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The Effects of Axial Ligation on the Ligand Field Spectra of Copper(II) β-Diketonates

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The effects of single and double addition of pyridine upon the ligand field spectrum of bis(hexafluoroacetylacetonato)copper(II) have been investigated in an attempt to apply group theoretical and qualitative crystal field predictions to the assignment of the d–d bands. Four-band Gaussian analyses are presented, the features of which are consistent with these predictions. An analogous treatment is found possible for the parent acetylacetonate of copper and its monopyridine adduct. The bis(hexafluoroacetylacetonato)copper(II)–water system has also been studied. It is postulated that both a mono- and a bis-aquo adduct exist in addition to the anhydrous chelate.

Introduction

The ligand field spectra of the copper(II) β-diketonates have been the subject of intense experimental and theoretical research for several years.[2-12] While the existence of a d_{xy} ground state seems to be fairly well established, the ordering of the excited d levels appears to be still an open question.

Fifth-position coordination of the copper acetylacetonates has also been recognized for some time.[13-15] When highly electronegative fluorine is substituted on the 1 and/or 5 carbon of the ligand, the affinity of the copper atom for axial ligation is increased to the extent that two molecules of base may be added.[16,17] Group theoretical principles lead to predictions regarding the effects of the progressive variation of symmetry which results from these axial ligations upon the ligand field band intensities. However, there appears to have been no concerted attempt to correlate these predictions with the spectra of such a series of intimately related complexes for the purpose of simultaneous solution of their electronic structures. The case of the pyridine adducts of bis(hexafluoroacetylacetonato)copper(II) (henceforth $Cu(hfacac)_2$) affords especially fertile ground for such a correlation since the stepwise coordination of the fifth and sixth positions provides a series of three stages, in contrast to the two-stage case for the nonfluorinated parent chelate.

Preliminary to the investigation of the above series, it seemed desirable to characterize the $Cu(hfacac)_2$–H_2O system since the diversity of previous results[18-21] suggested a three-membered series, analogous to the pyridine case, although this possibility had never been discussed.

Results and Discussion

The $Cu(hfacac)_2$–H_2O System.—In the solid state three distinctly differently colored species with varying water content have been observed. A yellow-green species initially isolated from aqueous solution has not been clearly characterized. It is stable if maintained in a moist atmosphere or if refrigerated, but under normal atmospheric conditions gradually turns grass green. The conversion from yellow-green to grass green is accelerated by exposure to vacuum over a desiccant, while the reverse process can be partially realized in a moist atmosphere, *e.g.*, on a humid day. The grass green species, which is stable in air, has been variously characterized as being anhydrous,[18,19] a monohydrate,[20] and a dihydrate.[21] A third species, the purple complex, has been clearly characterized as the anhydrous chelate.[17,21]

The visible and near-infrared spectra of the three species in the solid phase (Figure 1) show a distinct variation in the d–d transition envelope which is consistent with a postulate of varying coordination of the copper atom. The grass green complex is sparingly soluble in water to give a yellow solution whose spectrum (Figure 1) corresponds to that of the yellow-green adduct. Since it is not unexpected that both axial positions of the planar $Cu(hfacac)_2$ might be hydrated in water, it would appear that the yellow-green species is a bisaquo adduct. Accordingly, the grass green species—also a hydrate—appears to be a monoaquo adduct. This is supported by a determination of the amount of water absorbed by the purple species when allowed to revert to the grass green species in air. Duplicate trials yielded a mean weight gain for the purple complex of 3.70%. The theoretical gain for one molecule of water is 3.77%.

The spectra of the grass green species and the purple species in reagent grade CCl_4 are remarkably similar (Figure 2). However, a more careful investigation

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[1] NSF Graduate Fellow, 1966-1968.

[2] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

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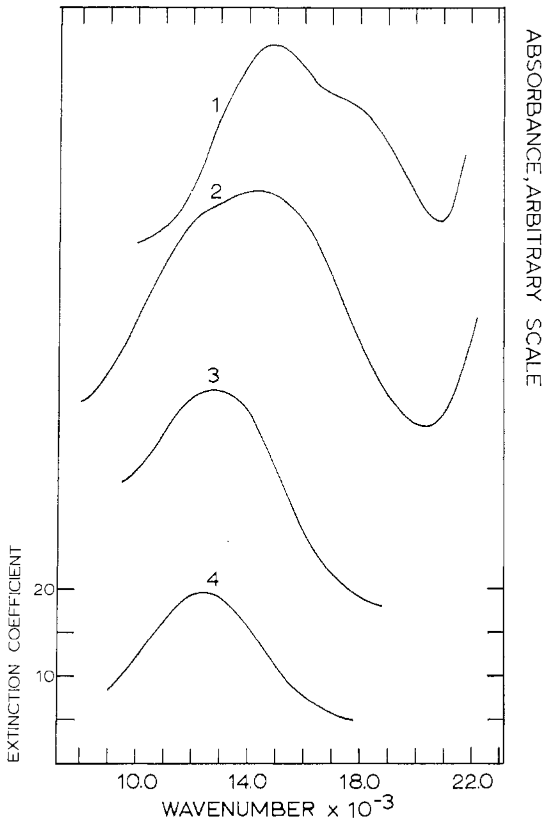

Figure 1.—Absorption spectra of Cu(hfacac)$_2$–H$_2$O adducts: (1) the purple anhydrous chelate, mull; (2) the grass green monohydrate, diffuse reflectance; (3) the yellow-green dihydrate, mull; (4) aqueous solution spectrum of the grass green monohydrate (1.58×10^{-3} *M*).

