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Electronic Spectra of β-Diketone Complexes. IV. γ-Substituted Acetylacetonates of Copper(II)

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The electronic spectra of a series of γ-substituted acetylacetonates of copper(II) are presented and discussed with the aid of Hückel molecular orbital calculations. Evidence is presented which substantiates the assignment of the band at ~296 mμ to a $\pi-\pi^*$ transition. Several new complexes are reported in this work.

In part III of this study,[2] the ultraviolet spectra of a series of α-substituted β-diketone complexes of copper(II) were discussed. In this paper we report the spectra of an extensive series of γ-substituted acetylacetonates of copper(II). Particular attention is given to the origin of the band[3] at ~296 mμ. Several of the complexes reported in this work are not described elsewhere, hence their preparation and characterization is presented in detail.

TABLE I

ANALYSIS OF COPPER(II) COMPLEXES OF γ-SUBSTITUTED ACETYLACETONE

γ-Substituent	Method of prepn.	Carbon (%)	Hydrogen (%)	Other (%)
CH_3	[c]	49.3 (49.7)[a]	6.3 (6.3)	
$CH_2—CH{=}CH_2$	[j]	56.1 (56.2)	6.3 (6.5)	
Cl	[d]	36.3 (36.3)	3.6 (3.7)	
Br	[e]	28.7 (28.6)	2.9 (2.9)	
NO_2[b]	[f]	34.3 (34.2)	3.4 (3.4)	N, 7.9 (8.0)
OCH_3	This work	44.7 (44.7)	5.6 (5.6)	
$NHCOCH_3$	This work	44.7 (44.7)	5.5 5.4)	N, 7.5 (7.5); Cu, 17.0 (17.0)
$OCOCH_3$	This work	44.3 (44.4)	5.2 5.1)	Cu, 17.0 (16.8)
CN	[g]	46.0 (46.2)	3.8 (3.9)	N, 9.0 (9.0)
$COOC_2H_5$	[h]	47.2 (47.3)	5.6 (5.5)	Cu, 15.1 (15.69)
$CH{=}CH—C_2H_5$	This work	58.5 (58.4)	7.2 (7.1)	
H	[i]	46.0 (45.9)	5.5 (5.4)	Cu, 24.3 (24.3)

[a] Calculated value in parentheses. [b] Bis-(3-nitro-2,4-pentanediono)-beryllium(II), m.p. 195–200°, was prepared in 38% yield utilizing a similar reaction. Only one proton n.m.r. peak was observed confirming substitution at the 3-position. [c] R. M. Mannyik, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 5030 (1953); G. T. Morgan and A. E. Rawson, *J. Soc. Chem. Ind.*, **44**, 462T (1925); R. B. Davis and P. Hurd, *J. Am. Chem. Soc.*, **77**, 3284 (1955). [d] M. Suzuki and M. Nagawa, *J. Pharm. Soc. Japan*, **73**, 394 (1953); *Chem. Abstr.*, **48**, 3295d (1954). [e] H. F. Holtzclaw and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3322 (1957). [f] C. Djordjevic, J. Lewis, and R. S. Nyholm, *Chem. Ind.* (London), 122 (1954). [g] J. P. Fackler, Jr., *J. Chem. Soc.*, 1957 (1962). [h] A. Spassow, *Org. Syn.*, **21**, 46 (1941). [i] W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957). [j] B. B. Martin and W. C. Fernelius, *J. Am. Chem. Soc.*, **81**, 2342 (1959).

Experimental

Preparation of Materials.—Several of the complexes used in this study were prepared by well established methods, for which references are listed in Table I. Analyses for carbon, nitrogen, and hydrogen were performed by S. M. Nagy, M.I.T., and Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Bis-(3-methoxy-2,4-pentanediono)-copper(II). Method A.—Diazoacetylacetone,[4] 2.5 g. (0.02 mole), dried over calcium sulfate, was cooled to −70° in a small tube. Boron fluoride etherate, 8 g. (Eastman), was added and the mixture warmed to allow solution, then quickly cooled. Thirteen ml. of methanol (absolute) was added and the solution slowly warmed to room temperature and allowed to stand for ~3.5 hr. The volume was reduced by approximately one third at 65° and, after cooling to 10°, dry potassium fluoride, 6 g., was added with shaking. After adding 25 ml. of ether, 20 ml. of water was slowly added, heat being evolved. The ether layer was removed and the solution extracted with an additional 10 ml. of ether. Ten ml. of water was added to the solution and the extraction repeated. The ether layers were combined and dried. Distillation gave ~0.5 g. (20% yield) of the diketone, b.p. ~50° (6 mm.); n^{22}D 1.4476. This small amount of liquid was not purified further. The copper(II) complex, m.p. ~180°, and the 2,4-dinitrophenylhydrazine derivative, m.p. 200–203°, were formed as described in method B.

