Investigation on Mixed Complex. I. Spectrophotometric Study of Mixed Complexes Formed by Cupric Ion and Bidentate Ligands

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If two kinds of cupric complexes having bidentate ligands are dissolved to make a solution, the mixed complex is to be formed; e. g., bisethylenediamine copper nitrate and potassium bisoxalato cupriate are expected to react in an aqueous solution and reach the following equilibrium.

$$[\mathrm{Cu\ en_2}]^{++}+[\mathrm{Cu\ ox_2}]^{--}\rightleftarrows 2[\mathrm{Cu\ en\ ox}]$$

(en = ethylenediamine, ox = oxalate ion)

This kind of equilibrium is expressed by the following general formula:

$$\mathrm{MA_2+MB_2}\rightleftarrows \mathrm{2MAB} \qquad (1)$$

$$Km=\frac{(\mathrm{MAB})^2}{(\mathrm{MA_2})(\mathrm{MB_2})} \qquad (2)$$

where, M is the metallic ion of the coordination number four, A and B are bidentate ligands. The reciprocal of Km corresponds to the dismutation constant introduced by Watters et al.[1)]

If the bond energies of M–A and M–B are not altered in the two sides of this equilibrium, and there is no interaction between MAB, $\mathrm{MA_2}$ and $\mathrm{MB_2}$, three complex species would be distributed entirely statistically; in this condition Km is equal to 4*.

When the value of Km is found to be far from 4, we can conclude that the bond energies of M–A and M–B are affected by each other in the mixed complex.

The determination of Km makes it possible to draw the absorption curve of the mixed complex by using the measured extinction data of the parent complexes, and it will be interesting to examine the absorption curves of the mixed complex and its parent complexes.

However, there was no investigation on the mixed complexes of this kind, until the investigations were reported by Watters et al. in very recent years[1)]. They succeeded in obtaining the formation constants of mixed complexes such as $[\mathrm{Cu\ en\ P_2O_7}]^{--}$ and [Cu en ox], by using a newly devised "isosbestic method". The present author modified Watters' isosbestic method, and by this method obtained the values of Km and the absorption spectra of the following three mixed complexes, [Cu en ox], $[\mathrm{Cu\ en\ aca}]^+$ and [Cu dgH aca], where aca and dgH denote acetylacetonate ion ($\mathrm{C_5H_7O_2^-}$) and dimethylglyoximate ion ($\mathrm{C_4H_7O_2N_2^-}$) respectively.

Determination of *Km*

From the equations (1) and (2) the following relations are derived.

$$Km=\frac{4x^2}{(c_1-x)(c_2-x)} \qquad (3)$$

$$x=\frac{D-\varepsilon_1c_1-\varepsilon_2c_2}{2\varepsilon_3-\varepsilon_2-\varepsilon_1}$$

$$D=\varepsilon_1(c_1-x)+\varepsilon_2(c_3-x)+2\varepsilon_3x \qquad (4)$$

where c_1 and c_2 are concentrations of $\mathrm{MA_2}$ and $\mathrm{MB_2}$ respectively**, and ε_1, ε_2 and ε_3 are the molar extinction coefficients of $\mathrm{MA_2}$, $\mathrm{MB_2}$ and MAB respectively. D is the measured optical density $\left(\log\frac{I_0}{I}\right)$ of the solution in equilibrium. $2x$ is the concentration of the mixed complex. From the equation (4)

$$x=\frac{D-\varepsilon_1c_1-\varepsilon_2c_2}{2\varepsilon_3-\varepsilon_2-\varepsilon_1}$$

is obtained. In the case of $\varepsilon_3=m\varepsilon_1$

$$x=\frac{D-\varepsilon_1c_1-\varepsilon_2c_2}{\varepsilon_1(2m-1)-\varepsilon_2} \qquad (5)$$

As will be seen from the following examples,

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1) R. De Witt and J. Watters, *J. Am. Chem. Soc.*, **76**, 3810 (1954). J. I. Watters, A. Aaron and J. Mason, ibid., **75**, 5212 (1953). J. I. Watters and E. D. Lougham, ibid., **75**, 4819 (1953).