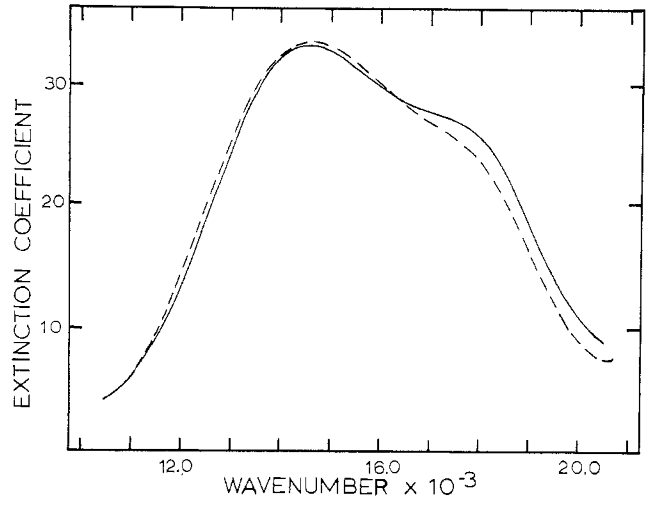

Figure 2.—Carbon tetrachloride solution spectra of (———) the purple anhydrous chelate and (– – – –) the grass green monohydrate.

using dried solvent with varying amounts of added wet solvent yields the spectra shown in Figure 3. The regular trend in spectra coupled with the maintenance of an isosbestic point suggests the existence of an equilibrium between the anhydrous complex and its monoaquo adduct. Note that the spectra of Figure 2 are intermediate between the extremes in Figure 3. Attempts to drive the equilibrium farther toward the monoaquo species by shaking CCl$_4$ solutions of the purple complex with small portions of water only led to precipitation of the yellow-green complex.

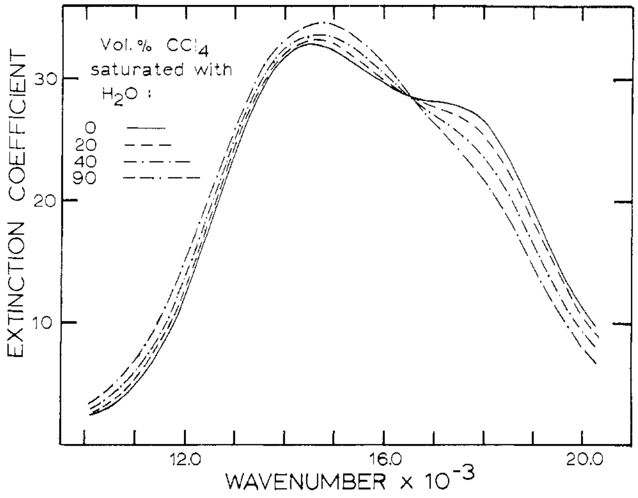

Figure 3.—Spectra of carbon tetrachloride solutions of the purple anhydrous chelate containing varying amounts of water. Concentration of chelate, 1.78×10^{-3} *M*. Concentrations of water: ———, 0.000 *M*; - - - -, 0.002 *M*; — · —, 0.003 *M*; and — — · — —, 0.007 *M*. These concentrations of water are based upon the room temperature solubility of water in CCl$_4$ taken as 0.008 *M*. This solubility is the one estimated by T. J. V. Findlay [*Australian J. Chem.*, **18**, 521 (1965)] from previous data [C. K. Rosenbaum and J. H. Walton, *J. Amer. Chem. Soc.*, **52**, 3568 (1930); J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A174**, 234 (1940)].

The visible spectrum of the green complex has been reported previously in reagent grade CHCl$_3$[18,19] and has been reproduced in Figure 4, curve 1. It has also been observed that the purple complex in the same solvent gives an identical spectrum.[21] However, reagent grade CHCl$_3$ contains up to 0.75% ethanol as a preservative, and if instead ethanol-free spectroscopic grade CHCl$_3$ is used, a spectrum practically identical with the CCl$_4$ spectrum is obtained for the purple complex (Figure 4, curve 2). Furthermore, by the addition of methanol to a CCl$_4$ solution of the purple complex, a spectrum similar to curve 1 was obtained. Obviously the alcohol present in reagent grade CHCl$_3$ and added to the CCl$_4$ solutions coordinates the copper atom. Thus it is apparent that the previously reported spectra of Cu(hfacac)$_2$ and Cu(hfacac)$_2$(H$_2$O) in chloroform which contained ethanol are significantly in error.

