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A Spectrophotometric Study of Tributyl Phosphate Adducts of Three Bis(β-diketonato)copper(II) Complexes in Carbon Tetrachloride

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Adduct formation equilibria between bis(2-thenoyltrifluoroacetonato)-, bis(trifluoroacetylacetonato)-, and bis(hexafluoroacetylacetonato)copper(II) chelates and tributyl phosphate (TBP) in water-saturated carbon tetrachloride were studied spectrophotometrically at 25 °C. The chelates added one TBP molecule and decreased the absorption, but not very much. The formation constants obtained from the changes in the absorption, given as a function of the TBP concentration, agreed very well with those obtained previously by a solvent-extraction method.

The adduct formation of uncharged metal chelates with neutral ligands in the organic phase in solvent-extraction systems enhances the metal-chelate extraction; this enhancement is often called "synergism." The equilibria of the adduct formation can be measured from an analysis of the enhancement of the extraction, which is determined as a function of the ligand concentration in the organic phase; also, the formation constants of the adduct metal chelates have been determined in several systems under various conditions.[1-4]

The formation of adducts may affect the spectral properties of the complex. This has been observed in several metal chelate systems,[5] especially when the adduct-forming ligands were organic bases, such as homologues or derivatives of pyridine and quinoline. The appearance of strong absorptions upon the addition of organic bases to metal chelates in the organic phase in solvent-extraction systems has been used in the colorimetry of the metal ion; the sensitivity has thus been found to be much higher than in the absence of the adduct-forming ligand.[6,7]

The change in the absorption by adduct formation as a function of the ligand concentration may also be used in the determination of the formation constants. In studies of the synergism of metal extraction as chelates on the addition of heterocyclic organic bases, the adduct-formation constants have been spectrophotometrically determined and discussed in relation to the synergism.[8,9] Such quantitative spectrophotometric studies of adduct chelate formation equilibria with heterocyclic organic bases have been reported several times.[10-22]

Another group of ligands which have been studied frequently in connection with their ability to form adduct chelates are neutral phosphorus compounds such as tributyl phosphate (TBP); the changes in the absorptions have also been discussed in relation to the enhancement of the extraction.[23,24] However, not much quantitative analysis of the changes in the absorption has been done, and few spectrophotometric determinations of the adduct formation constants with such neutral organophosphorus compounds have been made.

In the course of a series of studies of metal-chelate extraction with several β-diketones and their synergism with neutral ligands in our laboratory, it was found that the optical absorption also changed upon adduct-formation in the copper(II) extraction systems with β-diketones in conjunction with TBP and that the equilibrium constants obtained from these spectrophotometric data agreed very well with those obtained from the solvent-extraction data.

Experimental

The experimental conditions were the same as in the previous solvent-extraction study,[25,26] except that the changes in the absorption spectra were measured instead of those in the distribution ratio.

The bis(β-diketonato)copper(II) ($Cu(acac)_2$) and the β-diketones were supplied by the Dojindo Co., Kumamoto. The tributyl phosphate was supplied by the Tokyo Kasei Co., Tokyo, and was purified by the same method as before.[25,26] The carbon tetrachloride was an analytical-grade solvent. Two UV-VIS spectrophotometers (Hitachi type-556 and -139) were used.

A weighed amount of $Cu(acac)_2$ was dissolved in water-saturated carbon tetrachloride containing 0.1 mol dm^{-3} of 2-thenoyltrifluoroacetone (Htta), trifluoroacetylacetone (Htaa), or hexafluoroacetylacetone (Hhfa) and converted into $Cu(tta)_2$, $Cu(taa)_2$, or $Cu(hfa)_2$. These solutions were used as the stock solutions. A portion of a stock solution and a portion of a water-saturated carbon tetrachloride solution of TBP were mixed; when necessary, another portion of carbon tetrachloride was added in order to bring the initial concentrations of the bis(β-diketonato)copper(II), the β-diketone and TBP up to the wanted values. The solution was stored for 1 h, and the absorption spectrum was measured using a glass cell with a 1 cm light path. The temperature was kept at 25±0.3 °C.

