  Bull. Chem. Soc. Jpn., 53, 91—95 (1980)

Formation and Spectral Properties of Some Bis(β-diketonato)-copper(II)–Diazole Complexes

Tamizo KOGANE* and Reiko HIROTA**

Industrial Research Institute of Kanagawa Prefecture, Showa-machi, Kanazawa-ku, Yokohama 236

***Faculty of Science, Rikkyo University, Nishi-ikebukuro, Toshima-ku, Tokyo 171*

(Received May 19, 1979)

The reactions of bis(β-diketonato)copper(II) with pyrazole and imidazole gave the diazole adducts Cu(β-dik)$_2$(Hdzl) (β-dik=β-diketonate anion; Hdzl=diazole) and/or the μ-diazolato complexes [Cu(β-dik)(dzl)]$_n$ (n=2,4,....). The complexation reactions are very sensitive to the nature of the diazole and to the reaction conditions, sometimes giving different products depending upon the solvent used. In chloroform, Cu(β-dik)$_2$–pyrazole and Cu(β-dik)$_2$–imidazole complexes exhibited characteristic absorption maxima at approximately 570 and 555 nm, respectively, which are much shorter than the λ_{max} values of the starting Cu(β-dik)$_2$ chelates.

Nitrogen heterocycles react with bis(β-diketonato)-copper(II) complexes in different solvents forming 1:1 or 1:2 adducts.[1] There have been several reports concerning the reactions of bis(β-diketonato)copper(II) with bidentate ligands containing similar nitrogen atoms. For example, the ethylenediamine complex with bis(2,4-pentanedionato)copper(II),[2] as well as the 2,2′-bipyridine,[3] pyrazine,[4] 1,5-naphthyridine,[5] and 1,10-phenanthroline[6] complexes with bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), has been isolated and identified. Few papers have been published, however, on the reactions of bis(β-diketonato)copper(II) with heterocyclic bidentate ligands containing dissimilar nitrogen atoms.[7,8]

Pyrazole (Hpz) and imidazole (Him) are known to be versatile ligands which produce complexes with many metal ions or Lewis acids. These diazoles behave differently from pyridine and other six-membered nitrogen heterocycles in complex formation, since the NH protons are acidic and easily dissociate to give the corresponding anions.[9,10]

Diazole adducts of the bis(β-diketonato)copper(II) complexes, such as imidazole adducts of bis(fluorinated β-diketonato)copper(II)[7,8] and Cu$_2$(acac)$_2$(pz)$_2$ and Cu$_2$(acac)$_2$(OH)(pz) have been reported.[11] The reactions of diazoles with bis(β-diketonato)copper(II) in general, however, have not been studied systematically. The results of such studies and the behavior of the mixed complexes obtained, will be reported here.

Experimental

Materials. The β-diketonato chelates of copper(II) employed were Cu(dpm)$_2$, Cu(dibm)$_2$, Cu(dnbm)$_2$, Cu(dprm)$_2$, Cu(acac)$_2$, Cu(bzac)$_2$, Cu(tac)$_2$, Cu(fac)$_2$, and Cu(tfac)$_2$, where dpm, dibm, dnbm, dprm, acac, bazc, tac, fac, and tfac designate the anions of 2,2,6,6-tetramethyl-3,5-heptanedione, 2,6-dimethyl-3,5-heptanedione, 4,6-nonanedione, 3,5-heptanedione, 2,4-pentanedione, 1-phenyl-1,3-butanedione, 1-(2-thienyl)-1,3-butanedione, 1-(2-furyl)-1,3-butanedione, and 1,1,1-trifluoro-2,4-pentanedione, respectively. The chelates were prepared by mixing copper(II) acetate (1 mol) in aqueous solution with β-diketone (2 mol) in ethanol under stirring. The precipitate formed was filtered, dried, and recrystallized from chloroform or from a chloroform–ethanol mixture. Other materials and solvents were purified by standard procedures.

