Thermodynamics of 1:1 Adduct-formation of Bis(trifluoroacetylacetonato)copper(II) with Lewis Bases

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Formation constants and thermodynamic parameters for the 1:1 adduct-formation reactions of bis(trifluoroacetylacetonato)copper(II), $Cu(tfac)_2$, with alkylamines, α-picoline, 2,6-lutidine, and THF have been determined spectrophotometrically. The $\Delta H°-\Delta S°$ plots for primary and secondary alkylamines gave a linear relationship for the thermodynamic parameters of the $Cu(tfac)_2$–heterocyclic base systems. The plots for the 2,6-lutidine, THF and tertiary alkylamine systems have been found consistent with a correlation between $\Delta H°$ and $\Delta S°$ values for bis(acetylacetonato)copper(II)–heterocyclic base systems. It has been subsequently deduced that the 1:1 adducts of $Cu(tfac)_2$ with Lewis bases possess a square-pyramidal structure on the basis of the ESR data for the $^{63}Cu(tfac)_2$–Lewis base systems.

The 1:1 adduct-formation constants of copper(II) complexes of β-diketonates with pyridine and its derivatives have been reported.[1] The systematic studies reveal that (i) substitution of one or both terminal methyl groups in acetylacetone by the trifluoromethyl group increases the formation constant, (ii) the greater the basicity of the donor atom, the greater the stability of the adduct formed, and (iii) the stability of the adducts of α-picoline and 2,6-lutidine are lower than that of the pyridine adduct. The explanation for (i) has been ascribed to the decrease in electron density around the central copper ion by the electron-withdrawing trifluoromethyl group and in (iii) to the steric hindrance of the methyl group in α-positions.

Graddon *et al.* measured the thermodynamic parameters for the 1:1 adduct-formation reactions of copper(II) complexes of fluorinated β-diketonates with heterocyclic bases and noted that the high stability of the bis(trifluoroacetylacetonato)copper(II) ($Cu(tfac)_2$) adduct with pyridine was largely due to an entropy factor.[2,3] Drago *et al.* found that the enthalpy change of 1:1 adduct-formation reactions of bis(hexafluoroacetylacetonato)-copper(II) with several Lewis bases did not obey the double-scale enthalpy equation proposed and brought this into close connection with the formation of different isomers in solution.[4] The 1:1 adduct of bis(3-trifluoromethyl-*d*-camphorato)copper(II) with α-picoline has been shown by the authors to be more stable than the pyridine adduct.[5] These results suggest that the factors affecting 1:1 adduct-formation equilibria of bis(β-diketonato)copper(II) with Lewis bases need further investigation. In this paper the 1:1 adduct-formation constants and thermodynamic parameters for the 1:1 adduct-formation reactions of $Cu(tfac)_2$ with alkylamines, THF, α-picoline and 2,6-lutidine will be reported together with an ESR investigation of the 1:1 adducts of $^{63}Cu(tfac)_2$ in an attempt to elucidate the geometries in solution. The adduct-formation constants have been determined spectrophotometrically.

Experimental

Materials and Measurements. $Cu(tfac)_2$ was prepared by the addition of an ethanol solution of trifluoroacetylacetone to an aqueous solution of copper acetate. The solution upon recrystallization from toluene gave dark blue crystals (Found: C, 32.67; H, 2.36; F, 31.14%). In the ESR spectra of $Cu(tfac)_2$, $^{63}Cu(tfac)_2$ was prepared from isotopically pure ^{63}CuO (99.8%). The bases were obtained commercially and distilled at reduced pressure. Dodecylamine and tertiary alkylamines were used without further purification. Reagent grade benzene was used without further purification as the solvent. Optical absorption measurements were made on a Hitachi 323 automatic recording spectrophotometer equipped with a water cooled cell holder. The temperature of the samples was maintained constant within ±0.1 °C. The absorbances were measured at 540 nm for THF and at 700 nm for the other bases. ESR measurements were made with a JEOL-ME-3X X-band ESR spectrometer at 77 K. The spectra were calibrated with Mn^{2+} in MgO and DPPH.

