Title

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Authors

Belford, R Linn
Martell, A E
Calvin, M

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INFLUENCE OF FLUORINE SUBSTITUTION ON THE PROPERTIES OF METAL CHELATE COMPOUNDS. I. COPPER (II) CHELATES OF BIDENTATE LIGANDS[1]

R. Linn Belford,[2] A. E. Martell,[3] and M. Calvin

Radiation Laboratory and Department of Chemistry,
University of California, Berkeley, California

June 9, 1955

ABSTRACT

The ultraviolet, visible, and infrared absorption spectra of six β-diketones and their copper (II) chelates are presented and discussed in relation to the structure of these molecules. Infrared assignments are made. The 300-mμ bands of the metal chelates are shown to be shifted enolate ion absorptions. The order of magnitude and direction of those shifts are predicted correctly by a simple molecular orbital-electrostatic calculation. Visible chelate spectra are correlated with the nature of the chelating agent. The correlation agrees with crystal field theory predictions. Preparations of most substances studied are described in full, as also are some problems arising from the preparations.

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[2] National Science Foundation Predoctoral Fellow, 1953-4 and 1954-5.

[3] On leave during summer of 1953 from Clark University, Worcester, Massachusetts.

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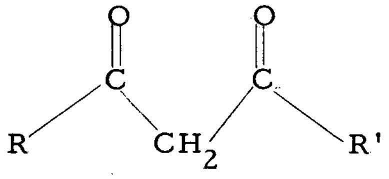
Introduction

This is the first of three articles dealing with the influence of fluorine substitution in the ligand on the properties of metal chelate compounds. Although the primary purpose of this project was to study the influence of fluorine substitution on the properties -- particularly light absorption -- of uranyl compounds, copper chelates were chosen for preliminary study as model substances, because they are easily prepared. Since a number of fluorinated bidentate ligands are available or may be readily prepared, it was decided to investigate copper (II) chelates of these substances first. The ligands selected for this study are represented by Formula I, and the corresponding metal chelate compounds by Formula II. The names and structures of the metal chelate compounds prepared are given in Table I by defining the substituent groups R and R' in each case.



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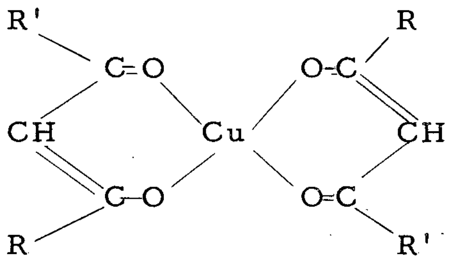

II

Although bis-acetylacetono-Cu(II) was first studied early in the development of coordination chemistry,[4, 5, 6] the fluoro derivatives of acetylacetone and similar ligands have not been available until recently, and relatively little has been done with the corresponding metal chelates. Trifluoroacetylacetone

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[4] A. Combes, Compt. rend. 105, 868 (1887).

[5] L. Claisen and E. Ehrhardt, Ber. 22, 1009 (1889).

[6] H. Ley, Ber. 47, 2948 (1915).

Table I

Bidentate ligands and Cu(II) chelates

Name of Ligand	Formula[a]		References[b]	
	R	R'	Ligand	Cu(II)Chelate
Acetylacetone	CH_3	CH_3	...	4,5,6
Trifluoroacetylacetone	CF_3	CH_3	7, 8	8, 9, 10
Hexafluoroacetylacetone	CF_3	CF_3	10	10
Ethylacetoacetate	CH_3	OC_2H_5	12	9, 12
Ethyltrifluoroacetoacetate	CF_3	OC_2H_5	...	9, 10
Acetoacetic acid diethylamide	CH_3	$N(C_2H_5)_2$	11	11

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[a] R and R' refer to the corresponding groups in Formulas I and II.

[b] Reference numbers refer to footnotes in main body of paper.

has been studied by a number of investigators.[7,8] Although the stability of bis-(trifluoroacetylacetono)-Cu(II) was reported in 1945,[9] the first reports of the preparation of the compound appeared somewhat later.[~~5~~,8] Some reactions of hexafluoroacetylacetone have been studied by Haszeldine et al.[10]

Of the remaining substances listed in Table I, the diethylamide of acetoacetic acid, and its copper (II) chelate, have been investigated by Utzinger.[11] Also, the stability of the copper chelate of ethylacetoacetate has been reported by Calvin and Wilson,[9] and an absorption maximum in the ultraviolet has been reported by Morton and Rasney.[12]

Experimental

Bis-(Trifluoroacetylacetono)-Cu(II)

To 10.0 g (0.050 mole) of cupric acetate monohydrate dissolved in 150 ml of warm water was added a solution of 15.4 g (0.010 mole) of trifluoroacetylacetone in 25 ml of ethanol. The reaction mixture was warmed and stirred, 1.2 g of anhydrous sodium carbonate was added, and the heating was continued for 15 minutes more. The blue precipitate that had first appeared when the solutions were mixed was filtered off and recrystallized from 50 % aqueous ethanol. The hot solution was green, but turned greenish-blue on cooling, and a robin's-egg-blue alcoholate crystallized out. The product was filtered and air-dried, whereupon it became blue-lavender in appearance. The final yield was 17.1 g, or 92% of the theoretical amount. The compound was found to be soluble in cold chloroform, toluene, and benzene to give blue solutions, and is very soluble in hot chloroform, toluene, and benzene to give green solutions. It is not readily recovered from

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[7] A. Henne, M. Newman, L. Quill, and R. Staniforth, J. Am. Chem. Soc. 69, 1819 (1947).

[8] J. C. Reid and M. Calvin, J. Am. Chem. Soc. 72, 2948 (1950).

[9] M. Calvin and K. Wilson, J. Am. Chem. Soc. 67, 2005 (1945).

[10] R. N. Haszeldine, W. K. Musgrave, F. Smith, and L. M. Turton, J. Chem. Soc. 1951 609.

[11] G. E. Utzinger, Helv. Chim. Acta 35, 1359 (1952)

[12] R. Morton and W. Rasney, J. Chem. Soc. 1926, 707.

these solutions by cooling, but it may be recrystallized easily by cooling a hot carbon tetrachloride solution. It sublimes readily; a relatively large sample was obtained in one hour at 100° and 0.1 mm pressure. An attempt to determine the melting point resulted in slow sublimation above 140°C. The melting point obtained is 189°, in agreement with that reported by Reid and Calvin[8] and by Park et al.[13]

Analysis: Calc. for $C_{10}H_8O_4F_6Cu$: C, 32.5; H, 2.2. Found: C, 32.3; H, 2.5.

Hexafluoroacetylacetone

A 50 g sample (approximately 0.20 mole) of hexafluoroacetylacetone dihydrate, obtained from the Caribou Chemical Company, was shaken with approximately three times its volume of 98% sulfuric acid until the material was completely dispersed. The heat evolved during the initial stages of dehydration was removed by immersion of the flask in cold water for a short time. After the mixture had been allowed to stand overnight, the anhydrous hexafluoroacetylacetone was seen to separate as a colorless liquid over the sulfuric acid, which was deeply colored by decomposed organic material. Dehydration of the product was repeated with a fresh batch of sulfuric acid. The final product was siphoned off and distilled. It was found that about 98% of the liquid distilled between 70.0 and 70.2°C. Qualitative observation indicated that the liquid has a low viscosity, low surface tension and high vapor pressure and that it hydrates rapidly when exposed to the atmosphere. Its density, measured by weighing the liquid delivered from a 0.02-ml micropipette, was found to be 1.46 g/ml.

Analysis: Calc. for $C_5H_2O_2F_6$: C, 28.82; H, 0.97. Found: C, 28.81; H, 1.13.

Acidic Hydrogen: Calc. mol. wt. 208. Found: 205.

Bis-(Hexafluoroacetylacetono)-Cu (II)

(Method I).

To 10.0 g (0.05 mole) of cupric acetate dissolved in 150 ml of water, 25 g (0.1 mole) of hexafluoroacetylacetone dihydrate was added with stirring. The solution turned green and pale green crystals gradually appeared. Upon the slow addition of 25 ml of 4.0 M sodium hydroxide, the solution deepened in color and the amount of crystalline precipitate increased. After the reaction mixture was heated on a steam bath for an hour, it was cooled and

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[13] J. D. Park, H. A. Brown, and J. R. Lacher, J. Am. Chem. Soc. 75, 4754 (1953).

the product was filtered off. When it was recrystallized from 50% aqueous ethanol, a greenish-yellow solvate consisting of long, flat, radiating needles was obtained. On standing in air, the solvate decomposed and the needles crumbled, forming a green finely-divided solid. The product weighed 14.0 g, or 55% of the theoretical amount, calculated as the dihydrate. It was found to be insoluble in water, but soluble in ethanol, dioxane, and organic solvents containing polar groups. It sublimed readily onto a cold finger in a drying pistol heated by boiling chloroform, and a moderate-sized sample was collected in five hours. Its melting point was found to be 135°.

Analysis : Calc. for $C_{10}H_2O_4F_{12}Cu \cdot 2H_2O$: C, 23.4; H, 1.17. Found: C, 23.16; H, 1.16.

(Method II).

A 2.0-g sample of cupric acetate monohydrate was dissolved in 10 ml of anhydrous hexafluoroacetylacetone by boiling for five minutes. The excess reagent was evaporated off, and the residue was recrystallized from carbon tetrachloride. The yield of the resulting grass-green crystalline product weighed 4.5 g, or 80% of the theoretical amount.

Bis-Ethylacetoacetate-Cu (II)

To 10 g (0.05 mole) of cupric acetate dissolved in 100 ml of hot 50% aqueous ethanol was added 13 g (0.1 mole) of ethylacetoacetate dissolved in 25 ml of ethanol. The mixture was heated on a steam bath until most of the alcohol had been expelled, and was cooled. The green-blue powder obtained upon filtration and air-drying was likely a hydrate. It was recrystallized twice successively from hot ligroin-chloroform mixture, the first time yielding a bluish powder, the second, large green plates. They melt at 193°C with decomposition.

Analysis : Calc. for $C_{12}H_{18}O_6Cu$: C, 44.8; H, 5.64; Cu, 19.8. Found: C, 44.94; H, 5.78; Cu, 19.9.