Method B.—With vigorous stirring, glacial acetic acid, 48.0 g. (0.8 mole) at 0° was saturated with gaseous boron fluoride until a powdery white solid formed. A mixture of 17.6 g. (0.2 mole) of methoxyacetone[5] and 0.8 g. (0.4 mole) of acetic anhydride (Eastman) was added to the stirred powder during 10 min. The ice bath was removed after 0.5 hr. and stirring was continued for 4 hr. The mixture was shaken with aqueous sodium acetate (100 ml. of a saturated solution) and extracted with six 60-ml. portions of ether. The ether extracts were combined and washed with aqueous sodium bicarbonate, then water, and dried. Distillation gave 3.5 g. (13% yield) of the diketone, b.p. 43–70° (15 mm.). Approximately 2 g. of the material distilled at 65–68° (15 mm.), n^{22}D 1.4515. The 2,4-dinitrophenylhydrazine derivative (pyrazole) was formed in ethanol, m.p. 205–207°.

To form the copper(II) complex, methoxyacetylacetone was added to a slight excess of saturated aqueous copper(II) acetate. The complex did not precipitate so the aqueous solution was extracted with chloroform. The green chloroform solution was evaporated to dryness after dehydrating with magnesium sulfate. The complex was dried thoroughly under vacuum at 70° and redissolved in chloroform. This solution was filtered to remove some copper acetate present and evaporated. Recrystallization was accomplished from a 1:1 toluene–ligroin mixture. The complex appears to be hygroscopic, especially when powdered. When dry it is soluble in most organic solvents. The copper complex, prepared from method A, gave no "free" carbonyl band in the infrared.[6]

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(1) Communications regarding this paper should be directed to J. P. F., Department of Chemistry, Case Institute of Technology, Cleveland, Ohio.

(2) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

(3) R. Linn Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(4) L. Wolff, *Ann.*, **325**, 139 (1902). The compound shows an infrared band at 2125 cm.$^{-1}$, characteristic of a diazo group.

(5) R. P. Marietta and J. L. Leech, *J. Am. Chem. Soc.*, **71**, 3558 (1949).

(6) By modifying method A, hydrolyzing the methanol solution containing boron fluoride and diazoacetylacetone with aqueous copper(II) acetate, bis-(3-acetoxy-2,4-pentanediono)-copper(II) was obtained instead of the expected methoxy derivative.

Anal. Calcd. for $CuC_{12}H_{18}O_6$: C, 44.68; H, 5.64. Found: Method A: C, 44.68; H, 5.64. Method B: C, 44.68; H, 5.56.

To determine if the condensation of methoxyacetone with acetic anhydride produced the desired γ-derivative, 1-methoxy-2,4-pentanedione was prepared[7] and its properties compared with that of the products obtained by methods A and B. In accord with expected differences between properties of α- and γ-substituted β-diketones, materials from methods A and B gave purple ferric chloride tests and a green copper(II) derivative while the α-methoxy diketone gave a red ferric chloride test and a blue copper(II) derivative. Other properties including infrared spectra showed the materials from methods A and B to be identical and different from 1-methoxy-2,4-pentanedione.

Bis-(N-acetyl-3-amido-2,4-pentanediono)-copper(II).—Since "isonitrosoacetylacetone," $(CH_3CO)_2CNOH$, is known to produce $(CH_3CO)_2CHNH_3Cl$ in acid solution upon reduction with zinc,[8] a procedure[9] similar to that used to form the N-acetyl-2-amido derivative of ethylacetoacetate was used here.

