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Formation and Absorption Spectra of Mixed Copper(II) Chelates Containing Acetylacetone and 2,2′-Bipyridine or 1,10-Phenanthroline

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The formation and absorption spectra of a number of mixed copper(II) chelates of the general type [CuAB], where A is bip or phen and B is en, gly or ox, were studied by Sone, Utsuno and Ogura.[1] The extension of this study to the systems

(1) $[Cu\ bip_2]^{2+} + [Cu\ aca_2] \rightleftarrows 2[Cu\ bip\ aca]^+$

(2) $[Cu\ phen_2]^{2+} + [Cu\ aca_2] \rightleftarrows 2[Cu\ phen\ aca]^+$

is reported here[2].

Figure 1 shows the visible absorption spectra of the solutions containing $[Cu\ bip_2](NO_3)_2 \cdot H_2O$ and $[Cu\ aca_2]$ in various proportions. The solvent used is 80% (v/v) dioxane, and the total concentration of the two chelates is 10^{-2} M in every case. Existence of two isosbestic points is evident; one at 704 mμ is observed in solutions in which the ratio $[Cu\ bip_2]^{2+}$: $[Cu\ aca_2]$ is 0 : 10 to 5 : 5, and another at 628 mμ is found in solutions where the ratio is 5 : 5 to 10 : 0. In Fig. 1, the curves for the solutions of the ratios 3 : 7, 4 : 6, 6 : 4 and 7 : 3 are not shwon. However, each of them passes the corresponding isosbestic point. The absorption bands of $[Cu\ bip_2]^{2+}$ at 740 and 950 mμ (ε=88 and 78, respectively) disappear almost completely in the solution where the ratio is 5 : 5, and a new band appears, the λ_{max} of which (610 mμ; ε=62) is smaller than those of $[Cu\ bip_2]^{2+}$ and even than that of $[Cu\ aca_2]$ (620 mμ; ε=39). Essentially similar data are obtained with $[Cu\ phen_2](NO_3)_2 \cdot H_2O$ and $[Cu\ aca_2]$ in 72% dioxane, where the

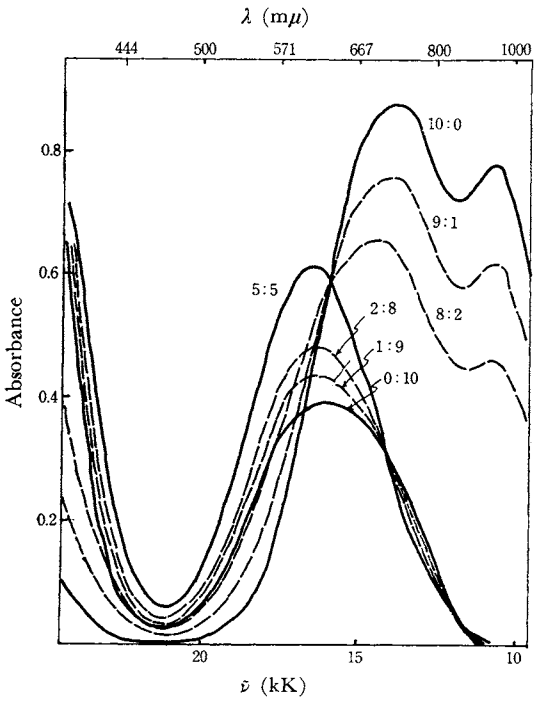

Fig. 1. Absorption spectra of $[Cu\ bip_2]^{2+}$ - $[Cu\ aca_2]$ mixed solutions in 80% dioxane. The molar ratio of the component chelates ($[Cu\ bip_2]^{2+}$: $[Cu\ aca_2]$) is shown for each curve.

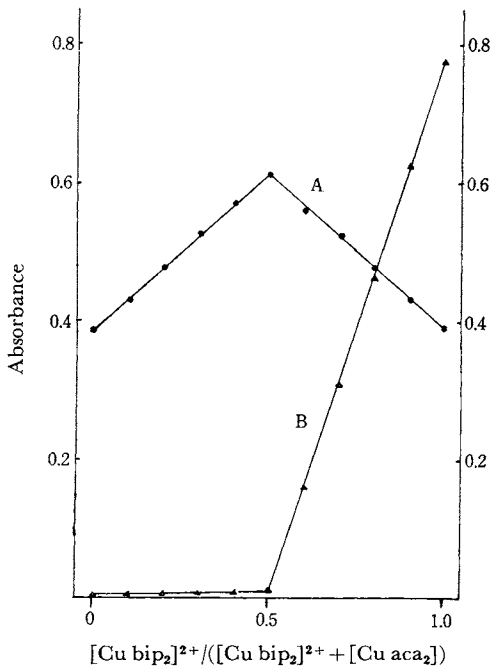

Fig. 2. Application of continuous variation method to the data of Fig. 1. The wavelength used: (A) 600 mμ; (B) 940 mμ.

