DETERMINATION OF STABILITY CONSTANTS OF COPPER COMPLEX WITH
O-CARBOXYPHENYLHYDRAZODIETHYLMALONATE
SPECTROPHOTOMETRICALLY

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The complex formation of copper–o–carboxyphenylhydrazodiethylmalonate (o–CPHM) is studied spectrophotometrically. The composition of the complex is 1:1 and its stability constant as determined spectrophotometrically by three different methods,is 5.11, 5.45 and 5.39. The UV and IR spectra of the pure organic ligand as well as copper solid complex are given and the configuration of this complex is proposed.

INTRODUCTION

Diethylmalonate or generally β–diketones are known to act as strong complexing agents with transition metals [1], as do many of the azo compounds [2]. Although the coupling compound phenylhydrazodiethylmalonate was prepared by Adams [3] little is known about its use as a complexing agent. This may be due to its insolubility in water. However, the carboxy-derivatives of the compound are water soluble in their potassium form. For this reason, the o–CPHM was prepared in this laboratory, and used as a complexing agent for a series of divalent metal ions.

It is expected that the coupling compounds of these two types of ligands would also act as chelating agents. Recently, some of these coupling compounds have been prepared and used as complexing agents [4,5].

In the present paper the composition and the stability in solution of o–carboxyphenylhydrazodiethylmalonate – copper complex are determined spectrophotometrically. The IR and UV spectra of the ligand as well as of its copper complex are given.

EXPERIMENTAL

Copper nitrate (A.R. Grade) solution was standardized by complexometric [6] titration. Other chemical reagents were purified by recommended methods.

Reagents

(1) o–Carboxyphenylhydrazodiethylmalonate (o–CPHM): Diazotized anthranilic acid was coupled with diethylmalonate in presence of sodium acetate medium [3]. The pure organic product was obtained after crystalli-zation several times from aqueous alcoholic solvent as a light yellowish needle crystals, m.p. 135° (Found C, 54.33; H, 4.95; N, 9.01; $C_{14}H_{16}O_6N_2$; required C, 54.51; H, 5.10; N, 9.09 %).

(2) o–Carboxyphenylhydrazodiethylmalonate – Cu(II) complex: Aqueous solution of cupric ions (1 x 10^{-1} M) with a potassium salt of the ligand o–CPHM (2 x 10^{-2} M.) were mixed at 50° and pH 5.5 to 6.0. Deep green crystals were gradually precipitated and complete preciptation obtained overnight. The solid complex was washed thoroughly with water and alcohol, and dried in vacuum desiccator. It shrinks at 270°. The result of analysis agrees well with the composition 1:1 (Ligand:metal) stoichemetry (Found C, 45.63; H, 3.87; N, 7.80; Cu, 16.83; for Cu $C_{14}H_{14}O_6$ N_2; required C, 45.40; H, 3.79; N, 7.55 and Cu 17.1%) The solid complex is soluble in alcohol and other organic solvents and decomposes by concentrated mineral acids.

Measurements

pH measurements were carried out using Pye–Unicam-290 pH-meter. The IR spectra were measured by Perkin–Elemr–437 spectrometer on mull of the complex with potassium bromide discs, from 4000 to 200 cm^{-1}, visible and UV spectra on Pye-Unicam Sp 1800 recording spectrophotometer, connected with a thermostated cell holder. Atomic absorption Varian was used in determination of percentage of copper in solid copper complex.

RESULTS AND DISCUSSION

(I) Absorption Spectra of o–CPHM–Cu(II) Solutions.
An aqueous solution of the ligand exhibits a band maximum

at 358 mμ with a shoulder at 250 mμ. On adding cupric ion to the ligand, a green color is developed with a red slight shift of the previous band to 363 mμ and the appearance of a new band at 410 mμ which is characterisitc of the formed complex. The absorbance at this band increases with pH upto 6.0 (Fig. 1).

(II) Composition of the Complex. The composition of the complex was determined spectrophotometrically following Job's continuous variation method [7], slope ratio [8] and the limiting logarithmic method [9]. Measurements were carried out at constant ionic strength 0.1 M. and 30°. As seen from Fig. 2, representing the Job's method, the complex has 1:1 composition which is confirmed by the other two methods.
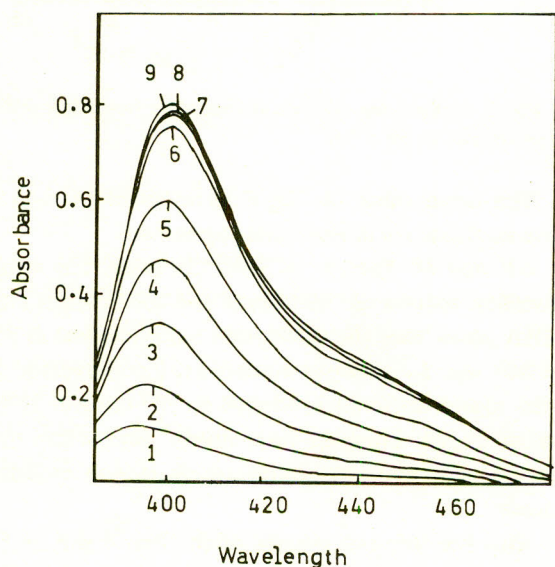

