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BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2970—2972 (1970)

Alpha-Benzildioxime Complexes of Copper(II) — A Study by Solvent Extraction —

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(Received November 12, 1969)

It is well known that α-benzildioxime forms complexes with nickel(II) and palladium(II), and has been used as a gravimetric or a spectrophotometric reagent for these metals[1] as a substitute for dimethylglyoxime. Studies have also been made on cobalt(II)[2] and iron(II)[3] complexes of α-benzildioxime. However, little has been made on copper(II) complex of α-benzildioxime, except for the determination of the formation constants of the complex in 50% dioxane-water system by the potentiometric method.[4] During the course of studies on the reaction of copper(II) with α-benzildioxime by the solvent extraction method, we found that copper(II) forms two kinds of complexes with α-benzildioxime; one is light brown bis(α-benzildioximato)copper(II) and the other light greenish yellow mono(α-benzildioximato)copper(II). This paper gives some results of the study on the complexes by the solvent extraction method.

Experimental

Reagents. A copper(II) solution (0.618 mg Cu(II)/m*l*) was prepared from copper(II) sulfate pentahydrate with the addition of a small amount of sulfuric acid to prevent the hydrolysis of copper(II). The solution was used with dilution to an appropriate concentration. Alpha-benzildioxime (Wako Pure Chemicals Ind., Ltd.) was recrystallized from methanol and a 0.02% methanolic solution of the purified reagent (mp 237°C) was used. A 2.5 M solution of ammonium nitrate was used as the ammonium salt solution.

Apparatus. Absorption spectra were recorded with a Hitachi automatic recording spectrophotometer, model EPS-3T, and other absorption measurements were carried out with a Hitachi spectrophotometer, model 139, with 10-mm quartz cells. A pH meter of Toa Dempa Co., Ltd., model HM-5A, was used for pH measurements. Solvent extraction was carried out with an Iwaki universal shaker, model V-D, at the rate of 300 rpm. All the experiments were carried out at about 23°C.

Results and Discussion

Absorption spectra of copper(II)-α-benzildioxime complex extracted into benzene are shown

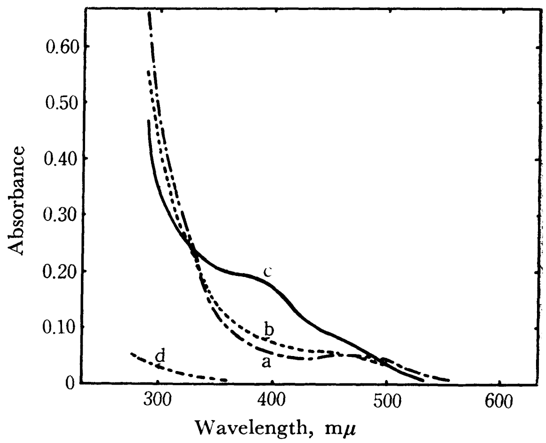

Fig. 1. Absorption spectra of copper(II)-α-benzildioxime complex in benzene.
[α-Benzildioxime]: 3.87×10^{-5} M.
a : [Cu(II)]/[α-Benzildioxime] = 0.6 (mole fraction of Cu(II) = 0.38).
b : [Cu(II)]/[α-Benzildioxime] = 2.5 (mole fraction of Cu(II) = 0.67).
c : [Cu(II)]/[α-Benzildioxime] = 5.0 (mole fraction of Cu(II) = 0.83).
d : α-Benzildioxime alone.
pH value of equilibrated aqueous phase: 8.2.
λ_{max} of curve a: 460 mμ.