1) K. Sone, S. Utsuno and T. Ogura, *J. Inorg. Nucl. Chem.*, **31**. 117 (1969).

2) Abbreviations used in this paper are: bip=2,2′-bipyridine; phen=1,10-phenanthroline; en=ethylenediamine; gly=glycinate anion; ox=oxalate anion; aca=acetylacetonate anion.

total concentration of the two chelates is 0.8×10^{-2} M; here the band of $[Cu\ phen_2]^{2+}$ at 720 and 980 mμ (ε=46 and 41, respectively) practically disappears in the 5 : 5 mixture, and a new band appears instead at 615 mμ (ε=48). These facts, and especially the application of continuous variation method to these data (*cf.* Fig. 2), clearly indicate that the mixed chelates [Cu bip aca]$^+$ and [Cu phen aca]$^+$ are formed nearly quantitatively in the respective mixed solutions. Estimation from these spectral data indicates that the equilibrium constants (K) of the two systems (1) and (2) are both very large ($K \geqq 10^4$), showing the remarkably high stability of these mixed species. It was also found that dark-green crystalline chelates [Cu bip aca]X and [Cu phen aca]X (X=NO_3 or ClO_4) can be readily obtained by evaporating equimolar mixtures of [Cu aca_2] and [Cu bip_2]X_2 or [Cu $phen_2$]X_2 dissolved in aqueous ethanol. The results of elemental analyses are as follows; Found: C, 47.21; H, 3.99; N, 10.96%. Calcd for [Cu bip aca](NO_3): C, 47.29; H, 3.97; N, 11.03%. Found: C, 41.47; H, 4.00; N, 6.50%. Calcd for [Cu bip aca](ClO_4)·H_2O: C, 41.29; H, 3.94; N, 6.42%. Found: C, 47.39; H, 4.23; N, 9.84%. Calcd for [Cu phen aca](NO_3)·1.5 H_2O: C, 47.27; H, 4.21; N, 9.73%. Found: C, 44.37; H, 3.80; N, 6.17%. Calcd for [Cu phen aca](ClO_4)·H_2O: C, 44.35; H, 3.73; N, 6.09%.

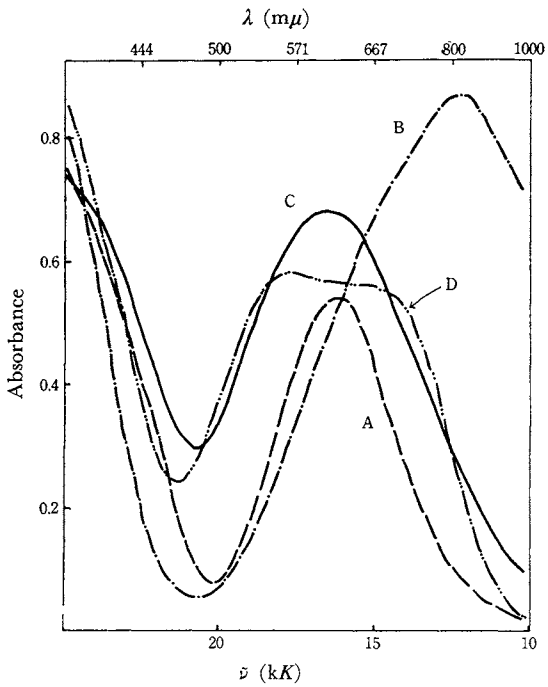

Fig. 3. Spectral data of the chelates in the system $[Cu\ bip_2]^{2+}-[Cu\ aca_2]$. Curve A: absorption spectrum of [Cu bip aca]$^+$ in 80% dioxane; curves B, C and D: reflectance spectra of [Cu bip_2](NO_3)$_2$·H_2O, [Cu bip aca](NO_3) and [Cu aca_2], respectively.