Eighty g. (0.61 mole) of 3-oxime-2,4-pentanedione,[4] m.p. 74°, was placed in a 2000-ml. flask fitted with a condenser, stirrer, and thermometer. Glacial acetic acid, 50 ml., anhydrous ethyl ether, 400 ml., and acetic anhydride, 130 g. (1.28 mole), were added. The solution was stirred vigorously and 80 g. of zinc dust was added slowly over a period of 1.5 hr., maintaining a temperature between 40 and 50°. Stirring was continued an additional 2 hr. at 50°, after which the solution was cooled, filtered, and evaporated under reduced pressure. When evaporation was complete, 100 ml. of water was added and removed by evaporation. The last procedure was repeated three times giving ~75 g. (79% yield) of crude product. Since the material appeared to be somewhat hygroscopic, purification was difficult but was accomplished by crystallization, first from benzene using activated charcoal, followed by two crystallizations at −50° from 1:1 ethyl ether–alcohol and a final crystallization from benzene–ligroin. Ten g. of pure material, m.p. 97°, was recovered.

Anal. Calcd. for $C_7H_{11}O_3N$: C, 53.17; H, 7.10. Found: C, 53.71; H, 7.01.

The copper(II) complex was obtained by dissolving 10 g. of the ligand in 35 ml. of hot water containing 6.5 g. of copper(II) acetate monohydrate and evaporating. The solution–evaporation procedure was repeated with water, twice with 95% ethanol, and twice with absolute ethanol, followed by a crystallization from 2:1 ethanol–ether. The green product, 7.1 g., was dried at 60° *in vacuo* and recrystallized from a minimum quantity of ethanol upon addition of an equal volume of *t*-butyl alcohol.

Anal. Calcd. for $CuC_{14}H_{20}O_6N_2$: C, 44.73; H, 5.36; N, 7.46; Cu, 16.95. Found: C, 44.66; H, 5.49; N, 7.47; Cu, 17.0.

A KBr disk infrared spectrum showed bands characteristic of β-diketone complexes as well as peaks at 1650 cm.$^{-1}$ (amide carbonyl) and 3260 cm.$^{-1}$ (N–H stretch). The ultraviolet spectrum confirmed the presence of the usual six-membered chelate ring formed with β-diketones.

Bis-(3-acetoxy-2,4-pentanediono)-copper(II).—γ-Acetoxyacetylacetone was prepared from lead tetraacetate and acetylacetone using the method of Cocker and Schwarz[10]; b.p. 101–120° (15 mm.), $n^{24}D$ 1.4386 (lit.,[18] b.p. 100–105° (15 mm.)). A 4.5-g. sample of the product (0.027 mole) was dissolved in 10 ml. of ethanol and saturated aqueous cupric acetate was added until precipitation was complete. The gray precipitate was recrystallized from ethanol containing a few drops of chloroform; yield, 3.9 g. (73%).

Anal. Calcd. for $CuC_{14}H_{18}O_6$: C, 44.38; H, 5.06; Cu, 16.8. Found: C, 44.26; H, 5.19; Cu, 17.0.

Spectral evidence strongly favors the usual six-membered chelate structure for this complex. An ester carbonyl peak is observed at 1775 cm.$^{-1}$ in the infrared.

Bis-(3-Δ'-butenyl-2,4-pentanediono)-copper(II).—An approximately 50% yield of γ-butylideneacetylacetone,[11] b.p. 83–85.5° (9 mm.) (lit.[11] 81–83° (8 mm.)) was obtained by the reaction of *n*-butyraldehyde with acetylacetone according to the method of Payne.[11]

The copper(II) complex was formed by filtering a solution containing 4 g. of copper(II) acetate in 25 ml. of water into 100 ml. of ethanol containing 6 g. of γ-butylidenecetylacetone. The green precipitate which formed was redissolved by warming the solution. After cooling overnight, the green, crystalline complex was filtered off, washed with water, and crystallized from an ethanol–water solution, followed by two recrystallizations from cold benzene with the addition of ligroin. The complex, which has not been reported previously, appeared to decompose in benzene when the solution was heated; m.p. 141.5° with decomposition.

Spectral Measurements.—Ultraviolet and visible spectra of the copper(II) complexes were obtained as described in part III.[2]

Results

In part III[2] the spectrum of a typical β-diketone complex, bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-copper(II), was presented. The spectra of the γ-substituted complexes are generally similar and will be discussed in terms of the five clearly separated bands, I–V. Table II lists the wave lengths and intensities observed for these bands in chloroform and cyclohexane. In only three cases was it possible to observe the high energy band I with the γ-substituted derivatives because of their limited solubility in cyclohexane.