In summary, the question of the characterization of the hydrate of Cu(hfacac)$_2$ appears resolved by the concluded existence of two distinct hydrates in addition to the anhydrous form. The first and last members of the series are unstable in air with respect to the monohydrate, in contrast to Cu(acac)$_2$ whose weaker axial affinity prohibits even a monohydrate adduct. Accordingly, somewhat greater caution must be exercised in the characterization of solution spectra of the fluorinated analog, it having been shown by this work that even minute concentrations of ligating components can give misleading spectra which obscure the real and sig-

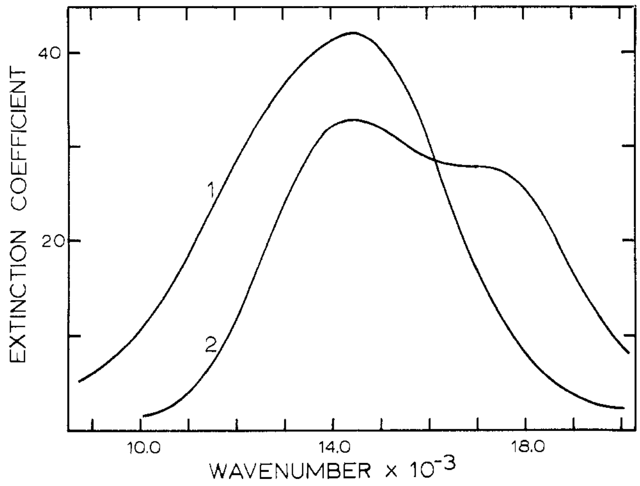

Figure 4.—Spectra of (1) the grass green monohydrate in reagent grade chloroform (1.81×10^{-2} *M*) and (2) the purple anhydrous chelate in spectroscopic grade chloroform (3.22×10^{-2} *M*).

nificant differences which result from more populous coordination spheres. Such differences are better demonstrated by the following study of the Cu(hfacac)$_2$–pyridine system.

The Cu(hfacac)$_2$–Pyridine System.—The spectra of solutions containing constant amounts of Cu(hfacac)$_2$ and varying quantities of pyridine are shown in Figure 5. The presence of isosbestic points indicates the primary equilibria to be between Cu(hfacac)$_2$ and its monopyridine adduct in Figure 5A and between the mono and bispyridine adducts at the higher concentrations of the base in Figure 5B. A similar experiment using approximately one-tenth the concentration of metal complex yielded similar results indicating the validity of Beer's law for this system.

Calculations based upon the absorption in curves 1–6 of Figure 5A at 10,000 cm^{-1} and known quantities of added base indicate that the formation of the mono adduct is essentially complete at these concentrations. On this basis curve 8 was obtained as the spectrum of the mono adduct by using the mean of the extinction coefficients calculated from the data in curves 2–6. The maximum mean deviation of any point in curve 8 is 0.7 l./mole-cm. The calculated curve corresponds quite closely to curve 7 which represents approximately a 1:1 mole ratio. In contrast, the formation of the bispyridine adduct, as might be expected, is not complete until a large excess of the base has been added as demonstrated in Figure 5B. Solid phase spectra of the mono- and bispyridine adducts gave band positions corresponding to curves 8 and 14 in Figure 5, respectively.

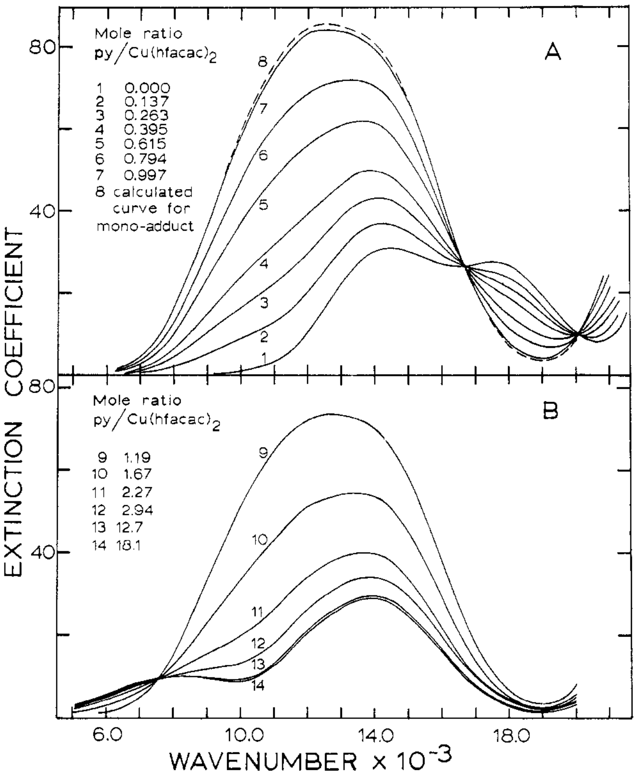

Figure 5.—Spectra of dry carbon tetrachloride solutions of Cu(hfacac)$_2$ containing varying amounts of pyridine. Concentration of chelate, 1.192×10^{-2} *M*.

Stereospectral Considerations in the Cu(hfacac)$_2$–Pyridine System.—There is ample theoretical and experimental evidence indicating that all of the ligand field transitions in the copper acetylacetonates are congregated under the envelope which generally occurs in the 8000–22,000-cm^{-1} region.[6,8,10–12] Furthermore, there seems to be sufficient evidence to believe that the usual assignment of d$_{xy}$ as the ground state is the correct one.[6,9,10–12] We have predicated our analysis on these two premises.

The symmetry of the copper acetylacetonates has sometimes been approximated as D$_{4h}$.[2] In this symmetry two excited levels, d$_{xz}$ and d$_{yz}$, remain degenerate in the E$_g$ representation; hence only three transitions are theoretically observable. The actual symmetry of the system is closer to D$_{2h}$ in which the E$_g$ representation is reduced to B$_{2g}$ and B$_{3g}$. Four transitions are then theoretically observable. *A priori*, there is no basis for choosing which of these two symmetries is effective. However, there is precedent for observing four bands in this region.[8,12,22] We have attempted to resolve the spectra of Cu(hfacac)$_2$ and its mono- and bispyridine adducts *via* Gaussian analysis. The analyses led repeatedly to four bands, the features of which are consistent with the predictions of group theory and qualitative crystal field theory. An analogous treatment was found applicable for the parent compound, Cu(acac)$_2$, and its monopyridine adduct (next section).