Bis-(ethyltrifluoroacetoacetato)-Cu (II)

To a solution of 2.0 g (0.010 mole) copper (II) acetate monohydrate in 100 ml of dioxane was added 3.68 g (0.02 mole) of ethyltrifluoroacetoacetate. The blue color of the copper acetate was quickly changed to deep green. The reaction mixture was warmed for 15 minutes with 1.0 g of potassium carbonate, the excess base was filtered off, and the solution was diluted with an equal volume of water. After the light green crystalline product that separated was filtered, washed, and air-dried, it was found to weigh 3.7 g, which corresponds to 86% of the theoretical yield. This product was recrystallized from 150 ml of carbon tetrachloride; it was obtained in the form of deep green crystals. It was found to be very soluble in acetone, chloroform, and dioxane, but insoluble in ligroin and water. Its melting point was 188°.

Analysis: Calc. for $C_{12}H_{12}O_6F_6Cu$: C, 33.5; H, 2.8; Cu, 14.8. Found: C, 31.2; H, 2.9; Cu, 15.0.

Reaction of diethylamine with ethyltrifluoroacetoacetate.

To 50 ml of anhydrous diethylamine was added dropwise, with stirring, 15 g (0.08 mole) of ethyltrifluoroacetoacetate. To the reaction mixture was added 100 ml i-octane, and the solution was reduced to 20% of its original volume by low-pressure distillation. Upon cooling to 0°C, it yielded 12 g of white crystals. They were washed with ice-cold i-pentane, recrystallized from i-octane, and dried in vacuo. The product is soluble in all organic solvents tried -- from saturated hydrocarbons to ketones and alcohols -- at room temperature. Its melting point was 82°.

Analysis: Calc. for $C_8H_{12}NO_2F_3$(N, N-diethyltrifluoroacetoacetamide): C, 45.5; H, 5.69; N, 6.64. Calc. for $C_{10}H_{16}NO_2F_3$ (β-diethylamino ethyltrifluorocrotonate): C, 50.0; H, 6.76; N, 5.84. Found: C, 51.7; H, 6.97; N, 5.55.

Basic groups: Calc. for $CF_3C\left[N(C_2H_5)_2\right]CHCO_2C_2H_5$: 1 basic amino group/239 g. Found: 1 basic group/238 g.

Reaction of β-diethylamino ethyltrifluoroarotonate with Cu (II)

To 21.1 g (0.10 mole) of the above product dissolved in 100 ml of warm absolute etanol was added 10 g (0.05 mole) of cupric acetate monohydrate. The metal salt gradually dissolved when the reaction mixture was boiled for 10 minutes, and a deep green solution was formed. After the solution had been cooled and diluted with an equal volume of water, a deep green crystalline precipitate was isolated. The weight of product obtained was 21 g, or 86% of the theoretical yield based on the expected copper (II) chelate. The product was recrystallized from a small amount of chloroform by adding n-heptane. After further recrystallization from carbon tetrachloride, it was obtained in the form of deep greenish-blue crystals, very soluble in chloroform, acetone, and alcohols, sparingly soluble in carbon tetrachloride and in ligroin, and nearly insoluble in cold n-heptane.

Analysis: Found: N, 0.0; Cu, 15.1.

Titrations

All titration curves were measured with a glass electrode in conjunction with a Beckman pH meter. Frequent checks were made against standard buffer solutions.

Hexafluoroacetylacetone was pipetted and the weight was calculated from the measured density (1.46 g/ml). It was titrated with 0.100 N NaOH.

One sample of β-diethylamino ethyltrifluorocrotonate was titrated with 0.385 N HCl. The resulting solution, at pH 1.9, was allowed to stand on a steam bath for two thours. A titration with 0.83 N KOH showed that no reaction had occurred in the hot acidic solution.

Absorption spectra

The infrared absorption spectra were measured with a Model 21 Perkin-Elmer Recording Double-Beam Spectrophotometer with NaCl optics. The liquid ligands were measured as thin films, whereas the solid ligands, hexafluoroacetylacetone dihydrate and β-diethylamino ethyltrifluorocrotonate, as well as all the metal chelate compounds, were measured in the form of nujol mulls. Frequencies are estimated accurate to 10 cm^{-1}.

Some of the absorption spectra in the visible and ultraviolet were measured with a Cary Model 11 recording spectrophotometer; the others in the near infrared, visible, and ultraviolet, were measured with a prototype of the Beckman DK Recording Spectrophotometer at fast speed in the ultraviolet and at medium speed in the visible and infrared. Quartz cells of 1 cm thickness were employed. The solutions were first made up by weight to 0.01 M, and these solutions were then successively diluted by syringe-type pipettes until absorption of the sample could be accurately measured. With few exceptions, the spectroscopic solvent employed was Eastman Kodak No. S337 spectro grade chloroform. Sodium-dried B and A reagent-grade ether, distilled water, Phillips spectro grade cyclohexane, and absolute methanol were used in the special cases.

Experimental Results

Figure 1 shows the ultraviolet absorption spectra of β-diethylamino ethyltrifluorocrotonate in a variety of solvents. The ultraviolet absorption spectra of the ligands are given in Figs. 2 and 3, and the corresponding spectra of the copper (II) chelate compounds are given in Figs. 3 and 4. Figures 5 and 6 illustrate the visible absorption spectra of the six copper (II) chelate compounds reported in this investigation. In each case molar extinction

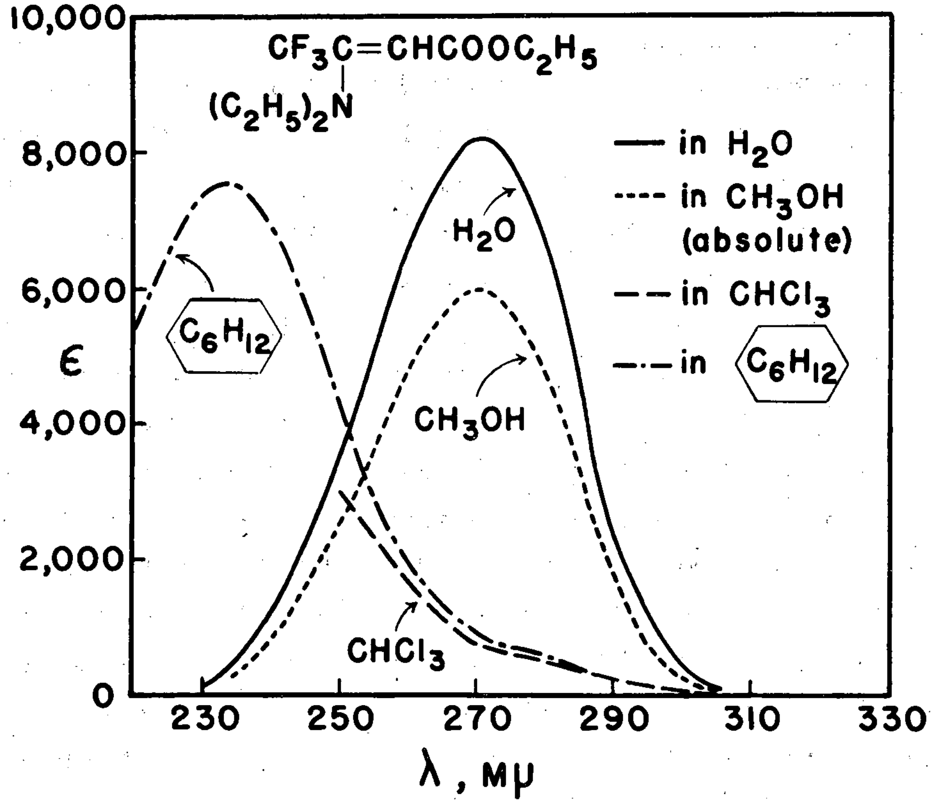

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Fig. 1. Ultraviolet spectra of β-diethylamino ethyltrifluorocrotonate, 10^{-4} M in water, methanol, chloroform, and cyclohexane.

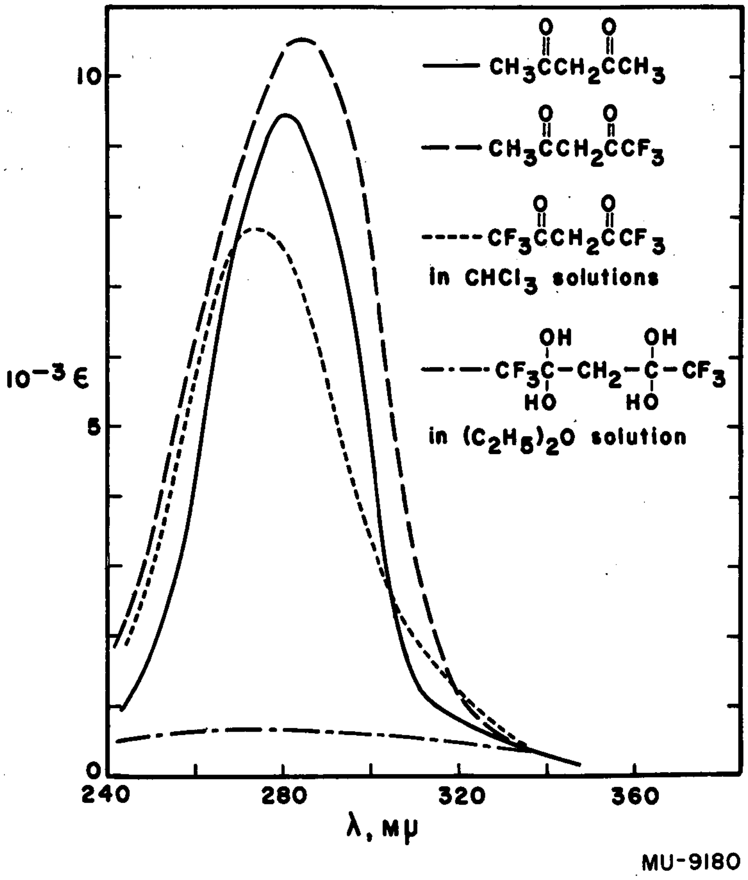

Fig. 2. Ultraviolet absorption spectra of acetylacetone, ——, trifluoroacetylacetone, — — ; and hexafluoroacetylacetone, · · · ·; 4.0 x 10^{-5} M in $CHCl_3$; of hexafluoroacetylacetone dihydrate, 4.0 x 10^{-5} M in ether.