The position of band II is found to vary only slightly with changes in the γ-substituent but band III shifts markedly to longer wave lengths with increasing *ortho–para* (toward benzene) directing capabilities of the group. A poorly resolved shoulder is found on band III, ~20 mμ to longer wave lengths from the maximum. In some cases it was impossible to establish clearly the presence of this shoulder due to overlap with the main peak.

The ultraviolet tail of band III extends considerably into the visible region of the spectrum in many of the γ-substituted complexes. This accounts for the gray-green color which seems to be characteristic of the γ-substitution in β-diketone complexes of copper(II). When the ultraviolet tail is subtracted, the visible spectrum (bands IV and V) is similar to the spectrum of the unsubstituted copper(II) acetylacetonate except in the case of bis-(3-cyano-2,4-pentanediono)-copper. In the latter complex only one rather broad band is observed (Fig. 1) reminiscent of the spectrum[2] of the hexafluoroacetylacetonate complex.

Discussion

The primary purpose of this investigation was to determine the effect of γ-substituents on the 296 mμ

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[7] M. Renard and A. Maquiney, *Bull. soc. chim. Belges*, **55**, 98 (1946).

[8] H. Henecka, ' Chemie der Beta-Decarbonyl Verbindungen," Springer-Verlag, Berlin, 1950, p. 330.

[9] H. O. House, private communication.

[10] W. Cocker and J. C. P. Schwarz, *Chem. Ind.* (London), 390 (1951).

[11] G. B. Payne, *J. Org. Chem.*, **24**, 1830 (1959). Payne showed that γ-butylideneacetylacetone has properties characteristic of enolized β-diketones, *e.g.*, a positive ferric chloride test. He indicated the structure to be C_2H_5—CH═CH—C_R═C(OH)CH_3, R = $COCH_3$. In discussing the copper(II) complex, we will name the ligand as 3-Δ'-butenyl-2,4-pentanedione, after its tautomeric isomer.

TABLE II

SPECTRA OF γ-SUBSTITUTED ACETYLACETONATE COMPLEXES OF COPPER(II)

		λ (mμ); log ϵ				
R_3	Solvent	I	II	III	IV	V
CN	$CHCl_3$	...	243; 4.127	294.2; 4.396 (305)[d]		650; 1.718
NO_2	$CHCl_3$	...	246; 4.061	295.2; 4.380 (308)		650; 1.785[a]
H	$CHCl_3$	...	246; 4.198	296.0; 4.415 [310; 3.7]	...	...
$COOC_2H_5$	$CHCl_3$	...	244; 4.233	296.2; 4.387 (310)	555; 1.580	660; 1.623
$NHCOCH_3$	$CHCl_3$	...	243; 4.042	299.5; 4.301 [319; 3.6]		640; 1.681[a]
$OCOCH_3$	$CHCl_3$	...	...	305.7; 4.480 (320)	(550); 1.505	670; 1.577
$CH_2CH{=}CH_2$	$CHCl_3$	...	245.5; 4.049	308.0; 4.461 (324)	...	...
	C_6H_{12}	205; 3.832[b]	246.0; 3.992	308.1; 4.346 (322)	...	...
Br	$CHCl_3$	...	248; 4.185	308.4; 4.413 ...	...	...
CH_3	$CHCl_3$	...	...	309.6; 4.442 ...	...	...
	C_6H_{12}	200; 4.20[b]	243.5; 4.076	309; 4.417 ...	(510); 1.653	650; 1.664
$CH{=}CHC_2H_5$	$CHCl_3$	...	245; 4.225	313; 4.505 ...	(530); ...[c]	660; 1.706
Cl	$CHCl_3$	...	...	313.4; 4.439 (330)	(540); ...[c]	670; 1.607
OCH_3	$CHCl_3$	...	...	315.0; 4.471 [329; 3.3]	(530); ...[c]	660; 1.628
	C_6H_{12}[b]	206.5; ...	243.5; ...	314.2; ... (328)	...	...
C_2H_5	C_6H_{12}	206.5; 4.18	245; 4.041	309; 4.375	...	...