Syntheses of Pyrazolato and Imidazolato Mixed Complexes (Substitution Complexes). Cu$_2$(acac)$_2$(pz)$_2$, Cu$_2$(dprm)$_2$(pz)$_2$, and Cu$_2$(dnbm)$_2$(pz)$_2$ were obtained by reacting the β-diketonato complex with equimolar pyrazole in suitable solvents such as chloroform, acetone and ethanol. Cu(β-dik)(im) was obtained as a precipitate by the reaction of Cu(β-dik)$_2$ with an excess of imidazole in ethanol. The results of elemental analyses are given in Tables 1 and 3.

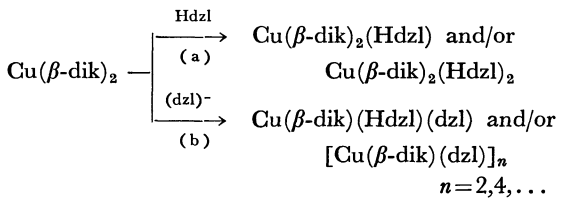
Synthesis of Pyrazole Adduct. Cu(bzac)$_2$(Hpz) and Cu(tfac)$_2$(Hpz): Cu(bzac)$_2$ or Cu(tfac)$_2$ was allowed to react with an equimolar quantity of pyrazole in cyclohexane under reflux for 5 min. After cooling, a light green or green precipitate was separated by filtration and dried *in vacuo*. Found: C, 60.88; H, 4.75; N, 5.95%. Calcd for $CuC_{23}H_{22}N_2O_4$: C, 60.85; H, 4.88; N, 6.17%. Found: C, 35.77; H, 2.62; N, 6.23%. Calcd for $CuC_{13}F_6H_{12}N_2O_4$: C, 35.67; H, 2.76; N, 6.40%.

Cu(tac)$_2$(Hpz) and Cu(fac)$_2$(Hpz): An equimolar mixture of pyrazole and Cu(tac)$_2$ or Cu(fac)$_2$ was dissolved in dichloromethane. The solvent was allowed to evaporate *in vacuo* and a green or light green solid was obtained as a residue. Found: C, 49.25; H, 4.04; N, 5.96%. Calcd for $CuC_{19}H_{18}N_2O_4S_2$: C, 48.97; H, 3.89; N, 6.01%. Found: C, 52.01; H, 4.09; N, 6.28%. Calcd for $CuC_{19}H_{18}N_2O_6$: C, 52.59; H, 4.18; N, 6.46%.

Spectra Measurement. The electronic absorption and diffuse reflectance spectra were recorded on a Hitachi Model 356 spectrophotometer and IR on a Hitachi Model 225 grating infrared spectrophotometer. ^{1}H-NMR spectra were obtained on a JEOL JNM C-60H spectrometer. Mass spectra were measured on a Hitachi RMU-6L mass spectrometer by introducing the sample through a direct inlet system.

Results and Discussion

The bis(β-diketonato)copper(II) complexes were treated with diazoles in solutions, and one or both of the reactions (a), (b) shown in Scheme 1 took place. Reaction (a) forms five or six coordinated bis(β-diketonato)copper(II) adducts, Cu(β-dik)$_2$(Hdzl) or Cu(β-dik)$_2$(Hdzl)$_2$, while (b) is a substitution reaction forming mononuclear Cu(β-dik)(Hdzl)(dzl) or polynuclear [Cu(β-dik)(dzl)]$_n$.[12]



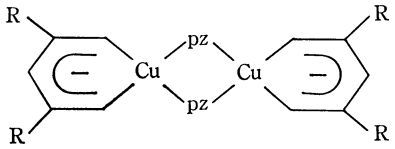
Scheme 1. Reaction paths of bis(β-diketonato)copper(II) with diazoles.

The complexation reactions are very sensitive to the nature of the solvent and to the reaction conditions, giving different products depending upon the solvent used. Hereafter, reactions (a) and (b) are referred to as addition and substitution reactions, respectively. The former proceeds *via* coordination of the neutral diazole molecules to the apical positions of the chelate, while the latter proceeds apparently by replacement of a β-diketonate anion of the chelate with one or two molecules of the diazolate anion.