Calculation of 1:1 Adduct-formation Constant. The 1:1 adduct-formation constants in the primary alkylamine systems were determined graphically from the following equation:[6]

$$1/K_1 = \frac{A-A_0}{\varepsilon_2-\varepsilon_1} - a_0 - b_0 + a_0 b_0 \frac{\varepsilon_2-\varepsilon_1}{A-A_0} \quad (1)$$

where ε_1 and ε_2 are the molar extinction coefficients of $Cu(tfac)_2$ and the adducts formed, and a_0 and b_0 are the initial concentration of $Cu(tfac)_2$ and that of the primary alkylamine added, respectively, and $A_0=\varepsilon_1 a_0$, for the 1 cm cells were used in this study. The formation constants in secondary alkylamine systems are given by:

$$K_1 = \frac{A-A_0}{A_\infty-A} \times \frac{1}{b_0-a_0(A-A_0)/(A_\infty-A_0)} \quad (2)$$

where $A_\infty=\varepsilon_2 a_0$. K_1 and ε_2 cannot be experimentally evaluated at the same time. Thus the K_1 value giving the smallest standard deviation was found using various A_∞ values.[7] In the case that a_0 and b_0 are much greater than the concentration of adduct formed, Eq. 1 transforms into Eq. 3:

$$\frac{a_0}{A-A_0} = \left(a_0+\frac{1}{K_1}\right) \times \frac{1}{(\varepsilon_2-\varepsilon_1)} \times \frac{1}{b_0} + \frac{1}{\varepsilon_2-\varepsilon_1}. \quad (3)$$

Under the experimental conditions that $b_0-c \fallingdotseq b_0$, where c is the concentration of adduct formed, Eq. 1 transforms into a modified Benesi equation:[6]

$$\frac{a_0}{A-A_0} = \frac{1}{K_1(\varepsilon_2-\varepsilon_1)} \times \frac{1}{b_0} + \frac{1}{\varepsilon_2-\varepsilon_1}. \quad (4)$$

K_1 and ε_2 of α-picoline and 2,6-lutidine were determined from the plots of $a_0/(A-A_0)$ *vs.* $1/b_0$ according to Eq. 3, and those of the tertiary alkylamines and THF according to Eq. 4.

Results and Discussion

1:1 Adduct-formation Constant and Thermodynamic Param-

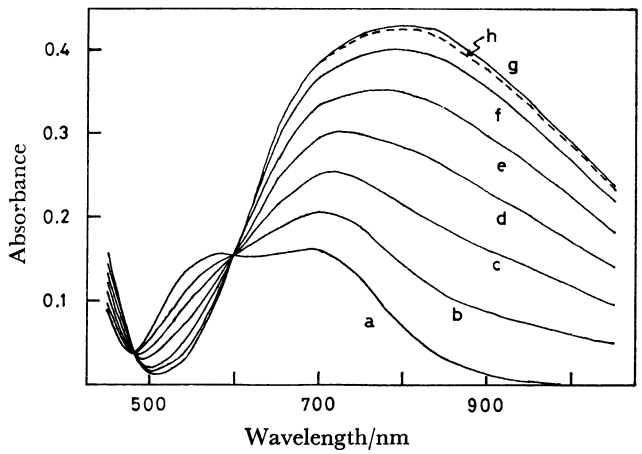

Fig. 1. Spectral change of $Cu(tfac)_2$ in benzene by the addition of octylamine at 20 °C. $a_0=5.43_4\times10^{-3}$ M, b_0/a_0; a: 0.0, b: 0.2, c: 0.4, d: 0.6, e: 0.8, f: 1.0, g: 3.0, h: 5.0 (1 M=1 mol dm^{-3}).