Statistical

In this paper, the chemical species with the subscript "aq" are those in aqueous solutions, while the lack of any subscript indicates those in carbon tetrachloride solutions.

The ligand-exchange equilibria of acetylacetonate ions in $Cu(acac)_2$ with a β-diketone, Ha, may be written as:

$$\mathrm{Cu(acac)_2 + Ha \rightleftharpoons Cu(acac)(a) + Hacac} \quad (1)$$

$$\mathrm{Cu(acac)_2 + 2Ha \rightleftharpoons Cu(a)_2 + 2Hacac} \quad (2)$$

$$K_{x1} = [\mathrm{Cu(acac)(a)}][\mathrm{Hacac}][\mathrm{Cu(acac)_2}]^{-1}[\mathrm{Ha}]^{-1} \quad (3)$$

$$K_{x2} = [\mathrm{Cu(a)_2}][\mathrm{Hacac}]^2[\mathrm{Cu(acac)_2}]^{-1}[\mathrm{Ha}]^{-2}. \quad (4)$$

The values of K_{x1} and K_{x2} can be obtained from the solvent-extraction constants as follows:

$$\mathrm{Cu^{2+}(aq) + 2Hacac \rightleftharpoons Cu(acac)_2 + 2H^+(aq)} \quad (5)$$

$$\mathrm{Cu^{2+}(aq) + Hacac + Ha \rightleftharpoons Cu(acac)(a) + 2H^+(aq)} \quad (6)$$

$$\mathrm{Cu^{2+}(aq) + 2Ha \rightleftharpoons Cu(a)_2 + 2H^+(aq)} \quad (7)$$

$$K_{\mathrm{ex(acac)}} = [\mathrm{Cu(acac)_2}][\mathrm{H^+}]^2_{\mathrm{aq}}[\mathrm{Cu^{2+}}]^{-1}_{\mathrm{aq}}[\mathrm{Hacac}]^{-2} \quad (8)$$

$$K_{\mathrm{ex(mix)}} = [\mathrm{Cu(acac)(a)}][\mathrm{H^+}]^2_{\mathrm{aq}}[\mathrm{Cu^{2+}}]^{-1}_{\mathrm{aq}} \times [\mathrm{Hacac}]^{-1}[\mathrm{Ha}]^{-1} \quad (9)$$

$$K_{\mathrm{ex(a)}} = [\mathrm{Cu(a)_2}][\mathrm{H^+}]^2_{\mathrm{aq}}[\mathrm{Cu^{2+}}]^{-1}_{\mathrm{aq}}[\mathrm{Ha}]^{-2}. \quad (10)$$

Here, the statistical values of $K_{\mathrm{ex(mix)}}$ are obtained as:[27]

$$K_{\mathrm{ex(mix)}} = 2\sqrt{K_{\mathrm{ex(acac)}}K_{\mathrm{ex(a)}}}. \quad (11)$$

Although the statistical value of $K_{\mathrm{ex(mix)}}$ could, to some extent, be different from the experimental value, it may be used in this study, taking its concentration as an approximate value.

$$K_{\mathrm{x1}} = K_{\mathrm{ex(mix)}}K^{-1}_{\mathrm{ex(acac)}} \quad (12)$$

$$K_{\mathrm{x2}} = K_{\mathrm{ex(a)}}K^{-1}_{\mathrm{ex(acac)}}. \quad (13)$$

The formation equilibrium of the adduct can be written as:

$$\mathrm{Cu(a)_2 + tbp \rightleftharpoons Cu(a)_2(tbp)} \quad (14)$$

$$\beta_{\mathrm{1(org)}} = [\mathrm{Cu(a)_2(tbp)}][\mathrm{Cu(a)_2}]^{-1}[\mathrm{tbp}]^{-1}. \quad (15)$$

When the molar extinction coefficients of the $\mathrm{Cu(a)_2}$ and $\mathrm{Cu(a)_2(tbp)}$ species at a certain wavelength are ε_0 and ε_1 respectively, then the optical density can be written as:

$$E = \varepsilon_0[\mathrm{Cu(a)_2}] + \varepsilon_1[\mathrm{Cu(a)_2(tbp)}]. \quad (16)$$

The following equations may be valid in these systems:

$$[\mathrm{Cu(II)}]_{\mathrm{total}} = [\mathrm{Cu(a)_2}] + [\mathrm{Cu(a)_2(tbp)}] \quad (17)$$

$$[\mathrm{tbp}]_{\mathrm{total}} = [\mathrm{tbp}] + [\mathrm{Cu(a)_2(tbp)}]. \quad (18)$$

By using a least-squares program, the values of $\beta_{\mathrm{1(org)}}$ and ε_1 can be computed by successive approximation procedures.

