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INFLUENCE OF FLUORINE SUBSTITUTION ON THE PROPERTIES OF METAL CHELATE COMPOUNDS. II. COPPER(II) CHELATES OF TETRADENTATE LIGANDS

A. E. Martell, R. Linn Belford, and M. Calvin

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ABSTRACT

The ultraviolet, visible, and infrared absorption spectra of four Schiff bases derived from β-diketones and their copper(II) chelates are described and discussed in relation to the structure of these molecules. Infrared assignments are made where possible. The influence of fluorine substitution and ring size on the ultraviolet and visible spectra of the chelate compounds is discussed, and interrelationships between structure, stability, and absorption spectra are suggested.

INFLUENCE OF FLUORINE SUBSTITUTION ON THE PROPERTIES OF METAL CHELATE COMPOUNDS. II. COPPER(II) CHELATES OF TETRADENTATE LIGANDS

A. E. Martell,* R. Linn Belford,† and M. Calvin

Radiation Laboratory and Department of Chemistry
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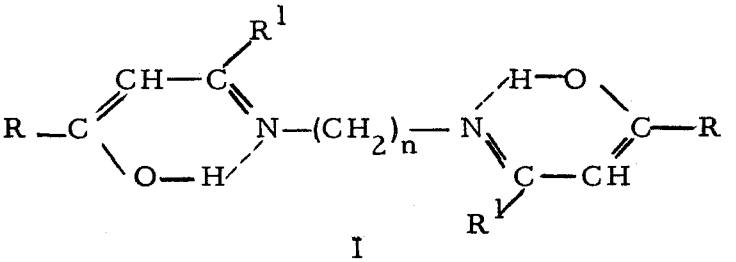
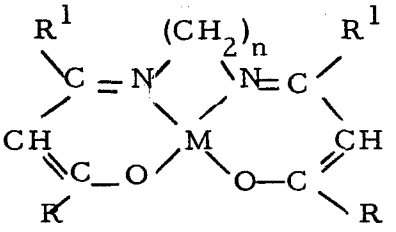
In a previous publication,[1] the influence of fluorine substitution on the spectra of copper(II) chelates of a number of β-diketones was reported. A second class of ligands, which would seem to offer structures of interest in this study, are the Schiff bases derivable from diamines and β-diketones, as indicated in Formula I. Thus acetylacetone or its tri-fluoromethyl derivatives, linked together by a hydrocarbon chain through Schiff-base formation, would provide a series of tetradentate chelating agents capable of conforming to the steric requirements of the Cu(II) and UO_2(VI) ions. The structures of the corresponding Cu(II) chelates is indicated by Formula II.



I



II

These compounds are analogous to those described in the first paper in this series in that they are derived from the same β-diketones.

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[1] Linn Belford, Martell, and Calvin, J. Inorg. Nucl. Chem. 2, 11 (1956).

The only ligands corresponding to Formula I that have been reported prior to this investigation are bisacetylacetoneethylenediimine ($R = R^1 = CH_3$; $n = 2$), described by Combes and Combes;[2] and a number of its metal chelates, studied by Morgan and Smith.[3] More recently a series of these substances have been prepared by McCarthy et al.[4] as model compounds for dipole moment studies. Exchange of the metal ion has been studied with bisacetylacetoneethylenediimino-Cu(II) by Duffield and Calvin[5] and with bisacetylacetoneethylenediimino-Zn(II) by Leventhal and Garner.[6]

Experimental Procedure

Bisacetylacetoneethylenediimine. To 20.0/g (0.2 mole) of acetylacetone dissolved in 25 ml of absolute ethanol as a moderator for the reaction, , 6.0 g of anhydrous ethylenediamine diluted with an equivalent volume of absolute ethanol was added in a dropwise fashion with cooling of the reaction mixture. The resulting yellow solution was evaporated to dryness under reduced pressure with a stream of dry air at about 50°. The yellow crystalline product was recrystallized twice from toluene and twice from carbon tetrachloride. The yield was 18 g, or 80% of the theoretical amount, of a colorless solid which melted at 113°. It is also soluble in water, from which it crystallizes as a solvate in the form of large needles. Water is unsatisfactory for crystallization since recovery is poor, because of possible partial hydrolysis of the Schiff base.

Anal. Calcd for $C_{12}H_{20}O_2N_2$: C, 64.29; H, 8.96; N, 12.5. Found: C, 65.18; H, 8.96; N, 12.2.

Bisacetylacetoneethylenediimino-Cu(II). To a solution of 2.0 g (0.01 mole) of copper(II) acetate monohydrate in 150 ml warm dioxane was added 3.5 g (0.015 mole) of bisacetylacetoneethylenediimine. The red solution was heated on a steam bath for 15 minutes, diluted with 200 ml of water, and allowed to stand overnight. The dark red needles which crystallized out were filtered off. Further dilution of the filtrate did not result in the crytallization of additional product, but a second small amount of product was recovered after evaporation of the mother liquor to a small volume. The combined relatively pure product thus obtained weighed 2.6 g or about 90% of the theoretical yield. Further purification was carried out, with little loss, by recrystallization from ligroin. The product was found to be very soluble in cold chloroform and carbon tetrachloride. Its melting point was 145°C.

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[2] A. Combes and C. Combes, Compt. rend 108, 1252 (1889).