eters. The spectral change of $Cu(tfac)_2$ by the addition of octylamine at 20 °C is shown in Fig. 1 as an example. In the concentration-ratio range of 0—5.0 of the amine to $Cu(tfac)_2$ (b_0/a_0), three isosbestic points were observed at 426, 479, and 598 nm. The absorbance in the near-infrared region decreases at high concentration-ratio. The change in absorbance at 700 nm is large when $b_0/a_0<1$, but extremely small when $b_0/a_0>2$. Thus it has been concluded that only the 1 : 1 adduct is formed when the concentration-ratio is less than 1. Figure 2 shows a set of curves of $1/K_1$ *vs.* $\varepsilon_2-\varepsilon_1$ for the $Cu(tfac)_2$–octylamine system at 20 °C. Each curve was calculated from the observed $A-A_0$ value at one of the base concentrations according to Eq. 1. The coordinates for the intersection on the curves give the common solution for K_1 and ε_2. The set of curves calculated from Eq. 1 for the secondary alkylamine systems give only a dull intersecting point in a range of concentration-ratio (b_0/a_0) exhibiting isosbestic points. Thus the formation constants for the systems have been estimated according to the method described above.

Table 1 shows the 1 : 1 adduct-formation constants and the thermodynamic parameters calculated from the

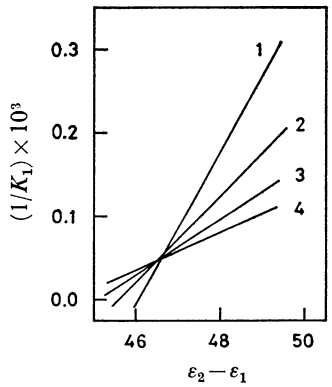

Fig. 2. Curves of $1/K_1$ *vs.* $\varepsilon_2-\varepsilon_1$ for $Cu(tfac)_2$–octylamine system at 20 °C. $a_0=5.12_7\times10^{-3}$ M, b_0; 1: $1.01_0\times10^{-3}$ M, 2: $3.03_0\times10^{-3}$ M, 3: $4.03_9\times10^{-3}$ M, 4: $5.04_9\times10^{-3}$ M (1 M=1 mol dm^{-3}).

Table 1. 1:1 Adduct-formation constants and thermodynamic parameters for 1 : 1 adduct-formation reactions of $Cu(tfac)_2$ with Lewis bases in benzene

Base	log K_1 at 20 °C (1/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
Butylamine	4.64±0.05	−54±6	−96±20
Hexylamine	4.50±0.16		
Octylamine	4.30±0.02	−58±2	−116±6
Dodecylamine	4.32±0.02		
Dibutylamine	3.35±0.02	−37±3	−61±10
Dihexylamine	3.55±0.07		
Dioctylamine	3.50±0.02	−36±3	−57±9
Tributylamine	$K_1=3.9\pm0.1$	−20±2	−55±12
Trioctylamine	$K_1=3.5\pm0.1$	−14±2	−39±13
Pyridine[a)]	3.00	−30.9	−48
γ-Picoline[a)]	3.33	−30.7	−41
α-Picoline	$K_1=83\pm4$	−33±4	−75±15
2,6-Lutidine	$K_1=9.5\pm0.7$	−40±3	−118±11
THF	$K_1=5.4\pm0.3$	−17±3	−43±11

a) From Ref. 3. log K_1 at 20 °C was calculated from the thermodynamic parameters.

van't Hoff plots of ln K_1, together with the K_1 values and the thermodynamic data of the pyridine and γ-picoline systems reported by Graddon and Ong.[3] The effect of self-association of primary alkylamine has not been taken into account because of the low concentration of the amines.[8] The 1 : 1 adducts of primary alkylamines are more stable than that of pyridine. The formation constants of the alkylamines increase in the order: primary alkylamine>secondary alkylamine≫tertiary alkylamine. The number of carbon atoms in the alkyl chains do not significantly affect the value of the formation constant. The formation constants of the bulky heterocyclic bases and THF, which is a weak base, are remarkably small, as previously reported. The enthalpy term for 2,6-lutidine which exhibits steric hindrance is smaller than that of pyridine. The magnitude of the enthalpy change for the pyridine and α-picoline systems is approximately equal. The thermodynamic data for the heterocyclic base systems show that the remarkably small formation constants of the α-picoline and 2,6-lutidine systems may be ascribed to the decrease in the entropy term. The enthalpy term of the primary alkylamines is smaller than that of the heterocyclic bases due to the strong basicity and the enthalpy change of the secondary alkylamines is larger than that of the primary alkylamines due to steric effects.

