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Adduct-Formation Constants of Bis(3-trifluoroacetyl-*d*-camphorato)copper(II) with Lewis Bases

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Synopsis. The formation constants of the mono-adducts of bis(3-trifluoroacetyl-*d*-camphorato)copper(II) with the Lewis bases, such as pyridine, α-picoline, β-picoline, γ-picoline, isopropylamine, and *d*- and *l*-α-methylbenzylamine, were determined spectrophotometrically.

Some metal complexes of β-diketones react further with heterocyclic bases, amines, and phosphorate esters,[1–4] and this adduct formation reaction plays an important role in the synergistic effect for solvent extraction.[5–9]

We investigated the adduct-formation between bis(3-trifluoroacetyl-*d*-comphorate)copper(II) and heterocyclic bases and amines, including chiral amines, because this β-diketone is chiral and bulky, and determined spectrophotometrically the formation constants.

Experimental

3-Trifluoroacetyl-*d*-camphor (Hfacam) was synthesized from ethyl trifluoroacetate and *d*-camphor using a procedure similar to that described by Hammond.[10] The copper complex, Cu(facam)$_2$, was prepared by adding an ethanol solution of the ligand to an aqueous solution of copper acetate at 60 °C. After cooling, the green crystals which precipitated were filtered off. This product was recrystallized from benzene and then sublimed three times *in vacuo* at 160 °C. (Found: C, 51.54; H, 5.14; F, 20.37%. Calcd for $C_{24}H_{28}O_4F_6Cu$: C, 51.66; H, 5.06; F, 20.43%)

The absorption spectra in benzene at 25 °C were recorded on a Hitachi 323 automatic recording spectrophotometer.

The formation constant K_1 of the mono-adduct was calculated by an equation similar to that of Rose-Drago.[11,12]

$$\mathrm{Cu(facam)_2} + \mathrm{B(Lewis\ base)} \underset{K_1}{\rightleftharpoons} \mathrm{Cu(facam)_2B} \qquad (1)$$

$$\frac{C_AC_B}{A-A_0} = \left[C_A+C_B-\frac{A-A_0}{\varepsilon_3-\varepsilon_1}\right]\frac{1}{\varepsilon_3-\varepsilon_1}+\frac{1}{(\varepsilon_3-\varepsilon_1)K_1} \qquad (2)$$

where A and A_0 are the absorbances at a chosen wavelength in the presence and absence of B, and C_A and C_B are the initial concentrations of Cu(facam)$_2$ and B, respectively. ε_1 and ε_3 are the extinction coefficients of Cu(facam)$_2$ and Cu(facam)$_2$B, respectively. The least-squares method was applied to obtain the best K_1 and ε_3 values.

Results and Discussion

The spectrum of Cu(facam)$_2$ in benzene (*cf.* Fig. 1-(a)) exhibited two maxima at 574 and 680 nm; it resembles those of bis(acetylacetonato)copper(II), Cu(acac)$_2$, and bis(trifluoroacetylacetonato)copper(II), Cu(tfa)$_2$, with a square-planar symmetry.[3,13] When the concentration ratio of pyridine to Cu(facam)$_2$ was in the range 0—0.6, two clear isosbestic points were present, indicating the formation of a mono-adduct. The isosbestic points vanished with increase of the pyridine concentration, and a maximum appeared at 800 nm in the pyridine solution. Moreover, the analytical results of the crystals isolated from the pyridine solution agreed with the calculated values for Cu(facam)$_2$(Py)$_2$. Therefore, the spectrum in the pyridine solution may be due to Cu(facam)$_2$(Py)$_2$. Similar spectral changes of Cu(facam)$_2$ caused by the addition of β- and γ-picolines and the analytical results of the crystals isolated from the β- and γ-picoline solutions proved the existence of the bis-adducts, Cu(facam)$_2$(β-pic)$_2$ and Cu(facam)$_2$(γ-pic)$_2$. With α-picoline, two isosbestic points were observed in the concentration-ratio range smaller than 1.0, suggesting a mono-adduct formation.