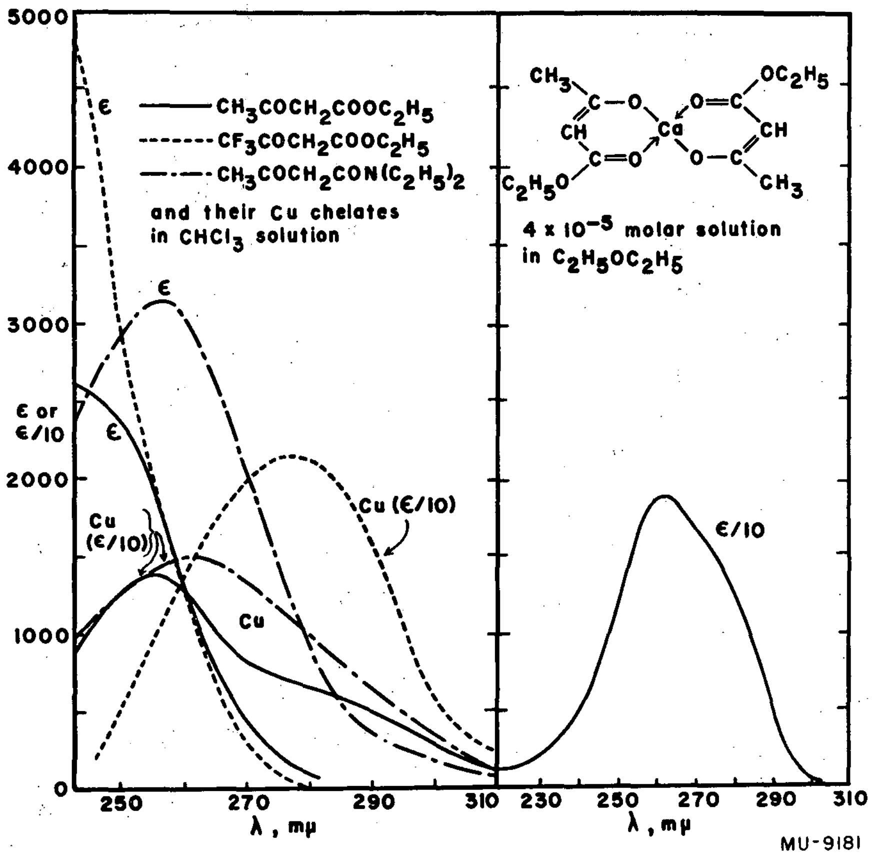

Fig. 3. Ultraviolet absorption spectra of (left): ethyl acetoacetate, ——; ethyl trifluoroacetoacetate, · · · ; and N, N-diethylacetoacetamide, —— · —— , 2×10^{-4} M in $CHCl_3$. The corresponding Cu chelates, 2×10^{-5} M or 1×10^{-5} in $CHCl_3$, are labeled "Cu". (right): bis-ethylacetoacetate-Ca (II), 4×10^{-5} M in absolute ether.

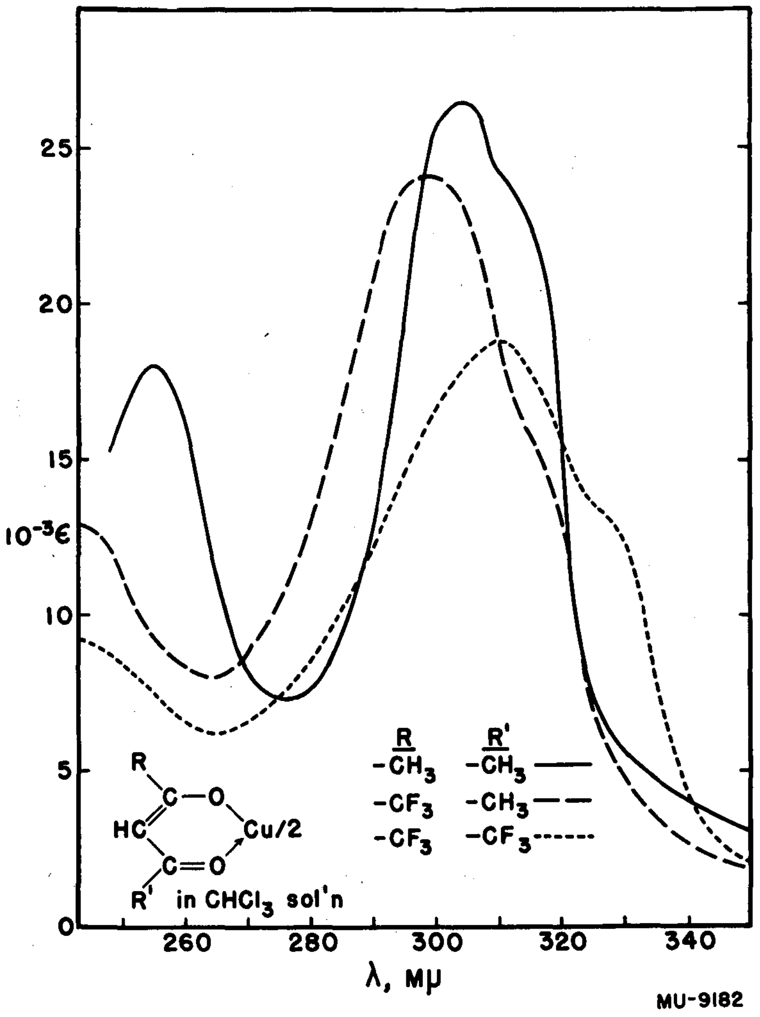

Fig. 4. Ultraviolet absorption spectra of 2×10^{-5} M bis-acetylacetono-Cu (II), —— ; 2×10^{-5} M bis-trifluoroacetylacetono-Cu (II), — — — ; and 1×10^{-5} M bis-hexafluoroacetylacetono-Cu (II), · · · · ; in $CHCl_3$.

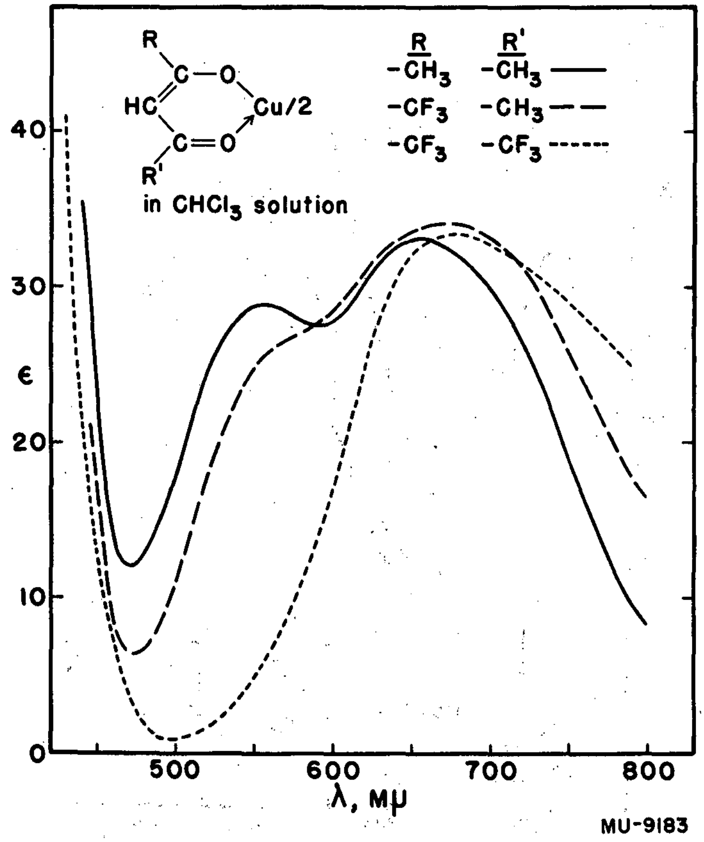

Fig. 5. Visible absorption spectra of bis-acetylacetono-Cu (II), ——; bis-trifluoroacetylacetono-Cu (II), —— ——; and bis-hexafluoroacetylacetono-Cu (II), · · · ; 0.010 M in $CHCl_3$.

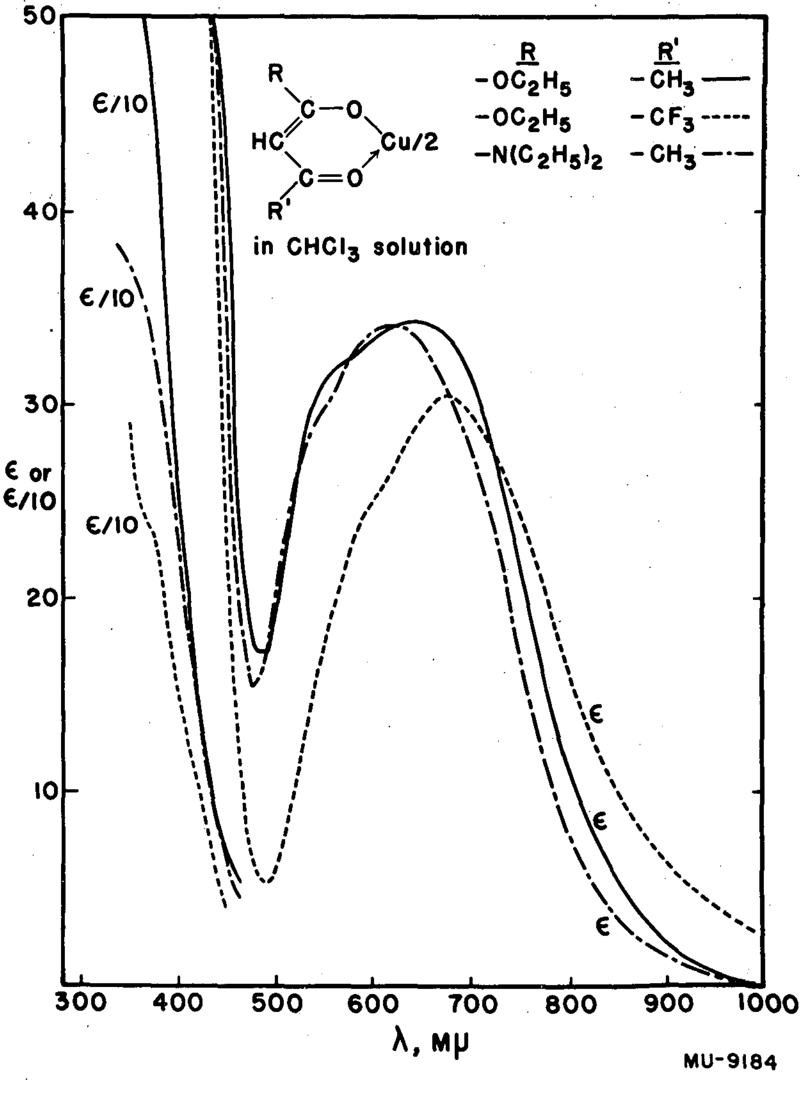

Fig. 6. Visible absorption spectra of bis-ethylacetoacetato-Cu (II), —— ; bis-ethyltrifluoroacetoacetato-Cu (II), · · · · ; and bis- N, N-diethylacetoacetamido-Cu (II), —— · —— · ; 0.010 M in $CHCl_3$. Left-hand curves obtained with 0.0010 M solutions.