Fig. 1. Effect of the pH on absorption spectra of Cu$-o-$CPHM complex. (1) 3.3.(2) 3.6.(3) 3.8.(4) 4.1(5) 4.35. (6) 5.6. (7) 6.7. (8) 8.3.(9) 9.3.
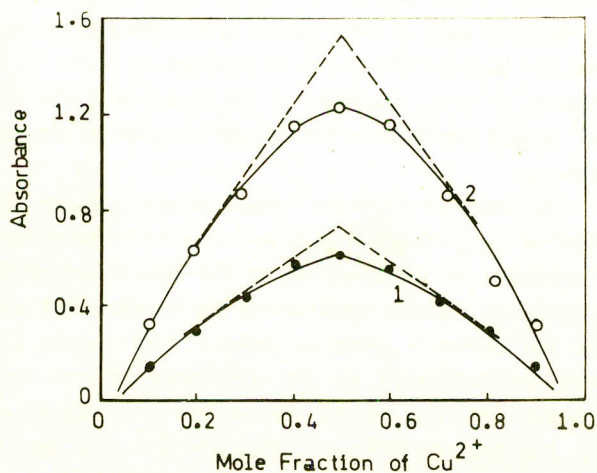

Fig. 2. The continuous variation method (1) Total molar conc. = 2.5x10^{-4}M. (2) Total molar conc. =5.0x10^{-4}M.

(III) Formation Constant of Cupric-o-CPHM Complex. The formation constant of the 1:1 Cu-o-CPHM complex was calculated using the spectrophotometric method of Yoe and Jones [10] as follows:

$$Cu \; + \; L \quad \rightleftharpoons \quad CuL$$
$$(a-x) \quad (b-x) \qquad\qquad x$$

Assuming that association of complex is complete, absorbance will arrive to a constant value "A_m" in presence of excess of ligand and one chooses a wavelength at which the ligand does not absorb, therefore, the absorbance for the complex "A" is proportional to its concentration "X". Thus:

$$\frac{X}{a} = \frac{A}{A_m} \text{ or } X = a^{A/A_m} \quad \cdots \quad (1)$$

and the stability constant equals:

$$K = \frac{A/A_m}{(b - a \; A/A_m)(1 - A/A_m)} \quad \cdots \cdots \quad (2)$$

Table 1 shows the formation constant of 1: Cu-o-CPHM complex, measured at 410 mμ; pH = 6.0 and ionic strength 0.1; [a] = [Cu(II) = 6.0 x 10^{-5}M, Am = 0.40.

Table 1. The formation constant of 1:1 Cu$-o-$CPHM complex.

[o--CPHM] 10^5	A	K x 10^{-5}	log K
1.0	0.06	1.764	5.25
2.0	0.11	1.083	5.05
3.0	0.16	1.111	5.05
4.0	0.22	1.740	5.24
5.0	0.25	1.330	5.12
6.0	0.27	1.065	5.03
7.0	0.30	1.216	5.10
10.0	0.35	1.280	5.11
12.0	0.35	1.037	5.06
18.0	0.40	. . . .	. . . .

Mean value log K = 5.11 ± 0.07

Also the formation constant is calculated from the data obtained in continuous variation method at two different concentrations (C_t = 5x10^{-4} M and C_t = 2.5x10^{-4} M). The stability constant of the complex (ML$_n$) can be obtained from:

$$K = \frac{C_3}{(C_t(1-x)-C_3 \; (C_t x-nC_3)^n}$$

$$= \frac{C_3'}{(C_t(1-x)-C_3') \, (C_t' x-nC_3')^n} \cdots \cdots (3)$$

Hogenmullar [11] found that, if only ML complex is formed i.e. $x = 0.5$ and $n = 1$, then equation (3) can be written in the following simple formula:

$$K = \frac{C_3}{(0.5 \, C_t - C_3)^2} = \frac{C_3'}{(0.5 C_t' - C_3')^2} \cdots (4)$$

where $A/A' = C_3/C_3'$, C_3 and C_3'' are the concentrations of the formed complex. Fig. 2. gives absorbance $A = 0.73$ and $A = 1.54$ at 410 mμ and the values of log k as 5.45 and 5.46 respectively. The third method for calculation of the formation constant of 1:1 copper –o–CPHM complex is the Haymann's method [12] using the following relations:

$$A \; + \; B \; \rightleftharpoons \; A \, B$$

$$K_{AB} \; = \; \frac{c_{AB}}{(C_A - c_{AB}) \, (C_B - c_{AB})} \; \cdots \cdots (5)$$