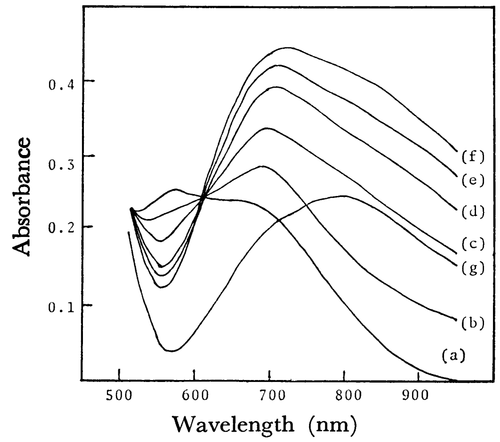

Fig. 1. Spectral change of Cu(facam)$_2$ in benzene caused by the addition of pyridine. $C_A = 4.3\times10^{-3}$ M, ratio of C_B/C_A; (a) 0.0; (b) 0.2; (c) 0.4; (d); 0.6; (e) 0.8; (f) 1.0; (g) pyridine.

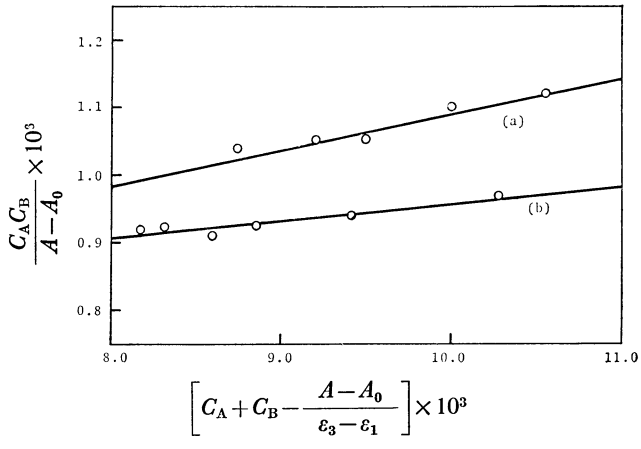

Fig. 2. Plots of $C_AC_B/(A-A_0)$ *vs.* $\left[C_A+C_B-\frac{A-A_0}{\varepsilon_3-\varepsilon_1}\right]$ for α-methylbenzylamine at 700 nm. (a) *l*-α-Methylbenzylamine, (b) *d*-α-methylbenzylamine.

Table 1. Formation constants of mono-adducts between $Cu(facam)_2$ and bases at 25±1 °C

Base	K_1 (M^{-1})
Pyridine	31.1± 4.5
α-Picoline	83.3±24.6
β-Picoline	30.9± 6.4
γ-Picoline	21.9± 5.6
Isopropylamine	26.4± 6.7
d-α-Methylbenzylamine	33.2±12.9
l-α-Methylbenzylamine	84.3±21.0

These isosbestic points vanished with the increase of the α-picoline concentration, and the spectrum in the α-picoline solution exhibited a maximum at 750 nm, with a shoulder at 850 nm. For isopropylamine, two isosbestic points at 520 and 610 nm were found in the concentration ratio range smaller than 1.0. For *d*- and *l*-α-methylbenzylamines, a dull isosbestic point at 600 nm was observed in the region smaller than 0.8, suggesting the formation of a mono-adduct.

An example of the calculation of formation constants is given in Fig. 2, and the K_1 values are summarized in Table 1. The solid lines are drawn on the basis of the calculated ε_3 and K_1 values. The agreement of the plots with the solid lines confirms the plausibility of the calculated ε_3 and K_1 values.

The comparison of the K_1 values reported in the literature[1,2,14–16] with the present data shows that the K_1 values, except that of α-picoline, increase in the order $Cu(tfa)_2 > Cu(facam)_2 > Cu(acac)_2$. This suggests that the rigid and bulky 3-trifluoroacetyl-*d*-camphor hinders the formation of the mono-adduct with bases, but that the electron-withdrawing property of the CF_3-group is still effective. The K_1 value of α-picoline is smaller than those of the other pyridine derivatives for $Cu(acac)_2$ and $Cu(tfa)_2$, whereas the relation is reversed for $Cu(facam)_2$. The K_1 values of *d*- and *l*-α-methylbenzylamine are remarkably different; this difference is difficult to explain, due to the lack of information on their mono-adducts.

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