Results and Discussion

The equilibrium constants for the ligand exchange in Eqs. 3, 4, 12, and 13 were calculated from the extraction constants in the literature, as listed in Table 1. Since the maximum amount of Hacac produced by the ligand exchange should be twice that of the $\mathrm{Cu(acac)_2}$ chelate added, it should be lower than 1×10^{-3} mol dm^{-3}. Thus, it may be seen from Eqs. 12 and 13 and the values of the constants in Table 1 that more than 99% of the initial bis(acetylacetonato)copper(II) should be converted into the complexes when the β-diketone concentration is 0.1 mol dm^{-3}. It was also confirmed by spectrophotometric measurements that the optical-absorption spectrum of the solution thus obtained by the ligand exchange was identical to that of the solution of each β-diketone complex within the limits of experimental error. This exchange formed free acetylacetone and decreased the concentration of that β-diketone. The change in the absorption caused by the changes in these concentrations was corrected on the basis of the molar extinction coefficients of the β-diketones and the concentration of copper(II).

TABLE 1. EQUILIBRIUM CONSTANTS FOR THE LIGAND EXCHANGE OF COPPER(II) CHELATES IN $\mathrm{CCl_4}$

Ligand	log K_{ex}[a]	log $K_{\mathrm{ex(mix)}}$[b]	log K_{x1}	log K_{x2}
Hacac	−3.47	—	—	—
Htta	−1.08	−1.98	1.49	2.39
Htaa	−1.12	−2.00	1.47	2.35
Hhfa	−0.26	−1.57	1.90	3.21

a) When the aqueous phase was 0.1 mol dm^{-3}, $\mathrm{(Na,H)ClO_4}$. Taken from refs. 25 and 26. b) Calculated statistical values.

The total copper(II) concentration was maintained at 5×10^{-4} mol dm^{-3}. Optical measurements were carried out in the region where the molar extinction coefficient is higher than 2×10^2 and where the absorption due to the reagent is not high. This region was from 400 to 420 nm at twenty-one different points for the $\mathrm{Cu(tta)_2}$ chelate, from 350 to 400 nm at fifty-one different points for the $\mathrm{Cu(taa)_2}$ chelate, and from 370 to 390 nm at twenty-one different points for the $\mathrm{Cu(hfa)_2}$ chelate. The absorption of the $\mathrm{Cu(hfa)_2}$ chelate and its TBP adduct could not be measured below 370 nm because, in this region, the absorption of the reagent was very high. Absorptions were also measured up to 800 nm, but no high absorption due to the adduct formation ($\varepsilon_1 > 200$) was found in this region. Thus, the range of the wavelengths of the data used for the calculation was narrow in all the cases, as can be seen from Fig. 1. Several sets of data of the optical absorption, E, in Eq. 16 at this copper(II) concentration and various total TBP concentrations were obtained at each wavelength.