ESR Measurements. The ESR spectral change of isotopically enriched $^{63}Cu(tfac)_2$ in frozen toluene was measured by the addition of Lewis bases. Figure 3 illustrates the spectral change in the $g_{//}$ region by the addition of octylamine, which shows that only the 1 : 1 adduct is formed when $b_0/a_0<1$. The ESR data of the 1 : 1 adducts are given in Table 2. Trigonal-bipyramidal complexes of copper have a d_{z^2} ground state which gives rise to $g_\perp\simeq2.2$ and to $g_\perp<g_{//}$.[9,10] In the adducts studied here $g_{//}\simeq2.3$ and $g_\perp\simeq2.04$, which are typical values for square-pyramidal complexes with a $d_{x^2-y^2}$ ground state. Thus it has been assumed that the adducts possess a square-pyramidal structure. There are two

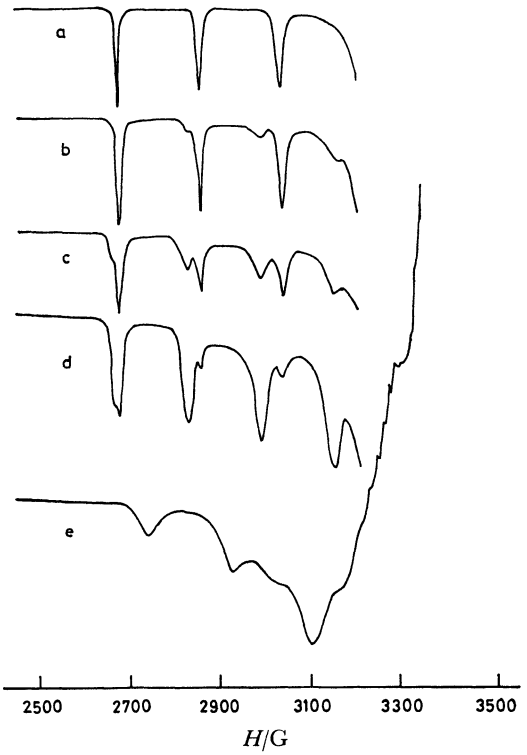

Fig. 3. ESR spectral change of $^{63}Cu(tfac)_2$ in toluene by the addition of octylamine at 77 K. $a_0=2.31_7\times10^{-3}$ M, b_0/a_0; a: 0.0, b: 0.3, c: 0.6, d: 0.9, e: 9.0 (1 M=1 mol dm^{-3}).

Table 2. ESR parameters for 1:1 adducts of $^{63}Cu(tfac)_2$ with Lewis bases in frozen toluene

Base	$g_{//}$	$g_\perp$	$A_{//}$	$A_\perp$
—	2.266	2.044	193	15.7
Octylamine	2.303	—	171	—
Dibutylamine	2.292	—	167	—
Tributylamine	2.300	2.019	164	34
Pyridine	2.296	—	182	—
α-Picoline	2.319	2.043	162	—
2,6-Lutidine	2.303	2.014	134	48
THF	2.296	—	180	—

A: 10^{-4} cm^{-1}.

isomers for the limiting square-pyramidal structure. One involves apical coordination of a Lewis base molecule and the other involves basal coordination. ^{14}N ligand hyperfine structure was found in the frozen solution ESR spectrum of the 1: 1 adduct of $Cu(hfac)_2$ with pyridine and it has been proposed that the adduct has a basal structure.[4,11] In the spectra of the adducts studied such ligand hyperfine splitting was not observed. This, however, does not necessarily indicate that the structure of the adducts is of an apical type.