coefficient, based on the presumed formula weight, is plotted vs wave length in mμ. The wave lengths of the maxima of the absorption bands found in the visible and ultraviolet regions of the spectrum are listed in Table II, along with the corresponding approximate molar extinction coefficients. In certain cases the irregular shape of a shoulder of the absorption band indicated probable additional bands adjacent to and partly obscured by the primary band. Such subsidiary bands for which it was possible to estimate approximate frequencies are indicated in parentheses in Table II.

The infrared absorption frequencies are listed in Table IIIa for the ligands and in Table IIIb for the corresponding metal chelate compounds. Here, also, frequencies of very weak or doubtful bands are enclosed in parentheses.

Titration curves are given in Figs. 7 and 8. From Figs. 7 and 8 we estimate the pK_A for hexafluoroacetylacetone to be about 4.6; for ethyltrifluorocrotonate β-diethylammonium ion, about 8.1.

Table II

Absorption bands of $CHCl_3$ solutions in the visible and ultraviolet regions

Compound	Molarity	max	max
I Acetylacetone	4×10^{-5}	280	9,500
II Trifluoroacetylacetone	4×10^{-5}	284	10,500
III Hexafluoroacetylacetone dihydrate*	4×10^{-5}	none	. . .
IIIa Hexafluoroacetylacetone	4×10^{-5}	273	7,800
IV Ethylacetoacetate	2×10^{-4}	<246	$\sim 2{,}600$
V Ethyltrifluoroacetoacetate		<246	$\sim 4{,}900$
		(~ 290)	
VI N, N-diethylacetoacetamide	2×10^{-4}	256	3,200
	(Utzinger gives λmax=253, log ϵ = 4.0)*		
I-Cu bis-acetylacetono-Cu(II)	2×10^{-5}	254	18,000
		304	26,000
		(313)	. . .
		(390)	. . .
		552	29
		660	33
II-Cu bis-trifluoroacetylacetono-Cu(II)	2×10^{-5}	298	24,000
		(316)	. . .
	1×10^{-2}	(566)	. . .
		680	34
III-Cu bis-hexafluoroacetylacetono-Cu(II)	1×10^{-4}	310	18,700
		(329)	. . .
	1×10^{-2}	710	40
IV-Cu bis-ethylacetoacetato-Cu(II)	2×10^{-5}	254	14,000
		(281)	. . .
	1×10^{-2}	(560)	. . .
		650	34
V-Cu bis-ethyltrifluoroacetoacetato-Cu(II)	2×10^{-5}	277	22,000
	1×10^{-2}	(590)	
		680	30
VI-Cu bis-N, N-diethylacetoacetamido-Cu(II)	1×10^{-5}	260	$\sim 16{,}000$
	1×10^{-2}	(540)	. . .
		620	34

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* Dissolved in diethyl ether rather than $CHCl_3$

Table IIIa

Infrared absorption bands of bidentate ligands

Region	I	II	III	IIIa	IV	V	VI	VII*
OH str.	3550	3360	3330	3120	3550	3360	3480	((3500))
		(3120)				(3100)		((3100))
CH str.	2960	2980	(2500)	2950	3050	2920	2960	
	(2620)		(2330)	(2580)				(2520))
	(2350)	(2350)	(2160)	2420		2340	(2350)	((2430))
				(2200)				
				2000				
C=O	(1725)	1775		1790	1735	1650	1720	1688
and	1708	1745		1765	1720	1608	1640	
C-C str.		(1713)		1680	1650	(1562)	1595	1635
	1620	1680		1625	(1640)	1545	(1560)	1560
						(1525)	(1545)	(1545)
		(1475)			1470	(1510)	1495	
						(1475)		
CH_2 and		1455		1450	1450	(1460)	1460	1495
CH_3 de-	1425	(1430)			1410	1425	1390	1390
form;	1365	1375	1340	(1350)	1370	1375	1365	1335
C-C str.	1305	1350					1315	
	1252	1282	1278	1270	(1265)	1285	1280	1275
		1230	1212	1220	1235	1207	1223	1190
		1200						
		1160	1188	1160	1190	1157	1205	1165
		1095	1138		1150		1142	1130
		1030	990	1085	(1115)	1112	1100	1110
		(990)	970		1096	(1030)	1080	1098
					1037		1038	(1065)
		900	910	913	(928)	(895)	1010	1030
							963	963
							943	
							920	913
		822	823	819	(855)	858	826	863
								837
	780	730	740	743	(740)	795	790	790
		700	720			726	775	
							725	725
		665	658	655	662		670	675

* β-diethylaminoethyltrifluorocrotonate

Table IIIb

Infrared absorption bands of bidentate Cu(II) chelates

I-Cu	II-Cu	III-Cu	IV-Cu	V-Cu	VI-Cu
(2360)	(2350)	(2350)	(2340)	(3110)	(2340)
1582	1615	1643	(1645)	1635	1565
(1560)	1535	(1615)	1600	1612	(1550)
1530		1565	1555	1564	1525
		1540	1538	(1550)	1500
		1490		1495	
(1425)	(1422)	(1450)	(1425)	(1432)	(1340)
(1362)	1312	1360	1290	1375	1398
1278	1230	(1340)	(1270)	1312	1363
1193	1198	(1300)	(1225)	1248	1343
	1157	1260	1180	1230	1302
	1142	1210		1228	(1280)
		1150		1188	1212
		1110		1155	1167
					1102
1020	1030	1080	1070	1092	1085
940	1015	1044	1022	1013	1075
(720)	952	(955)	985	985	1050
682	870	(895)	973	967	(1030)
	800	871	(865)	925	1000
	738	802	778	862	970
		746	(758)	842	960
		679		815	928
				802	830
				755	785
				732	728
				722	670
				698	

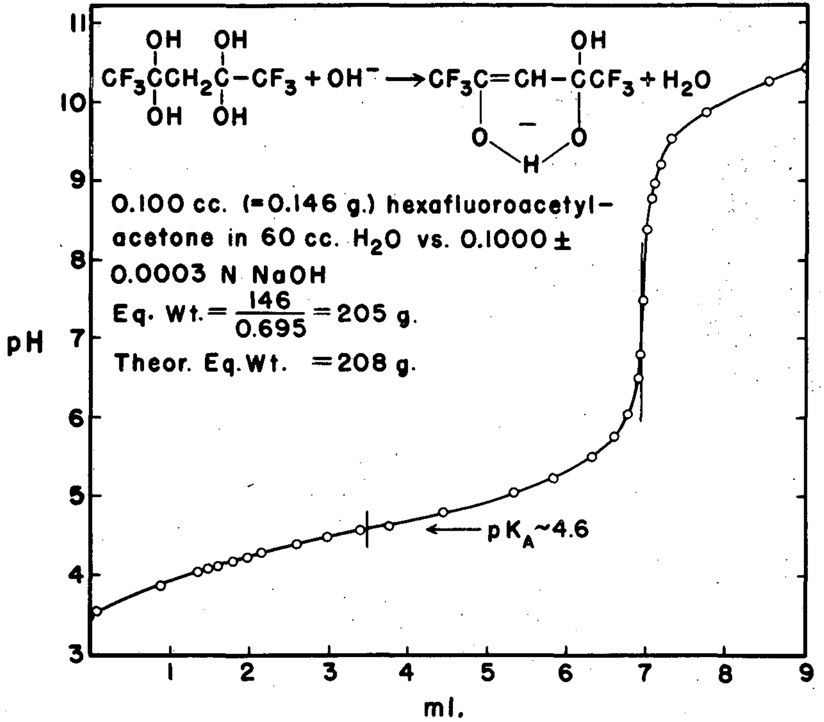

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Fig. 7. Titration of aqueous hexafluoroacetylacetone with sodium hydroxide solution.