* The statistical value of Km is found in the following way. Since, in this equilibrium, M exists always in combination with any one of pairs AA, BB and AB, instead of MAA, MBB and MAB. Let P_{AA}, P_{BB} and P_{AB} be the probabilities with which the pairs of AA, BB and AB are found, when two particles are picked out from the n particles of both A and B.

$$P_{AA}=P_{BB}=\frac{{}_nC_2}{{}_{2n}C_2}=\frac{n-1}{2(2n-1)}$$

$$P_{AB}=\frac{{}_nC_1\cdot{}_nC_1}{{}_{2n}C_2}=\frac{n}{2n-1}$$

$$\therefore\ \lim_{n\to\infty}P_{AA}=\lim_{n\to\infty}P_{EB}=\tfrac{1}{4}$$

$$\lim_{n\to\infty}P_{AE}=\tfrac{1}{2}$$

$$\therefore\ Km=\frac{(\mathrm{MAB})^2}{(\mathrm{MA_2})(\mathrm{MB_2})}=\frac{(\frac{1}{2}\times n)^2}{(\frac{1}{4}\times n)(\frac{1}{4}\times n)}=4$$

** c_1 and c_2 are concentrations of $\mathrm{MA_2}$ and $\mathrm{MB_2}$ respectively, when it is assumed that, in the mixed solution of $\mathrm{MA_2}$ and $\mathrm{MB_2}$, MAB is not formed at all. Hereafter such a concentration as the above mentioned will be called the "initial concentration" of $\mathrm{MA_2}$ or $\mathrm{MB_2}$.

the value of m is chosen for the convenience of the experiment (e. g., $m=1, 2, 3$ or 5.5 etc.); and the wavelength where ε_3 is equal to $m\varepsilon_1$ is found in the following procedure.

First, the optical densities of the solution containing MA_2 at the concentration c_0 are measured, and then those of the solution containing MA_2 and MB_2 at the initial concentrations c_0-c and c' are measured respectively. Provided that c and c' are very small compared to c_0, and the equilibrium is not much shifted towards the left side of the following equation, the relation of the concentrations may be considered to be:

$$\underset{(c_0-c-c')}{MA_2} + \underset{(0)}{MB_2} \rightleftarrows \underset{(2c')}{2MAB}$$

Therefore, the condition that the extinction curve of MA_2 (whose concentration is c_0) crosses with the extinction curve of the mixed solution at the wavelength where ε_3 is equal to $m\varepsilon_1$ is:

$$\varepsilon_1 c_0 = \varepsilon_1(c_0-c-c') + 2m\varepsilon_1 c'$$

or

$$c' = \frac{c}{2m-1} \tag{6}$$

Accordingly, if the initial concentrations of MA_2 and MB_2 are chosen as c_0-c and $c/2m-1$ respectively, (where c is a small variable value—e. g., 5×10^{-5} or 1×10^{-4} etc.), the extinction curves of this mixed solution have the isosbestic point at $\varepsilon_3=m\varepsilon_1$. Thus, from the isosbestic point of these extinction curves, the wavelength where ε_3 is equal to $m\varepsilon_1$ is readily found. Then, at this wavelength extinction measurements are made on the mixed solution of the parent complexes in appropriate concentrations (see the curves of 6, 7 and 8 in Fig. 1 and Table I). From these data and the relations (2) and (4), Km is readily obtained.

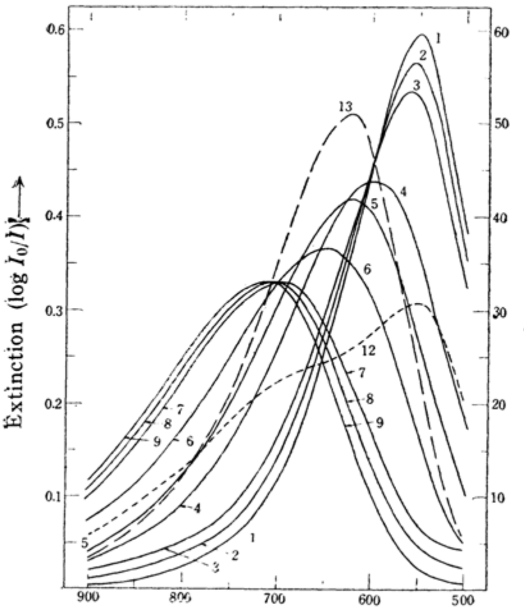

Fig. 1. (cf. Table I) (mμ)