The electronic selection rules are given in Table I for the symmetries appropriate to the problem. The salient feature is the fact that the transitions to the d$_{xz}$ and d$_{yz}$ levels gain electronic allowedness in the C$_{2v}$ symmetry of the monopyridine adduct while both of the other bands remain electronically forbidden in either symmetry. With regard to energy predictions, on the basis of qualitative crystal field theory one would expect increasing axial coordination to have

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(22) G. Basu, R. L. Belford, and R. E. Dickerson, *Inorg. Chem.*, **1**, 438 (1962).

Table I

Group Theoretical Selection Rules for Copper(II) in C_{2v} and D_{2h}

Transition	D_{2h} symmetry[a]		C_{2v} symmetry[b]	
$xy \rightarrow x^2 - y^2$	$B_{1g} \rightarrow A_g$	Forbidden	$A_2 \rightarrow A_1$	Forbidden
$\rightarrow z^2$	$\rightarrow A_g$	Forbidden	$\rightarrow A_1$	Forbidden
$\rightarrow xz$	$\rightarrow B_{2g}$	Forbidden	$\rightarrow B_1$	Allowed (y)
$\rightarrow yz$	$\rightarrow B_{3g}$	Forbidden	$\rightarrow B_2$	Allowed (x)

[a] For 0:1 and 2:1 adducts. [b] For 1:1 adduct.

Table II

Gaussian Components for the Spectra of Cu(hfacac)$_2$ and Its Pyridine Adducts[23]

Band	$\bar{\nu}$[a]	ϵ_{max}	$\delta_{1/2}$[a,b]	f[c]	$\bar{\nu}$	ϵ_{max}	$\delta_{1/2}$	f	$\bar{\nu}$	ϵ_{max}	$\delta_{1/2}$	
I	14.0	20	1.5	2.7	13.0	22	1.4	2.9	13.9	19	1.6	2.7
II	13.5	7	1.9	1.2	11.3	50	2.1	9.5	12.0	11	1.4	1.4
III	15.8	10	1.5	1.5	14.9	56	1.8	9.2	15.3	11	1.9	2.6
IV	18.0	24	1.7	3.7	10.2	22	1.8	3.8	8.1	10	2.3	2.1

[a] Frequency in cm^{-1} × 10^{-3}. [b] $\delta_{1/2}$ = half-width at $\epsilon_{max}/2$. [c] Oscillator strength × 10^{-4}.

its greatest effect upon the transition to the d_{z^2} level with much smaller effects upon the transitions to d_{xz} and d_{yz}. The transition to $d_{x^2-y^2}$ should remain relatively unaffected. In summary, then, the predictions are as follows.

(1) One band, $d_{xy} \rightarrow d_{x^2-y^2}$ (I), should show little or no effects in both intensity and position with changes in axial ligation.

(2) Two bands, $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$ (II and III), should show a significant increase in intensity in going to the monopyridine adduct and then lose intensity in the reversion to D_{2h} symmetry in the bis adduct; simultaneously relatively small red shifts are expected.

(3) The fourth band, $d_{xy} \rightarrow d_{z^2}$ (IV), should exhibit little or no change in intensity throughout the series but should show uniquely a large red shift in both cases.

A set of Gaussian analyses is presented in Figure 6 for the spectra of Cu(hfacac)$_2$ and its two pyridine adducts with the pertinent data for the individual components given in Table II.[23,24]

The foregoing considerations seem to be most consistent with the following interpretations.

(1) For the component denoted by I, neither the position nor the intensity is greatly affected by axial ligation; hence it is assigned to $d_{xy} \rightarrow d_{x^2-y^2}$.

(2) The bands designated as II and III are affected only slightly in position. However, they are greatly increased in intensity in the spectrum of the monopyridine adduct. These features identify them as the $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$ transitions.

(3) The remaining band, IV, shows relatively large red shifts with increasing axial ligation but only small changes in intensity. These are the features predicted for the $d_{xy} \rightarrow d_{z^2}$ transition.

One interesting feature of these analyses is the zigzagged effect obtained for the positions of bands I, II, and III. This could be taken to indicate that the copper atom is shifted slightly out of the plane in the monopyridine adduct resulting in a ground state lower

