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Mixed Acetylacetonato Complexes of Copper(II)

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Mixed β-diketone complexes of copper(II) have been prepared and characterized, and the effects of lowered symmetry on various spectral properties have been studied. Solutions of Cu(acac)(hfac), Cu(acac)(tfac), and Cu(tfac)(hfac) exhibit no detectable admixtures of the symmetrical systems according to infrared, optical, and esr studies. Solution mixtures of these symmetrical chelates exchange rapidly to produce the more stable mixed chelate systems.

Introduction

There have been three reports on the preparation of mixed chelates of Cu(II) involving β-diketones.[1-3] Kluiber[1] has isolated some Cu(II) complexes containing a thiopicolinamide and a β-diketone whereas Moore and Young[2] have detected, in solution, mixed-chelate systems of a β-diketone and a β-keto ester. Newman and Klotz[3] have detected equilibria in solution among a variety of mixed β-diketonate complexes of Cu(II). Although we have prepared a variety of mixed substituted acetylacetonato complexes of Cu(II), some of which apparently show disproportionation between the mixed and symmetrical chelates in solution, the purpose of this paper is to present those mixed systems which do not exhibit detectable equilibria in solution and to comment on the effects of the lowered symmetry upon various spectral properties.

Experimental Section

Mixed Cu(II) complexes of acetylacetonate (acac), trifluoroacetylacetonate (tfac), and hexafluoroacetylacetonate (hfac) are obtained from addition of an equimolar mixture of two ligands to a small excess of a suspension of $CuCO_3 \cdot Cu(OH)_2$ in chloroform. After filtration from unreacted solid material and evaporation of the solvent, the product is purified by recrystallization from toluene. The yields of all compounds prepared are greater than 80%.

Anal. Calcd for Cu(acac)(tfac): C, 38.04; H, 3.51. Found: C, 38.19; H, 3.66. Calcd for Cu(acac)(hfac): C, 32.48; H, 2.19; mol wt, 369.7. Found: C, 32.53; H, 2.17; mol wt, 375. Calcd for Cu(tfac)(hfac): C, 28.35; H, 1.19; F, 40.36. Found: C, 28.48; H, 1.27; F, 40.46.

Electron spin resonance spectra were recorded on a Varian V-4502 spectrometer in CH_2Cl_2 solution both at room temperature and in the frozen state at $-196°$. Optical spectra were obtained in CH_2Cl_2 solution on a Perkin-Elmer Model 450 ultraviolet–visible–near-infrared spectrophotometer. Infrared spectra of the samples were recorded as Nujol mulls between CsI disks on a Perkin-Elmer 221 spectrophotometer fitted with a CsBr interchange and as Nujol mulls and CH_2Cl_2 solutions on a Perkin-Elmer 521 grating infrared spectrophotometer.

Results

The melting points and esr and optical spectra are presented in Table I. The infrared frequencies of the mixed and symmetrical chelates in the 400–500-cm^{-1} region are presented in Table II. These frequencies were determined from the Nujol mull spectra obtained on the Perkin-Elmer 221 spectrophotometer, and the spectra are shown in Figure 1. The very weak bands in these spectra were subjected to ordinate expansion of 10 times in order that they might more easily be observed. The expansions are shown in the spectra where applicable.

Discussion

In order to present the spectral data as those of mixed chelate systems, one must first show that the results are inconsistent with equilibrium mixtures of mixed and symmetrical complexes. This evidence is now presented.

The first evidence for mixed complexation comes from examination of the infrared spectra of the complexes in the 400–500-cm^{-1} region, *i.e.*, the CuO stretching region. For the bis-chelate complexes, which are of molecular D_{2h} symmetry, two CuO stretching frequencies are predicted to be infrared active according to simple group theoretical considerations. For Cu(acac)$_2$, two CuO stretching frequencies have recently been assigned[4] at 451 cm^{-1} (B_{1u}) and 291 cm^{-1} (B_{2u}). Since the B_{2u} band has not been assigned in the spectra of substituted acetylacetonates, this discussion will be confined to the bands in the 400–500-cm^{-1} region.