[3] G. Morgan and J. Smith, J. Chem. Soc. 2034 (1925); 918 (1926).

[4] McCarthy, Hovey, Ueno, and Martell, J. Am. Chem. Soc. 77, 5820 (1955).

[5] R. B. Duffield and M. Calvin, J. Am. Chem. Soc. 68, 557 (1946).

[6] L. Leventhal and C. S. Garner, J. Am. Chem. Soc. 71, 371 (1949).

Anal. Calcd for $C_{12}H_{18}O_2N_2$ Cu: C, 50.4; H, 6.3; N, 9.81. Found: C, 49.2; H, 6.6; N, 9.77.

Bistrifluoroacetylacetoneethylenediimine. To 0.20 mole (30.8 g) of trifluoroacetylacetone dissolved in 200 ml of 95% ethanol was added 50 ml of an ethanol solution containing 6.0 g (0.10 mole) of anhydrous ethylenediamine. The yellow solution was refluxed for 30 minutes, diluted with an equal volume of water, and allowed to cool. The nearly colorless crystals thus obtained were separated, and a further small batch was recovered by dilution of the mother liquor with an equal volume of water and allowing it to stand for one day. The combined batches weighed 29 g, which is 87% of the theoretical amount. It was further recrystallized from 50% ethanol with only slight loss. It melted at 156°.

Anal. Calcd. for $C_{12}H_{14}N_2O_2F_6$: C, 43.1; H, 4.22; N, 8.44; Found: C, 42.7; H, 3.86; N, 8.28.

Bistrifluoroacetylacetoneethylenediimino-Cu(II). A solution of 2.0 g (0.010 mole) of copper(II) acetate monohydrate in 150 ml of dioxane was treated with 4.0 g (0.012 mole) of bistrifluoroacetylacetoneethylenediimine according to the general procedure described above for the copper(II) chelate of bisacetylacetoneethylenediimine. The lavender-colored crystalline precipitate weighed 3.8 g, or 96% of the theoretical amount.

Red form. The product was dissolved in a small amount of chloroform and treated with twice its volume of warm ligroin. When the solution was slowly cooled, 1.6 g (approximately 40%) of wine-red needles melting at 256° was obtained.

Anal. Calcd for $C_{12}H_{12}O_2N_2F_6$ Cu: C, 36.6; H, 3.1; N, 7.12; Found: C, 36.2; H, 3.2; N, 6.95.

Blue form. An equal volume of ligroin was added to the mother liquor obtained after separation of the red product described above. After the resulting solution was allowed to stand overnight, a batch of blue needles was obtained. A further small amount of the same material was recovered by evaporating the mother liquor to a small volume and adding ligroin. The combined batches of blue needles weighed 1.8 g, or about 45% of the theoretical amount. Its melting point was found to be 197°, with softening beginning at 190°.

Anal. Calcd for $C_{12}H_{12}O_2N_2F_6$ Cu: C, 36.6; H, 3.1; N, 7.12. Found: C, 37.0; H, 3.8; N, 7.39.

Both the red and the blue forms produced blue solutions having the same color and shade, and showed similar solubility characteristics in polar solvents such as chloroform.

Bisacetylacetonetrimethylenediimine. To 20.0 g (0.20 mole) of acetylacetone dissolved in about 200 ml of anhydrous ethyl ether, 7.4 g (0.10 mole) of anhydrous trimethylenediamine was added dropwise with stirring and cooling.

Slow addition was necessary to prevent too rapid refluxing of the ether as the result of the large heat of reaction, and a considerable proportion of the Schiff base was seen to precipitate during the addition. The reaction was completed by stirring the refluxing mixture for thirty minutes, and the product was isolated by cooling the mixture to 0° with a small amount of anhydrous ether. The yield of product was 18.0 g, or 80% of the theoretical amount. It is very soluble in water and in most organic solvents, including toluene, carbon tetrachloride, chloroform, and the like. It is quite hygroscopic and readily absorbs sufficient moisture from the atmosphere to go into solution. It is best recrystallized from dry ether by strong cooling. The melting point was found to be 51°.

Anal. Calcd for $C_{13}H_{22}O_2N_2$: C, 65.80; H, 9.25; N, 11.75. Found: C, 65.92; H, 9.56; N, 11.57.

Bisacetylacetonetrimethylenediimine - Cu(II). A 2.0-g sample (0.010 mole) of copper(II) acetate was treated with 3.5 g (0.015 mole) of bisacetylacetonetrimethylenediimine according to the general procedure described above. The finely divided crystalline material obtained was dissolved in 200 ml of ligroin, evaporated to 50 ml, and allowed to stand. Most of the product (1.6 g) was thus obtained as glistening greenish-black needles. Further evaporation of the mother liquor resulted in the isolation of 0.5 g more as fine dark-green needles. The total yield, melting at 97°, amounted to 70% of the theoretical amount.

Anal. Calcd for $C_{13}H_{20}N_2O_2$ Cu: C, 52.0; H, 6.77; N, 9.34. Found: C, 51.5; H, 6.9; N, 9.21.