The Pyrazole Complexes. Equimolar amounts of pyrazole and $Cu(acac)_2$ were mixed in chloroform, which gave $Cu_2(acac)_2(pz)_2$ (**1**) which was isolated as a light blue precipitate. The precipitate was identified by elemental analysis and spectroscopy, the results of which are in accordance with those previously reported by Barraclough *et al.*[11] who showed that it is a binuclear complex. The reaction of pyrazole with $Cu(dprm)_2$ and $Cu(dnbm)_2$ also gave the pyrazolato complexes **2** and **3**, respectively (Table 1).

TABLE 1. THE DIFFUSE REFLECTANCE SPECTRA AND CHEMICAL ANALYSES OF THE PYRAZOLATO COMPLEXES

Complex	λ_{max}/nm	Found (Calcd) (%)		
		C	H	N
$Cu_2(acac)_2(pz)_2$	630	41.72 (41.83)	4.37 (4.39)	12.37 (12.19)
$Cu_2(dprm)_2(pz)_2$	618	46.54 (46.59)	5.60 (5.47)	10.65 (10.87)
$Cu_2(dnbm)_2(pz)_2$	635	50.19 (50.43)	6.13 (6.35)	9.97 (9.80)



1 R=CH_3
2 R=C_2H_5
3 R=n-C_3H_7

The other bis(β-diketonato)copper(II) complexes examined gave no pyrazolato complexes of this type. Bis(β-diketonato)copper(II) complexes with bulky substituents such as isopropyl and *t*-butyl resist the formation of pyrazolato complexes, probably because of steric hindrance.

In order to investigate the substitution reactions further, the NMR spectra of ternary $Cu(\beta\text{-dik})_2$–diazole–chloroform-*d* system were measured. The signals of the OH and CH protons (*ca.* 16.0 ppm and 5.7 ppm, respectively) characteristic of the intramolecularly hydrogen-bonded enolic form of β-diketone are observed when diazole is added to $Cu(\beta\text{-dik})_2$ in chloroform. The signals are attributed to the β-diketone liberated during the reaction of $Cu(\beta\text{-dik})_2$ with diazole. The enolic CH and OH signals are also observed in cases when the substituents are bulky and the solid substitution products are not isolated. For example, the system $Cu(dpm)_2$–Hpz shows the following signals: ($CDCl_3$) δ=1.2 (s, *t*-butyl), 4.3 (br, ring), 5.73 (s, CH), and 16 (br, OH), suggesting that pyrazole, in solution, is coordinated in the anionic form even to the $Cu(\beta\text{-dik})_2$ chelates with bulky alkyl group, liberating the β-diketone.

The reaction of $Cu(bzac)_2$ with equimolar pyrazole in cyclohexane gave a light green precipitate, which was shown to be a 1:1 addition complex, $Cu(bzac)_2$-(Hpz).[13] The product undergoes extremely slow breakdown on standing for several months to give measurable amounts of $Cu(bzac)_2$ and pyrazole. $Cu(bzac)_2$(Hpz) exhibits a rather broad band at 3310 cm^{-1} which has been assigned to ν(N–H), showing that pyrazole is present as the neutral ligand in this complex. An analogous addition complex is also obtained by reacting pyrazole with $Cu(tfac)_2$ in cyclohexane. The diffuse reflectance spectra of the pyrazole complexes are shown Fig. 1. $Cu(bzac)_2$(Hpz) has a broad maximum at 675 nm, while that of $Cu(tfac)_2$-(Hpz) is broader and somewhat split, with the maximum at >700 nm. In general, the addition of a nitrogen base to bis(β-diketonato)copper(II) causes a shift in the visible absorption maximum of the original copper chelate to a longer wavelength, when the base is coordinated at an apical position.[14,15]

The electronic absorption spectrum of the ternary system, $Cu(tfac)_2$–pyrazole–chloroform, showed two isosbestic points at 597 and 483 nm, when the amount of pyrazole was altered. $Cu(tfac)_2$(Hpz) was also obtained from this ternary system. This addition complex has an absorption maximum at 700 nm in chloroform. The addition complex $Cu(bzac)_2$(Hzp), however, behaves differently from $Cu(tfac)_2$(Hzp) in the same solvent, having an absorption maximum at 568 nm (Fig. 2). In this case, no isosbestic point was

