BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2656—2660 (1968)

Studies on Adduct Formation of β-Diketone Chelates with Heterocyclic Bases

Tsunenobu Shigematsu, Masayuki Tabushi, Masakazu Matsui
and Megumu Munakata

Institute for Chemical Research, Kyoto University, Uji, Kyoto

(Received April 27, 1968)

Stability constants of the 1 : 1-adducts with heterocyclic Lewis bases on copper chelates of six β-diketones and two ethylesters of β-ketoacids ($Cu(ligand)_2 \cdot base$) were determined by spectrophotometric measurements in visible region and the effects of β-diketone substituents, Lewis bases and organic solvents on the stability constants were studied. Terminal alkyl groups of β-diketones hardly hindered the adduct formation, because the adducts of β-diketone chelates except acetylacetone chelate had similar stability constants. Solvent effect was due to the formation of the solvates of the chelates or the solvation of N-base with solvent. This is related to the abnormal position of chloroform in the order of the adduct stability compared with oxygen-containing solvents. Infrared spectra indicate that the metal-oxygen bonding, as well as the basicity of Lewis bases is considered as an essential factor in the adduct formation of metal β-diketone chelates.

As already stated by many investigators, the adduct-formation of metal β-diketonates plays an important role in the synergistic enhancement of the solvent extraction, and therefore the adduct-forming reaction and the structure of the adducts have the interest for analytical and coordination chemists. Recently, many adducts of transition metal acetylacetone (AA) chelates were prepared and their properties studied. Nakamoto and his coworkers(1) suggested from the infrared spectra that adduct-forming Lewis bases coordinated directly to the central metal atom in the adduct of metal acetylacetonates such as $Ni(AA)_2$, $VO(AA)_2$ and $UO_2(AA)_2$. Adducts of copper(II) β-diketonates have been extensively investigated. The behavior of Lewis base, chelate ligand and solvent on the adduct-formation were studied by Graddon and Watton(2) using nitrogen-containing heterocyclic bases (N-bases), and by Rao and Li(3) using some organo-phosphorus compounds. They mentioned that (i) the base effect reflected partly donor power of the base and partly steric effect; (ii) the ligand effect related to the transfer of negative charge from the ligand to metal ion, and consequently to the residual positive charge on the metal

---

(1) K. Nakamoto, Y. Morimo and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4533 (1961).

(2) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).

(3) G. N. Rao and N. C. Li, *ibid.*, **28**, 2931 (1966).

atom; and (iii) the solvent effect was attributed to change in the solvation energy.

The present research was carried out in order to ascertain and to discuss Graddon's conclusion. Copper chelates were prepared by using six β-diketones and two methylesters of β-ketoacids; the stability constant of the 1 : 1-adducts with several N-bases (Cu^{II}(chelate ligand)$_2$N-base) was determined by means of spectrophotometric measurements, and various factors affecting the stability of the adduct were investigated. Especially, the solvent effect seemed to result from the change in the thermodynamic concentration of the Lewis base and from the solvation which took place between some oxygen-containing solvents and β-diketone chelates with CF_3 terminal group. Furthermore, the chelates were prepared, and the problem on metal ligand bonding, which had not been clarified, was discussed from the results of infrared absorption.

Experimental

Apparatus. A Hitachi Perkin-Elemer 139 UV-VIS spectrophotometer and a Shimadzu automatic recording spectrophotometer, model IV-50, were used for the visible spectrophotometeric measurements. Infrared spectra were obtained by the KBr disk method with a Perkin-Elmer, Model 521 infrared spectrophotometer.

Materials. Acetylacetone (AA), ethylacetyl acetate (EAA), ethylbenzoyl acetate (EBA), trifluoroacetylacetone (TAA) and benzoyltrifluoroacetone (BFA) were obtained from the Dojindo Co. Ltd., Research Laboratories or from Tokyo Kasei Kogyo Co., Ltd. Dipropionylmethane (DPrM), diisobutyrylmethane (DIBM) and pivaloylacetone (PvA) were prepared by the acylation of methylketones with the ethyl esters of carboxylic acids in the presence of sodium amide or sodium methoxide. These β-diketones were precipitated as copper chelates, and recrystallized from benzene. The analytical data are listed below (calculated values are shown in parentheses):

$Cu(DPrM)_2$	C: 52.88 (52.69)	H: 6.92 (7.05)
$Cu(PvA)_2$	C: 55.80 (56.70)	H: 7.69 (7.52)
$Cu(DIBM)_2$	C: 57.37 (57.80)	H: 8.27 (8.03)

Preparation of Metal Chelates. Copper chelates were prepared in the following manner: To 50 m*l* of 0.5 M copper(II) chloride solution, 20 m*l* of 2.5 M β-diketone methanol solution and 25 m*l* of 2 M sodium acetate solution were successively added under continuous stirring. After heated for a short while on a hot plate, the mixture was allowed to stand in a refrigerator for several hours. The crystalline solid was filtered off on a Buchner funnel, washed with water and dried in a desiccator. After recrystallized from benzene, the crystalline chelate was dried overnight at 60°C in an evacuated vessel. The results of elementary analysis of the chelates are shown in Table 1.