Bistrifluoroacetylacetonetrimethylenediimine. A 15.4-g sample (0.010 mole) of trifluoroacetylacetone was treated with 3.7 g (0.050 mole) of anhydrous trimethylenediamine according to the procedure described above for the preparation of bistrifluoroacetylacetoneethylenediimine. The 13.5 g (77% of the theoretical yield) of colorless crystalline product thus obtained melted at 52° and was sufficiently pure for most purposes without further purification.

Anal. Calcd. for $C_{13}H_{16}N_2O_2F_6$: C, 45.1; H, 4.63; N, 8.10. Found: C, 44.8; H, 4.87; N, 7.96.

Bistrifluoroacetylacetonetrimethylenediimino - Cu(II). The procedure outlined for the preparation of the copper(II) chelate of bistrifluoroacetylacetoneethylenediimine was followed. The deep green dioxane reaction solution thus obtained was diluted with 1.5 times its volume of water, and 4.0 g (approximately 98% of the theoretical yield) was obtained. After recrystallization from carbon tetrachloride, it was isolated in the form of dark-green needles melting at 214°.

Anal. Calcd for $C_{13}H_{14}O_2N_2F_6$ Cu: C, 38.3; H, 3.4; N, 6.89. Found: C, 37.5; H, 5.8; N, 7.03.

Diethyl (ethylenebis-β-aminocrotonate). A 26.0-g (0.2-mole) sample of ethylacetonacetate was treated with 6.0 g (0.10 mole) of ethylenediamine in

the manner described above for the preparation of bistrifluoroacetylacetone-ethylenediimine. The product was obtained in the form of nearly colorless needles weighing 25.0 g, which represents 93% of the theoretical yield. It was recrystallized from aqueous ethanol.

Anal. Calcd for $C_{14}H_{24}N_2O_4$: C, 59.2; H, 8.4; N, 9.85. Found: C, 59.4; H, 8.4; N, 9.6.

Absorption Spectra

Visible and ultraviolet absorption spectra were measured with a Cary Model 11 recording spectrophotometer, or with a prototype of the Beckman DK1 Recording Spectrophotometer, and with quartz cells of 1 cm thickness. The solutions were made up to 0.0100 M concentration by weight and progressively diluted with syringe-type pipettes until the proper concentration for absorption measurements was obtained. The spectroscopic solvent used was Eastman Kodak No. S337 Spectro-Grade chloroform.

The infrared measurements were made with a Model 21 Perkin-Elmer Recording Double-Beam Spectrophotometer with NaCl optics. All ligands and chelate compounds were measured anujol mulls.

Experimental Results

The structures of the ligands actually prepared in this investigation are indicated in Table I. In all cases the procedures employed in their preparation were sufficiently different from those of previous investigators to warrant the brief description given in the experimental part.

The ultraviolet absorption spectra of the ligands are given in Fig. 1, and those of the corresponding Cu(II) chelates are illustrated in Fig. 2. The visible absorption spectra of the metal chelates are given in Fig. 3. In these diagrams, the molar extinction coefficient was determined on the basis of the assumed molecular weight of the compound, and was plotted vs wave length in mμ. In Table II are listed the wave lengths of the absorption maxima found in the visible and ultraviolet regions, and the corresponding approximate molar extinction coefficients. Frequencies are enclosed in parentheses in cases where the band is weak and occurs as a shoulder or irregularity on a much stronger band.

The infrared absorption frequencies of both the ligands and the metal chelates are given in Table III, with the very weak or doubtful bands indicated in parentheses. The bands have been marked arbitrarily as weak or strong on the basis of the appearance of the spectra.

TABLE I

Ligands and metal chelates of this study

Name of ligand	Formula			References	
	R	R^1	n	Ligand	Cu(II) Chelate
Bisacetylacetone-ethylenediimine	CH_3	CH_3	2	5, 7	6, 7
Bistrifluoroacetyl-acetoneethylenediimine	CH_3	CF_3	2	7	7
Bisacetylacetone-trimethylenediimine	CH_3	CH_3	3	7	7
Bistrifluoroacetyl-acetonetrimethylenediimine	CH_3	CF_3	3	--	--