TABLE I

(cf. Figs. 1 and 2)

Curve	$c_1\times10^2$	$c_2\times10^2$
1	1	0
2	0.95	0.05
3	0.9	0.1
4	$\frac{2}{3}$	$\frac{1}{3}$
5	$\frac{1}{2}$	$\frac{1}{2}$
6	$\frac{1}{3}$	$\frac{2}{3}$
7	0.1	0.9
8	0.05	0.95
9	0	1
10	$0.05\times\frac{1}{3}$	0.95
11	$0.1\times\frac{1}{3}$	0.9
12	$\frac{\varepsilon_1+\varepsilon_2}{2}$	
13	extinction of [Cu en ox] (calcd.)	

c_1: initial concentration of $[Cu\ en_2]^{++}$
c_2: initial concentration of $[Cu\ ox_2]^{--}$

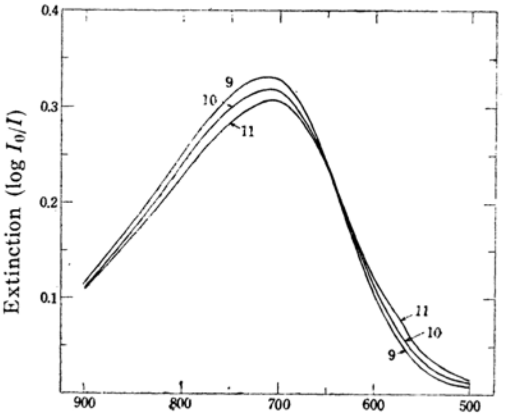

Fig. 2. (cf. Table I) (mμ)

In the case of $\varepsilon_3=m\varepsilon_2$ the procedure of determining Km is quite similar to that above mentioned.

[Cu en ox]: The wavelength where ε_3 is equal to ε_1 was determined to be 600 mμ by curves 1, 2 and 3 in Fig. 1. The wavelength where ε_3 is equal to $2\varepsilon_1$ was determined to be 650 mμ by curves 9, 10 and 11 in Fig. 2. The wavelength where ε_3 is equal to ε_2 was determined to be 706 mμ by curves 7, 8 and 9 in Fig. 1. At these three wavelengths Km of

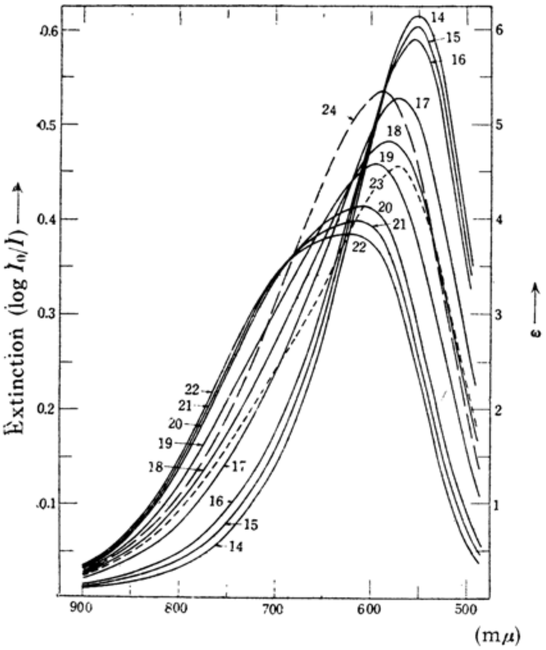

Fig. 3. (cf. Table II)