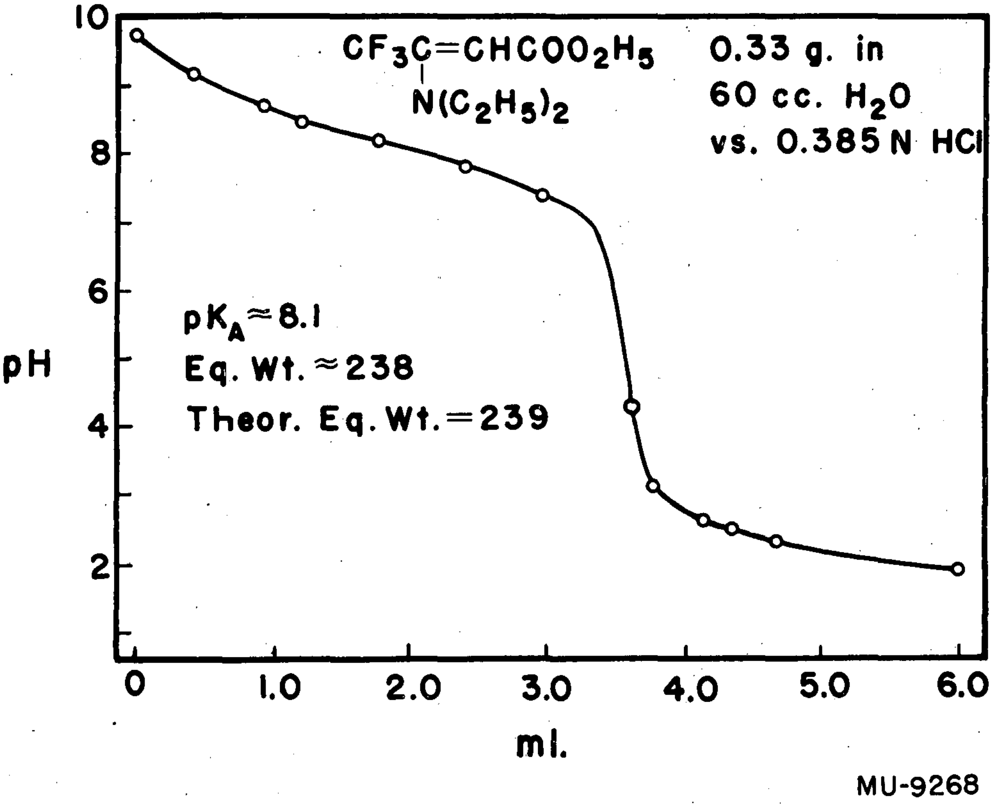


Fig. 8. Titration of aqueous β-diethylamino ethyltrifluorocrotonate with hydrochloric acid.

Discussion

Preparation of Ligands and Cu(II) Chelate Compounds

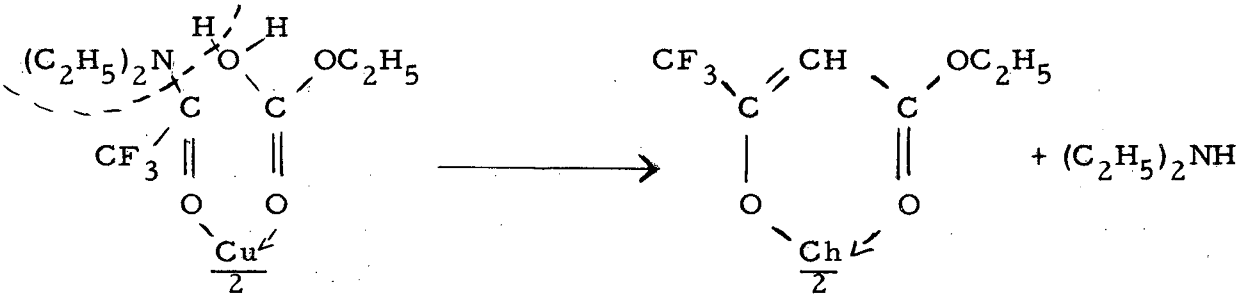
All the ligands excepting N, N-diethylacetoacetamide and β-diethylamine ethyltrifluorocrotonate were available from commercial sources. The former compound, and its Cu(II) chelate, were kindly donated by Dr. G. E. Utzinger.[11] The product obtained from the reaction of diethylamine with ethyltrifluoroacetate always contained less nitrogen than that calculated for the desired product, N, N-diethyltrifluoroacetoacetamide, but corresponded quite closely to the value calculated for β-diethylamino ethyltrifluorocrotonate. This structure for the product was confirmed by titration curves, absorption spectra, and failure to obtain a nitrogen-containing copper chelate.

The method described for the preparation and purification of hexafluoroacetylacetone from the dihydrate has not been reported previously and seems to be an improvement over the method given by Haszeldine et al.,[10] which involves the treatment of an ether solution of the hydrate with metallic sodium. The resulting solution was used for synthesis of other metal salts, rather than for the preparation of the pure diketone. The boiling point range found in this investigation is quite narrow, and differs somewhat from the values reported by Haszeldine et al.[10] (54-85°) and by Henne et al.[7] (63-65°). The apparently impure fraction obtained by Haszeldine and co-workers was obtained by treatment with sodium sulfate in ether, and probably was a partially dehydrated mixture.

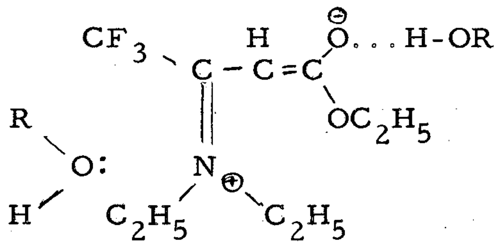
The procedures used for the preparation of the copper (II) chelates of trifluoroacetylacetone, ethylacetoacetate, and ethyltrifluoroacetoacetate are sufficiently different from the procedures previously reported[7, 8, 10, 11] to warrant the brief descriptions given here. The preparation of the copper (II) chelate compound of trifluoroacetylacetone given above has not been described previously although it has apparently been prepared by Henne et al.[7] In the preparation of bis-hexafluoroacetylacetato-Cu(II) the results of the present investigation indicate that, contrary to the findings of Haszeldine et al.,[10] the metal chelate is formed in the presence of water. On the other hand, there is general agreement in that the yield of metal chelate seems much higher in nonaqueous media.

The reaction of copper (II) acetate monohydrate with β-diethylamino-ethyltrifluorocrotonate in boiling ethanol resulted in a product free of nitrogen.

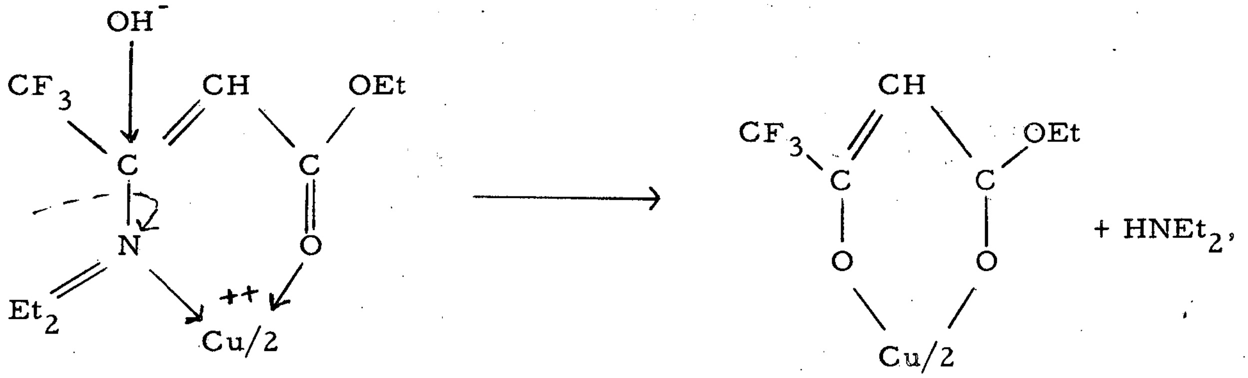
The analytical results checked the throretical values of bis-ethyltrifluoroacetoacetato-Cu(II) and -- with the exception of some rather minor differences-- the infrared and ultraviolet spectra of the latter compound also corresponded very closely to those of the reaction product. It seems, therefore, that the diethylamino group was replaced by a hydroxy group. That this process of hydrolysis (or alcoholysis) must be metal-catalyzed is shown by the previously mentioned titration experiments; one should certainly observe hydrolysis products by titration, since the pK_A of the liberated diethylamine would be > 11. However, prolonged heating of the free amino crotonic ester in aqueous solutions ranging from neutral to quite acid yielded quantitatively the initial undecomposed amine, $pK_A \sim 8.1$. A likely mechanism for metal-catalyzed hydrolysis would involve the hydrate either in the transition state or as stable intermediate:



Accordingly, ultraviolet spectra of the crotonate (Fig. 1) were examined for that disappearance of high-intensity bands which would mark extensive conversion of the crotonate to a solvent (HOH or ROH) addition product across the double bond. No such evidence is to be seen; indeed, in the hydroxylated solvents not only is the principal band quite as strong as in cyclohexane or chloroform, but it has undergone a shift from 234 to 270 mμ. This indicates that the hydroxylated solvents must assist excitation of the conjugated system, perhaps through such forms as



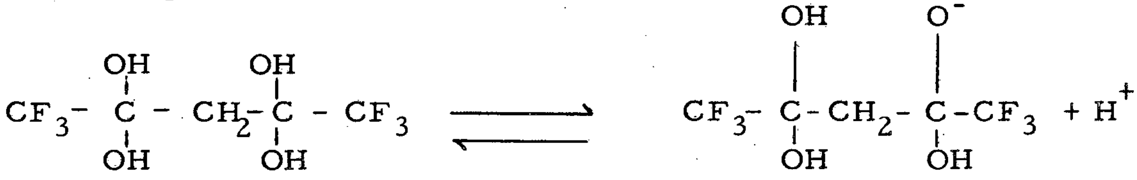
The question that this interpretation leaves unanswered is why chloroform, a hydrogen-bonding agent, does not exhibit a similar effect. Perhaps the steric hindrance would be sufficient to prevent useful approach of chloroform, or perhaps chloroform's H-bonding power is just not great enough to be observed here. Since there appears to be no positive evidence for large equilibrium quantities of $(C_2H_5)_2NC(CF_3)(OH)CH_2CO_2C_2H_5$ when the crotonate is dissolved in water or alcohol, the above elimination reaction may not involve such a species at all. Instead, it may proceed through some such mechanism as the following,



which invokes the polarizing power of the doubly charged cation to weaken the C-N bond.

The low metal and carbon analyses of bis-hexafluoroacetylacetono-Cu(II) and a high hydrogen analysis indicate the possibility of a dihydrate, but this chelate compound sublimed very readily without change in color or composition. Also, there were no hydroxyl bands in the infrared. Since it is unlikely that a hydrate of any kind could be produced without the retention of O-H bonds, the conclusion is inevitable that the analytical results are in error and that the chelate is anhydrous, with a structure corresponding to Formula I.