The least-squares calculation of the values of $\beta_{\mathrm{1(org)}}$

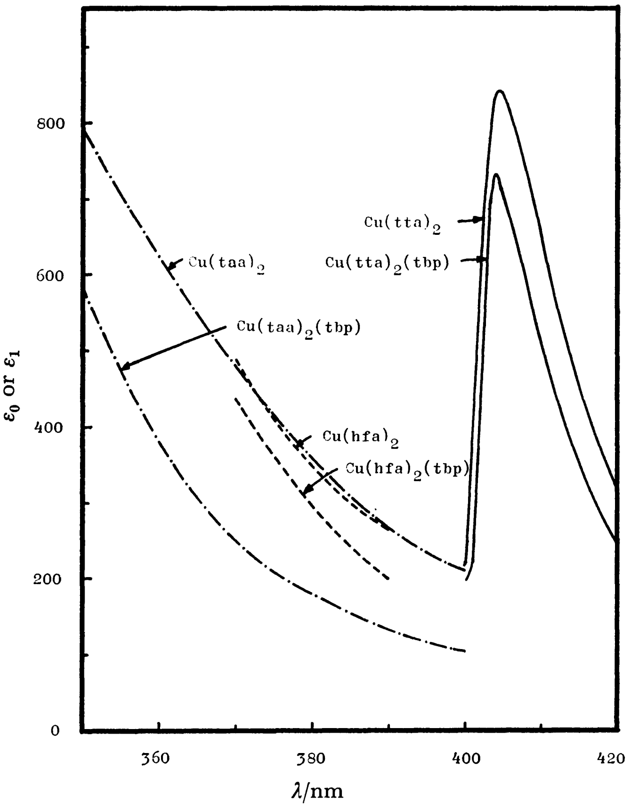

Fig. 1. Absorption spectra of bis(β-diketonato)copper(II) chelates and their tbp adducts given by molar absorptivity as a function of wavelength.

TABLE 2. SUMMARY OF FORMATION CONSTANTS OF TBP ADDUCT CHELATE COMPLEXES

Chelate	log $\beta_{1(org)}$[a] (by spectrophotometry)	log $\beta_{1(org)}$[b] (by solvent extraction)
$Cu(tta)_2$	2.21 ± 0.1	2.27
$Cu(taa)_2$	2.15 ± 0.1	2.16
$Cu(hfa)_2$	4.63 ± 0.1	4.60

a) Present work; the limit of error is 3σ. b) Refs. 25 and 26.

and ε_1 at each wavelength were carried out from the set of data, together with the ε_0 of that bis(β-diketonato)-copper(II) which was determined at that wavelength in the absence of TBP. The variation in the values of $\beta_{1(org)}$, the formation constants of the TBP adducts, obtained from the data at different wavelength was rather small; the values are listed in Table 2, together with the corresponding values obtained by the solvent-extraction method in the previous study. The constants obtained by these two different methods agreed very well, as may be seen in Table 2. The values of ε_1, the molar extinction coefficient of the TBP adducts, were also obtained from the experimental data by these calculations. The values of ε_1 are shown in Fig. 1, together with the values of ε_0 of the bis(β-diketonato)-copper(II) complexes.

Since the carbon tetrachloride solutions were saturated by water, the effect of water in the carbon tetrachloride on the adduct-formation equilibrium should be identical with that in solvent extraction systems. However, if spectrophotometric experiments were to be made at various water concentrations, the effect of water in the solvent which can not be made by the solvent extraction method could be determined.

As may be seen from Fig. 1, the absorption spectra of each bis(β-diketonato)copper(II) complex and its TBP adduct are rather similar, although the absorption curve of the bis(hexafluoroacetylacetonato)complex and of its TBP adduct become a little closer in the lower-wavelength region. In all the cases, the molar extinction coefficient of the adduct is smaller than that of the chelate ($\varepsilon_1/\varepsilon_0$ is 0.75 to 0.85 with $Cu(tta)_2$, 0.50 to 0.65 with $Cu(taa)_2$, and 0.75 to 0.90 with $Cu(hfa)_2$). However, the $\varepsilon_1/\varepsilon_0$ values are not far from 1, so the adduct formation by TBP seems to have only a slight effect on the electronic state of the complex. This is quite different from the observation that, by the formation of bis(β-diketonato)complexes with organic bases, a strong absorption appears in the higher wavelength region.[6,7]

The difference in the two absorption spectra is not large, but the adduct-formation constants, $\beta_{1(org)}$, could be determined accurately in the present study. This indicates that the spectrophotometric determination may be used for the adduct-formation equilibria in several other systems. However, since the metal concentration can not be lowered very much for accurate optical measurements, the error in the constants must be larger than those obtained by the solvent extraction method, which can be studied even at tracer metal concentrations, if the value of $\beta_{1(org)}$ is very large, for example, as in the case of the $Cu(hfa)_2$ chelate.

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