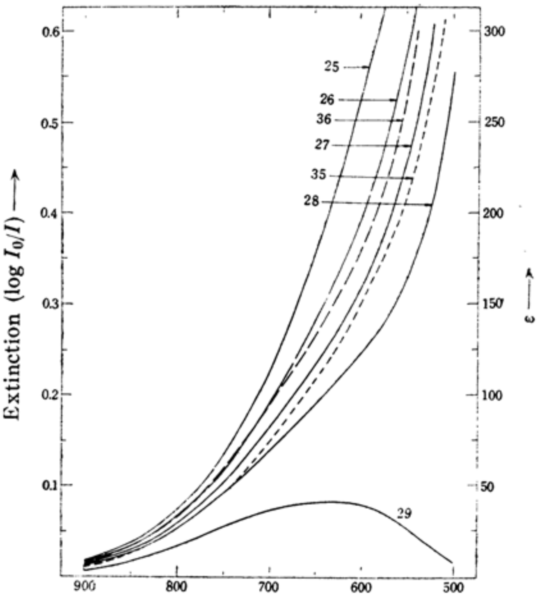

Fig. 4. (cf Table III) (mμ)

TABLE II
(cf. Fig. 3)

Curve	$c_1' \times 10^2$	$c_2' \times 10^2$
14	1	0
15	0.95	0.05
16	0.9	0.1
17	$\frac{2}{3}$	$\frac{1}{3}$
18	$\frac{1}{2}$	$\frac{1}{2}$
19	$\frac{1}{3}$	$\frac{2}{3}$
20	0.1	0.9
21	0.05	0.95
22	0	1
23	$\frac{\varepsilon_1' + \varepsilon_2'}{2}$	
24	extinction of [Cu en aca]$^+$ (calcd.)	

c_1': initial concentration of [Cu en$_2$]$^{++}$

c_2': initial concentration of [Cu aca$_2$]

TABLE III
(cf. Figs. 4, 5 and 6)

Curve	$c_1'' \times 10^2$	$c_2'' \times 10^2$
25	0.2	0
26	$0.2 \times \frac{2}{3}$	$0.2 \times \frac{1}{3}$
27	0.1	0.1
28	$0.2 \times \frac{1}{3}$	$0.2 \times \frac{2}{3}$
29	0	0.2
30	0	1
31	$0.05 \times \frac{1}{5}$	0.95
32	$0.1 \times \frac{1}{5}$	0.9
33	$0.05 \times \frac{1}{10}$	0.95
34	$0.1 \times \frac{1}{10}$	0.9
35	$\frac{\varepsilon_2'' + \varepsilon_1''}{2}$	
36	extinction of [Cu dgH aca] (calcd.)	

c_1'': initial concentration of [Cu(dgH)$_2$]

c_2'': initial concentration of [Cu aca$_2$]

[Cu en ox] was calculated according to (2) and (4) using the data of curves 1, 4, 5, 6 and 9 in Fig. 1. The results are given in Table V.

[Cu en aca]$^+$: The wavelength where ε_3 is equal to ε_1 was determined to be 588 mμ from curves 14, 15 and 16 in Fig. 3. The wavelength where ε_3 is equal to ε_2 was determined by curves 20, 21, and 22 in Fig. 3 to be 684 mμ. At these two wavelengths *Km* of [Cu en aca]$^+$ was calculated using the curves 14, 17, 18, 19 and 22 in Fig. 3 according to the method described above. The results are given in Table VI.

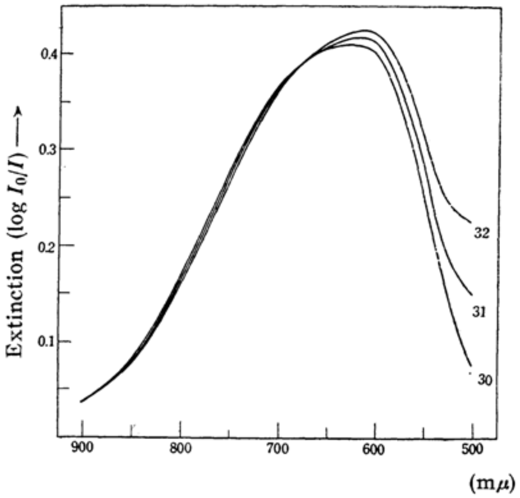

Fig. 5. (cf. Table III)