TABLE 1. ANALYSIS OF METAL COMPOUNDS

Complex	Analysis (%) C	Analysis (%) H
$Cu(AA)_2$	45.74(45.78)	5.38(5.35)
$Cu(EAA)_2$	44.54(44.72)	5.44(5.59)
$Cu(EBA)_2$	58.67(59.26)	4.89(4.93)
$Cu(TAA)_2$	32.39(32.43)	2.21(2.16)
$Cu(BFA)_2$	48.54(48.57)	2.39(2.43)

Calculated values are in parentheses.

Results and Discussion

It has been reported that copper β-diketonates react with one mole of N-base to form 1 : 1-adducts in solution. The fact is supported by the fact that a distinct isosbestic point is observed in Fig. 1. Since the visible band shifts to longer wavelength by coordination of the N-base (see Fig. 1), the stability constant of the adducts can be determined spectrophotometrically by the following equation[2];

$$K=\frac{[E_\infty-E_0][E-E_0]}{B_0[E_\infty-E]-C_0[E-E_0]}\times\frac{1}{E_\infty-E}$$

where E is the absorbance measured at a definite wavelength, such as that is indicated in Table 2,

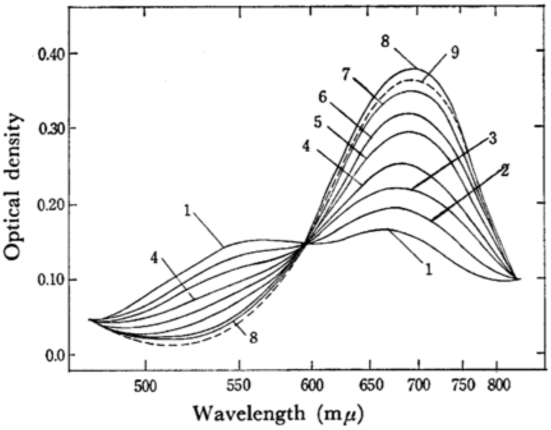

Fig. 1. Absorption spectra of 0.0025 M $Cu(TAA)_2$ and pyridine in benzene.
Pyridine concentration
1: 0; 2: 0.001 M; 3: 0.002 M; 4: 0.003 M;
5: 0.005 M; 6: 0.007 M; 7: 0.01 M; 8: 0.03 M;
9: 0.1 M.

TABLE 2. MAXIMUM WAVELENGTH (mμ) OF PYRIDINE ADDUCTS OF COPPER(II) β-DIKETONATES

Adduct	Solvent Benzene	Solvent Acetone	Solvent Chloroform
$Cu(AA)_2\cdot Py$*	660	660	660
$Cu(EAA)_2\cdot Py$	710	710	710
$Cu(EBA)_2\cdot Py$	714	714	720
$Cu(TAA)_2\cdot Py$	690	695	702
$Cu(BFA)_2\cdot Py$	706	710	710

* Py: Pyridine

and E_0 the absorbance obtained in the absence of the N-base, at the same wavelength. The value of E_∞ is that found, by trial and error, to give the most reproducible value of the stability constant, K. B_0 and C_0 are total concentrations of the base and the copper chelate, respectively.

Effect of Alkyl Group of β-Diketones. It was expected that the adduct formation would be influenced by the steric effect of the terminal groups of chelate ligands.[4] The stability constants of the adducts involving AA, DPrM, DIBM and PvA as β-diketone were measured: Each copper chelate of these β-diketones except that of AA seems to have stabilities of the same magnitude. The results presented in Table 3 indicate that the terminal alkyl group scarcely affects the adduct formation. It must be noted that the steric hindrance does appear not in the chelate ligand but in the adduct forming base, as described below.

Effect of N-Base. Tables 3 and 4 show that for each copper chelate and in each solvent, the stability constants of the adducts increased in the following order:

2-methylpyridine$<$pyridine$<$4-methylpyridine,
2-methylpiperidine$<$piperidine$<$4-methylpiperidine

The former order was already observed by Graddon and Watton in the copper(II) β-diketone chelates,[2] and they stated that the higher stability of the 4-methyl pyridine adducts reflected the increased donor property of nitrogen atom due to substitution, and the unexpected low stability of the 2-methyl pyridine adducts was probably caused by the steric interference. The latter order supports this concept. Namely, the ability to form adducts is enhanced by the increasing basicity of the base, but weakened by the steric hindrance.