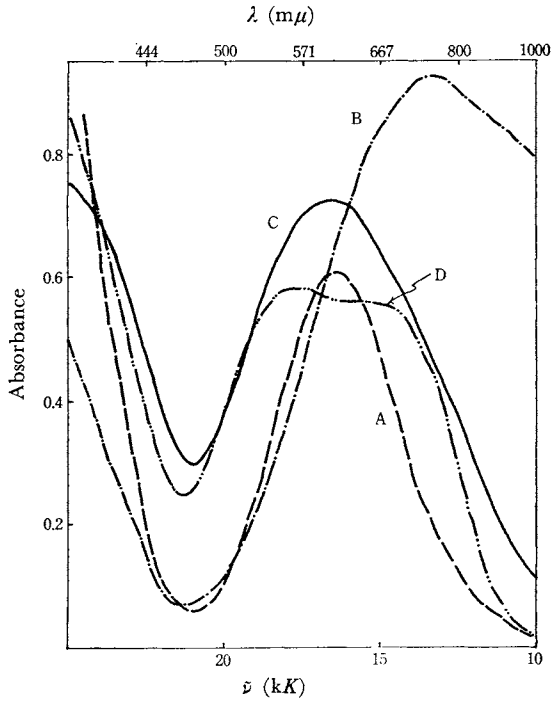

Fig. 4. Spectral data of the chelates in the system $[Cu\ phen_2]^{2+}$-[Cu aca_2]. Curve A: absorption spectrum of [Cu phen aca]$^+$ in 80% dioxane; curves B, C and D: reflectance spectra of [Cu $phen_2$](NO_3)$_2$·H_2O, [Cu phen aca](NO_3)·1.5H_2O and [Cu aca_2], respectively.

Figures 3 and 4 show that the λ_{max} values of the reflectance spectra of these newly obtained chelates agree fairly well with those in the absorption spectra of their 80% dioxane solutions; the latter spectra, on the other hand agree nearly exactly with the spectra of the corresponding 5 : 5 mixtures described above. These facts show that these crystalline chelates are true mixed chelates, and not the mere mixtures of the component chelates.

It is of interest to compare these data with the earlier data of Kida[3] on the formation of [Cu en aca]$^+$ from $[Cu\ en_2]^{2+}$ and [Cu aca_2] in water-dioxane. Although his experimental conditions are not exactly the same as ours, it is apparent that the stability of [Cu en aca]$^+$ with respect to its component chelates is very much lower than that of [Cu bip aca]$^+$ and [Cu phen aca]$^+$. The value of K calculated by Kida was only 2.6, and did not differ so much from the statistical value 4. He also found that the absorption band of [Cu en aca]$^+$ was nearly at the middle between those of $[Cu\ en_2]^{2+}$ and [Cu aca_2]. Thus the behavior of this mixed chelate seems to be quite normal in every respect.

The remarkably greater stability and apparently anomalous spectra of the mixed chelates can now

3) S. Kida, This Bulletin, **29**, 805 (1956).

be ascribed, as in the case of other bip- or phen-containing mixed chelates,[1] to the removal of the steric hindrance existing in $[Cu\ bip_2]^{2+}$ and $[Cu\text{-}phen_2]^{2+}$ by mixed chelate formation. As described in a previous paper,[1] scale model studies show that these chelates are considerably deformed from the square-planar structure normally favored by Cu^{2+}. On the other hand, the same studies show that the mixed chelates $[Cu\ bip\ aca]^+$ and $[Cu\ phen\ aca]^+$ are perfectly square-planar. Therefore, we can expect that they will be very readily formed in solution containing the component chelates, and the value of K will be very much higher than the statistical value. We can also expect that their λ_{max} values will be much smaller than those of $[Cu\ bip_2]^{2+}$ or $[Cu\ phen_2]^{2+}$, and even than that of $[Cu\ aca_2]$ as they are both $[Cu\text{-}N_2O_2]$-type chelates.[1),4)] It is apparent that these expectations agree quite well with our observations.

It is of some interest to note that the band of $[Cu\ aca_2]$ in Figs. 3 and 4 is notably split. This can probably be related to its crystal structure in which the chelate molecules are highly planar and each copper atom is practically 4-coordinate.[5)]

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4) It is noteworthy that the λ_{max} of $[Cu\ aca_2]$, which is a $[Cu\ O_4]$-type chelate, is quite small, and even somewhat smaller than that of $[Cu\ gly_2]$ (635 mμ) which is a $[Cu\ N_2O_2]$-type chelate. However, since the ligand field strength of bip or phen will be more or less comparable with that of en ($[Cu\ en_2]^{2+}$: λ_{max} = 550 mμ), we can anticipate what is stated in the text.

5) E. A. Shugan, *Dokl. Akad. Nauk SSSR*, **1951**, 853; H. Koyama, Y. Saito and H. Kuroya, *J. Inst. Polytech. Osaka City Univ.*, **C4**, 43 (1953); K. Mizutani, K. Sone and T. Sakaki, *Z. Anorg. Allg. Chem.*, **365**, 217 (1969).