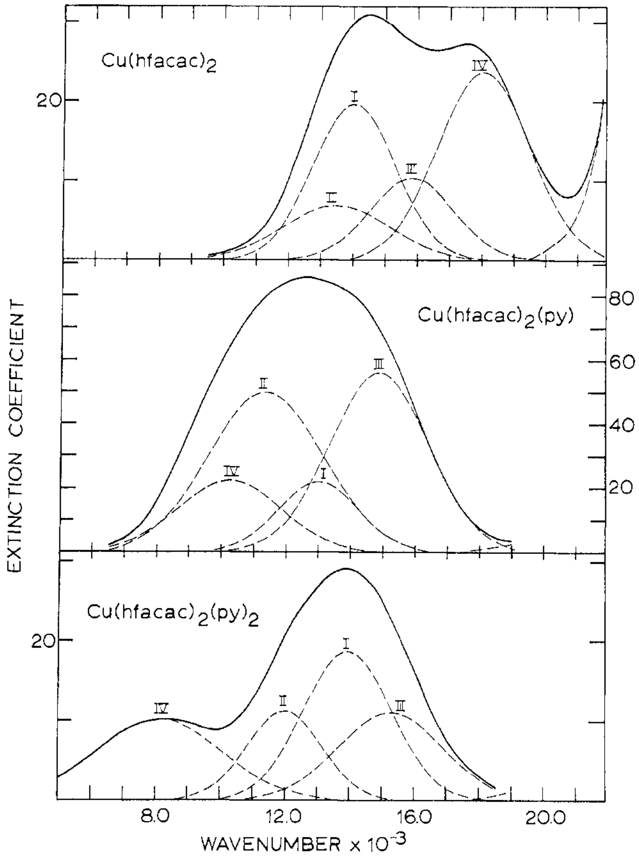

Figure 6.—Gaussian analyses for the Cu(hfacac)$_2$–py system.

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(23) In the latter stages of the preparation of this article for publication, it was discovered that the wavelength reading on the spectrophotometer which was used in obtaining the spectra was slightly in error. Since in the spectral region under study the instrument scan is approximately linear with energy, this error does not appreciably affect the band shape of our spectra. Therefore the Gaussian analyses and the conclusions drawn therefrom are unaffected. It must be noted, however, that all spectra and listed component band energies are approximately 100 cm^{-1} low.

(24) The analyses of the band envelopes were accomplished by trial and error, assuming a symmetrical and purely Gaussian shape for every component band. Strict criteria for acceptable fits were adhered to in each case. The maximum deviations of the sum of component bands from the experimental curves for the three low-intensity and the two high-intensity spectra were 0.4 l./mole cm and 1.0 l./mole cm, respectively. In each case a tail from allowed transitions in the ultraviolet was encountered in the blue region. It was found to be very impractical to estimate the shape of this tail from the characteristics of the ultraviolet band; therefore, its shape was arrived at merely by subtracting the Gaussian components from the envelope. It was discovered that arriving at an acceptable fit within strict criteria was a very delicate operation, and that small variation of component band parameters from those obtained led to a poor fit with the experimental curve. It appeared that only by making radical changes in band parameters and positions could other acceptable fits be achieved.

in energy and thus reducing the energy of all ligand field transitions.

The propriety of four-band rather than three-band analyses receives additional support from the shape of the spectrum of the monopyridine adduct. The intense, very broad band does not yield itself to an analysis containing a single high-intensity component which would be the case if the effective symmetry were C_{4v}. Instead, two regions of high intensity separated by about 3500 cm^{-1} are strongly implied.

Finally, it must be admitted that Gaussian analyses are by nature speculative, and this is particularly true in cases such as the present one in which component bands are confined under a single rather structureless envelope. For this reason the analyses presented here are offered as neither unique nor definitive. However, although each individual analysis may be open to question, it is felt that the strength of the treatment lies in its internal consistency and in its correlation with theoretical predications.

Stereospectral Consideration in the $Cu(acac)_2$–py System.—It is interesting to note that the shape of the band envelope in the visible spectrum of $Cu(acac)_2$ bears a remarkable resemblance to that of its fluorinated analog, the primary difference being that the spectrum of the latter is red shifted by approximately 500 cm^{-1}. This trend is consistent with the postulate of a reduced equatorial field in the fluorinated analog caused by the electron-withdrawing tendencies of fluorine and also implies that the energy separations of the excited d levels remain relatively constant. If the latter is true, then the spectra of $Cu(acac)_2$ and its monopyridine adduct should lend themselves to four-band analyses, and, in fact, a large separation between d_{xz} and d_{yz} has been suggested previously as an alternative to the three-band analyses which assume their degeneracy.[6] It was discovered that four-band analyses of the $Cu(acac)_2$ and $Cu(acac)_2py$ spectra, reminiscent of those of the fluorinated analogs, were possible, and these are presented in Figure 7 with the pertinent data in Table III. By reasoning analogous to that used earlier the following assignments may be postulated: (1) band I, $d_{xy} \rightarrow d_{x^2-y^2}$; (2) bands II and III, $d_{xy} \rightarrow d_{xz}, d_{yz}$; (3) band IV, $d_{xy} \rightarrow d_{z^2}$.

Critique.—It is frequently a feature of the electronic structural tendencies of transition metal complexes that ground states isolate themselves from excited states which remain relatively clustered. This clustering often occurs to an extent that typical electronic band widths prohibit the realization of as many spectral peaks as one might expect theoretically. Accordingly, the assignment of electronic spectra is truly a dual task, *i.e.*, first locating the bands and then differentiating between them.

This dual task has been a formidable one in the case of the acetylacetonates of copper(II). One can cite, for example, two very recent investigations which represent extensive efforts in this area. Each of these involved an attempt to interpret four observed "d–d" peaks in the crystal spectrum of a copper(II) β-diketonate. Their apparent failure to harmonize, either with each other or with the present work, deserves some consideration.