TABLE 3. EFFECT OF TERMINAL GROUPS OF β-DIKETONES ON STABILITY CONSTANTS OF ADDUCTS OF COPPER(II) β-DIKETONATES

Base		AA	DPrM	PvA	DIBM
	R	CH_3	C_2H_5	CH_3	$HC(CH_3)_2$
	R′	CH_3	C_2H_5	$C(CH_3)_3$	$HC(CH_3)_2$
Pyridine		9.2	6.9	6.8	5.8
γ-Picoline		14.0	11.8	11.7	11.8
α-Picoline		2.5	2.6	3.0	3.5
Pyperidine		41	48	44	57
γ-Pipecoline		52.0	—	—	—
α-Pipecoline		13.0	—	—	—

Solvent: Benzene

TABLE 4. EFFECT OF HETEROCYCLIC BASE ON STABILITY CONSTANT OF ADDUCTS

Cu-chelate	Lutidine	α-Picoline	Pyridine	γ-Picoline
$Cu(AA)_2$	—	2.5	9.2	14
$Cu(TAA)_2$	1.8×10^2	2.7×10^2	1.0×10^3	1.6×10^3

Solvent: Benzene

Effect of Organic Solvents. The effect of the solvent is shown in Table 5, which indicates that the order of the adduct stability partly depends on the presence of CF_3 terminal group of the chelate ligand. The general orders of increasing stability for $Cu(EBA)_2$ are

chloroform$<$butyl acetate$<$acetone$<$MIBK$<$benzene$<$cyclohexane.

While for $Cu(TAA)_2$ and $Cu(BFA)_2$ acetone$<$butyl acetate$<$MIBK$<$chloroform$<$benzene$<$cyclohexane.

Toluene and monochlorobenzene situate in the same position as of benzene. The stabilities of the $Cu(AA)_2$ adducts were obtained only in chloroform, acetone and benzene, because of their low solubility in the other organic solvents, and the order is quite the same with that reported by Graddon and Watton. They measured the stability of the pyridine adducts of $Cu(AA)_2$. $Cu(EAA)_2$ and $Cu(\text{benzoylacetone})_2$ in chloroform, acetone and benzene, and stated that the increasing order of the adduct stabilities, chloroform$<$acetone$<$benzene, did not agree with the order of the dipole moments, the dielectric constants or the splitting energy of ligand-field of the solvents, but it agreed with the decreasing order in the interaction between the solvents and the copper chelates or in the solvation energy of N-bases. However, it was thought to be difficult to distinguish these two effects, although they showed some evidence in favor of the latter.

In the two kinds of order found in this experiment, the solvation to the chelates may be discriminated from that of N-bases. The relative position of chloroform to MIBK, butyl acetate and acetone may bring a solution of this interesting problem. Clarke *et al.*[5] reported that the bonding energies of chloroform solvates of tervalent metal acetylacetonates were rather small, ranging from 2 to 6 kcal/mol, which lay in the region of hydrogen bonding or dipole-dipole interaction, and with copper(II)-, zinc(II)- and cadmium(II) acetylacetonates, even such weak solvates were not produced. Graddon and Watton pointed out that considerable heat was evolved on dissolving N-bases in chloroform. Such circumstances may lead to the conclusion that the large solvation energy of the N-bases loweres the stability of the adducts of $Cu(EAA)_2$, $Cu(EBA)_2$ and $Cu(AA)_2$ in chloroform. In other words, the thermodynamic concentration of the bases decreases by the interaction with chloroform through the hydrogen bonding.

On the contrary, for the adducts of $Cu(TAA)_2$

---

[4] G. A. Gutter and G. S. Hammond, *J. Am. Chem. Soc.*, **81**, 4686 (1959).

[5] F. R. Clarke, J. F. Steinbach and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **26**, 1311 (1964).