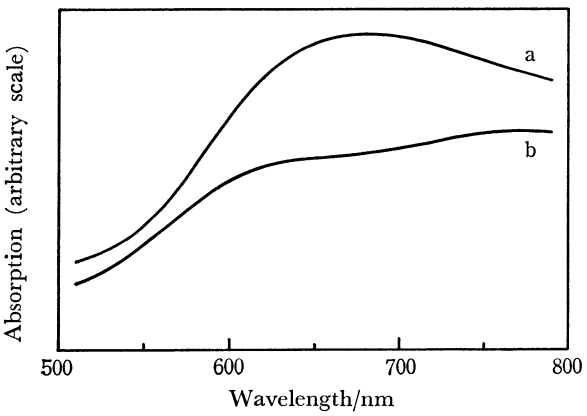


Fig. 1. The diffuse reflectance spectra of Cu $(bzac)_2$-(Hpz) (a) and $Cu(tfac)_2$(Hpz) (b).

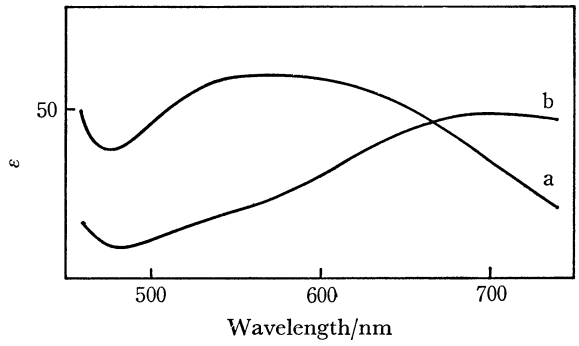


Fig. 2. The electronic spectra of $Cu(bzac)_2$(Hpz) (a) and $Cu(tfac)_2$(Hpz) (b) in chlorofrom.

observed with successive additions of pyrazole to a solution of $Cu(bzac)_2$. The spectral behavior suggests some structural change in the adduct, *e.g.* isomerization or partial dissociation, probably accompanied by apical-equatorial transfer of Hpz. Evaporation of chloroform, however, left a residue composed mainly of normal $Cu(bzac)_2(Hpz)$ and therefore the structural change in solution is apparently reversible.

As mentioned above, the adduct is obtained when the β-diketonato ligand is Hbzac and not when the ligands are aliphatic β-diketone. This suggests that the adduct $Cu(bzac)_2(Hpz)$ is more stable than the pyrazole adducts of bis(1,5-dialkyl-2,4-pentanedionato)-copper(II) chelates. This is in agreement with conclusions from the stability constants[15] of the $Cu(\beta\text{-dik})_2$(pyridine) and probably due to the contribution of phenyl group to the resonance stabilization of the adduct.[16]

Similarly, $Cu(tac)_2$ and $Cu(fac)_2$ formed stable 1:1 adducts with pyrazole. Equimolar quantities of pyrazole and either $Cu(tac)_2$ or $Cu(fac)_2$ were dissolved in dichloromethane. Evaporation of the solvent *in vacuo* left a green or light green residue, which was a 1:1 adduct of $Cu(tac)_2(Hpz)$ or $Cu(fac)_2(Hpz)$. The adducts lost pyrazole on standing for a long period in the atmosphere. The spectral data of the addition complexes are shown in Table 2, where it may be seen that the spectra are similar to that of $Cu(bzac)_2(Hpz)$, showing again characteristic absorption maxima at *ca.* 570 nm in solution.

The Imidazole Complexes. Using imidazole, 1:1 and 1:2 adducts of bis(fluorinated β-diketonato)copper-(II) have been isolated.[7] Those without fluorine substituents have, however, not been isolated because of their instability. An equimolar mixture of imidazole and $Cu(acac)_2$ in chloroform, when refluxed for 1 h, gave crystals which were isolated and shown to have a composition corresponding to Cu(acac)(im) by elemental analysis, IR and mass spectra. By the successive addition of imidazole to a solution of $Cu(acac)_2$ in chloroform, further displacement occurs. The product has not been identified, however. The displacement reaction in ethanol, however, gave Cu(acac)(im) exclusively. Consequently, Cu(β-dik)(im) was prepared by the reaction of the bis(β-diketonato)copper-(II) complex with an excess of imidazole in ethanol. Characteristic data on the substitution complexes are given in Table 3.

