Thermodynamic Study on Adduct Formation of Copper(II) β-Diketonates with Heterocyclic Bases

Kazumasa UEDA

Department of Industrial Chemistry, Faculty of Technology, Kanazawa University, Kodatsuno, Kanazawa 920

(Received September 14, 1977)

The stability constants and thermodynamic functions for 1:1 adduct formation of unidentate heterocyclic bases with copper(II) β-diketonates were determined in non-aqueous solvents by the spectrophotometric method. The main factors controlling the stability of the adducts were investigated and the bases were classified into two groups in adduct formation from the plots of the stability constants against pK_H values of the bases: steric hindered and unhindered bases. Large negative entropy changes were observed for pyridine, β-picoline, and γ-picoline; these were ascribed to the π-bond character of the adduct bonds. A solvent effect was observed; the order of increasing adduct stability was as follows: acetone < butyl acetate < 4-methyl-2-pentanone < chloroform < nitrobenzene < toluene ≃ benzene < chlorobenzene. This order agreed with the decreasing order of the solvent-chelate interaction and of the solvent-base interaction. In all cases, the adducts were stabilized by large exothermic enthalpy changes. Moreover, the introduction of a CF_3 group into β-diketones also brought about a considerable entropy change which promoted the stabilization of the chelate. The effect of the other terminal groups was not clearly observed.

It is well known that copper(II) β-diketonates behave as Lewis acids and react with nitrogen bases to form addition compounds.[1] The formation equilibria of such synergistic adducts have been widely investigated for many metals under a variety of conditions.[2,3]

Most investigations of the adduct formation have been carried out by means of solvent extraction. Therefore, complications inherent to the heterogeneous equilibrium, *e.g.*, the displacement reaction of a Lewis base for water molecules in metal chelates, would be involved.

Since the direct observation of the equilibria in non-aqueous solvents is free from these complications, some detailed studies have been undertaken by using spectrophotometric,[4-6] titrimetric,[7,8] ESR, and NMR[9,10] techniques. Planar, four-coordinate copper(II) complexes of β-diketones react with Lewis bases to form five-coordinate 1:1 adducts and six-coordinate 1:2 adducts, and the formation constants for 1:1 adducts with various bases have been determined. Nevertheless, comparatively little information is available about the thermodynamics of these equilibria.

In the present investigation, the author has undertaken to obtain the thermodynamic data for the adduct formation of several different β-diketonato complexes of copper with a variety of bases, and quantitative information on factors affecting the stability of the adducts formed in non-aqueous solvents.

Experimental

Apparatus and Materials. The absorption measurements were carried out with a Hitachi 124 spectrophotometer equipped with a thermostated cell holder, which was held at the required temperature by water from a HAAKE FJ thermoelectric circulating bath. β-Diketones with a CF_3 terminal group such as benzoyltrifluoroacetone(Hbfa), 2-thenoyltrifluoroacetone(Htta), 2-furoyltrifluoroacetone(Hfta), pivaloyltrifluoroacetone(Hpta), trifluoroacetylacetone(Htaa), and the nonfluorinated β-diketones such as acetylacetone(Haa), benzoylacetone(Hba), and dipivaloylmethane(Hdpm) were commercially available and used without further purification. All the nitrogen bases were of guaranteed grade and usually dried over potassium hydroxide; a constant boiling fraction was collected under a reduced pressure. Solvents were of guaranteed grade and freshly distilled before use.

Preparation of Copper Chelates. The copper chelates were prepared by mixing equivalent quantities of copper(II) chloride solution and β-diketone methanol solution and adding 2M sodium acetate solution under continuous stirring. The mixture was allowed to stand in a refrigerator for several hours, after heated for a short while on a hot plate. The filtered complex was washed with water and dried in a desiccator. After being recrystallized from benzene, the crystalline chelate was dried by standing over diphosphorus pentaoxide *in vacuo*. The results of elementary analysis are shown in Table 1.