1) For example: Y. Uzumasa and S. Washizuka, This Bulletin, **29**, 403 (1956); W. Wawrzyczek, H. Majkowska and J. Soboczynska, *Z. Anal. Chem.*, **188**, 88 (1962).
2) C. Matsumoto, I. Masuda and K. Shinra, *Nippon Kagaku Zasshi*, **88**, 46 (1967).
3) C. Matsumoto, Y. Yamano and K. Shinra, *ibid.*, **89**, 44 (1968).
4) K. Burger and I. Ruff, *Talanta*, **10**, 329 (1963).

in Fig. 1. Curve a in Fig. 1 is a spectrum of the complex obtained with an excess of α-benzildioxime (mole fraction of copper(II): 0.38) and has an absorption maximum at the wavelength of 460 mμ. The complex obtained under these conditions is light brown and moderately soluble in benzene, irrespective of the presence of ammonium salt in the aqueous phase. Curve c in Fig. 1, on the contrary, is a spectrum of the complex obtained with a large excess of copper(II) (mole fraction of copper(II): 0.83) and has no absorption maximum in the near ultraviolet and visible regions. The complex is light greenish yellow, and its solubility in benzene is very low unless ammonium salt is present in the aqueous phase. (Curve b in Fig. 1 can be considered as an intermediate of the above-mentioned two limiting cases).

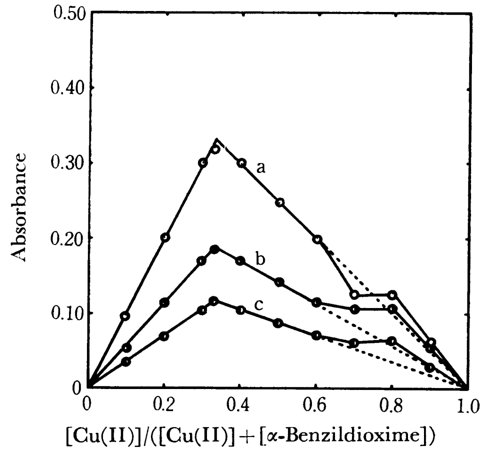

Fig. 2. The method of continuous variations.
λ; a: 350 mμ, b: 380 mμ, c: 430 mμ
[Cu(II)]+[α-Benzildioxime]: 1.54×10^{-4} M
pH value of equilibrated aqueous phase: 8.2
$\mu=0.15$ (NH_4NO_3)

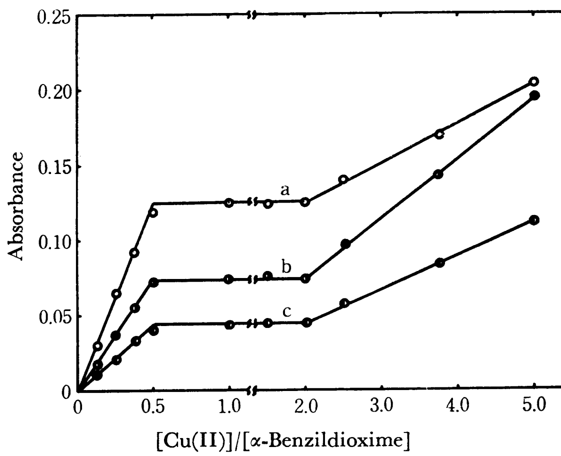

Fig. 3. The molar ratio method.
λ; a: 350 mμ, b: 380 mμ, c: 430 mμ
[α-Benzildioxime]: 3.87×10^{-5} M
pH value of equilibrated aqueous phase: 8.2
$\mu=0.15$ (NH_4NO_3)

Figures 2 and 3 show the results obtained by the method of continuous variations and the molar ratio method, respectively. The results indicate that there exists a 1 to 2 (metal to ligand) complex when mole fraction of copper(II) is less than about 0.6 (ratio of copper(II) to α-benzildioxime: about 2), and another kind of copper(II) complex is formed when copper(II) is in a large excess over α-benzildioxime (mole fraction of copper(II) is larger than about 0.8). As we could not determine the composition of the latter complex from these results, chemical analysis of the complex extracted with a large excess of copper(II) was carried out. The results are presented in Table 1. We see that the light greenish yellow complex has a composition of 1 to 1 (metal to ligand).