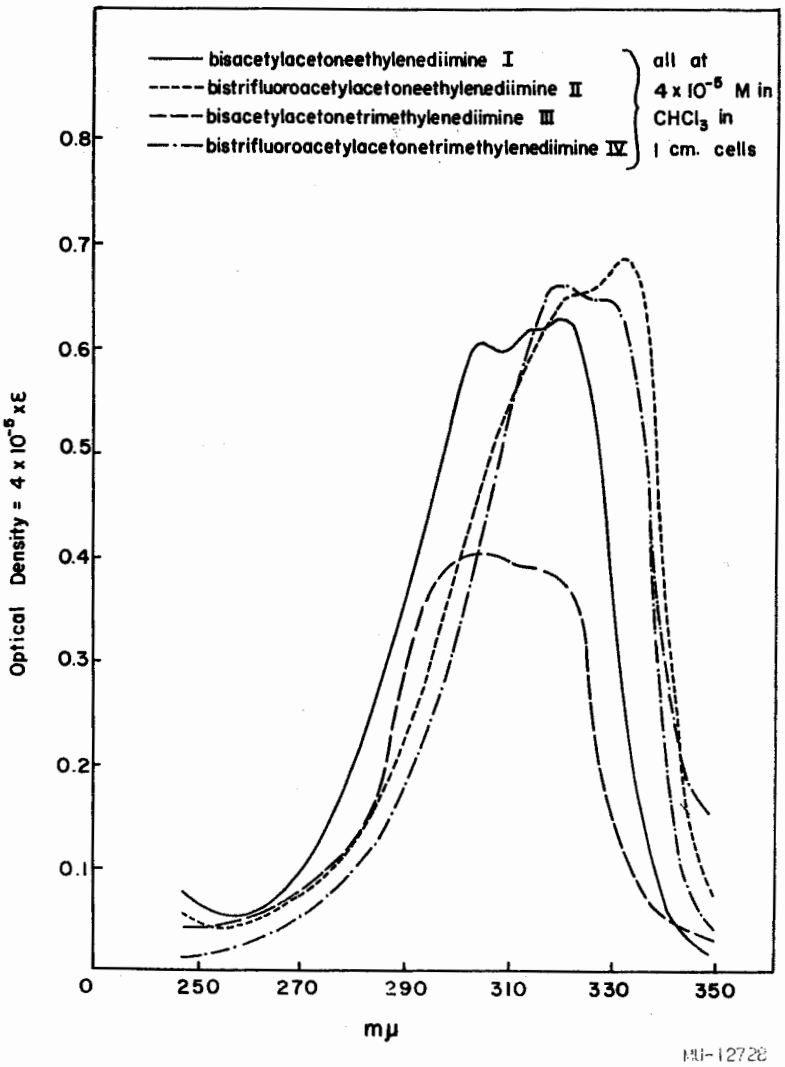


Fig. 1. Ultraviolet absorption spectra of ligands

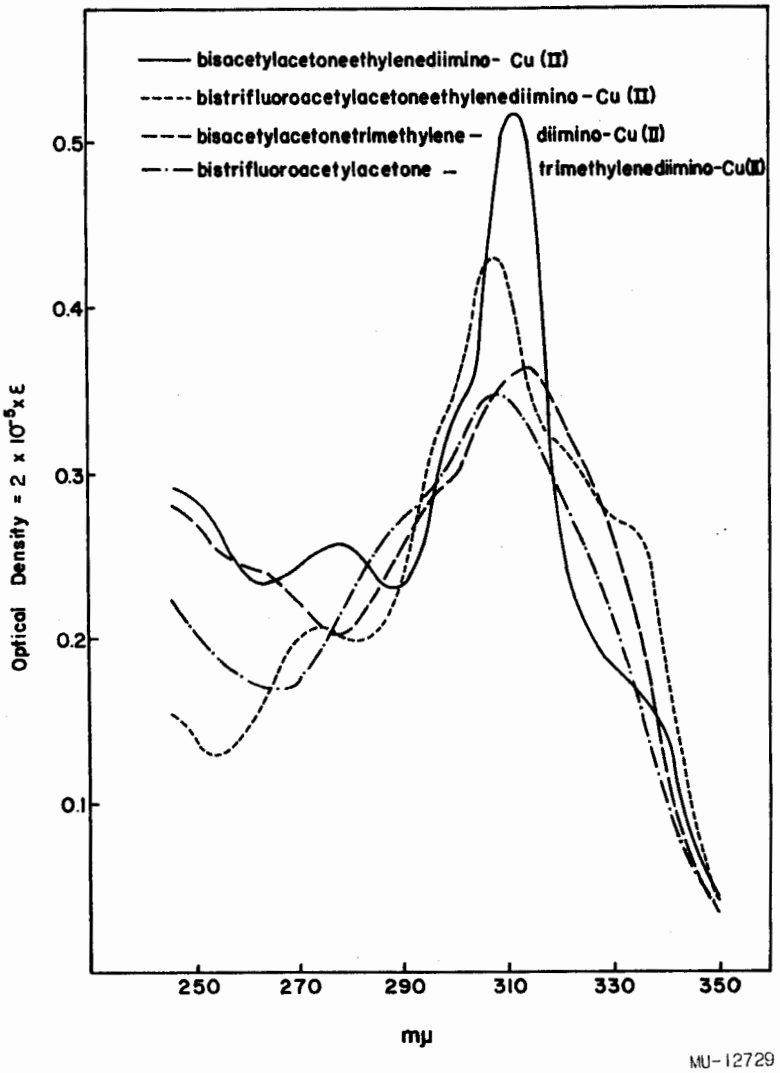


Fig. 2. Ultraviolet absorption spectra of metal chelates

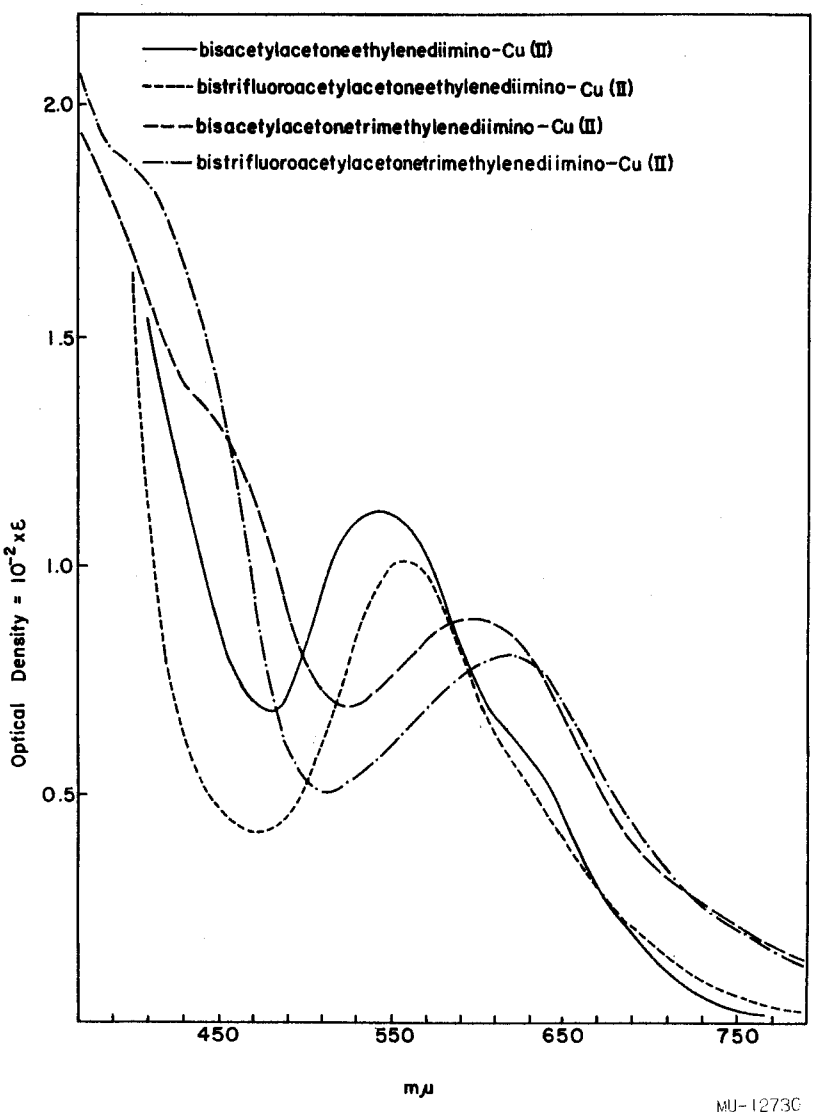


Fig. 3. Visible absorption spectra of metal chelates.

TABLE II

Absorption Bands of $CHCl_3$ Solutions in the Visible and Ultraviolet Regions

Compound	Molarity	λ_{max}	ϵ_{max}
I Bisacetylacetoneethylenediimine	4×10^{-5}	305	15, 000
	4×10^{-5}	321	15, 800
II Bistrifluoroacetylacetone-ethylenediimine	4×10^{-5}	322	16, 200
	4×10^{-5}	337	17, 000
III Bisacetylacetonetrimethyl-enediimine	4×10^{-5}	305	10, 000
		320	9, 500
IV Bistrifluoroacetylacetone-trimethylenediimine	4×10^{-5}	321	16, 500
	4×10^{-5}	331	16, 100
V Bisacetylacetoneethylenediimino-Cu(II)	2×10^{-5}	(~246)	------
		276	13, 000
		(299)	------
		312	26, 000
		(336)	------
	10^{-2}	543	112
		(635)	---
VI Bistrifluoroacetylacetoneethylene-diimino - Cu(II)	2×10^{-5}	274	10, 600
		(295)	------
		308	21, 600
		(326)	------
		(334)	------
	10^{-2}	555	101
VII Bisacetylacetonetrimethylenediimino-Cu(II)	2×10^{-5}	(258)	------
		(298)	------
		314	18, 500
	10^{-3}	375	950
	10^{-2}	(460)	------
		600	89
VIII Bistrifluoroacetylacetonetrimethylene-diimino - Cu(II)	2×10^{-5}	(290)	------
		308	17, 500
	10^{-2}	(450)	------
		618	81