Calculation of Stability Constants and Thermodynamic Functions. The stability constants of the 1:1 adduct in non-aqueous solvent were obtained by the following equation:

$$K = \frac{[\text{Adduct}]}{[\text{Diketonate}][\text{Base}]} = \frac{1-\alpha}{\alpha[\text{Base}]}. \quad (1)$$

The concentration of the free base is

$$[\text{Base}] = B_0 - C_0(1-\alpha), \quad (2)$$

where α is the fraction of the free diketonate and B_0 and C_0 are the total concentrations of the base and the copper chelate. Since the bases do not absorb at the wavelength concerned,

$$A = A_0\alpha + A_\infty(1-\alpha), \quad (3)$$

where A and A_0 are the absorbances of the system and the diketonate only. A_∞ is the absorbance found, by trial and error, to give the most reproducible value of K.[4,11] The stability constant can be expressed in terms of the absorbance

Table 1. Analysis of copper(II) chelates

Chelate	Found (Calcd) %		
	C	H	Cu
$Cu(bfa)_2$	48.55 (48.64)	2.48 (2.44)	12.84 (12.86)
$Cu(tta)_2$	38.00 (37.99)	1.60 (1.59)	12.54 (12.56)
$Cu(fta)_2$	40.53 (40.56)	1.71 (1.70)	13.45 (13.41)
$Cu(pta)_2$	41.84 (42.34)	4.37 (4.44)	14.08 (14.00)
$Cu(taa)_2$	32.38 (32.48)	2.11 (2.18)	17.17 (17.18)
$Cu(ba)_2$	62.14 (62.24)	4.62 (4.70)	16.38 (16.38)
$Cu(aa)_2$	45.65 (45.88)	5.35 (5.39)	24.10 (24.09)
$Cu(dpm)_2$	61.51 (61.43)	8.86 (8.90)	14.73 (14.71)

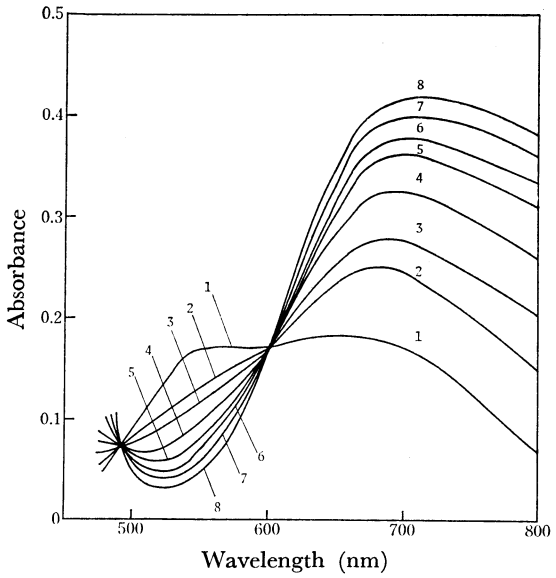

Fig. 1. Absorption spectra of $Cu(bfa)_2$–pyridine system in benzene at 298 K. $[Cu(bfa)_2]=0.005$ M, [pyridine]; 1: 0, 2: 0.002 M, 3: 0.003 M, 4: 0.005 M, 5: 0.007 M, 6: 0.01 M, 7: 0.015 M, 8: 0.04 M.

from Eqs. 1, 2, and 3:

$$K=\frac{[A-A_0]}{[A_\infty-A]B_0-C_0[A-A_0]/[A_\infty-A_0]}. \quad (4)$$

At least ten experimental points were used in each system and each measured absorbance was the average of three independent determinations. The standard molar thermodynamic functions were calculated by the usual methods: $-RT\ln K=\Delta G^\circ=\Delta H^\circ-T\Delta S^\circ$ and $\Delta H^\circ/RT^\circ=\mathrm{d}\ln K/\mathrm{d}T$. ΔH° was constant within the experimental error over the range of temperature, as shown in Fig. 3. Under the present experimental conditions, the values of $\log K$ were reproducible within ±0.05, values of ΔG within ±0.9 kJ mol^{-1}, and the values of ΔS within ±0.2 J K^{-1} mol^{-1}.