The solid-state infrared spectra (Nujol mulls) of mixtures of bis chelates are, of course, superimposed spectra of the individual complexes. The spectra of the mixed chelates in the 400–500-cm^{-1} region show bands which are shifted with respect to the symmetrical chelates and, in fact, show no trace of bands due to the presence of bis chelates. Infrared spectra in the CuO stretching region of the mixed complexes in CH_2Cl_2 solutions are virtually identical with those obtained as Nujol mulls, even when spectra of very concentrated solutions are taken. The solution spectra show no bands arising from the presence of symmetrical chelate systems. The very close similarity of the solid state and solution infrared spectra rule out the possibility that crystal site splitting or mixtures of crystalline forms contribute to the bands in the spectra.

Solution spectra of an equimolar mixture of two bis chelates are identical with those of mixed chelates, showing that a rapid, essentially quantitative exchange of chelates occurs to produce the mixed systems. In-

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[1] R. W. Kluiber, *Inorg. Chem.*, **4**, 1047 (1965).

[2] T. S. Moore and M. W. Young, *J. Chem. Soc.*, 2694 (1932).

[3] L. Newman and P. Klotz, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967, No. L119.

[4] M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **A23**, 1037 (1967).

TABLE I

MELTING POINTS AND OPTICAL AND ESR SPECTRA OF MIXED AND SYMMETRICAL β-DIKETONATE COMPLEXES OF COPPER(II)

		Near-ir-visible[b]		Esr[b]	
Complex	Mp,[a] °C	ν_{max}, cm^{-1}	ϵ[c]	g	10^4A(Cu), cm^{-1}
Cu(acac)$_2$	236	15,200	33.0	2.123	76.2
		18,200	28.7		
Cu(tfac)$_2$	189	14,850	29.6	2.129	72.2
		17,400	26.2		
Cu(hfac)$_2$	95–98	14,600	29.1	2.135	67.0
		16,800	26.1		
Cu(acac)(tfac)	230–232	15,100	35.0	2.125	75.15
		17,800	30.4		
Cu(acac)(hfac)	170–173	14,900	34.3	2.126	73.1
		17,600	31.6		
Cu(tfac)(hfac)	110–112	14,750	31.4	2.131	70.35
		17,250	27.9		

[a] Uncorrected. [b] CH_2Cl_2 solution. [c] In l. mol^{-1} cm^{-1}.

TABLE II

INFRARED SPECTRA (400–500 CM^{-1}) OF MIXED AND SYMMETRICAL β-DIKETONATE COMPLEXES OF COPPER(II)[a]

Complex	Bands in 400–500-cm^{-1} region
Cu(acac)$_2$	456 s, 432 w
Cu(tfac)$_2$	445 s
Cu(hfac)$_2$	415 vw
Cu(acac)(tfac)	457 s, 449 m, 433 w
Cu(acac)(hfac)	466 s, 420 m, 403 vw
Cu(tfac)(hfac)	442 sh, 437 m, 406 vw

[a] Abbreviations: m, medium; w, weak; v, very; sh, shoulder. The underlined frequencies are ν(CuO), assigned elsewhere: K. Nakmoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 224, 225.

deed, isolation of the products of these exchange reactions shows that the mixed chelate systems are formed. This is confirmed by comparing melting points and solid-state infrared spectra with those of the mixed chelates, and these are identical in every way.

Electron spin resonance spectra of the mixed chelates in CH_2Cl_2 solution at room temperature give g and A(Cu) values approximately intermediate between those of the corresponding bis-chelate systems. To guard against the possibility that time-averaged spectra are observed in equilibrium mixtures, these spectra were recorded in the frozen state at −196°. The frozen-state spectra indicate the presence of only one species. In Figure 2 the esr spectrum of a frozen solution of Cu(acac)(tfac) is shown. Whereas the very weak peaks to the high-field side of the spectrum cannot be accounted for at present, except to say that they are due to extremely small amounts of impurities of some kind, the possibility that they are due to the presence of small amounts of the corresponding bis chelates may be ruled out immediately, since these bands occur some 75–100 G to higher fields than do the highest Cu(acac)$_2$ or Cu(tfac)$_2$ signals. Furthermore, the infrared spectra, both in the solid state and in relatively concentrated solutions, conclusively support the esr evidence that there is a predominance of one species present in solutions of mixed chelates. Additional support is afforded by thin layer chromatographic studies, with the use of benzene as the eluting solvent. Only one species is detected in chromatograms of mixed chelates, and its R_f value is intermediate between those of the corresponding bis chelates. For example, in typical chromatograms, Cu(acac)$_2$, Cu(acac)(tfac), and Cu(tfac)$_2$ show R_f values of 0.15, 0.14, and 0.13, respectively.