Table 2. The electronic and IR spectra of the pyrazole adducts

Adduct	Electronic: Reflectance λ_{max}/nm	Electronic: In chloroform λ_{max}/nm	Electronic: In chloroform ε_a[a]	IR ν_{N-H}^{KBr}/cm^{-1}
$Cu(bzac)_2(Hpz)$	675	568	60	3310
$Cu(tac)_2(Hpz)$	673	567	56	3310
$Cu(fac)_2(Hpz)$	685	569	51	3300
$Cu(tfac)_2(Hpz)$	—	700	48[b]	3310

a) Apparent molar absorptivity. b) This value appears to correspond to the true molar absorptivity, since the addition complex is, probably, the only chemical species present in solution under the experimental conditions.

Cu(acac)(im) exhibits no N–H absorption band in the infrared spectra, and imidazole is shown to be present as the imidazolate anion. This complex has a magnetic moment of 1.59 BM which is less than the spin-only value of 1.73 BM for bivalent copper. The value of the magnetic moment is similar to that of a blue (1.57 BM) or a green (1.62 BM) modification of bis(imidazolato)copper(II).[17] The subnormal magnetic moment suggests the exsistence of spin interaction between the copper atoms through imidazole rings in the complex. The imidazolate anion thus acts as a bridging bidentate ligand linking two copper ions. Cu(acac)(im) was insoluble in ordinary solvents and is thus suspected to be polymeric, or tetranuclear as reported on a similar complex,[18] in structure rather than binuclear as in **1**.

The diffuse reflectance spectra of Cu(acac)(im) and **1** are shown in Fig. 3. The former complex has a maximum at 540 nm, while the latter has at 630 nm (Table 1). The binuclear complex $Cu_2(acac)_2(pz)_2$

Table 3. Characteristic data on the imidazolato complexes

Complex	Color	Found (Calcd) (%) C	H	N	Diffuse reflectance spectra λ_{max}/nm
Cu(acac)(im)	violet	41.74 (41.83)	4.41 (4.39)	12.28 (12.19)	540
Cu(dprm)(im)	purple	46.37 (46.59)	5.49 (5.47)	10.88 (10.87)	542
Cu(dnbm)(im)	black	50.36 (50.43)	6.22 (6.35)	9.65 (9.80)	563
Cu(dibm)(im)	dark blue	50.53 (50.43)	6.56 (6.35)	9.68 (9.80)	580
Cu(dpm)(im)	dark blue	53.38 (53.57)	7.07 (7.06)	8.91 (8.92)	554
Cu(bzac)(im)	dark green	53.50 (53.51)	4.12 (4.15)	9.52 (9.60)	572
Cu(tac)(im)	dark green	44.27 (44.36)	3.26 (3.38)	9.10 (9.41)	574
Cu(fac)(im)	gray	47.22 (46.89)	3.67 (3.58)	9.83 (9.94)	559

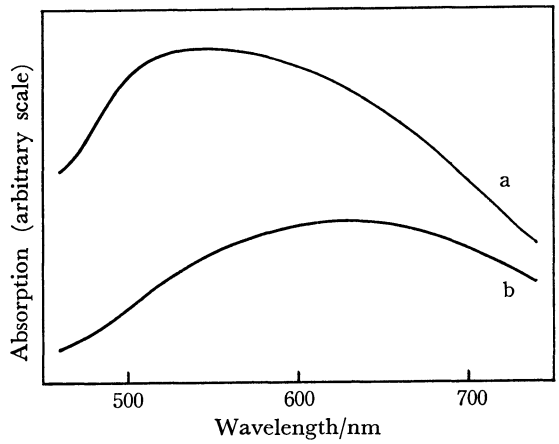


Fig. 3. The diffuse reflectance spectra of Cu(acac)(im) (a) and $Cu_2(acac)_2(pz)_2$ (b).