Results and Discussion

It has already been recognized that copper(II) β-diketonates react with nitrogen bases to form several adducts and that the 1:1 adduct is preferentially formed in non-polar organic solvents.[2,12] The absorption spectra of $Cu(bfa)_2$–pyridine system are shown in Fig. 1, as a typical example. These spectra form a family with isobestic points at these intersections, indicating the formation of a mono-adduct. Similar spectra with sharp isobestic points are obtained for all the bases employed. The analytical results by the molar ratio method also show that the present chelates form only 1:1 type adducts and 1:2 type equilibria do not take place, as shown in Fig. 2. Therefore, the author investigated only 1:1 type adduct formation equilibria with unidentate nitrogen bases, though several types of adducts with unidentate nitrogen bases have been identified, especially when the neutral ligand is a strong base and the chelate ligand contains an electron withdrawing nitro- or cyano-group.[13,14]

Stability Constants of Base Adducts. Figure 3 shows the changes in the stability constants of $Cu(bfa)_2$ adduct as a function of temperature. The stabilities decrease

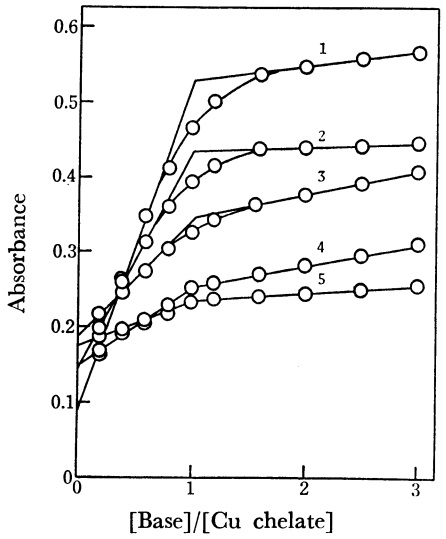

Fig. 2. Determination of the adduct composition by mole ratio method in benzene at 298 K. [Cu chelate] $=0.005$ M. 1: $Cu(bfa)_2$-2-methylpiperidine (850 nm), 2: $Cu(tta)_2$-γ-picoline (740 nm), 3: $Cu(fta)_2$-2,4-lutidine(700 nm), 4: $Cu(taa)_2$-α-picoline (690 nm), 5: $Cu(pta)_2$-pyridine (620 nm).

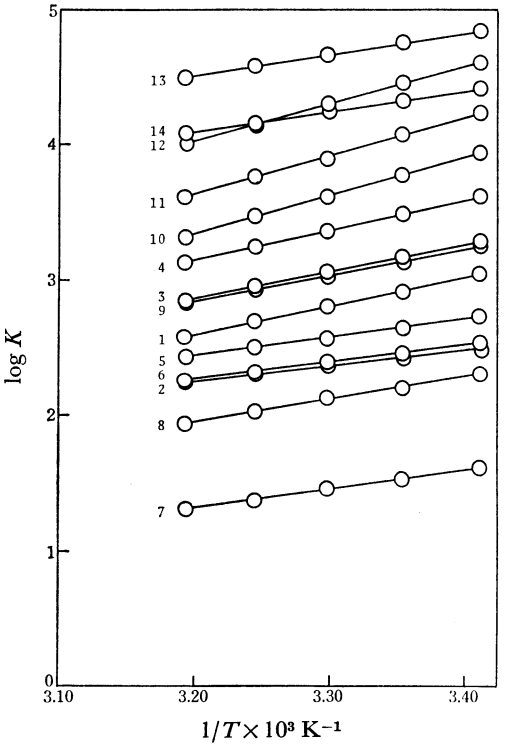

Fig. 3. Temperature dependence of stability constants for $Cu(bfa)_2$ adduct. For numerals, see Table 2.

linearly on every base as temperature rises. The adduct chelate dissociation must be much enhanced with the increase of thermal energy. From the slope of these linear plots, the standard enthalpy change of adduct formation was obtained. It seems remarkable that the enthalpies for pyrrolidine and piperidine show smaller changes in spite of their high stabilities. The stability constants increase in the following order: 2,6-lutidine $\ll$ quinoline $<$ α-picoline $\leq$ 2,5-lutidine $<$ 2,4-lutidine $<$ pyridine $<$ isoquinoline $<$ β-picoline $<$