Another experience would indicate that hexafluoroacetylacetone anion is indeed no more than monohydrated. The titration with 0.100 N base (Fig. 7) shows hexafluoroacetylacetone to be an acid slightly stronger than acetic acid. However, the equilibrium



$$\mathrm{CF_3-\underset{OH}{\overset{OH}{C}}-CH_2-\underset{OH}{\overset{OH}{C}}-CF_3 \rightleftharpoons CF_3-\underset{OH}{\overset{OH}{C}}-CH_2-\underset{OH}{\overset{O^-}{C}}-CF_3 + H^+}$$

would probably have a much higher pK_A; other known alcohols very highly substituted with trifluoromethyl groups have acid pK values no smaller than about ten (e.g. $(C_3F_7)_2CHOH$, $pK_A = 10.66$; $(C_3F_7)_3COH$, $pK_A = 10.1$.[14] (One

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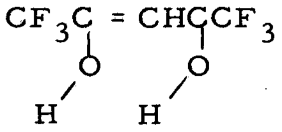
[14] A. Henne, J. Am. Chem. Soc. 75, 991 (1953), and R. N. Haszeldine, referred to therein.

might conjecture that the four hydroxy-groups would increase the acidity of each other and of the methylene hydrogens. Likely this effect could not account for such great acidity as we observe, however. An inductive-effect calculation, with consideration of the statistical factor, sets a lower limit on the pK_A for the dihydrate of ca 8.) The alternative reaction would seem to be one involving dehydration,

$$CF_3C(OH)_2CH_2C(OH)_2CF_3 + OH^- \rightleftharpoons CF_3C(OH) = CH_2C(OH)_2CF_3 + H_2O.$$

The pK_A value observed should then correspond to the acid structure



III

in fact, 4.6 would be a reasonable value for this enol.

Morgan and Moss[15] have pointed out that metal chelate compounds of type II, in which two beta-diketonic residues are bound to a transition metal, form stable addition compounds with two other donors to give complexes in which the metal coordinate linkages are presumed to have an octahedral arrangement. In this investigation no addition compounds were obtained under the conditions employed in the production of bis-acetylacetono-Cu(II). However, this tendency was apparent in the case of bis-trifluoroacetylacetono-Cu(II), for which an unstable solvate was formed in cold 50% aqueous ethanol, and gradually decomposed to the anhydrous form when exposed to air over the period of a few hours. It is perhaps surprising that more stable addition compounds were not obtained for the hexafluoroacetylacetone chelate, since the tendency of the trifluoromethyl groups to decrease stability[9] would be expected to enhance the affinity of the metal ion for additional donor groups. However, an unstable solvate, perhaps also an alcoholate, was first isolated when the chelate was recrystallized from aqueous ethanol. Samples of bis-hexafluoroacetylacetono-Cu(II) prepared from the dihydrate of the ligand in aqueous media, and from the diketonic form of the ligand in anhydrous media, both gave products with identical properties and spectra.

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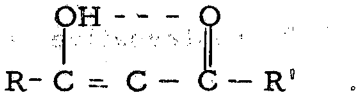
[15] G. T. Morgan and H. W. Moss, J. Chem. Soc. 105, 189 (1914).

Ultraviolet and Visible Absorption Spectra

All the ultraviolet absorption bands of ligands in Figs. 2 and 3 are high-intensity bands arising from electronic transitions in the conjugated system

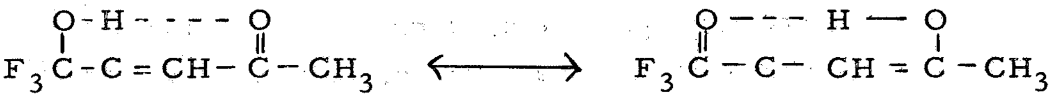


$$R-\overset{\overset{OH\text{ - - - }}{|}}{C}=C-\overset{\overset{O}{\|}}{C}-R' \quad .$$

IV

Such bands are sometimes called "K" transitions.[16] This enolic system, in which R may be methyl or trifluoromethyl, and R' may be methyl, trifluoromethyl, ethoxy or diethylamino, is common to all the ligands investigated.

In Fig. 1, a simple comparison may be made between the spectra of acetylacetone and its trifluoro and hexafluoro derivatives. The maximum of the intense absorption band of acetylacetone is shifted to longer wave lengths and further intensified by the substitution of an electron-attracting trifluoromethyl group at one end of the conjugated system. In this case two isomeric enol forms are possible



$$F_3\overset{\overset{O-H\text{ - - - -}}{|}}{C}-C=CH-\overset{\overset{O}{\|}}{C}-CH_3 \longleftrightarrow F_3\overset{\overset{O\text{ - - - }H\text{ — }}{\|}}{C}-C-CH=\overset{\overset{O}{|}}{C}-CH_3$$

VI A VI B

The influence of the trifluoromethyl group increases enolization;[8] one may surely suppose that A has greater acidity than B and therefore that B is likely present in higher concentration than A. The absorption band of hexafluoroacetylacetone, on the other hand, is considerably decreased in intensity, while its frequency is also decreased. A rough quantitative comparison of these spectra on the basis of relative intensities is possible even though the relative degrees of enolization are not known exactly. From published data on the absorption intensity of the pure enol of acetylacetone, one would guess it to be approximately 50% enolized in the solvent used in this investigation. Meyer[17] reports the enol content of the acetylacetone to be 79% at 20°C in chloroform. Assuming this to be correct, and making reasonable estimations for the enol contents of

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[16] A. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Ltd., London, England (1954).

[17] K. H. Meyer, Ber. 45, 2843 (1912).

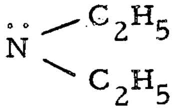
trifluoro-[8] and hexafluoroacetylacetone of ~95% and ~100% respectively, one obtains the following values:

Enol of	Approx. % enol	λ_{max}	Approx. ϵ_{max} for enol
Acetylacetone	73-79	280	12,500 ± 500
Trifluoroacetylacetone	90-100	284	11,100 ± 600
Hexafluoroacetylacetone	100	273	7,800

While these values are not precise, one can safely draw from them the conclusion that an increase in the electron-donating power of the groups R and R' produces a corresponding increase in the intensity of K-absorption. This point is borne out by other substitutions as well. Taking the degree of enolization into account, one finds that when R is $-CH_3$, the K-band intensities for various R'-groups increase in the order $-CF_3 < -CH_3 < -OC_2H_5 < -N(C_2H_5)_2$.

The wave-length shifts with fluorine substitution are what one would expect: an increase when a strong electron-attracting group is placed on one end of a conjugated system, and a decrease when such electron-attracting groups are placed on both ends of the system.

The spectrum of acetylacetone given in Fig. 1 is in rough agreement with those given by Haszeldine et al.[10] and by Acly and French[18] for alcohol solutions. Close agreement would not be expected in view of the wide variation with solvent of both frequency and intensity of β-dicarbonyl compounds reported by Haszeldine et al.[10] Subject to the same qualifications, the absorption curves of ethylacetoacetate and of ethyltrifluoroacetoacetate given in Fig. 3 and Table II agree with the values reported previously.[10] In this work, however, no secondary absorption band at higher wave length was observed for ethyltrifluoroacetoacetate, as was reported for this substance in cyclohexane.[10] It is of interest to note that an increase in intensity is produced by a modification of the structure of ethylacetoacetate. In the trifluoromethyl analogue, the effect is probably due to an increase in the degree of enolization of the compound. On the other hand, the intensity increase, accompanied by an increase in λ_{max}, observed for N, N-diethylacetoacetamide is due to the effect on a conjugated system of replacing an electron-donating group, $-\ddot{\underline{O}}-C_2H_5$, by a stronger electron-donating group,


$\ddot{N}(C_2H_5)_2$

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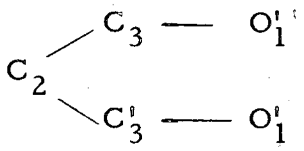
[18] H. E. Acly and H. S. French, J. Am. Chem. Soc. 49, 847 (1927).

The ultraviolet absorption spectra of bis-acetylacetono-Cu(II), and of its two fluoro analogues, shown in Fig. 4, show some resemblance to those of the ligands themselves. The main absorption band of the keto enol seems to be considerably intensified in the chelates, and to be split more clearly into double bands. Furthermore, there seems to be a weaker K-type band at lower wave length, although the maxima are below the range of the measurements for the fluorinated chelates.

In reference to the shift to lower frequencies ($\sim 2800\ \mathrm{cm}^{-1}$ decrease) of the main ultraviolet band of acetylacetone anion upon replacement of H^+ by Cu^{++}, it is interesting to see what a crude theoretical calculation predicts. We calculate, by the LCAO molecular orbital method, an electron distribution for the ground and first excited states of acetylacetonate ion. Then, supposing the dominant effect of replacing H^+ by Cu^{++} to be increased Coulombic interaction of cation and anion due to the additional cation charge, we compute the effect of this change upon the difference in energy between the ground and the first excited state.

a. <u>LCAO-MO treatment</u>. We consider the pi-system of five p_z orbitals containing six electrons for the pictured



skeleton, symmetry C_{2v}. Symbols are defined as usual:

$H_{ij} (= H_{ji}) \equiv \int \psi_i^* \, H \psi_j \, d\tau$, where H is the Hamiltonian for the system and ψ_i the p_z eigenfunction of atom i. Let us neglect all overlap integrals and all integrals connecting nonadjacent atoms. The secular equation is factored into a cubic and a quadratic by forming combinations of the ψ_i as follows:

$\psi_a \equiv (\psi_1 - \psi_1')/\sqrt{2}$; $\psi_b \equiv (\psi_3 - \psi_3')/\sqrt{2}$; $\psi_d \equiv (\psi_3 + \psi_3')/\sqrt{2}$; $\psi_f \equiv (\psi_1 + \psi_1')/\sqrt{2}$.

$$\begin{vmatrix} H_{22} - W & \sqrt{2}\, H_{23} & 0 & & \\ \sqrt{2}\, H_{23} & H_{33} - W & H_{13} & & \bigcirc \\ 0 & H_{13} & H_{11} - W & & \\ & \bigcirc & & H_{11} - W & H_{13} \\ & & & H_{13} & H_{33} - W \end{vmatrix} = 0$$

is the secular equation, where the solutions, W, give the five energy levels.