It must be concluded, therefore, that any equilibria existing in solutions of these mixed chelates lie so far to the side of the mixed complexes that they cannot be detected by the instrumental methods mentioned above.

If the infrared spectra of the mixed chelates are examined in the 400–500-cm^{-1} region, then it is apparent that two CuO stretching modes may be assigned for each mixed complex. That this is so comes from the observation that the spectra of the mixed chelates in this region contain the same number of bands as the total contributed by the two corresponding symmetrical species. In addition, relative intensities and band shapes are generally retained in corresponding spectra (see Figures 1 and 3).

With regard to the nmr study of mixed chelate complexes of Ni(II) by Eaton and Philips,[5] it might be expected that an increase in the CuO bond strength would occur for the more electron-donating ligand at the expense of the lesser one. This expectation is supported in the case of Cu(acac)(hfac), where the obvious assignments for ν(CuO) are 461 and 400 cm^{-1}; the higher frequency band arises from ν(CuO) of the Cu(acac) whereas the lower is due to the CuO absorption of the Cu(hfac) part of the molecule. A line spectrum of Cu(acac)(hfac) is presented with those of Cu(acac)$_2$ and Cu(hfac)$_2$ in Figure 3; the arrangement of the spectra show the contribution of the bis chelates to the spectrum of the mixed chelate. For Cu(acac)(tfac), the tendency is in the same direction as with Cu(acac)(hfac) but is not quite as pronounced. However, for Cu(tfac)(hfac), it appears that the CuO stretching bands for both the tfac and hfac parts of the complex decrease in frequency. An explanation for this apparent exception is not at all obvious, and further experiments on similar systems must be completed before one may draw any conclusions.

Two effects of mixed chelation are readily observed in the optical spectra in the near-infrared and visible regions. First of all, the bands in the spectra of the mixed chelates are intermediate in position between those of the corresponding bis chelates. Since the two observed bands presumably contain all four expected d–d transitions,[6] one cannot, at this stage, undertake a quantitative discussion of the effects of mixed chelation on the individual d orbitals; however, the decrease in transition energies is consistent with the expectation that the in-plane σ orbital is affected most by a change in the equatorial ligand field. The second effect is the slight increase in extinction coefficients of the mixed chelates with respect to those of the corresponding bis chelates. The observation that the change is small may be compared to the optical studies by Belford and

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(5) D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, **43**, 392 (1965).

(6) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 917 (1967).