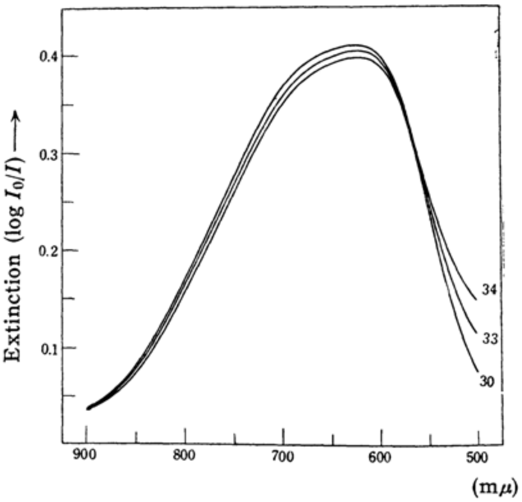

Fig. 6. (cf. Table III)

TABLE IV

RESULTS OF THE EXPERIMENTS ON THE EQUILIBRIUM $[Cu\,en_2]^{++}+[Cu\,ox_2]^{--} \rightleftarrows 2[Cuen\,ox]$, AT 20° IN AQUEOUS SOLUTION, IONIC STRENGTH WAS ADJUSTED TO 0.25 BY $NaNO_3$

Wavelength (mμ)	$c_1\times10^2$	$c_2\times10^2$	D	ε_1	ε_2	ε_3	log Km
600	$\frac{2}{3}$	$\frac{1}{3}$	0.440	45.8	10.3	ε_1	1.12
600	$\frac{1}{2}$	$\frac{1}{2}$	0.404	〃	〃	〃	1.38
600	$\frac{1}{3}$	$\frac{2}{3}$	0.315	〃	〃	〃	0.91
706	$\frac{2}{3}$	$\frac{1}{3}$	0.249	11.4	33.4	ε_2	1.12
706	$\frac{1}{2}$	$\frac{1}{2}$	0.291	〃	〃	〃	1.11
706	$\frac{1}{3}$	$\frac{2}{3}$	0.322	〃	〃	〃	1.05
650	$\frac{2}{3}$	$\frac{1}{3}$	0.379	26.2	23.9	$2\varepsilon_2$	1.05
650	$\frac{1}{2}$	$\frac{1}{2}$	0.395	〃	〃	〃	1.13
650	$\frac{1}{3}$	$\frac{2}{3}$	0.369	〃	〃	〃	1.03

Mean value of log Km=1.10

c_1, c_2: initial concentrations of $[Cu\,en)^{++}$ and $[Cu\,ox]^{--}$ respectively
D: optical bensity of the solution
ε_1, ε_2, ε_3: molar extinction coefficients of $[Cu\,en_2]^{++}$, $[Cu\,ox_2]^{--}$ and [Cu en ox] respectively

[Cu dgH aca]: The wavelength where ε_3 is equal to $3\varepsilon_1$ was determined to be 674 mμ from curves 30, 31 and in Fig. 5. The wavelength where ε_3 is equal to 5.5 ε_1 was determined to be 582 mμ from curves 30, 33 and 34 in Fig. 6. At these two wavelengths Km of [Cu dgH aca] was calculated using curves 25, 26, 27, 28 and 29 in Fig. 4. The results are given in Table VI.

TABLE V

RESULTS OF THE EXPERIMENTS ON THE EQUILIBRIUM, $[\mathrm{Cu\ en_2}]^{++} + [\mathrm{Cu\ aca_2}] \rightleftharpoons 2[\mathrm{Cu\ en\ aca}]^{+}$, AT 20° IN 75% DIOXANE SOLUTION WHICH CONTAINS $NaNO_3$ IN THE CONCENTRATION OF 0.1 M

Wavelength	$c_1' \times 10^2$	$c_2' \times 10^2$	D	ε_1'	ε_2'	ε_3'	$\log Km$
588	$\frac{2}{3}$	$\frac{1}{3}$	0.510	53.2	35.9	ε_1'	0.42
588	$\frac{1}{2}$	$\frac{1}{2}$	0.484	〃	〃	〃	0.40
588	$\frac{1}{3}$	$\frac{2}{3}$	0.452	〃	〃	〃	0.42
684	$\frac{2}{3}$	$\frac{1}{3}$	0.272	17.0	35.8	ε_2'	0.49
684	$\frac{1}{2}$	$\frac{1}{2}$	0.305	〃	〃	〃	0.39
684	$\frac{1}{3}$	$\frac{2}{3}$	0.334	〃	〃	〃	0.43