Correlation between Thermodynamic Parameters. Figure 4 shows the relationship between $\Delta H°$ and $\Delta S°$ values. The $\Delta H°-\Delta S°$ plots of the primary and secondary alkylamines fit a linear relationship for the thermodynamic parameters of $Cu(tfac)_2$–heterocyclic base systems. The plots for THF and the bulky heterocyclic bases except α-picoline are consistent with a correlation between the thermodynamic parameters of bis(acetylacetonato)-

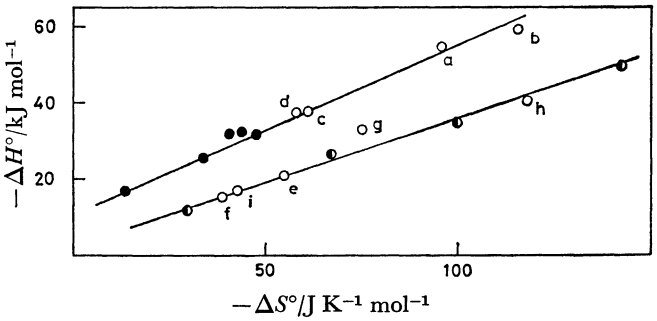

Fig. 4. Relationships between $\Delta H°$ and $\Delta S°$ values. ● Plots for $Cu(tfac)_2$–heterocyclic base systems from Ref. 3. ◐ Plots for $Cu(acac)_2$–heterocyclic base systems from Ref. 1 (b). ○ Present work; a: butylamine, b: octylamine, c: dibutylamine, d: dioctylamine, e: tributylamine, f: trioctylamine, g: α-picoline, h: 2,6-lutidine, i: THF.

copper(II) ($Cu(acac)_2$)–heterocyclic base systems. One of the conditions for the existence of a set of reactions having such a linear relationship is that they should share a common interaction mechanism.[12] The fact that $\Delta H°$ of 2,6-lutidine is smaller than that of pyridine may also mean that the interaction mechanism in the 2,6-lutidine and pyridine systems is different. The ESR data show that the 1: 1 adducts in this study exist in two square-pyramidal structures. The adduct of $Cu(acac)_2$ with quinoline is of an apical type.[13] Therefore, Fig. 4 suggests that the 1: 1 adducts of $Cu(tfac)_2$ with THF and the bulky heterocyclic bases except α-picoline possess an apical structure and that those of pyridine and the primary and secondary alkylamines have a basal structure. It is known that in 1: 1 adducts of bis(β-diketonato)copper(II) with Lewis bases, which have a square-pyramidal structure, the axial bond length is longer than the equatorial bond length.[13-15] Thus the axial ligation of a Lewis base molecule to $Cu(tfac)_2$ results in the formation of new, relatively longer Cu–N or Cu–O bonds normal to the almost undisturbed CuO_4 plane. The steric hindrance of the bulky heterocyclic bases may be weakened by this interaction mechanism. The structure of the adduct of α-picoline cannot, however, be presumed on the basis of the data in this study. It is reported that the 1: 1 adduct of bis(α-nitroacetophenonato)copper(II) with α-picoline has a basal structure in which the methyl group in the α-position sticks out toward the sixth coordination position.[16]

There is a linear relationship between the log K_1 values of pyridine, γ-picoline and butylamine and the log K_H values in the aqueous solutions, while the plots for the secondary alkylamines lie below the line due to steric effects. This linear relationship is explainable by the fact that the strength of the bond between a ligand and a metal ions is determined to a first approximation by the same factors as those which determine the strength of protonation of the ligand. Butylamine is a σ-donor and γ-picoline has a considerably stronger σ-donor property. Thus it is suggested that in the adduct-formation of $Cu(tfac)_2$ with the heterocyclic bases, the σ-bond may play a more important role than the π-bond.

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