was assumed to take a square-planar configuration.[11] The electronic spectra in Fig. 3 show that the coordination around the copper atom of the imidazolato complex is clearly different from that of the pyrazolato complex. Square-planar coordination around each copper atom with a coplanar arrangement of the two imidazole rings and one 2,4-pentanedionato ligand appears sterically difficult, and the coordination around the copper atom may be considerably distorted from square-planar towards a tetrahedral. The similarity of the spectra in the series of Cu(β-dik)(im) suggests similar structures. The spectra in chloroform solutions[19] (Fig. 4) are also similar to the corresponding solid spectra, so the arrangement of the ligands around the copper(II) ions in such solutions is assumed to be analogous to that in the solid complexes.

The reaction of $Cu(tfac)_2$ with diazoles gave the diazole adducts, and did not yield the μ-diazolato complexes under the experimental conditions described above. The introduction of a CF_3 group into β-diketone greatly increases the stability of Lewis base adducts of the chelates,[16,20] making it difficult to transform to the μ-diazolato complexes. 2-Methylimidazole and 3-methylpyrazole exclusively form addition

Table 4. Products of the reaction of $Cu(RCOCHCOR')_2$ with nitrogen bases

Substituent		Base			
R	R′	Pyrazole		Imidazole	
		Path	Product	Path	Product
CH_3	CH_3	(b)	binuclear	(b)	polynuclear
C_2H_5	C_2H_5	(b)	binuclear	(b)	polynuclear
n-C_3H_7	n-C_3H_7	(b)	binuclear	(b)	polynuclear
i-C_3H_7	i-C_3H_7	(b)	(substitution)[a]	(b)	polynuclear
t-C_4H_9	t-C_4H_9	(b)	(substitution)[a]	(b)	polynuclear
C_6H_5	CH_3	(a)	1:1 adduct	(b)	polynuclear
C_4H_3S	CH_3	(a)	1:1 adduct	(b)	polynuclear
C_4H_3O	CH_3	(a)	1:1 adduct	(b)	polynuclear
CF_3	CH_3	(a)	1:1 adduct	(a)	1:1 and 1:2 adducts[b]

a) Reaction was found to proceed in solution. No solid product was isolated, however. b) Ref. 7.