We take a method of choosing parameters which we have previously used and found satisfactory for computing "resonance energies" of oxygenated molecules:[19]

$$\frac{H_{13}}{H_{23}} \approx \frac{\text{C = O energy - C - O}^{-}\text{ energy}}{\text{C = C energy - C - C energy}} \approx 1.8$$

We first guess at the Coulomb integrals: $H^o_{33} = H^o_{22} = H^o_{11} - 2\,H_{23}$. Then the method given by Branch and Calvin[20] and used by Jaffé[21] and others to account for the induction effect is applied to correct these to

$$H_{ii} = \sum_k \left(\frac{1}{3}\right)^{n_{ik}} H^o_{kk} ,$$

where $n_{ik}-1$ is the number of atoms between i and k. Our complete set of Coulomb integrals is $H_{22} = 0$; $H_{33} = 0.52\,H_{23}$; $H_{11} = 1.8\,H_{23}$. Solution of the secular equation yields the following set of energy levels and orbital functions:

(I) $W_I = 3.30\,H_{23}$; $\psi_I = 0.264\,\psi_2 + 0.617\,\psi_d + 0.741\,\psi_f$,

(II) $W_{II} = 3.09\,H_{23}$; $\psi_{II} = 0.818\,\psi_a + 0.577\,\psi_b$,

(III) $W_{III} = 0.66\,H_{23}$; $\psi_{III} = 0.754\,\psi_2 + 0.352\,\psi_d - 0.555\,\psi_f$,

(IV) $W_{IV} = -0.75\,H_{23}$; $\psi_{IV} = 0.578\,\psi_a - 0.817\,\psi_b$,

(V) $W_V = -1.64\,H_{23}$; $\psi_V = 0.607\,\psi_2 - 0.705\,\psi_d + 0.368\,\psi_f$.

From the orbital functions is obtained the electron density distribution for an electron in any orbital

		Oxygen 1 or 1'	Carbon 3 or 3'	Carbon 2
e^- Density in	I	0.274	0.191	0.070
	II	0.334	0.166	0
	III	0.154	0.062	0.569
	IV	0.166	0.334	0
	V	0.068	0.248	0.368

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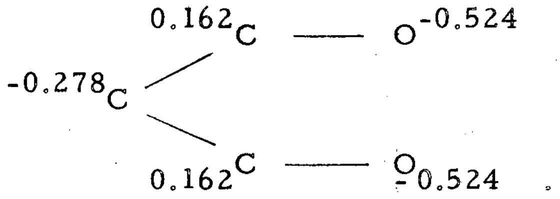
[19] R. L. Belford, (thesis), University of California, Berkeley (1955); University of California Radiation Laboratory Report No. UCRL-3051 "Bonding and Spectra of Metal Chelates: Ultraviolet, Visible, Infrared, and Electron Resonance Absorption".

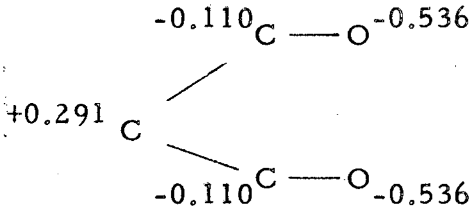
[20] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry", Prentice-Hall, Inc., New York, New York (1941).

[21] H. H. Jaffé, J. Chem. Phys. 20, 279 (1952).

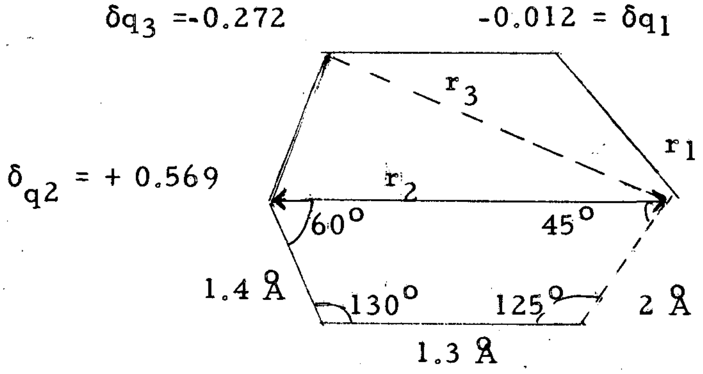
Six electrons would fill I, II, III with resulting ground-state distribution of the single anion charge as follows:



The first excited state would have I and II filled, III and IV each half-filled, with a resulting charge distribution



b. <u>Electrostatic effect</u>. From the foregoing we take the differences in charge density between the first excited and ground states for the anion and place a single positive charge as shown below:



The change of transition energy (III → IV) upon increasing cation charge by one unit is then given by

$$\Delta_E = \left(2 \frac{\delta q_1}{r_1} + 2 \frac{\delta q_3}{r_3} + \frac{\delta q_2}{r_2} \right) e^2;$$

for the geometry and δq's shown above $\Delta E_{calc} = -3200\ cm^{-1}$. The observed shift of -2800 $cm.^{-1}$ agrees fantastically well. It should be mentioned that if one performs the above calculation assuming that all exchange integrals have the same value and that all Coulomb integrals have the same value (i.e. ignoring the differences between carbon and oxygen), one obtains a calculated shift of $\Delta E_{calc} = -2500\ cm^{-1}$. Thus it appears that the treatment we use will give the observed direction and order of magnitude for the shift regardless of chosen values for the integrals (within reasonable limits, of course).

For the copper (II) chelates of the β-keto esters and amide illustrated in Fig. 3, the spectra resemble those of the ligands much more closely than is the case with the β-diketones. Here, also, the effect of the metal is to intensify the absorption bands of the ligand and to shift them to longer wave lengths.

It is interesting to observe the spectrum, in this range, of the calcium chelate of ethylacetoacetate (Fig. 3). It resembles, both in intensity and band placement, that of the corresponding Cu chelate. This unmistakably points to the origin of the ultraviolet bands of the chelates as transitions in the enolate ions; charge-transfer spectra would surely exhibit drastic changes upon the replacement of Cu^{++} by Ca^{++}.

The absorption spectra of the copper (II) chelates in the visible region, shown in Figs. 5 and 6, clearly indicate that the influence of substitution by trifluoromethyl groups in the ligand is to shift the absorption bands to longer wave lengths, thus passing more light in the low-wave-length region and accounting for the typically green color of copper chelates of fluorinated ligands. This shift of the absorption bands increases as the number of trifluoromethyl groups increases, and thus correlates with a decrease in the stability of the metal chelate.[22]

Another interesting inference may be drawn from the similarity of the spectra of the copper (II) chelates of ethylacetoacetate and N, N-diethylacetoacetamide. The fact that these curves are almost superimposable indicates that the copper (II) ion is bound only through the oxygen atoms of both ligands, as indicated by formulas Va and Vb.

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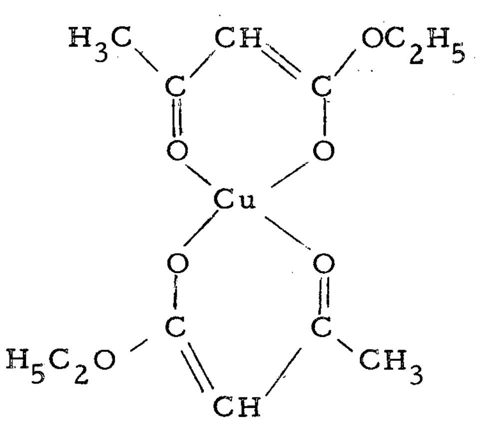
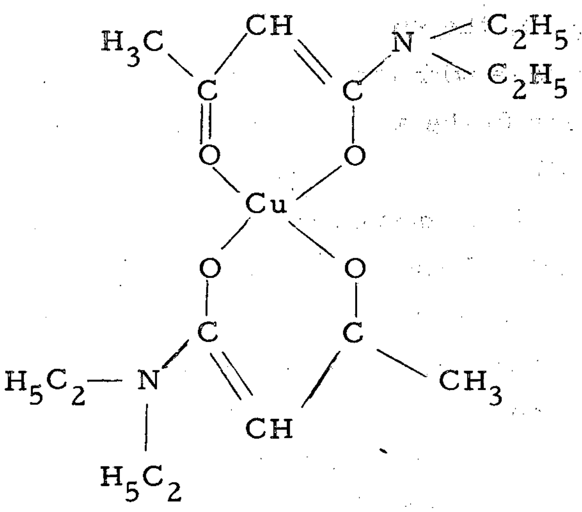
[22] An increase in the acidity of the ligand, and a decrease in the affinity for Cu(II) ion, was demonstrated by Calvin and Wilson[9] to accompany the replacement of one methyl group of acetylacetone by a strongly electron-attracting CF_3 group. It is believed that the replacement of the second methyl group will further decrease the donor power of the ligand.



Va

Bis-ethylacetoacetato-Cu(II)



V

Bis-N, N-diethylacetoacetamido-Cu(II)

It is seen that all the copper chelate spectra in the visible region consist of at least two overlapping absorption bands. We believe that these are transitions between d-orbitals of the Cu(II) ion; the strong molecular field of the ligands partially removes the 3d orbital degeneracy, permitting transitions in the visible. The two strong bands that appear for chloroform solutions of the molecules reported in this paper are likely the transitions of the hole in configuration $3d^9$ from the ground state, the d_{xy}-orbital (if we consider ligands to be centered near the lines x=y and x=-y), to the higher-energy d-orbitals, d_{xz}, d_{yz}, and $d_{x^2-y^2}$. The supposition that such transitions are responsible for the visible and near infrared absorption bands of the transition metal hydrates as well as some complex ions has been under investigations by several workers very recently.[23]

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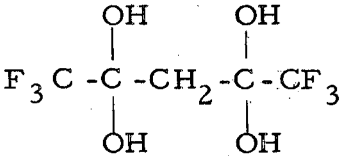
[23] (a) L. E. Orgel, J. Chem. Soc. 1952, 4756.
(b) O. Holmes, Ph.D. Thesis, University of California, 1955.
(c) C. J. Ballhausen, Dan. Mat. Fys. Medd. 29, No. 4 (1954).
(d) J. Bjerrum, C. J. Ballhausen, and C. K. Jorgensen, Acta Chem. Scand. 8, 1275 (1954).
(e) B. R. McGarvey, private discussions.

It will be shown in a later paper that if the visible chelate absorption is of this sort, a decrease in donor base strength and covalent bonding tendency such as one expects from the series acetylacetone – trifluoroacetylacetone – hexafluoroacetylacetone should cause a shift of both bands to the red and a slight increase in the ratio of wave length of the higher-wave-length band to that of the lower. For the acetylacetone series this seems to hold true. Upon passing from ethylacetoacetato-Cu(II) to the corresponding trifluoro derivative, one notes the proper shift of both bands to the red; their ratio appears to be little changed.