Table 2. The effect of nitrogen bases on adduct formation

No.	Base	log K_{298}	$-\Delta G_{298}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S_{298}$ (J K^{-1} mol^{-1})
1	Pyridine	2.91	16.61	44.31	92.89
2	α-Picoline	2.43	13.85	22.80	30.03
3	β-Picoline	3.17	18.07	38.70	69.18
4	γ-Picoline	3.48	19.87	41.63	72.97
5	2,4-Lutidine	2.64	15.06	26.40	38.03
6	2,5-Lutidine	2.46	14.01	23.01	30.17
7	2,6-Lutidine	1.53	8.70	25.44	56.13
8	Quinoline	2.20	12.55	31.96	65.11
9	Isoquinoline	3.13	17.91	35.69	59.64
10	2-Methylpiperidine	3.77	21.55	54.73	111.28
11	3-Methylpiperidine	4.08	23.26	55.18	107.06
12	4-Methylpiperidine	4.45	25.39	53.22	93.32
13	Pyrrolidine	4.76	27.19	30.37	10.66
14	Piperidine	4.32	24.64	29.87	17.54

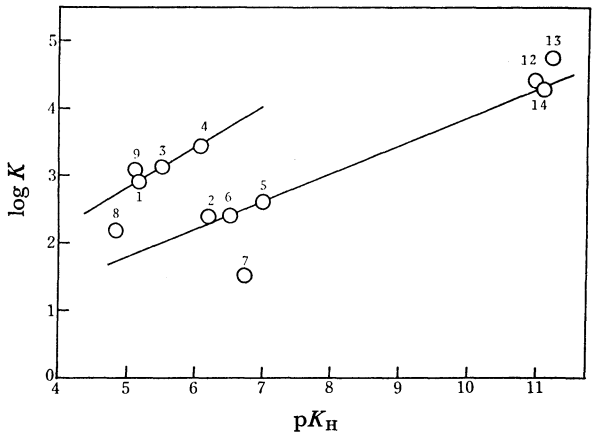

Fig. 4. Plots of log K *vs.* pK_H in benzene at 298 K. For numerals, see Table 2.

γ-picoline < 2-methylpiperidine < 3-methylpiperidine < piperidine < 4-methylpiperidine < pyrrolidine. The order is related not only to the basicity of the bases, but also to the steric effect due to substitution. The high stabilities in the secondary cyclic amines correspond to their large donor properties. The higher stability of γ-picoline as compared with that of pyridine also reflects the increased donor power of the nitrogen atom due to the introduction of a methyl group. A similar effect would be expected for α-picoline and lutidines from these pK_H values, but much lower stabilities were observed. This fact may be caused by the steric interference of the α-methyl group. In order to make the point clearer, the stability constants of these mono-adducts are plotted against the pK_H values of the bases, as shown in Fig. 4. The values of the stability constants are classified roughly into two types, the higher and lower stability groups. The values of 2,6-lutidine and quinoline lie apart from these two groups. The lower stabilities of the second group compared to those of the first may be attributed to the steric hindrance of the methyl group in the α-position. This interference is significant in 2,6-lutidine. Owing to the steric hindrance from the hydrogen atom attached to the nitrogen atom of pyrrolidine and piperidine, the adduct stabilities of those bases are reduced to the second group. The lower stability of quinoline may be caused by the steric effect of the adjacent benzene ring. Thus, both the pK_H and the steric hindrance of the bases have an effect on the stability of the base adduct.

Thermodynamics of Adduct Formation. The stability constants of Cu(bfa)$_2$ adduct in benzene at 298 K and some related thermodynamic functions are summarized in Table 2. The values of ΔG for all the donor systems are negative, so it is obvious that the acceptor mother chelate is stabilized by the adduct chelate formation. Both the enthalpy and the entropy terms contribute to the negative values of the free energy. The introduction of a fluorine atom into β-diketone greatly increases the stability of its base adduct.[6,15] This is supported by the highly negative values of ΔH.