TABLE III

Infrared Absorption Bands of Nujol Mulls*

Region	I	II	III	IV	V	VI	VII	VIII	IX
	eA	eT	tA	tT	Cu-eA	Cu-eA	Cu-tA	Cu-tT	
C-H,						(3400)	3500 s	(3360)	
N-H	3120 b	3140 s	(3220)	3160 s		(3140)			3260 s
	(2700)b	(3060)							
	(2320)	(2340)	(2350)	(2320)	(2320)	(2350)	(2340)	(2340)	
									1730 w
		(1710)	(1665)				1673 s		1645 s
C___O,	1615 s	1612 s	1610 s	1615 s		1627 s	1645 w	1631 s	1607 s
C___C,	1585 s	1585 s	1570 s	1590 s	1592 s	1573 s	1588 s		1565 w
								1552 s	1545 w
C___N	(1550)	1533 s	(1550)	(1550)		1545 s	(1535)	(1515)	1510 s
	1525 s	(1510)	1516 s	1525 w	1515 s	(1510)	1512 s	(1490)	
			1448 s	1450 s	1440 w	(1443)	1415 s	(1452)	1445 s
		1395 w	1357 s	1395 w	1422 s		1360 s		1368 w
C-N	1360 w	1345 w	(1300)	1365 w	1356 s				1338 s
			1320 w	1317 w		1300 s	1325 w	1305 s	1305 s
	1295 s	1287 s	1285 s	1292 s	1285 s		1283 s	1273 w	1290 s
	1258 w	1267 w	1247 s	1250 s	(1255)	1256 s	1253 s	1255 w	1270 s
	1227 w	1248 s	1215 s		1229 s	1228 s	1235 s		
C-C							1217 s	1218 s	1225 s
	1208 w	1208 s	1200 w		(1215)		1200 s		
		1190 s		1195 s		1183 s		1192 s	1183 w
						1150 s	1145 s	1178 s	1168 s
		1135 s	1140 s	1137 s		1130 s	(1130)	1151 s	1150 s
	1145 w							1128 s	
		1120 s		1115 s	1117 s	1105 w		1100 s	1115 s
	1087 s	1080 s	1092 s	1085 w	1073 s	1093 s	1090 w	1087 w	1092 s
	1020 s	(1055)		1070 w	1043 s	1073 w	1043 s		1067 s
			1028 s	1025 w	1028 w	(1035)	1020 s	1023 w	(1037)
		1007 w	1000 s		1018 s	1020 w	1000 w		1020 s
	975 s		975 w	990 w	988 s		(970)	(970)	978 s
			956 s		948 s	(950)	955 w		
	940 w	943 s	933 s	903 s			945 s		
							(932)		935 w
		880 s	887 w	888 s	(880)	897 s		895 s	
	850 s	(870)	865 w	875 s			872 s	865 w	
				848 s		845 s			830 w
	835 w	832	(830)	830 w					
				803 w	805 w				
		780 w	780 s	785 s		792 s	(792)	783 w	777 s
		775 s		767 s		787 s	785 s	773 s	
	740 s		750 s		753 s	742 w			757 w
		755 s		747 s			750 s	733 s	
	720 w								
		723 s	725 s	725 s	738 s	732 s	(740)	720 w	720 s
			645 w		670 w		670 w	(660)	
					645 w				

* eA = ethylene diimine-bis-Acetylacetone
eT = ethylene diimine-bis-Trifluoroacetylacetone
tA = trimethylene diimine-bis-Acetylacetone
tT = trimethylene diimine-bis-Trifluoroacetylacetone

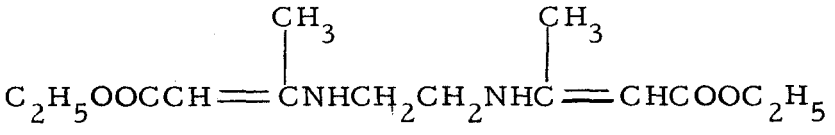
Bands are classed arbitrarily as "s"-strong; "w"-weak; or "b"-broad.

Discussion

Preparation of Ligands and Cu(II) Chelates

The methods employed in the investigation reported here differ from those previously reported in the use of ethanol as a moderator for the formation of the Schiff bases, and in the use of aprotic solvents for their recrystallization. For these reasons, the yields of the ligands appear to be somewhat better than those reported by McCarthy et al.[4]

All attempts to prepare Schiff bases of hexafluoracetylacetone, ethylacetoacetate, and ethyltrifluoroacetoacetate resulted in failure. In the case of ethylacetoacetate the reaction product with ethylenediamine proved to be the diethyl ester of ethylenebis-β-aminocrotonate (Formula III). This substance was found to produce a deep blue solution when attempts were made to convert it to the chelate by the dioxane method.



III

On dilution with water, however, cupric hydroxide precipitated. Apparently the metal chelate formed in the organic phase is relatively unstable, and breaks up in water solution.

Since no condensation was obtained between hexafluoroacetylacetone and ethylene-diimine, an attempt was made to prepare the desired chelate compound directly by combining cupric acetate with ethylenediamine and hexafluoroacetylacetone under varying conditions of solvent and temperature. In all cases the only reactions that were detectable corresponded to separate reactions of the metal ion with ethylenediamine and with the β-diketone.

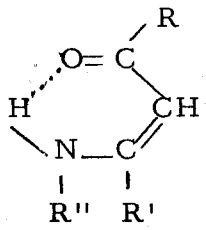
The general procedure employed for the preparation of the metal chelates, involving formation of the compound in dioxane and precipitation by the addition of water, differs considerably from the methods previously employed, which usually involved combination of the ligand with the freshly-precipitated metal hydroxide or hydrous oxide.[4] The method used in this investigation gives yields that are at least as good as those previously described.

It is interesting to note that the Cu(II) chelate of bistrifluoroacetylacetone-ethylenediimine was obtained in two forms by fractional crystallization from chloroform and ligroin. The less soluble red form, had a melting point 66° higher than the more soluble blue compound. The infrared, ultraviolet, and visible spectra (in chloroform) were found to be identical, and analytical results were also the same within experimental error. These substances, therefore are probably crystal modifications of the same compound.

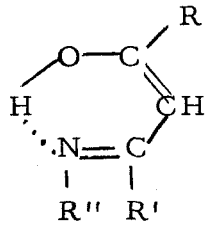
In accordance with its lower solubility and higher melting point, it is possible that the red modification involves intermolecular interactions that are absent in the blue one, and that these interactions probably involve metal-metal forces. That the red color is lost in such polar solvents as chloroform and acetone seems to support this point of view, particularly since both substances give identical blue solutions.