We have noticed that the visible absorption spectra of some of the Cu(II) chelates exhibit interesting solvent effects. These will be reported in another paper.

Infrared Spectra

For the free ligands, acetylacetone and the corresponding trifluoro and hexafluoro analogues, there is an OH stretching vibration indicating strong enolization of one of the carbonyl groups. It is interesting that the influence of one trifluoromethyl group results in a shift of the OH band from 3550 cm^{-1} in acetylacetone to 3360 cm^{-1}, in the trifluoromethyl derivative. This correlates with the fact that the enol of trifluoroacetylacetone is more acidic than that of acetylacetone itself. The further shift of the OH band in anhydrous hexafluoroacetylacetone to 3120 cm^{-1} is then just as one should expect. In the dihydrate of hexafluoroacetylacetone there are four hydroxyl groups, as indicated by Formula VI, which result in a very intense broad band at 3330 cm^{-1}.



$$F_3C-\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}-CH_2-\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}-CF_3$$

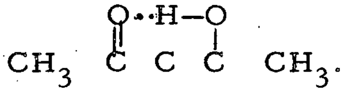
VI

Hexafluoroacetylacetone dihydrate

Other bidentate ligands show a similar effect of the trifluoromethyl group in displacing the OH bond vibration to longer wave lengths. Thus the enol band of ethylacetoacetate (3550 cm^{-1}) is displaced to 3360 cm^{-1} in the trifluoromethyl derivatives.

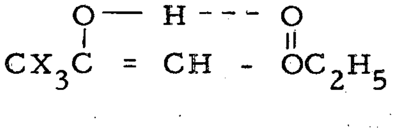
Additional evidence for the assignment of these absorption bands to OH stretching vibrations may be found in the complete absence of these bands in the spectra of the corresponding metal chelate compounds. Since all the enolic hydrogens are replaced by metal ions in the chelates, as is indicated by Formula II, it is apparent that all the OH bands should disappear.

All the ligands have absorption frequencies that may be assigned to free carbonyl groups, with shifts to higher (or lower) frequencies when a CF_3 group is present. Thus the normal carbonyl frequencies of acetylacetone 1708 and 1725 cm^{-1} are shifted to 1775 cm^{-1} and 1745 cm^{-1} in trifluoroacetylacetone; to 1790 cm^{-1} and to 1765 cm^{-1} in hexafluoroacetylacetone. For all three ligands there is a strong, broad band, 70 to 90 cm^{-1} below the free carbonyl bands, which must be due to the conjugated, hydrogen-bonded carbonyl group characteristic of the enolic form of the β-diketone:



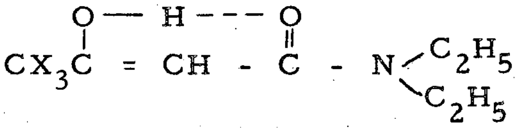
$$\begin{array}{ccccc} & O & \cdots H- & O & \\ & \| & & | & \\ CH_3 & C & C & C & CH_3. \end{array}$$

Since the free-carbonyl frequencies of ethylacetoacetate and the corresponding amide should be close to that of acetylacetone, the 1720 cm^{-1} bands may be given this assignment. In ethylacetoacetate, the band found at 1735 cm^{-1}, 15 cm^{-1} above the free carbonyl band, has been assigned to the ester carbonyl. The highest carbonyl frequency of ethyltrifluoroacetoacetate, found at 1650 cm^{-1}, may possibly be assigned to the ester carbonyl group, and the next lower frequency, 1608 cm^{-1}, to the free carbonyl vibration. In the case of acetoacetic acid diethylamide, there can be no ester carbonyl bands, in agreement with the observed spectra. The frequency observed at 1640 cm^{-1} may be assigned to the typical amide I frequencies (tertiary amide). The lowest of the three carbonyl frequencies observed for each ester and amide may be assigned to the H-bonded (chelated) form of the ester or amide carbonyl, according to formulas VII and VIII, where X may be H or F. These frequencies appear at about 100 cm^{-1} lower than corresponding ester carbonyl, and from 120 to 140 cm^{-1} below the frequency assigned to the amide carbonyl group. For acetylacetone and ethylacetoacetate our assignments agree with those of Bellamy and Beecher.[24]



$$\begin{array}{ccccc} O & — H & --- & O & \\ | & & & \| & \\ CX_3C & = CH & - & OC_2H_5 & \end{array}$$

VII



$$\begin{array}{cccccc} O & — H & --- & O & & \\ | & & & \| & & \\ CX_3C & = CH & - & C & - & N\begin{matrix} \diagup C_2H_5 \\ \diagdown C_2H_5 \end{matrix} \end{array}$$

VIII

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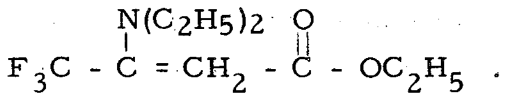
[24] L. J. Bellamy and L. Beecher, J. Chem. Soc. 1954, 4487.

Note: In the case of the ethylester of diethylamino trifluorocrotonic acid, the 1688 cm^{-1} line may be assigned to ester carbonyl (reduced by -CF$_3$ group and conjugation from normal position), and the 1638 cm^{-1} line to a C=C stretch of the crotonyl structure, corresponding to the formula



$$F_3C - \overset{N(C_2H_5)_2}{\overset{|}{C}} = CH_2 - \overset{O}{\overset{||}{C}} - OC_2H_5 \ .$$

An apparent anomaly, assuming the correctness of these tentative assignments, is the influence of CF$_3$ substitution on the carbonyl frequencies. In acetylacetone, a shift to higher frequencies is observed, whereas in ethylacetoacetate there is a very strong shift to lower frequencies. The corresponding shifts of the H-bonded (chelated) carbonyl frequencies, resulting from fluorine substitution, occur in the same direction and are of similar magnitude, as the shifts in the free carbonyl frequencies.

It is interesting that no C=C stretching frequencies have been assigned for the ligands, in analogy with the assignment of the 1633 cm^{-1} line of acetylacetone to this group. In all cases, however, other strong bands have appeared where this band would normally be expected, and the observed absorption bands may therefore be considered as combinations of the two component bands.

The bands observed in the 1300 - to 1500-cm^{-1} region of the spectrum must be due to CH$_3$ and CH$_2$ deformation vibrations, in accordance with the observed frequencies of other compounds.

Cu Chelate Spectra[*]

The metal chelate spectra given in Table III a are characterized by the absence of normal carbonyl, ester carbonyl, and amide carbonyl absorptions. In each case the carbonyl spectrum of the ligand is replaced by metal-chelated carbonyl absorptions at much lower frequencies. The absorption bands of bis-acetylacetono-Cu(II) at 1582 and 1530 cm^{-1} have been assigned to chelated carbonyl and C=C stretch, respectively, by Lecompte et al.[26, 27]

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[*] Attention is called to the work of Bellamy and Branch[25] on infrared spectra of CHCl$_3$ solutions of some metal chelates. Solution spectra for such chelates are not directly comparable with solid spectra, we feel.

[25] L. J. Bellamy and R. F. Branch, J. Chem. Soc. 1954, 4491.

[26] J. Lecompte, Discussions Faraday Soc. 1950, No. 9, 125.

[27] C. Duval, R. Freyman and J. Lecompte, Bull. Soc. Chim. France, 1952, 106.

Thus the chelate carbonyl absorptions of bis-acetylacetono-Cu(II), bis-trifluoroacetylacetono-Cu(II), and of bis-hexafluoroacetylacetono-Cu(II), occur at 1582, 1615, and 1643 cm^{-1}, respectively. There seems to be an increase in frequency of the carbonyl band as the stability of the metal chelate decreases. Thus, decreased interaction of the metal with the carbonyl groups results from increased fluorine substitution in the molecule. The frequencies of the C=C stretch vibrations, on the other hand, are increased only slightly as methyl groups are replaced by trifluoromethyl groups. In the case of bis-hexafluoroacetylacetono-Cu(II) there is an additional band at 1565 cm^{-1} which is difficult to assign; it is likely also due to C=C stretch.

The ester and amide chelate compounds, IV-Cu, V-Cu, and VI-Cu, seem to have double chelate carbonyl bands, corresponding to the ketonic carbonyl and the ester or amide carbonyl of the ligands. The 1600 cm^{-1} band of the ethylacetoacetate chelate has been assigned to the ester carbonyl chelated to the Cu(II) ion, and the lower-frequency band at 1555 cm^{-1} must correspond to the chelated ketonic carbonyl group. The frequencies of both these bands are therefore strongly shifted ($\sim$150 cm^{-1}) to lower frequencies by coordination with the metal ion. Another band at 1538 cm^{-1} is assigned to a C=C stretch vibration, analogous to the corresponding bands in the acetylacetone derivatives.

The frequency assignments made for bis-ethyltrifluoroacetoacetato-Cu(II) are completely analogous, with the exception that all the frequencies are somewhat higher than those of the ethylacetoacetate chelate. The shift to higher frequencies is much greater for the chelated ketonic carbonyl than for the chelated ester carbonyl, as would be expected from the position of the trifluoromethyl group. The C=C stretch frequency undergoes the smallest shift. The carbonyl frequencies of the N, N-diethylacetoacetamide chelate are considerably lower than the corresponding values for the esters, and coordination with the metal ion results in a smaller frequency decrease ($\sim$75 cm^{-1}) for the amide than was observed for the corresponding esters.

As in the case of the free ligands, a number of the absorption bands in the 1300- to 1500 - cm^{-1} region must be due to CH_2 and CH_3 deformations. Many of these bands are missing, however, because of the interference of two strong nujol bands in this region of the spectrum.

The authors would emphasize that some of their assignments of infrared frequencies may be in error; especially where two or more bands lie fairly close together, it is often impossible to decide how the likely assignments for that region should be distributed among them. However, it is felt that the general features of these spectra and the structure inferences drawn from them cannot be gross misinterpretations. The assignments have been examined quite carefully for consistency with known spectra whose interpretations are clear. A parallel infrared spectral study of the ligands and their chelates with appropriate isotopic substitutions might prove valuable in making assignments.