In the present system, the energy contribution from the structural rearrangement is significant. The enthalpy values for α-substituted pyridines are less negative and the entropy more positive than those for the other substituted pyridines. These differences may confirm the presence of some motional freedoms of α-substituted pyridines. In the α-substituted pyridines, the free rotation of the α-methyl group prevents any base with an α-methyl group from penetrating easily the chelate plane. Consequently, the approach of the base to the central copper atom will be hindered, and the chelate rings are distorted. Quinoline shows a structural difference from the α-substituted pyridines. The planar aromatic molecules will tend to arrange themselves in one of the two planes perpendicular to the coordination plane of the copper atom. Thus, the hydrogen atom of the ortho C–H group can easily penetrate the chelate plane; the rotational freedom of isoquinoline is more effective than quinoline.

In the case of pyrrolidine and piperidine, ΔG is exceedingly negative, while ΔH is not so much; as for ΔS, it is even close to zero. On the other hand, pyridine gives appreciably negative values of ΔH and ΔS, but not so great a negative value of ΔG. The difference between these two sets of data is probably owing, at least in part, to the smaller size of pyridine molecules. However, there is evidence that a π-bond is formed

Table 3. The effect of organic solvents on adduct formation

Solvent	$\log K_{298}$	$-\Delta G_{298}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S_{298}$ (J K^{-1} mol^{-1})
Chlorobenzene	3.07	17.53	44.26	89.67
Benzene	2.91	16.61	44.31	92.89
Toluene	2.87	16.40	28.99	42.24
Nitrobenzene	2.62	14.98	25.60	35.64
Chloroform	2.57	14.68	28.16	45.19
4-Methyl-2-pentanone	2.10	11.96	14.64	8.98
Butyl acetate	2.07	11.84	15.27	11.51
Acetone	1.91	10.92	14.22	11.08

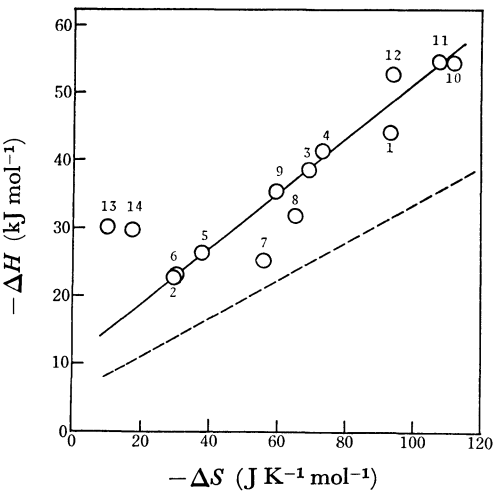

Fig. 5. Plots of $-\Delta H$ *vs.* $-\Delta S$ for $Cu(bfa)_2$ adducts (——) and non-fluorinated copper adducts (----). For numerals, see Table 2.

between the silver and the heterocyclic bases.[16] Though the systems are different, a π-bond is operative also in the case of the non-ortho-substituted pyridines. Thus, these pyridines make strong adduct bonds through their large π-bonding character, and the systems are generally rigid, owing to the restriction of rotational freedom. On the other hand, in pyrrolidine and piperidine there would be free rotation of the base molecule in the adduct bond with σ-bond character. The disorder of those systems will be attributed mostly to the rotational freedom of the bases. The smaller pyrrolidine has more kinetic freedom. It is surprising that the adduct bond in pipecolines is most rigid and is little influenced by the position of the substituent group. This will depend upon the larger size of the base molecules and their high basicity, even though the π-bond character is low.

Effect of Organic Solvents. The effect of solvents on the $Cu(bfa)_2$–pyridine system is shown in Table 3. The chelate is generally soluble in polar solvents but sparingly soluble in non-polar solvents, *e.g.*, hexane, cyclohexane, cyclohexanon, and carbon tetrachloride, though the latter solvents show a remarkable synergistic enhancement in the solvent extraction of metal chelates.[2,17] Among the non-polar solvents, benzene dissolves the chelate easily. The general order of increasing adduct stability is: acetone<butyl acetate <4-methyl-2-pentanone < chloroform < nitrobenzene < toluene≃benzene<chlorobenzene.