Mean value of $\log Km = 0.42$

c_1', c_2': initial concentrations of $[\mathrm{Cu\ en_2}]^{++}$ and $[\mathrm{Cu\ aca_2}]$, respectively

D: optical density of the solution

ε_1', ε_2', ε_3': molar extinction coefficients of $[\mathrm{Cu\ en_2}]^{++}$, $[\mathrm{Cu\ aca_2}]$ and $[\mathrm{Cu(en)\ aca}]^{+}$ respectively

TABLE VI

RESULTS OF THE EXPERIMENTS ON THE EQUILIBRIUM, $[\mathrm{Cu(dgH)_2}] + [\mathrm{Cu\ aca_2}] \rightleftharpoons 2[\mathrm{Cu\ dgH\ aca}]$, AT 20° IN 50% DIOXANE AND 50% ETHYL ALCOHOL MIXTURE

Wavelength (mμ)	$c_1'' \times 10^3$	$c_2'' \times 10^3$	D	ε_1''	ε_2''	ε_3''	$\log Km$
582	$\frac{3}{4}$	$\frac{2}{3}$	0.446	302	36.0	$5.5\varepsilon_1''$	$\bar{1}.87$
582	1	1	0.368	〃	〃	〃	$\bar{1}.99$
582	$\frac{2}{3}$	$\frac{3}{4}$	0.269	〃	〃	〃	$\bar{1}.98$
674	$\frac{3}{4}$	$\frac{2}{3}$	0.235	143	38.0	$3\varepsilon_1''$	$\bar{1}.96$
674	1	1	0.198	〃	〃	〃	$\bar{1}.97$
674	$\frac{2}{3}$	$\frac{4}{3}$	0.165	〃	〃	〃	$\bar{1}.97$

Mean value of $\log Km = \bar{1}.96$

c_1'', c_2'': initial concentrations of $[\mathrm{Cu(dgH)_2}]$ and $[\mathrm{Cu\ aca_2}]$, respectively

D: optical density of the solution

ε_1'', ε_2'', ε_3'': molar extinction coefficient of $[\mathrm{Cu(dgH)_2}]$, $[\mathrm{Cu\ aca_2}]$ and $[\mathrm{Cu\ dgH\ aca}]$ respectively

TABLE VII

THE VALUE OF $\log Km$

	$[\mathrm{Cu\ en\ P_2O_7}]^{--}$	$[\mathrm{Cu\ en\ ox}]$	$[\mathrm{Cu\ en\ aca}]^{+}$	$[\mathrm{Cu\ dgH\ aca}]$	Statistical Value
$\log Km$	1.70*	1.00*, 1.10	0.42	$\bar{1}.96$	0.60

* Data from the investigation of Watters and Lougham

Experimental

Apparatus.—All extinction measurements were made by the Beckman DU Spectrophotometer using 1 cm. quartz cells.

Materials.—$[\mathrm{Cu\ en_2}](\mathrm{NO_3})_2$ was prepared from copper nitrate and ethylenediamine, and purified by recrystallization from a mixture of water and alcohol. $\mathrm{K_2[Cu\ ox_2]}$ was obtained from cupric sulphate and potassium oxalate by heating them for a few hours on a steam bath, and purified by recrystallization from 0.1 M aqueous potassium oxalate solution. The crystal was heated in vacuum at 100°C., and desiccated over P_2O_5. $\mathrm{[Cu\ aca_2]}$ was prepared from cupric acetate and acetylacetone, and recrystallized from a mixture of benzene and chloroform. $\mathrm{[Cu(dgH)_2]}$ was prepared from equivalent amounts of cupric acetate, dimethylglyoxime and caustic soda, and it was recrystallized from alcohol.

All these complexes were analyzed for their copper contents by iodometric titration.