[a] Solvent contained 20% ethanol. [b] Saturated solution. [c] Very strong ultraviolet overlap. [d] Parentheses indicate shoulders and brackets enclose values obtained by approximate gaussian analysis.

band in copper acetylacetonate. This band is thought to be a π–π^* transition of the ligand,[2,3] and π-substitution therefore might be expected to shift such a band in a manner similar to spectral shifts observed in substituted benzenes[12] if the chelate ring system is quasi-aromatic (Fig. 2). Since shifts in the π–π^* transition of benzene produced by ring substitution have been correlated rather successfully with changes in the ionization potential of the substituent, it was hoped that there might be a direct relation between the shifts in substituted benzenes and those in the γ-substituted acetylacetonates of copper(II). However, the hypsochromic shifts observed for the γ-cyano- and γ-nitro-derivatives indicated that no such simple comparison could be made. The 260 mμ π–π^* transition in benzene always shifts to lower energies with ring substitution. Due to the presence of the copper(II) atom in the chelate ring, benzenoid aromaticity cannot be assumed in the copper(II) acetylacetonates without making some unreasonable assumptions concerning the bonding.[13] Since the electron density distribution in the ground and excited π levels of the complex can hardly be expected to be similar to the ground and excited states in benzene, comparisons were abandoned in favor of Hückel molecular orbital (HMO) calculations.[14]

A semi-empirical HMO treatment similar to that used previously by Barnum[15] for the tris-acetylacetonates of 3d transition elements was employed, neglecting the exchange integral, β_{Cu-A}, between the metal ion and the ligands.[2] The values used for the various coulomb, α_i, and exchange, β_{ij}, integrals are presented in Table III. These were computed employing the semi-empirical methods described by Dr. Barnum elsewhere.[15]

As indicated[2] in part III, the $\pi_3 \rightarrow \pi_4^*$ transition in copper(II) acetylacetonate will be split into two bands, $b_{1u} \rightarrow b_{3g}$ and $b_{3g} \rightarrow a_u$, depending on the extent of the metal–oxygen, dπ–pπ overlap, *i.e.*, the value of β_{Cu-O}. Since this splitting[2] is very small (~2500 cm.$^{-1}$) reasonable estimates of the energy for the π–π^* transitions with varying γ-substitution should be possible neglecting this splitting entirely. In Table IV the calculated and observed positions of the π–π^* transition occurring near 300 mμ are compared.

Considering that the calculations are based solely on β_{ij} and α_i values estimated from bond energies and

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(12) F. A. Matsen, "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience, Publ., New York, N.Y., 1956, Vol. IX, Chap. V, pp. 686–687.

(13) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(14) We are indebted to Dr. D. W. Barnum of Shell Development Co. for these computations.

(15) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961).

TABLE III

COULOMB AND EXCHANGE INTEGRALS IN HMO CALCULATION

	Energies in cm.$^{-1}$							
	H	$-C_1{\equiv}N$	$-N\begin{smallmatrix}O\\O\end{smallmatrix}$	$-\overset{O}{\overset{\|}{C_1}}-O_2-C_2H_5$	$-C_1{=}C_2H-C_2H_5$	-Br	Cl	$-OCH_3$
α_{Cu}	−62,000	−62,000	−62,000	−62,000	−62,000	−62,000	−62,000	−62,000
α_A	−65,700	−65,000	−64,400	−65,500	−65,500	−65,600	−65,600	−65,700
α_B	−60,900	−61,000	−62,300	−61,900	−60,900	−61,000	−61,000	−62,100
α_C	−58,700	−60,900	−63,100	−61,100	−58,900	−59,900	−60,000	−62,400
Others	$\beta_{C=O}$[a]	α_{C_1}	α_N	α_{C_1}	α_{C_1}	α_{Br}	α_{Cl}	α_O
	−32,900	−60,000	−69,900	−64,800	−58,000	−61,000	−62,300	−68,600
	$\beta_{C=C}$[a]	α_N	α_O	α_{O_1}	α_{C_2}	β_{CBr}	β_{CCl}	β_{CO}
	−22,100	−68,100	−78,800	−72,200	−57,000	− 6,600	− 8,900	−14,400
		$\beta_{C,N}$	β_{CN}	α_{O_2}	β_{CC_1}			
		−21,000	− 8,900	−68,600	−18,800			
		β_{C_1C}	β_{NO}	β_{C-C_1}	$\beta_{C_1C_2}$			
		−18,800	−17,500	−18,800	−22,100			
				$\beta_{C_1O_1}$				
				−32,900				
				β_{C_1O}				
				−14,400				

