

Within the framework of a vibronic mechanism operating only on the excited d states, the oscillator strength f_d for a Laporte-forbidden d-d transition $\psi_g \leftarrow \psi_{B_{1g}}$ of the energy E_d is given with the usual notation by^{33,34}

$$f_d = f_{CT} V_E a^2 \quad (5)$$

where $V_E = E_d/[E_{CT}^2(E_{CT} - E_d)]$ and $a^2 = \sum_i |\langle \psi_u | \partial V / \partial Q_i | \psi_g \rangle|^2 \times | \langle 0 | Q_i | 1 \rangle |^2 \times \coth(\hbar\nu_i/2kT)$. f_{CT} and E_{CT} are the intensity and energy, respectively, for an allowed charge-transfer transition of $\psi_u \leftarrow \psi_{B_{1g}}$. Belford et al. indicated that the

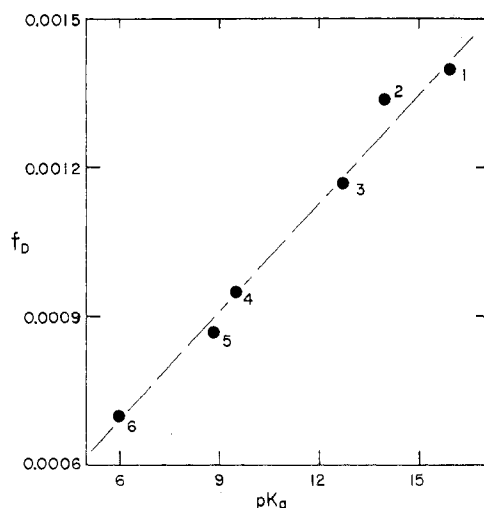


Figure 4. A plot of the d-d transition intensity f_D against the pK_a of the ligands: 1, Cu(dpm)₂; 2, Cu(dbm)₂; 3, Cu(acac)₂; 4, Cu(pta)₂; 5, Cu(tfac)₂; 6, Cu(hfac)₂.

Table IV. Visible Spectral and Related Parameters

Complex	E_D^a	f_D^a	$R(f_D)^b$	$f_{CT}V_E^c$ (=V)	$R(V)^b$
Cu(dpm) ₂	16.9	0.001 40	1.20	1.50	1.17
Cu(dbm) ₂	16.7	0.001 34	1.15	1.40	1.09
Cu(acac) ₂	16.6	0.001 17	1.00	1.28	1.00
Cu(pta) ₂	16.5	0.000 95	0.81	1.14	0.89
Cu(tfac) ₂	16.5	0.000 87	0.74	1.12	0.88
Cu(hfac) ₂	15.8	0.000 70	0.60	0.95	0.74

^a Values of E_D are in 10^3 cm^{-1} . E_D and f_D express the average energy and total intensity of the d-d transitions, respectively (see text). ^b $R(X)$ represents the ratio of X to the X of Cu(acac)₂. ^c All values are in 10^{10} cm^2 .

intensities of the y , x , and z polarizations of d-d transitions are effectively gained by admixtures of B_{3u} , B_{2u} , and A_u metal \leftarrow ligand charge-transfer states, respectively, into the excited d states.^{6,7} The transition of $A_u \leftarrow B_{1g}$, which corresponds to a metal \leftarrow ligand π -electron transfer, has been estimated to appear at a much higher energy than $E_1^{7,9}$ and, therefore, may contribute in the least degree to the gain of the overall d-d transition intensity.

It is of interest to see whether or not the relationship between f_D and the pK_a of the ligands can be explained by eq 5 on the basis of the assignment of band II to two charge-transfer transitions of B_{3u} and $B_{2u} \leftarrow B_{1g}$. By substituting E_{CT} and E_{II} , $f_{CT} = f_{II}$, and $E_d = E_D$ in eq 5, we calculated the values of $f_{CT}V_E$ and their ratios in units of the value for Cu(acac)₂; they are listed in Table IV. An inspection of this table indicates that the values of f_D and $f_{CT}V_E$ among the complexes vary in a parallel fashion. This means that the evaluation of a^2 as a constant for each charge-transfer transition in these complexes is almost valid, as has been previously proposed.³⁴ This evaluation seems understandable, because the complexes are of the same kind. It is concluded, therefore, that the d-d transitions in the present complexes may borrow the bulk of intensity from the pK_a -dependent band II. As one can see in this procedure, f_{CT} is as important as E_{CT} in the vibronic mechanism.

In conclusion, it is suggested that the d-d spectral intensity in bis(β -diketonato)copper(II) or related complexes increases with an increase in the ligand σ -donor ability, which results in the formation of strong σ bonding. This is considered just as a rule on d-d spectral intensity, which is applicable to all kinds of planar copper(II) complexes, except the ones whose ligand π -electron systems are exceptionally effective in the

vibronic mechanism. The validity of this rule is supported by the general observation that the d-d spectral intensity increases in order of planar CuO₄, CuO₂N₂, and CuN₄ chromophores.^{35,36} Accordingly, it is naturally to be expected that the intensity is extremely increased by the coordination of sulfur atoms.³⁷ In these cases, the apparent difference in molecular symmetry among the planar complexes does not seem to be an important factor in determining the intensity.³⁸ Further work on these problems is now in progress.

Acknowledgment. The author expresses his appreciation to Professor M. Iwaizumi for his interest in this work.

Registry No. Cu(dpm)₂, 14040-05-2; Cu(dbm)₂, 17653-77-9; Cu(acac)₂, 13395-16-9; Cu(pta)₂, 15716-66-2; Cu(tfac)₂, 14324-82-4; Cu(hfac)₂, 14781-45-4.

References and Notes

- Abbreviations for ligands used in this article are as follows: dpm⁻, 2,2,6,6-tetramethylheptane-3,5-dionate ion; dbm⁻, 2,6-dimethylheptane-3,5-dionate ion; acac⁻, pentane-2,4-dionate ion; pta⁻, 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionate ion; tfac⁻, 1,1,1-trifluoro-pentane-2,4-dionate ion; hfac⁻, 1,1,1,5,5,5-hexafluoropentane-2,4-dionate ion.
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