TABLE 5. EFFECT OF ORGANIC SOLVENTS ON STABILITY CONSTANTS OF ADDUCTS

Solvent	$Cu(BFA)_2$	$Cu(TAA)_2$	$Cu(EBA)_2$	$Cu(EAA)_2$	$Cu(AA)_2$
Benzene	9.8×10^2	1.0×10^3	129	31.0	9.2
Chloroform	354	320	14.5	4.8	2.0
Acetone	99.5	54.3	47.3	21.1	4.4
Methyl isobutylketone	142	113	75.4	35.5	—
Cyclohexanone	—	71.6	72.2	43.3	—
n-Butyl acetate	105	101	35.2	13.8	—
Cyclohexane	—	5.0×10^3	164	—	—
Monochlorobenzene	1.0×10^3	8.6×10^2	88.5	25.9	—
Toluene	8.5×10^2	8.5×10^2	101	34.4	—
Nitrobenzene	468	250	69.4	17.8	—

Base: Pyridine

and $Cu(BFA)_2$, the stability in chloroform is comparatively large: At least, the adducts in this solvent are more stable than those in MIBK, butyl acetate and acetone. The phenomena may be now explained by the solvation to the copper chelates. The electron-withdrawing CF_3 group in the chelating ligands decreases the electron density around the central copper atom, but at the same time, it enhances the ability to form the solvates with some oxygen-containing solvents. Consequently, the adduct formation with N-base is weakened owing to the competition reaction with the solvents. This fact must be an important reason for the phenomena that in MIBK, butyl acetate and acetone, the adducts containing CF_3 group in the chelate ligands show lower stabilities than that in chloroform.

Effect of Metal to Ligand Bonding. Table 5 shows that irrespective of the solvents used, the stability of the adducts increases in the order:

$$Cu(AA)_2 < Cu(EAA)_2 < Cu(EBA)_2 < Cu(TAA)_2 \simeq Cu(BFA)_2$$

Graddon and Watton concluded that this was the decreasing order of effect of ligand field and the increasing order of the residual positive charge on the copper atom; but they did not carry out systematic studies. In the present work, the infrared absorptions attributed to the M–O (metal to ligand bonding), C=O and C=C stretching, were obtained to ascertain their conclusion. The spectra of the copper chelates were measured as KBr disks, and the results were summarized in Table 6. The bands for these chelates were assigned on the basis of the data of metal(II) β-diketone chelates, which had been presented by Nakamoto *et al.*⁶⁾

It is important to examine the relationship between the stability constant of the adduct and the M–O or the C=O stretching frequencies and it will be expected that decrease in the M–O frequency reflects the increase in the stability constant of the adduct. Table 6 indicates that the order of both the C=C and the C=O stretching frequencies is

TABLE 6. M-O, C=O and C=C FREQUENCIES OF COPPER(II) β-DIKETONE CHELATES(cm^{-1})

Complex	$\nu_{C=O}$	$\nu_{C=C}$	ν_{M-O}
$Cu(AA)_2$	1575	1550 1526	455
$Cu(EAA)_2$	1595	1555 1530	452
$Cu(EBA)_2$	1595	1565 1545	460
$Cu(TAA)_2$	1604	1590	445
$Cu(BFA)_2$	1602	1590	443

$$Cu(BFA)_2 \simeq Cu(TAA)_2 > Cu(EBA)_2 \simeq Cu(EAA)_2 > Cu(AA)_2,$$

but the order of the M–O stretching frequency is

$$Cu(BFA)_2 \simeq Cu(TAA)_2 < Cu(EAA)_2 < Cu(AA)_2 < Cu(EBA)_2.$$

The M–O stretching frequency, except that of $Cu(EBA)_2$, is just in the reversed order to that of the C=C and C=O frequency, and decreased M–O frequency is closely concerned with the higher stability constants of the adducts as presented in Table 5. The M–O stretching frequency of $Cu(EBA)_2$ is abnormally high. The metal-oxygen bonding is weakened by the resonance between carbonyl group and lone pair electrons of ester oxygen in ketoesters such as EAA and EBA. In fact, effect of ligand field of EAA and EBA are lower than that of acetylacetone.²⁾ From the phenomena, the low M–O frequency must be anticipated for $Cu(EAA)_2$ and $Cu(EBA)_2$, and actually, the frequency of $Cu(EAA)_2$ is somewhat lower that of $Cu(AA)_2$. However, as described above, the M–O band of $Cu(EBA)_2$ shows higher frequency contrary to expection, and this is contradictory also to the fact that the higher C=O and C=C frequency results in the lower M–O one.⁷⁾ Then, it seems reasonable to consider that the M–O band of Cu

---

6) a) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960). b) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

7) K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066 (1961).

$(EBA)_2$ is not the pure metal-oxygen mode, but the M–O streching band couples with other band and subsequently, it shifts to higher frequency. It can be concluded, therefore that the chelates showing lower M–O stretching frequencies form the more stable adducts with N-base.

The results of this investigation led to the conclusion that (i) metal-oxygen (ligand) bonding—the localization of electron in the chelate ring and (ii) the basicity of Lewis bases are considered as the essential factors in the adduct formation of metal β-diketone chelates.

Furthermore, the stability constant of the adducts was influenced by (iii) steric factors of Lewis base and (iv) solvent effect due to the formation of the solvates of the chelates or the solvation of N-base.