Ultraviolet Absorption Spectra

All the ultraviolet absorption spectra in Figs. 1 and 2 are high-intensity K-type bands arising from electronic transitions in conjugated systems of the type shown in Formulas I and II. The characteristic double bands of the ligands would at first seem to arise naturally enough from the two tautomeric forms possible for each H-bonded ring of the ligand, indicated by Formulas IV and V.



IV



V

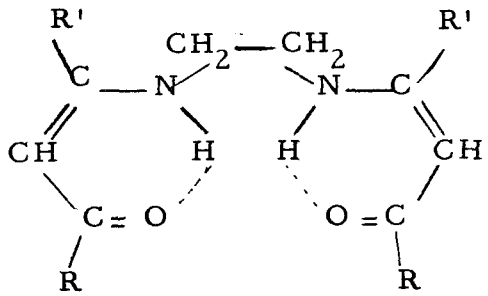
Independent measurements by Ueno and Martell[7] have shown that the relative intensities of the two bands are only slightly altered in 0.1 M NaOH solution. It seems probable, therefore, that each band is due to electronic transitions in the single conjugated system

$$R''N = C\text{-}CH = C - O^- \longleftrightarrow R''\ddot{N}\text{-}C = CH\text{-}C = O,$$

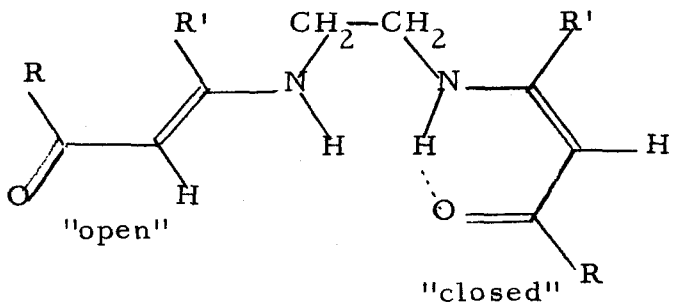
and that this is perhaps not very much affected by H-bonding to the oxygen or nitrogen.

The presence of two or three bands may possibly arise from different relative arrangements of the two conjugated systems arising from rotation through the ethylene or trimethylene bridge. Thus, the H-bonded rings may be relatively far apart as in Formula I, or close together as in Formula VI. This may be coupled with differing interactions arising from the isomeric "closed" or "open" forms as in Formula VIa.

[7] K. Ueno and A. E. Martell, J. Phys. Chem., 61 000 (1957).



VI



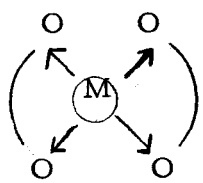
VIa

As with the bidentate ligands discussed previously,[1] the effect of introducing one trifluoromethyl group is to increase the wave lengths of the absorption maxima, and to increase somewhat the tendency to enolize. Because of the lack of a considerable increase in intensity on the addition of alkali, noted above, it seems that all the ligands are nearly completely enolized. As a first approximation, it seems that bisacetylacetone-ethylenediimine must be at least 90% enolized. If one then assumes that the corresponding trifluoro compound is 100% enolized, it is apparent from the relative absorption coefficients listed in Table II that substitution of the trifluoromethyl group results in little or no increase in the absorption intensity. It seems more logical, therefore, to assume complete enolization of both ligands derived from ethylenediamine, and an increase of 10% in the intensity of the absorption resulting from the introduction of a trifluoromethyl group at one end of the conjugated system.

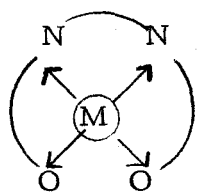
The large increase of intensity observed as the result of introduction of a trifluoromethyl group into the Schiff base derived from trimethylenediamine could be due to relatively incomplete enolization of the parent compound, and to what appears to be complete enolization of the trifluoromethyl derivative.

Unlike the bidentate ligands described previously, the ultraviolet spectra of the metal chelates of the Schiff bases bear little resemblance to those of the ligands. Instead of the simple double or triple bands present in the ligand, the metal chelates have complicated systems of at least five bands in each case, with one of much higher intensity than the others. The absorption curves shown in Fig. 2 indicate that the spectra can be divided into two similar pairs: (a) those involving the Schiff bases derived from ethylenediamine; and (b) the chelates derived from trimethylenediamine. It is apparent that changing the number of carbons in the hydrocarbon bridge from two to three has a greater influence on the spectra than substituting a trifluoromethyl group in each six-membered metal chelate ring.

It is perhaps not unreasonable that the spectra of the tetradentate chelates should differ so greatly from those of the β-diketones, when one considers the differences in the arrangement of the dipoles and charges in these two classes of compounds. If one makes the reasonable assumption that both classes of chelate compounds are square planar, one has the following arrangements of dipoles and charges about the metal ion:



Bidentate Chelate



Tetradentate Chelate

Thus, it is seen that the influence of the metal on the bidentate β-diketones is more symmetric than the effect on the ends of the conjugates systems in the Schiff bases. The greater number of distant pi-system energy levels in these compounds, indicated in Fig. 2, is probably related to that decreased symmetry.