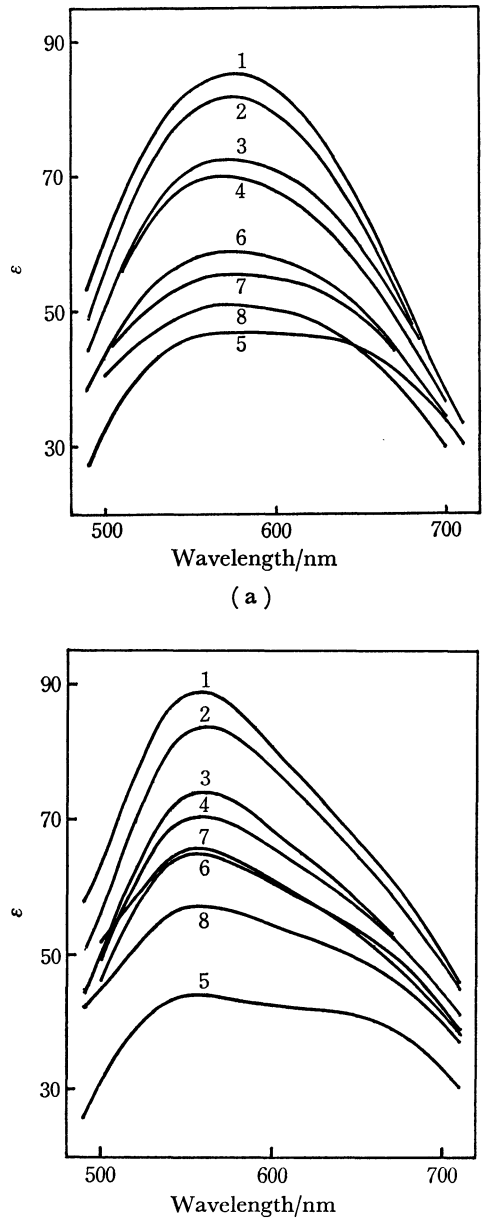


Fig. 4. The electronic spectra of Cu(β-dik)$_2$–pyrazole (4a) and Cu(β-dik)$_2$–imidazole (4b) complexes in chloroform: Cu(β-dik)$_2$ chelates are (1), Cu(dpm)$_2$; (2), Cu(dibm)$_2$; (3), Cu(dnbm)$_2$; (4), Cu(dprm)$_2$; (5), Cu(acac)$_2$; (6), Cu(bzac)$_2$; (7), Cu(tac)$_2$; (8), Cu(fac)$_2$.

complexes when reacted with $Cu(bzac)_2$. In these cases, the isomerization and the formation of substitution complex are prevented probably by steric hindrance.

In conclusion, the reactions of Cu(β-dik)$_2$ with diazoles proceed differently depending upon the nature of the substitutions on the β-diketonato ligands and also on the nature of nitrogen bases. The investigated nitrogen bases (pyrazole and imidazole) have both pyridine-like and imino nitrogen atoms in the same molecule, which enable them to react through two alternate paths here referred to as the addition and substitution reactions (Scheme 1). In the case of a

fluorinated β-diketonato ligand, the addition complex is favored irrespective to the nature of the nitrogen base. The substitution complex is always produced, on the contrary, when the β-diketone is aliphatic. The structures of the complexes appear to be different, however, depending on the nature of the bases in cases when aroyl- or hetaroylacetonato chelates are allowed to react. Addition complexes are obtained from pyrazole and substitution complexes from imidazole (Table 4). The greater ease of formation of the addition complexes in the former cases may be due to the π-donating power of the neighboring imino group in pyrazole.[16)]

The authors are grateful to Mr. Katsuo Hara of Yokohama National University for the measurement of ^{1}H-NMR spectra.

References

1) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).
2) T. Kurauchi, M. Matsui, Y. Nakamura, S. Ooi, S. Kawaguchi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **47**, 3049 (1974).
3) M. V. Veidis, G. H. Schreiber, T. E. Gough, and G. J. Palenik, *J. Am. Chem. Soc.*, **91**, 1859 (1969).
4) R. C. E. Belford, D. E. Fenton, and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, **1974**, 17.
5) H. W. Richardson, J. R. Wasson, and W. E. Hatfield, *Inorg. Chem.*, **16**, 484 (1977).
6) D. E. Fenton, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc., A*, **1971**, 1577.
7) J. T. Chen and S. M. Wang, *J. Chin. Chem. Soc.*, **18**, 213 (1971).
8) S. M. Wang and J. T. Chen, *J. Chin. Chem. Soc.*, **22**, 179 (1975).
9) S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972).
10) R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 471 (1974).
11) C. G. Barraclough, R. W. Brookes, and R. L. Martin, *Aust. J. Chem.*, **27**, 1843 (1974).
12) Hereafter diazole and β-diketone are abbreviated as Hdzl and Hβ-dik, respectively. Hβ-dik is used to designate non-fluorinated β-diketones in this report.
13) When the same reaction was conducted in chloroform, the reaction proceeds only partly and a mixture of the addition product and the starting materials was obtained.
14) R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).
15) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).
16) K. Ueda, *Bull. Chem. Soc. Jpn.*, **51**, 805 (1978).
17) M. Inoue, M. Kishita, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **39**, 1352 (1966).
18) G. Kolks, C. R. Frihart, H. N. Rabinowitz, and S. J. Lippard, *J. Am. Chem. Soc.*, **98**, 5720 (1976).
19) Since the polymeric solid of Cu(β-dik)(im) is sparingly soluble in chloroform, the spectra were obtained with 1:1 mixtures of $Cu(\beta\text{-dik})_2$ and imidazole. The spectra did not change in the course of polymerization and final deposition of the solid. The differences in the solubilities of these complexes may thus be ascribed to the differences in the degree of polymerization in the solids.
20) D. P. Graddon and W. K. Ong, *Aust. J. Chem.*, **27**, 741 (1974).