Solvent.—The solvent used for extinction measurements of [Cu en ox] was an aqueous solution of 0.01 M potassium oxalate. To this 0.17 M sodium nitrate was added to keep the ionic strength at about 0.25. Thus, solutions of 0.01 M $\mathrm{[Cu\ en_2]^{++}}$ and $\mathrm{[Cu\ ox_2]^{--}}$ were prepared by dissolving weighed amounts of each complex in this solvent. In the case of $\mathrm{[Cu\ en\ aca]^{+}}$ the mixture of 75% dioxane and 25% water was used for the solvent, which contained sodium nitrate in the concentration of 0.1 M. The solvent used for determining Km of [Cu dgH aca] was the mixture of 50% absolute ethyl alcohol and 50% dioxane.

Results and Discussion

The determination of Km by the method used in this investigation is possible only when hydrolysis such as, $\mathrm{MA_2+2H_2O \rightleftarrows MA(H_2O)_2+A}$, does not occur to a measureable extent. To fulfil this requirement, it is necessary that the concentration of $\mathrm{MA(H_2O)_2}$ be lower than 0.1% of that of $\mathrm{MA_2}$. Since the concentration of $\mathrm{MA_2}$ used in this experiment is the magnitude of 10^{-2}, the concentrations of $\mathrm{MA(H_2O)_2}$ and A must be lower than 10^{-5}. Accordingly, it is necessary that the second consecutive formation constant (k_2) of $\mathrm{MA_2}$ be greater than 10^8.

According to the data of other studies[2], k_2 of $\mathrm{[Cu\ en_2]^{++}}$ is $10^{9.05}$ and that of $\mathrm{[Cu\ aca_2]}$ is $10^{8.1}$. In both cases the above requirement is fulfilled.

As the formation constant of $\mathrm{[Cu(dgH)_2]}$ is not known, in the present experiment the extinction measurements were carried out in a water-free solvent in order to eliminate hydrolysis, though it is expected to be a considerably stable complex, from the analogy of the dimethylglyoxime complexes of other metals.

Since $\mathrm{[Cu\ ox_2]^{--}}$ is not so stable as to make it possible to ignore hydrolysis, $(k_1k_2=10^{8.3)})$[3], potassium oxalate was added to the solvent in the concentration 0.01 M to remove the error due to hydrolysis. On the other hand, the error due to the following equilibrium may be caused by the addition of the oxalate ion;

$$\mathrm{[Cu\ en_2]^{++}+ox^{--} \rightleftarrows [Cu\ en\ ox]+en.}$$

But the extinction measurements of the solution of $\mathrm{[Cu\ en_2]\ (NO_3)_2}$ containing 0.01 M potassium oxalate showed that the results agreed well with those of solutions containing no oxalate ion within the experimental error. Therefore, the error due to the addition of oxalate can be ignored.

If Watters' isosbestic method is adopted, such elaborate considerations as have been made above are not necessary. In his method only the total concentration of copper is known (0.01 M), and the concentration of the complexes in the solution is to be determined by calculation using the extinction data. For example, the concentration of $\mathrm{[Cu\ en_2]^{++}}$ can be determined by the following relation at the isosbestic point where ε_2 is equal to ε_3. Here ε_1. ε_2 and ε_3 mean the molar extinction coefficients of $\mathrm{[Cu\ en_2]^{++}}$, $\mathrm{[Cu\ ox_2]^{--}}$ and [Cu en ox] respectively.

$$(\mathrm{Cu\ en_2^{++}})=\frac{e-0.01\varepsilon_2}{\varepsilon_1-\varepsilon_2} \tag{7}$$

(where e is the extinction of the mixed solution).

While, in the present method, as the concentration of $\mathrm{[Cu\ en_2]^{++}}$ etc. is determined by direct weighing, its experimental error will be smaller than that calculated from the extinction data, and at the same time, will not be magnified in the process of calculation. (In the process of calculation after (7) the experimental error may be multiplied several times.)