[a] $\beta_{C=O}$; $\beta_{C=C}$ constant for all complexes.

electronegativities,[15] the correspondence between the observed and calculated sequences of relative shifts, $\Delta\tilde{\nu}$ (cm.$^{-1}$), is fairly good. In the case where coulomb and exchange integrals involve well known values, the —CH=CH—C_2H_5 derivative, the best agreement is obtained. Several factors contribute to a lack of consistently good agreement between calculated and observed shifts.

(1) Estimated values of β_{ij}, particularly between the methylene carbon atom and the first atom of the substituent, are subject to considerable uncertainty.

(2) The values of α_i based on electronegativities are not sufficiently reliable to expect good agreement.

(3) Some variations in β_{Cu-O} are expected with different γ-substituents.

(4) Steric repulsion by the methyl groups in some cases prevents a complete alignment of the γ-substituent so as to give maximum overlap of pπ orbitals on the substituent with the π system of the chelate ring.

As the methyl group produces a shift in the lowest energy π–π* transition of benzene,[12] it is not surprising that a shift is observed in the π–π* transition of the methylacetylacetonate. Since the methyl group has no non-bonding orbitals available for π-interaction with the chelate ring, the perturbing effect must be attributed to hyperconjugation.

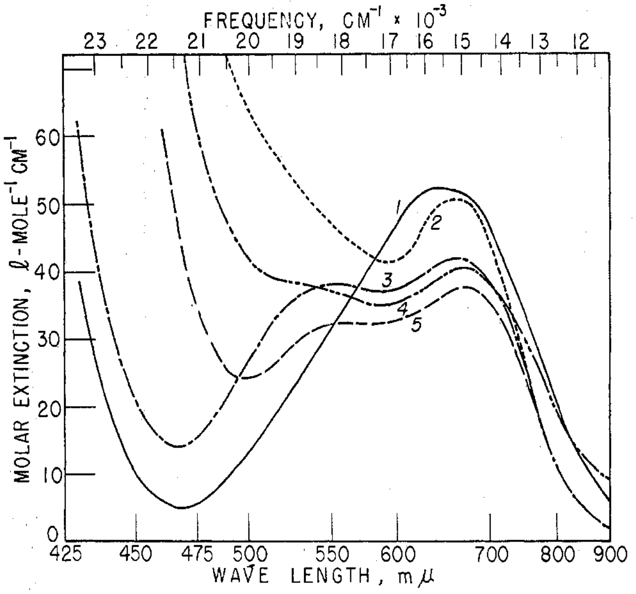

Fig. 1.—Visible spectra of some γ-substituted copper(II) acetylacetonates in chloroform: 1, bis-(3-cyano-2,4-pentanediono)-copper(II); 2, bis-(3-Δ'-butenyl-2,4-pentanediono)-copper(II); 3, bis-(3-carbethoxy-2,4-pentanediono)-copper(II); 4, bis-(3-chloro-2,4-pentanediono)-copper(II); 5, bis-(3-acetoxy-2,4-pentanediono)-copper(II).

TABLE IV

CALCULATED AND OBSERVED (IN CHLOROFORM) FREQUENCIES OF π–π* TRANSITION IN γ-SUBSTITUTED ACETYLACETONATES OF COPPER(II)

	Observed, cm.$^{-1}$		Calculated, cm.$^{-1}$	
R	$\tilde{\nu}$	$\Delta\tilde{\nu}$	$\tilde{\nu}$	$\Delta\tilde{\nu}$
CN	33,990	+210	33,830	+2,130
NO_2	33,880	+100	34,080	+2,380
H	33,780	0	31,700	0
$COOC_2H_5$	33,760	−20	33,150	+1,450
$NHCOCH_3$	33,390	−390	...	...
$OCOCH_3$	32,710	−1,070	...	...
CH_2—CH=CH_2	32,470	−1,320	...	...
Br	32,420	−1,360	26,680	−5,020
CH_3	32,300	−1,480	...	...
CH=CH—C_2H_5	31,950	−1,760	30,270	−1,430
Cl	31,910	−1,880	25,790	−5,910
OCH_3	31,750	−2,030	24,800	−6,900

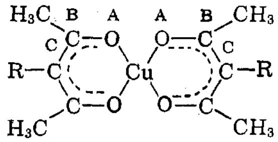

Figure 2.