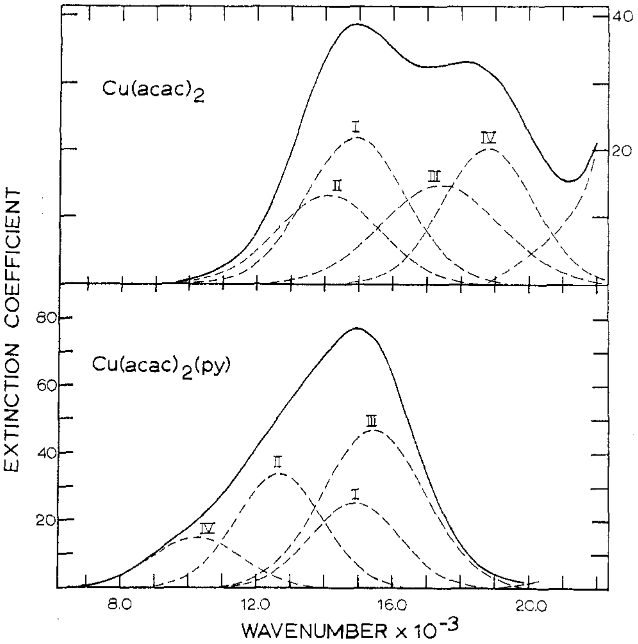

Figure 7.—Gaussian analyses for the $Cu(acac)_2$–py system.

TABLE III

GAUSSIAN COMPONENTS FOR THE SPECTRA OF $Cu(acac)_2$ AND ITS MONOPYRIDINE ADDUCT[23]

	$Cu(acac)_2$				$Cu(acac)_2py$			
Band	$\bar{\nu}^a$	ϵ_{max}	$\delta_{1/2}{}^{a,b}$	f^c	$\bar{\nu}$	ϵ_{max}	$\delta_{1/2}$	f
I	14.9	22	1.7	3.5	14.9	25	1.5	3.6
II	14.1	13	1.8	2.2	12.7	34	1.5	4.7
III	17.4	15	2.0	2.8	15.4	47	1.8	7.7
IV	18.8	20	1.6	2.9	10.2	15	1.6	2.2

[a] Frequency in $cm^{-1} \times 10^{-3}$. [b] $\delta_{1/2}$ = half-width at $\epsilon_{max}/2$. [c] Oscillator strength $\times 10^{-4}$.

The first of these studies, by Cotton and co-workers,[10–12] appeared during the intitial preparation of this paper. This work utilized the combination of an extended Hückel molecular orbital calculation[10] on a simplified model, $Cu[HC(CHO)_2]_2$, with both the electron spin resonance[11] and polarized crystal spectroscopy[12] of bis(dipivaloylmethanido)copper(II), $Cu(DPM)_2$. As a result, it was possible to establish conclusively only that the visible absorption is due to the four d–d transitions: $d_{xy} \rightarrow d_{z^2}, d_{xz}, d_{x^2-y^2}, d_{yz}$. The ordering (increasing in energy as given), however, could only be offered as a suggestion on the basis of the MO calculations which gave consistent results over considerable ranges in the parameters. The ordering was compatible with, though not demanded by, the esr data and was neither confirmed nor denied by any *a priori* conclusions of the polarization data.

The second recent study, by Belford and Carmichael,[25] appeared in the literature during the initial review of this paper. This work involved the polarized crystal spectroscopy of bis(3-phenyl-2,4-pentanedionato)copper(II), $Cu(3\text{-}Ph\text{-}acac)_2$, at several tem-

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[25] R. L. Belford and J W Carmichael, Jr., *J. Chem. Phys.*, **46**, 4515 (1967).

peratures in the range 299–6°K. Similarly to the above case, the authors found simple yes–no selection rules inconclusive in regard to spectral assignments. On the other hand, it was found that a more careful analysis of the spectra in terms of the temperature dependence of the intensities implied that the two lowest energy bands involve transitions (in D_{2h}) to A_g ($x^2 - y^2$, z^2) excited states, while the higher bands involve B_{2g} (xz) and B_{3g} (yz).[26]

Thus, it would appear that these two recent efforts together with the present one fail to provide the desirable element of agreement. However, it must be remembered that these studies all involved different copper chelates:[27] Cu(acac)$_2$, Cu(hfacac)$_2$, Cu(3-Ph-acac)$_2$,[25] Cu(DPM)$_2$,[11,12] and the hypothetical Cu[HC(CHO)$_2$]$_2$.[10] Thus, the most pertinent question is one of the similarity of the various chelates to each other or, more generally, of the sensitivity of electronic structure in copper(II) β-diketonates. In this regard, it is felt that much more needs to be learned about the nature of the equatorial bonding characteristics in such species before any generalization of even a definitive conclusion on a specific compound can be made.

The present approach is offered as neither redundant with nor to the exclusion of any potentially more definitive ones. Requiring the acceptance of a mathematical method of "locating" the bands, it then attempts to differentiate between them by their apparent vertical and horizontal motions throughout a series of homologous complexes, rather than by their observed polarizations within a particular complex.

For the case in point, the present results suggest that the ordering of the d orbitals is $d_{xy} \gg d_{xz}\ (d_{yz}) > d_{x^2-y^2} > d_{yz}\ (d_{xz}) > d_{z^2}$ for the effectively four-coordinate complex, with d_{z^2} becoming the highest filled orbital upon axial addition. Salient points either required or supported by the results are: (a) The energy of d_{z^2} is most sensitive to the degree of tetragonality of the ligand field. (b) The intensities of d_{xz} and d_{yz} are most sensitive to the effective coordination number about the central ion. (c) The above factors are primarily responsible for the sizable variation of the visible spectrum with crystal or solution environment. (d) The orthorhombic component of the ligand field is important. (e) The six-coordinate complex is centrosymmetric and the axial groups are geometrically equivalent. (f) The constancy of *Dq* and the existence of the five-coordinate complex as a "typically puckered" square pyramid are evidenced. (g) Acetylacetonate presents a stronger equatorial field than does its hexafluoro derivative and this may be inversely related to the facility of axial addition.