Visible Spectra

The absorption spectra of the copper(II) chelates in the visible region, shown in Fig. 3, are similar to those of the copper(II) chelates of the bidentate ligands, and presumedly arise from the same type of 3d orbital transitions. One would expect that the polar fields of the donor atoms of the Schiff bases would be more effective than the simple β-diketones in removing the d-orbital degeneracy of Cu(II) because of the greater interaction of the former with the metal ion. That this is actually the case may be seen qualitatively in the fact that the frequencies of the principal absorption bands in the visible region occur at much shorter wave length and are much more intense for the Schiff bases. In some cases the absorption maxima of the β-diketone is found displaced 100 mμ or more toward longer wave length than that of the Schiff base derived from the same β-diketone.

The absorption spectra in Fig. 3 indicate that the influence of trifluoromethyl groups is to shift the absorption bands of the metal chelates to longer wave lengths. This is in the same direction as the shifts observed in the Cu(II) chelates derived from the bidentate ligands. As indicated previously, this shift to the red correlates with a decrease in stability of the metal chelate and decreased interaction of the charges of the ligand with the electrical field of the metal ion.

Perhaps even more interesting is the greater increase in wave length of the visible copper(II) band when the ethylene bridge is replaced by a three-carbon chain. It is well known that increasing the size of the metal chelate ring formed between the two basic nitrogen atoms decreases the stability of the chelate compound. The common explanation of this correlation between stability and ring size, involving an entropy effect, does not seem

to offer an explanation of the shift in the spectra. Unlike the trifluoromethyl groups, which obviously influence the donor-metal interaction by an inductive removal of electrons, it is difficult to see how the size of the aliphatic chelate ring, per se, could affect so greatly the metal ion transitions. However, it is obvious from the shifts in Fig. 3 that the influence of increasing ring size is greater than that resulting from the substitution of trifluoromethyl groups on the ligand, in agreement with the conclusions drawn above from the ultraviolet spectra. A possible explanation would be that steric considerations involving the three metal chelate rings as a whole might actually force the nitrogens closer to the Cu(II) ion when the central (diamine) ring contains five members than when the ring contains six atoms. Greater proximity between the nitrogens and the Cu(II) ion in the ethylene diamine derivatives would result in more spreading of the d-orbital energy levels of the Cu(II) by the amino group charges and dipoles. It is quite likely that insertion of an extra methylene into the enthylenediamine bridge produces some more profound change in the chelate bi-ring structure.

Infrared Spectra

All the free ligands have a broad absorption band near 3150 cm^{-1} which is assigned to the NH or OH stretching frequency. The broadness of these bands is a good indication that the group is involved in hydrogen-bond formation.

The effect of introducing CF_3 groups in the ligands results in a higher NH or OH stretching frequency, possibly indicating weaker hydrogen bonds. This effect may be due to the interference of the electron-attracting trifluoromethyl group with the resonance of the conjugated system to which it is attached. It is also possible that the basicity of the donor atoms is also decreased sufficiently by fluorine substitution to affect hydrogen bonding, or that the frequency shift is primarily the result of direct influence through the hydroxyl oxygen or amino nitrogen.

The foregoing assignment of the broad bands in the 3200 to 3100 cm^{-1} region is further strengthened by the disappearance of these bands in the metal chelates, in which the enolic or amino hydrogens are completely displaced by the copper(II) ion.

It is interesting that, unlike the β-diketones discussed previously, the Schiff-base ligands in the investigation presented here do not show free carbonyl bands. All the Schiff bases have strong bands in the frequency range 1610 to 1615 cm^{-1}, which can only be due to H-bonded carbonyl stretching vibrations. These appear at lower frequencies than do the corresponding bands of the β-diketones, indicating stronger hydrogen bonding in the former compounds.

Another band, in the region 1570 to 1585 cm^{-1} sometimes occurring with a subsidiary band, may be assigned to C=C stretch in the H-bonded rings. It is to be noted that these frequencies are considerably lower than the corresponding bands of acetylacetone and other β-diketones, possibly as a result of stronger resonance of the conjugated rings in the Schiff bases.

The bands appearing at 1525 ± 1 cm^{-1} are assigned to C=N stretching vibrations, displaced from their usual positions at 1690 to 1640 cm^{-1} as the result of strong hydrogen bonding. These absorptions are, of course, absent in the spectra of the β-diketones discussed in the first paper of this series. The band appearing at 1510 cm^{-1} in the spectrum of the crotonic acid derivative, Formula V, is probably not due to >C=N stretch, since this group must be absent, but may be due to an N-H deformation vibration, which usually appears in this region. Although these assignments correspond to those of Ueno and Martell[8] for a somewhat different series of compounds, it is quite possible that the true C=C and C=N assignments have been inverted in all Schiff bases.

The bands observed in the 1300–1500 cm^{-1} region are likely CH_3 and CH_2 deformation vibrations. A number of bands in the 1120–1282 cm^{-1} region, which appear only in the spectra of the trifluoro derivatives, may be assigned to C-F stretching vibrations.

The structure assigned to the crotonic acid derivative, Formula III, is in conformity with the presence of the ester carbonyl band at 1730 cm^{-1}, as well as a band at 1645 cm^{-1} which may be due to the H-bonded carbonyl group. The lower-frequency bands may be due to C=C stretching vibrations of the various modifications (H-bonded, etc.) that are present. There may even be weak contributions from small amounts of the imino tautomer.

This work was done under the auspices of the U.S. Atomic Energy Commission.

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[8] K. Ueno and A.E. Martell, J. Phys. Chem. 59, 998 (1955).