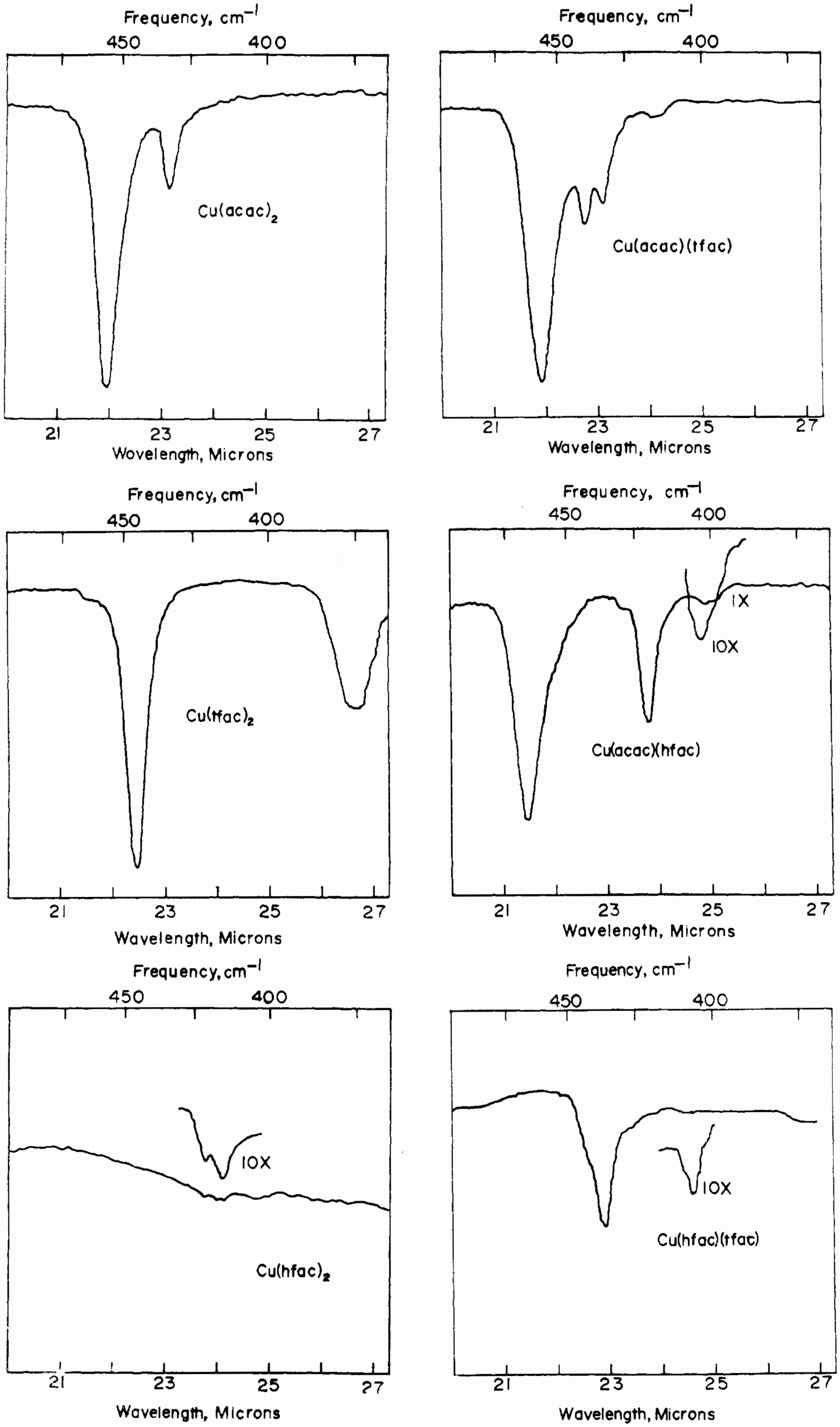

Figure 1.—Infrared spectra of symmetrical and mixed acetylacetonato complexes of copper(II) in the 400–500-cm^{-1} region.

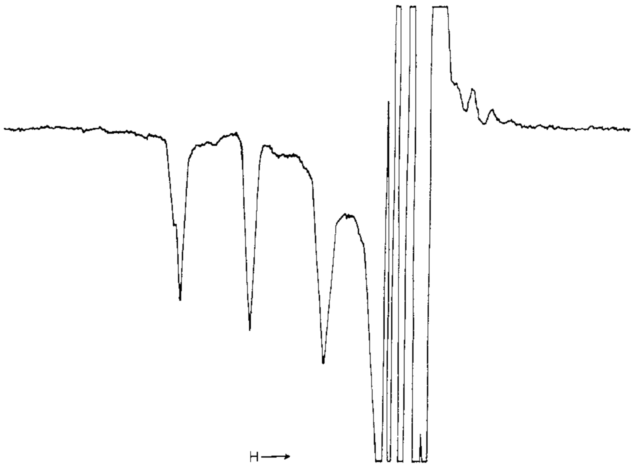

Figure 2.—Electron spin resonance spectrum of Cu(acac)(tfac) recorded in solution at 77°K.