Finally, it should be pointed out that a possible alternative to the ordering suggested for the filled orbitals in the four-coordinate case could be $d_{z^2} > d_{x^2-y^2} > d_{xz}\ (d_{yz}) > d_{yz}\ (d_{xz})$ — retaining $d_{z^2} > d_{xz}\ (d_{yz}) > d_{x^2-y^2} > d_{yz}\ (d_{xz})$ for the 1:1 and 2:1 adducts, as proposed. Although this secondary picture is not grossly inconsistent with the criteria used to derive the primary one, the authors do not find it as attractive on the basis of the absolute and relative energy shifts expected for d_{z^2} and the two "e levels." On the other hand, it is worthy of note and may be significant that the secondary scheme would afford a greater correspondence to the orderings recently suggested by the LCAO–MO calculation of Cotton, Harris, and Wise[10] and the temperature-dependence studies of Belford and Carmichael.[25] These both favored $d_{xy} \rightarrow d_{z^2}$ as a low-energy d–d transition whereas the primary scheme of the present study specifies it as the highest one. The secondary scheme, however, with $d_{xy} \rightarrow d_{z^2} < d_{x^2-y^2} < d_{xz}\ (d_{yz}) < d_{yz}\ (d_{xz})$, not only specifies the transition to d_{z^2} as the lowest of the four but also places the other three in the sequence required by the scheme of Belford and Carmichael[25] if the d_{z^2} transition is lowest.

Experimental Section

Preparation of Cu(hfacac)$_2$(H$_2$O).—The method followed was similar to that of Bertrand and Kaplan.[21] The yellow-green precipitate which resulted turned grass green after drying in air. This latter product was purified by sublimation. It had a closed-capillary melting point of 133–136°.

Preparation of Cu(hfacac)$_2$.—Following the published procedure,[17] the anhydrous complex was obtained by placing the grass green hydrate under vacuum over P_2O_5. The resulting purple solid reverted back to the grass green complex when exposed to the air. In handling the purple species for solution preparation it was kept under dry nitrogen or in a closed weighing bottle except during transfer.

Preparation of Cu(hfacac)$_2$(py)$_2$.—The isolation of this species has been reported previously by Walker and Li.[17] We prepared it by two different methods: a solid-phase reaction of Cu(hfacac)$_2$ with pyridine vapor and precipitation from CCl_4 solution containing excess pyridine. The latter method seems to be more facile. The material sublimes at 60–70° as fine, light green needles, having a closed-capillary melting point of 150–152°. *Anal.* Calcd for $CuC_{20}H_{12}O_4N_2F_{12}$: C, 37.78; H, 1.90; N, 4.40. Found: C, 37.81; H, 2.40; N, 4.70.

Preparation of Cu(hfacac)$_2$py.—Following the procedure used for the isolation of the 4-methylpyridine adduct,[17] a CCl_4 solution of the anhydrous chelate and pyridine in 1:1 stoichiometric proportions was allowed to evaporate. A dark green, crystalline residue was obtained. Similar dark green crystals may be obtained by prolonged exposure of the bispyridine adduct to vacuum. These crystals melt at 75–76°. The residue from the evaporation may be purified by thorough grinding with a mortar and pestle followed by sublimation at 70°, keeping only the later fractions which melt sharply at 75–76°. The process of grinding and subliming is then repeated. The primary volatile contaminant, which is probably Cu(hfacac)$_2$(H$_2$O), is more volatile and tends to sublime first. *Anal.* Calcd for $CuC_{15}H_7O_4NF_{12}$: C, 32.35; H, 1.27; N, 2.51. Found: C, 33.00; H, 1.12; N, 2.12.

Preparation of Cu(acac)$_2$.—The synthesis followed the established techniques for preparation of metal β-diketonates.[28] Purification was accomplished by sublimation *in vacuo* at 125°.

Spectra.—Diffuse reflectance spectra were obtained on a Beckman Model DU spectrophotometer. Where these were not at-

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[26] Perhaps even more important than Belford and Carmichael's proposed ordering are their arguments that the bulk of the intensity of all four "d–d" transitions is borrowed from a single charge-transfer transition [nonbonding oxygen B_{3u} (σ) to antibonding copper B_{1g} (xy)] under the influence of all types of vibrational modes. The significance of this inference lies in the fact that it focuses on a dominant perturbing excited level rather than on effective perturbing vibrations.

[27] In addition, one could make the point that significant differences (especially in d_{z^2}) might also be expected on the basis of variations in axial environment, *e.g.*, in solutions *vs.* crystals.

[28] W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 489 (1966).

tainable because of instability of the species in the atmosphere or the limited range of the instrument, crude qualitative spectra were obtained on Nujol mull smears on filter paper using a Beckman Model DK2A ratio-recording spectrophotometer. Visible and near-infrared solution spectra were obtained on the Beckman DK2A. There being no apparent sensitivity of the spectra to temperature, no attempt was made to control it.

Solvents.—Except where noted, solvents were from freshly opened bottles of the reagent grade chemical. Dry CCl_4 was obtained by shaking the reagent grade solvent with P_2O_5 and distilling from fresh P_2O_5, discarding the first and last portions. Wet CCl_4 was prepared by prolonged shaking with water in a separatory funnel with warming and then allowing the two phases to separate.