In summary, therefore, it appears that shifts in band III with variation of the γ-substituent are in accord with the assignment of the band as a $\pi-\pi^*$ transition, and therefore provide support for this assignment.

It also will be noted that the energy of band II is practically insensitive to variation in the γ-substituent. Such behavior is in accord with the proposed assignment of this band as a charge transfer band as discussed in part III.[2] In particular, the possibility that bands II and III might be the two components of a $\pi_3 \rightarrow \pi_4^*$ transition is rendered very unlikely by the very different degrees of sensitivity of these two bands to γ-substituents.

Acknowledgment.—We thank Dr. Dennis Barnum very cordially for his kindness in making the HMO calculations and we are grateful to both him and Professor R. H. Holm of Harvard University for helpful discussion. This work was supported in part by grants from the National Science Foundation and the U. S. Atomic Energy Commission.

Contribution from McPherson Chemical Laboratory,
Ohio State University, Columbus, Ohio

A Study of the Stability and Basicity of the Copper(II) Pyrophosphate Complexes Using the Dropping Amalgam Electrode[1]

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The extent of association of hydrogen ions with copper pyrophosphate complexes has been evaluated on the basis of potential measurements using a dropping copper amalgam electrode. Correlations have been made between the number of associated hydrogen ions and the stability as well as the basicity of the complex. In terms of concentrations the stepwise formation constants of $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$ are $10^{9.07}$ and $10^{4.58}$, respectively, at an ionic strength adjusted to unity with tetramethylammonium nitrate at 25°. One hydrogen ion associates readily with each PO_4 tetrahedron. The stepwise formation constants for the successive addition of hydrogen ions to $CuP_2O_7^{2-}$ are $10^{5.25}$ and $10^{3.31}$. For $Cu(P_2O_7)_2^{6-}$ they are $10^{6.76}$, $10^{5.78}$, $10^{4.40}$, and $10^{3.21}$. The association with hydrogen ions greatly decreases the stability of the complex. Some association of alkali metal ions with $Cu(P_2O_7)_2^{6-}$ is indicated by the slightly increased stability of this complex ion in the presence of up to 0.1 *M* Na^+ or K^+.

Introduction

The purpose of the present study was to establish the extent of association of hydrogen ions with copper(II) pyrophospate complexes and to determine the effect of this association on the stability of the complex. In addition, various effects which decreased the accuracy of previous studies were eliminated.

It has been known for a long time that pyrophosphate is capable of forming complexes in acidic solutions. Kolthoff and Watters[3] obtained potentiometric evidence that manganese(III) forms a complex with $H_2P_2O_7^{2-}$, while Laitinen and Onstott[4] obtained polarographic evidence for the existence and stability of the copper(II) complexes $CuHP_2O_7^{1-}$ and $Cu(HP_2O_7)_2^{4-}$. Spectrophotometric evidence for the existence and stability of the species $Cu(P_2O_7)^{2-}$ and $Cu(P_2O_7)_2^{6-}$ has been obtained in this Laboratory[5] and confirmed in other laboratories.[6-8]

The tendency of polyphosphate ions even when complexed with a metal ion to associate with hydrogen ions results in fairly complicated equilibria, so that calculations based on the assumption that particular species predominate in particular ranges of pH and ligand concentrations may lead to inaccurate results. Modern functions such as those of Leden, Bjerrum, and Froneus[9] eliminate the need for approximations of this type. As shown in earlier papers,[10,11] Leden's function expressed in terms of electrode potentials can be readily applied when the complexed, as well as the free, ligands tend to associate with hydrogen ions.

A further complication is the fact that alkali metal ions are known to form complexes with pyrophosphate[3,12] and triphosphate.[13] In the present study, alkali metal ions were replaced by tetramethylammonium ion in both the polyphosphate and in the supporting electro-

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