The values of $\log Km$ determined are given in Table V. It can readily be seen from the table that the order of the value of Km is

$$\mathrm{[Cu\ P_2O_7\ en]^{--} > [Cu\ en\ ox] >}$$
$$\mathrm{[Cu\ en\ aca]^{+} > [Cu\ dgH\ aca].}$$

Watters and De Witt ascribed the variety of the value of Km to the difference of the mutual ionic repulsion of ligands from their data of $\mathrm{[Cu\ P_2O_7\ en]^{--}}$ and [Cu en ox]. The results of the present study also seem to support their suggestion. It is reasonable

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[2] G. A. Carlson, J. P. Mc Reynolds and F. H. Verhoek, *J. Am. Chem. Soc.*, 67, 1334 (1945); M. Calvin and K. W. Wilson, ibid., 67, 2003 (1945).

[3] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", (1952), p. 516.

TABLE VIII

COMPARISON OF THE ABSORPTION MAXIMUM OF THE MIXED COMPLEX WITH IT PARENT COMPLEXES

	ν_{max}	ε_{max}		ν_{max}	ε_{max}		ν_{max}	ε_{max}
[Cu en$_2$]$^{++}$	54.9 (55.1*)	59.8 (63.1*)	[Cu en$_2$]$^{++}$	54.5	61.4	[Cu en$_2$]$^{++}$	54.3*	63.0*
[Cu ox$_2$]$^{--}$	42.0 (42.3*)	33.2 (34.7*)	[Cu aca$_2$]	48.0	38.0	[Cu(P$_2$O$_7$)$_2$]$^{6-}$	40.6*	27.5*
Mean value	48.45 (48.7*)	46.5 (48.9*)	Mean value	51.25	49.85	Mean value	47.45*	45.25*
[Cu en ox]	48.5 (48.2*)	51.0 (49.8*)	[Cu en aca]$^{+}$	51.1	53.6	[Cu en P$_2$O$_7$)$^{--}$	47.5*	43.0*

$\nu_{max} \times 10^{13}$: the frequency of the absorption maximum (sec^{-1})

ε_{max}: molar extinction coefficient of the absorption maximum

* Data from the investigation of Watters and Lougham1).

to consider that, in the case of [Cu en ox], electrical repulsion between ethylenediamine and oxalate ion is smaller than that between two oxalate ions, therefore, *Km* is greater than the statistical value. On the other hand in the case of [Cu en aca]$^{+}$ and its parent complexes, the contribution of electrical repulsion of the ligand to *Km* is negligibly small, so the value of *Km* of this complex is expected to be near the statistical value. But the found value is smaller than the expected value. This fact cannot be sufficiently explained by mere electric repulsion. For the complete interpretation further investigations will be necessary.

The absorption curves of the mixed complexes are shown with broken lines in Fig. 1, Fig. 3 and Fig. 4. These curves were determined from extinction data of parent complexes and the mixed solution, and *Km* by using the relations (3) and (4).

The absorption curve of the mixed complex is generally higher than the mean extinction curve of parent complexes which is shown with a dotted line in Fig. 1, 3 and 4. This is a very interesting fact for the investigation of the electronic state of metallic complexes, considering together the previous data4,5,6) of aquo-ammine mixed complex of Cu(II), Ni(II), Cr(III) and Co(III) in which the similar relations are found.

The absorption maxima of the mixed complexes are shown in Table VIII. From these data, it is readily seen that the frequency of the maximum absorption of a mixed complex coincides with the mean value of the parent complexes. This fact is also interesting in consideration of the study of Shimura and Tsuchida6), in which the shift of the frequency of the first absorption maximum of Co(III) ammine complexes was found to be proportional to the number of substituted ligands.

The detailed discussion of the absorption spectra of mixed complexes will be reported later.

Summary

The dismutation constants of the three mixed complexes [Cu en ox], [Cu en aca]$^{+}$ and [Cu dgH aca] were determined photometrically. The negative logarithms of their dismutation constants were found to be 1.10, 0.42 and $\bar{1}.96$ respectively.

By the use of determined, dismutation constants absorption spectra of these mixed complexes were found. The frequency of the absorption maximum was found to coincide with the mean value of the parent complexes. At the same time the absorption of the mixed complex is generally stronger than the mean absorption of the parent complexes.

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4) J. Bjerrum "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen (1941); R. Tsuchida, "The Colors and the Structure of Metallic Compounds", Zoshindo, Osaka (1948) (in Japanese).

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