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Kinetics of the Ligand Substitution Reaction of the Zinc(II)–4-(2-Pyridylazo)resorcinol Complex with (Ethylene glycol)bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic Acid

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The kinetics of the ligand substitution reaction of the zinc(II)–4-(2-pyridylazo)resorcinol complex (Zn(II)–PAR) with (ethylene glycol)bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA) has been studied spectrophotometrically in the pH range 8.7–10 at $\mu = 0.1$ and at 25°. The reaction involves a dissociation equilibrium of the Zn(II)–PAR complex: $-d[ZnR_2^{2-}]/dt = 10^{6.4}[ZnR_2^{2-}][H^+][Y']/[HR^-] = 10^{4.4}[ZnR][Y']$, where R^{2-} is the divalent anion of PAR (H_2R) and Y' is the free EGTA not combined with any metal. The release of PAR from the reaction intermediate PAR–Zn(II)–EGTA is the probable rate-determining step. The stability constants of sodium– and lithium–EGTA complexes at $\mu = 1.5$ and at 25° are kinetically determined as 24 ± 4 and 15 ± 2, respectively. The rate of the substitution of Zn(II)–PAR decreases in the order: free EGTA > sodium–EGTA complex > lithium–EGTA complex. The different reactivity of these species is discussed. In connection with the kinetic study the stability constants of the Zn(II)–PAR complexes have been determined spectrophotometrically at $\mu = 0.1$ and at 25°: $[ZnR]/[Zn^{2+}][R^{2-}] = 10^{11.9\pm0.1}$, $[ZnR_2^{2-}]/[ZnR][R^{2-}] = 10^{10.3\pm0.2}$, $[ZnHR^+]/[ZnR][H^+] = 10^{5.90\pm0.05}$, $[ZnHR_2^-]/[ZnR_2^{2-}][H^+] = 10^{7.55\pm0.05}$, $[ZnH_2R_2]/[ZnHR_2^-][H^+] = 10^{6.45\pm0.05}$.

Introduction

Though a great number of works have been devoted to the kinetics of the complex formation and the substitution of metal chelates with metal ions, little attention has, as yet, been given to the substitution of metal chelates with multidentate ligands. There are only a few examples such as the works of Bosnich, Dwyer, and Sargeson,[1] of Rogers, Aikens, and Reilley,[2] and of Margerum, *et al.*[3–5] Recently Yatsimirskii, *et al.*, have made an account of the kinetics of the reaction of rare earth complexes of xylenol orange with EDTA.[6] We are interested in the substitution of multidentate ligands, which is often involved in the complexometric titration and the solvent extraction of metal chelates. It seems important to study kinetic phenomena arising from the presence of some different bulky ligands competing for coordination sites on the same metal ion. The system

$$\text{Zn(II)–PAR} + \text{EGTA} \rightleftharpoons \text{Zn(II)–EGTA} + \text{PAR} \quad (1)$$

was chosen for the present study, where PAR and EGTA represent 4-(2-pyridylazo)resorcinol and (ethylene glycol)bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid, respectively, and are abbreviated as H_2R (tridentate) and H_4Y (hexadentate), respectively.

Experimental Section

Reagents. Zinc(II) Perchlorate.—Zinc metal (99.999%) was dissolved in perchloric acid to prepare zinc perchlorate solution.

PAR.—The acid form of PAR was obtained from Dojin-do Chemical Co., Kumamoto, Japan, and purified by recrystallization from aqueous methanol. PAR dried in an air bath at 80° was dissolved in 2 equiv of borax.

EGTA.—Reagent grade EGTA, obtained also from Dojin-do Chemical Co., was purified by recrystallization from distilled water, dried in an air bath at 80°, and dissolved in 2 equiv of borax. The solution was standardized complexometrically against a standard cadmium solution. The values agreed with the theoretical values within 0.3%, and thus the purified EGTA could be used as a primary standard.

Boric Acid and Borax.—Boric acid and borax were recrystallized twice from distilled water.

Sodium Perchlorate.—Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid. Heavy metal impurities in the sodium perchlorate were precipitated as hydroxides at pH 8.5 and extracted as oxinates with chloroform four times at pH 8.5. Sodium perchlorate was then recrystallized twice from distilled water.

Sodium Hydroxide.—Sodium hydroxide solution was prepared by electrolysis of the solution of sodium perchlorate obtained as described above. About 2 *M* aqueous sodium perchlorate solution with a slight excess of perchloric acid was taken in a polyethylene bottle and electrolyzed at about 30 mA with platinum foil electrodes. The polyethylene bottle was connected with an anode chamber by a bridge containing sodium perchlorate.

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[1] B. Bosnich, F. P. Dwyer, and A. M. Sargeson, *Nature*, **186**, 966 (1962).

[2] D. W. Rogers, D. A. Aikens, and C. N. Reilley, *J. Phys. Chem.*, **66**, 1582 (1962).

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[4] R. A. Libby and D. W. Margerum, *Biochemistry*, **4**, 619 (1965).

[5] J. D. Carr, R. A. Libby, and D. W. Margerum, *Inorg. Chem.*, **6**, 1083 (1967).

[6] K. B. Yatsimirskii, T. V. Mal'kova, and L. I. Budarin, "Proceedings of the Xth International Conference on Coordination Chemistry," Tokyo and Nikko, Japan, Sept 1967, p 290.