Where c_{AB} is the concentration of the complex, C_A and C_B are the original concentration of A and B. For small concentrations of A and B and assuming that the absorbance D at the specific wave length 410 mu is only due to the complex AB, then

$$D = \epsilon_{AB} \, C_{AB} \qquad \cdots (6)$$

and equation (5) can be written as:

$$\frac{C_A \, C_B}{D} = \frac{1}{K_{AB} \, \epsilon_{AB}} + \frac{C_A + C_B}{\epsilon \, AB} -$$

$$\frac{K_{AB} \, C_A \, C_B}{\epsilon \, AB} \cdots (7)$$

If $C_A = C_B$, and both are small then the last term in equation (7) can be neglected. Hence a plot of $C_A \, C_B/D$ against $(C_A + C_B)$ will not be completely linear. Fig. 3 shows the straight line relation between $[C_L] \, [C_M] /D$ vs $[C_L] + [C_M]$, confirming the formation of 1:1 complex and from its slope and intercept, the value of formation constant $K_{AB} = 2.468 \times 10^5$ and log $K_{AB} = 5.39$.
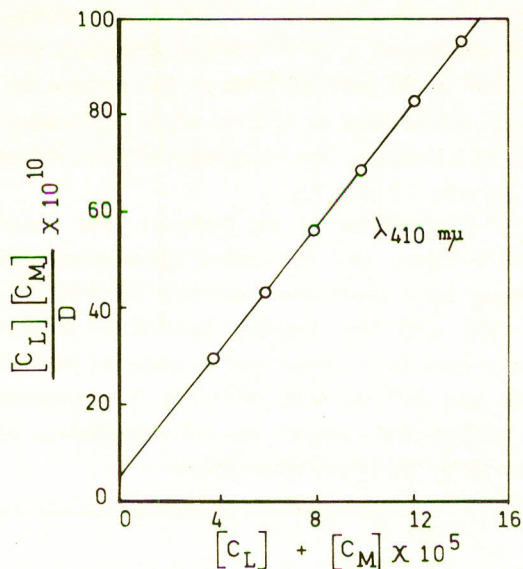

Fig. 3. Straight-line relation showing the formation of Cu--o-CPHM complex at pH = 6.0.

The mean value for log K as obtained by each of the above methods are in reasonable agreement.

UV and IR Spectra of Solid Complex. The electronic absorption spectra of solid ligand and solid copper complex in DMF show that the absorption band maxima at 252 mμ and 347 mμ, for diethylmalonate [13] and hydrazo groups of the ligand, suffered a red shift to 267 mμ and 378 mμ in case of copper complex respectively, supporting that the carbonyl and hydrazo groups are sharing in coordination process.

Also the infrared spectra of the ligand and its Cu (II) solid complex were carried out to help in identification the structure of the formed complex. The $3100 - 2500$ cm^{-1} absorption bands (NH & OH) [14] in the ligand disappear completely in the solid copper complex showing that not only is the hydrazo group involved in chelation, but also the OH of the carboxy group, while $\nu_{C_2H_5}$ vibration [15] in spectrum of the ligand at $2500-2400$ cm^{-1} is still observed in the copper complex at the same frequency.

The observed 1680 cm^{-1} band, which is always attributed to $\nu_{C=O}$ vibration [14] and may be to other modes of vibration in the spectrum of the ligand, was shifted to 1580 cm^{-1} in the spectrum of the complex, indicating that the carbonyl group is chelated with copper [16]. These are confirmed by the appearance of new bands of a Cu-- N band [5, 17, 18] at 543 cm^{-1} and Cu — O [16, 19] band at 445 cm^{-1}. This would suggest that the hydrogen atoms of hydrazo and the carboxyl groups are replaced by copper and that the third chelating group is an oxygen atom of a carbonyl group. Due to the steric

requirements, the fourth position may be occupied by a solvent molecule, which in this case would be water. There is a weak band in the IR at 3450 cm^{-1} which could be assigned to water.

From the above results we can expect that 1:1 Cu (II)–*o*–CPHM complex has a square planar structure and the four coordination sites are through nitrogen of hydrazo group, oxygen of carbonyl group of the diethylmalonate branch, carboxyl group and the fourth position is occupied by solvent molecule.

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