The extraction equilibrium of bis(α-benzildioxi-

Table 1. Composition of the complex extracted under the large excess of copper(II) (%)

	Cu	C	H	N
I	19.3	49.5	5.1	17.1
II	19.5	49.8	5.2	16.9
III	18.92	50.06	4.80	16.68

Note I: The complex extracted under 10 times as much as copper(II) against α-benzildioxime and obtained as solid state by evaporation of benzene under vacuum at room temperature.
II: Those extracted under 20 times as much as copper(II) and obtained by the same procedure as described in I.
III: Calcd for $Cu(C_{14}H_{10}N_2O_2)(NH_3)_2$.

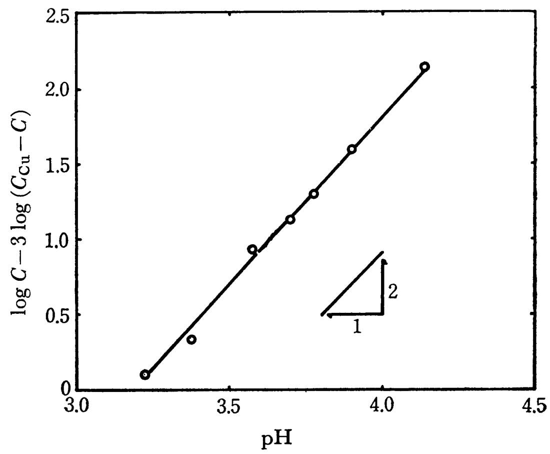

Fig. 4. Reaction between $\log C-3\log(C_{Cu}-C)$ and pH.

($\log C-3\log(C_{Cu}-C)=\log 4K_{ex}+2\cdot\text{pH}$)
C_{Cu}: 1.21×10^{-4} M ($C_{H_2L}=2C_{Cu}$)
$\mu=0.05$ (HCl+KCl)
$V/V_{(org)}=1$, ($V_{(org)}=10$ ml)

mato)copper(II) complex might be expressed as follows:

$$Cu^{2+} + 2H_2L_{(org)} \rightleftharpoons Cu(HL)_{2(org)} + 2H^+$$

$$K_{ex} = [Cu(HL)_2]_{(org)} \cdot [H^+]^2/[Cu^{2+}] \cdot [H_2L]^2_{(org)} \quad (1)$$

where H_2L denotes the undissociated α-benzildioxime, K_{ex} the extraction constant of the copper(II) complex, the suffix *org* the organic phase and no suffix the aqueous phase, respectively. To ascertain the validity of the extraction equilibrium represented above, the following considerations were made. Provided that the partition coefficients of α-benzildioxime and its copper(II) complex are sufficiently large and that the equilibrium concentrations of the intermediate species of α-benzildioxime and its copper(II) complex are negligibly low, $[Cu^{2+}]$ and $[H_2L]_{(org)}$ can be expressed in terms of the total concentration of copper(II). C_{Cu}, and that of α-benzildioxime, C_{H_2L}, when volumes of aqueous and organic phases are equal:

$$[Cu^{2+}] = C_{Cu} - [Cu(HL)_2]_{(org)} \quad (2)$$

$$[H_2L]_{(org)} = C_{H_2L} - 2[Cu(HL)_2]_{(org)} \quad (3)$$

When C_{Cu} and C_{H_2L} are taken so as to make $2C_{Cu} = C_{H_2L}$, Eq. (4) can be obtained by inserting Eqs. (2) and (3) into Eq. (1) and writing in logarithmic form:

$$\log C - 3 \log (C_{Cu} - C) = \log 4K_{ex} + 2\mathrm{pH} \quad (4)$$

where C denotes the term $[Cu(HL)_2]_{(org)}$. Figure 4 shows the results obtained under the condition $2C_{Cu} = C_{H_2L}$ with varying pH values of the aqueous phase, which reveals that the extraction equilibrium of bis(α-benzildioximato)copper(II) complex can be correctly expressed as represented above.