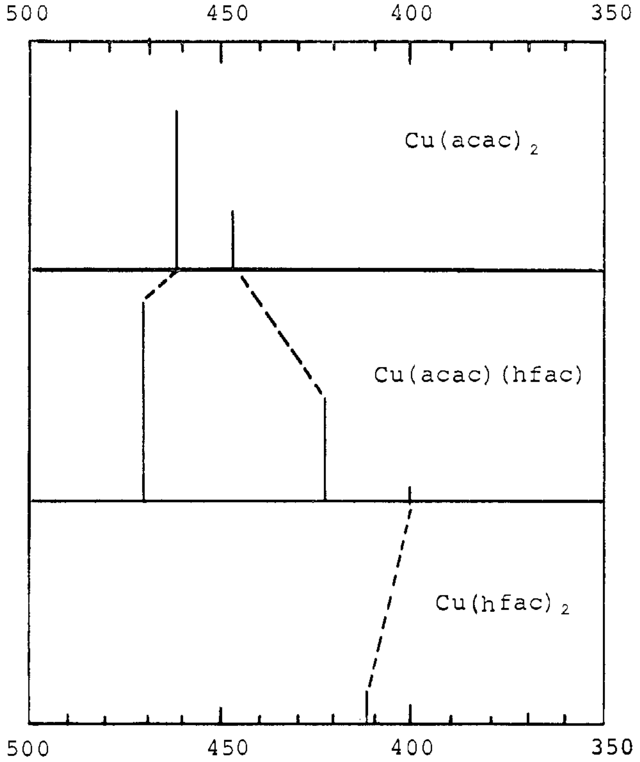

Figure 3.—Comparison of positions and relative intensities of the infrared spectra in the 400–500-cm^{-1} region for Cu(acac)$_2$, Cu(acac)(hfac), and Cu(hfac)$_2$.

Yeranos.[7] In their work, it was shown that only a small increase in extinction coefficients occurred as the symmetry was lowered from bis(acetylacetonato)-copper(II) to bis(acetylacetone iminato)copper(II) and bis(acetylacetone N-methyliminato)copper(II). Although the symmetry is lowered from D_{4h} for Cu(acac)$_2$ to C_{2h} for the iminato complexes, the center of symmetry is maintained in these compounds. When the center of symmetry is removed, as in the case of bis(acetylacetone ethylenediiminato)copper(II), then a large increase in the extinction coefficients occurs.

In the compounds studied in this work, the center of symmetry is removed in the case of the mixed chelate compounds. The fact that the increase in extinction coefficients is slight is probably attributable to the very small change in environment near the copper ion. Since these compounds contain copper surrounded by four oxygen donors in a square-planar environment, the effect of substituent change four atoms removed apparently does not alter the *effective* symmetry around the copper ion appreciably.

In Figure 4 it is seen that there is a relatively linear relationship between the esr *g* and *A* values and the Hammett σ factors,[8] indicating that, to a first approximation, the general esr behavior can be explained simply by considering the total basicity of the two ligands. For example, there is only a small difference in esr values when the two CF_3 groups are on the same ligand or on different ligands as in Cu(acac)(hfac) and Cu(tfac)$_2$.

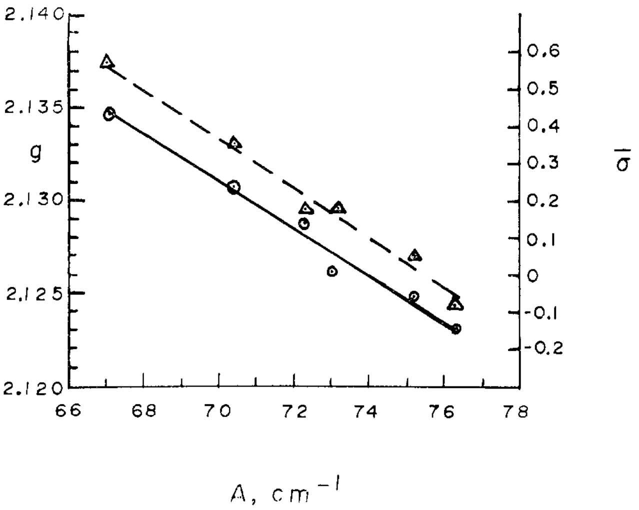

Figure 4.—Plots of esr *g* values *vs.* esr *A* values (solid line) and esr *A* values *vs.* average Hammett σ factors ($\sigma_{R_1} + \sigma_{R_2} + \sigma_{R_3} + \sigma_{R_4}$)/4 for Cu(OCR$_1$CHCR$_2$O)(OCR$_3$CHCR$_4$O) (dotted line).

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[7] R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963).

[8] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).