This order does not agree with that of the dipole moments, the dielectric constants, nor the transition energy of ligand field of the solvents, but it agrees with the decreasing order of the interaction between the solvent and the copper chelate or of the solvation energy of pyridine with various solvents. Libutti[18] measured the solvation energy of pyridine in benzene(−0.01 kcal/mol) and chloroform(−1.82 kcal/mol) and suggested that chloroform interacts very strongly with pyridine through hydrogen bonding. Data from NMR[19] and calorimetry[20] convince us of a weak interaction of pyridine with benzene. The existence of a large solvation energy will lower the activity and base strength of pyridine. This leads to the decrease of adduct stability and would account for the less exothermic nature observed in nitrobenzene and chloroform. On the contrary, chlorobenzene and benzene form weak solvates, which serve to reduce the endothermic effect of deaggregating pyridine molecules in these solvents. In 4-methyl-2-pentanone, butyl acetate, and acetone, the adduct stabilities are very low, and the reactions are least exothermic. This phenomena may be explained by the solvation of the copper chelate. The electron-withdrawing CF_3 group of the chelate ligand decreases the electron density around the central copper atom and, at the same time, it enhances the ability to solvate with such polar oxygen-containing solvents as 4-methyl-2-pentanone, butyl acetate, and acetone, although even weak solvates are not produced in non-fluorinated β-diketonate chelates.[21] It will require much energy to substitute a solvent molecule in addition to removing the dipole interaction of the pyridine with the solvent, and this fact promotes the irregular nature of the systems.

Effect of Chelate Ligands. Adduct stability will be much influenced by the Lewis acidity of the chelate, which is affected by the terminal group of the chelate ligand. The effect of chelate ligands involving non-fluorinated β-diketones in the pyridine system is shown in Table 4. The adduct stabilities in the fluorinated ligands differ little from those expected from the pK_H values. The constants increase in the following order: Hdpm < Haa < Hba ≪ Htaa < Hpta ≤ Hbfa < Hfta< Htta. For the fluorinated ligands, the electron-withdrawing effect of the CF_3 group is quite large, and the effect of the other terminal substituent is not so obviously recognized. But the order seems to correlate with the pK_H values, except Hpta, and to be just the reverse of the trend that the weaker the acidity of

Table 4. The effect of chelate ligands on adduct formation

Ligand	Base	$\log K_{298}$	$-\Delta G_{298}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S_{298}$ (J K^{-1} mol^{-1})
Htta	Pyridine	3.27	18.66	42.76	80.83
(6.28) [a]	α-Picoline	2.55	14.56	22.17	25.54
	γ-Picoline	3.62	20.67	38.95	61.32
	2,4-Lutidine	2.82	16.11	24.02	26.52
	2,6-Lutidine	1.74	9.91	26.61	55.99
Hfta	Pyridine	3.18	18.11	42.05	80.27
(6.18)	α-Picoline	2.46	14.06	28.24	47.57
	γ-Picoline	3.57	20.37	36.44	53.88
	2,4-Lutidine	2.79	15.94	24.27	27.92
	2,6-Lutidine	1.69	9.62	28.45	63.15
Hbfa	Pyridine	2.91	16.61	44.31	92.89
(6.01)	γ-Picoline	3.48	19.87	41.63	72.97
Hpta	Pyridine	3.02	17.24	44.60	91.77
(6.90)	α-Picoline	2.38	13.60	33.01	65.11
	γ-Picoline	3.43	19.58	37.07	58.65
	2,4-Lutidine	2.58	14.68	24.64	33.40
	2,6-Lutidine	1.61	9.16	23.76	48.98
Htaa	Pyridine	2.99	17.03	35.27	61.18
(6.09)	α-Picoline	2.25	12.84	22.01	30.73
	γ-Picoline	3.33	18.99	33.60	48.97
	2,4-Lutidine	2.48	14.14	20.58	21.61
	2,6-Lutidine	1.60	9.12	20.29	37.46
Hba	Pyridine	1.25	7.15	18.49	38.03
(8.55)					
Haa	Pyridine	1.07	6.11	14.43	27.92
(8.99)					
Hdpm	Pyridine	0.81	4.64	19.50	49.81

a) The pK_H values in parentheses are taken from T. Sekine, R. Murai, M. Niitsu, and N. Ihara, *J. Inorg. Nucl. Chem.*, **36**, 2569 (1974).

the ligand is, the weaker is the adduct stability.[17] To a certain extent, thenoyl, furoyl, and phenyl groups contribute to the resonance stabilization of those adducts, and the pivaloyl group shows some steric interference. However, we have no independent data available on the dissociation constants of the β-diketones in benzene solution; hence, further investigation will be required before a detailed discussion can be done. Nevertheless, the effect of bases definitely appears in the present experiment.

In the reaction of non-fluorinated copper chelates with nitrogen bases, Graddon pointed out a linear relationship between ΔH and ΔS, which was interpreted as indicating a common interaction mechanism.[22] The isoequilibrium temperature of the system containing 2-substituted 1,3-diketones was 310 K in benzene solution. A similar relationship was observed in the present fluorinated ligands, though a few points did not fit well in the case of Hbfa, as shown in Fig. 5. The line itself is situated considerably above that for the non-fluorinated ligands, and possesses a large slope. The isoequilibrium temperature is 413 K. These facts indicate rather clearly that fluorinated adducts are entropy-stabilized, while the non-fluorinated adducts show higher entropy-resistance. Thus, the extra stability of fluorinated adducts can mainly be ascribed to the entropy factor.

The author wishes to express his deep gratitude to Professor Shunzo Ueda, of Kanazawa University, for his continual encouragement and advice throughout this work. The author also wishes to express his thanks to Professor Tsunenobu Shigematsu and Assistant Professor Masakazu Matsui, of Kyoto University, for their valuable guidance and discussion.

References

1) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).
2) Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, London (1969), p. 815.
3) T. Sekine, *Nippon Kagaku Zasshi*, **90**, 951 (1969).
4) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).
5) T. Shigematsu, M. Tabushi, M. Matsui, and M. Munakata, *Bull. Chem. Soc. Jpn.*, **41**, 2656 (1968).
6) W. Partenheimer and R. S. Drago, *Inorg. Chem.*, **9**, 47 (1970).
7) E. F. Kassierer and A. S. Kertes, *J. Inorg. Nucl. Chem.*, **34**, 3209 (1972).
8) D. P. Graddon and W. K. Ong, *J. Inorg. Nucl. Chem.*, **37**, 469 (1975).
9) A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.*, **91**, 866 (1969).
10) T. Kogane, H. Yukawa, and R. Hirota, *Chem. Lett.*,

1974, 477.
11) P. Gans and H. M. N. H. Irving, *J. Inorg. Nucl. Chem.*, **34**, 1885 (1972).
12) W. R. Walker and N. C. Li, *J. Inorg. Nucl. Chem.*, **27**, 2255 (1965).
13) L. L. Funch and T. R. Ortolano, *Inorg. Chem.*, **7**, 567 (1968).
14) T. M. Shepherd, *J. Chem. Soc., Dalton Trans.*, **1972**, 813.
15) D. P. Graddon and W. K. Ong, *Aust. J. Chem.*, **27**, 741 (1974).
16) R. K. Murman and F. Basolo, *J. Am. Chem. Soc.*, **77**, 3484 (1955).
17) T. Honjyo and T. Shigematsu, *Kagaku*, **23**, 708 (1968).
18) B. L. Libutti, B. B. Wayland, and A. F. Garito, *Inorg. Chem.*, **8**, 1510 (1969).
19) J. N. Murrell and V. M. S. Gill, *Trans. Faraday Soc.*, **60**, 248 (1965).
20) P. R. Garrett, J. M. Pollock, and K. W. Morrow, *J. Chem. Thermodyn.*, **3**, 135 (1971).
21) F. R. Clarke, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964).
22) D. P. Graddon and K. B. Heng, *Aust. J. Chem.*, **24**, 1781 (1971).