The Effects of the BF_2- and $B(C_2H_5)_2$-substitution for Bridging Hydrogen Atoms in the Cobalt(II), Nickel(II), and Copper(II) Complexes with Some Oximate Ligands

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Cobalt(II), nickel(II), and copper(II) complexes with dioximes substituted by BF_2- and $B(C_2H_5)_2$-groups for bridging hydrogen atoms were prepared. The BF_2-substitution caused a red-shift of d-d band and increase of $g_{//}$-value for copper(II) complexes and positive shift of polarographic half wave potential of nickel(II) complexes. In the case of the $B(C_2H_5)_2$-substituted complexes, such variations were not observed. The BF_2-substituted cobalt(II) complexes are stable under an open atmosphere at room temperature in a solid state and in a DMF solution. These were interpreted in terms of the electron-withdrawing ability of BF_2-group in the ligand.

In 1962, nickel(II) complexes with BF_2- or BR_2($R=CH_3$, n-C_3H_7, n-C_4H_9, and i-C_4H_9)-linked dioximes were prepared and characterized by Schrauzer[1] (the structures and abbreviations of these complexes are shown in Fig. 1). In the electronic spectra of these complexes, little change due to the introduction of BF_2- or BR_2-group was observed. Therefore, it was concluded that these substituents exert no effect on the ligand field around the nickel ion. Recently, Gagnè[2] obtained the dark purple complex, $Cu(tnomBF_2)ClO_4$, from brown $Cu(tnomH)ClO_4$:

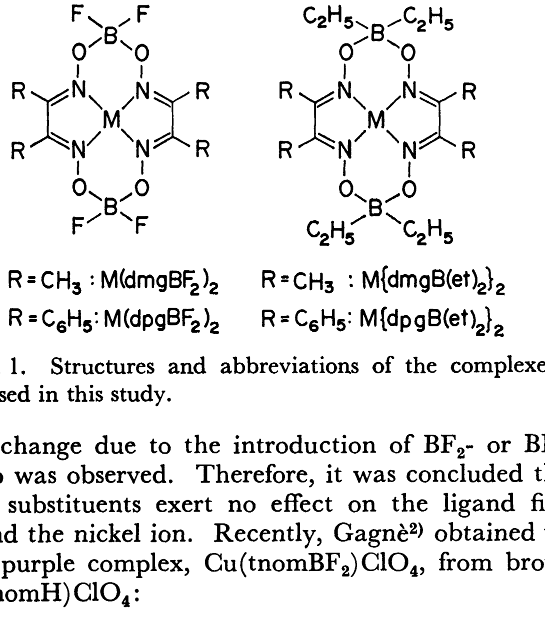
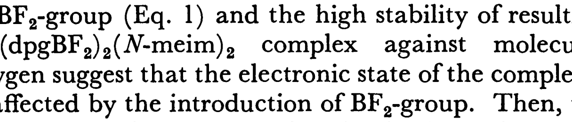


Fig. 1. Structures and abbreviations of the complexes used in this study.



(1)

$Cu(tnomH)ClO_4$ $Cu(tnomBF_2)ClO_4$

Drago and Gaul[3] found that $Co(dpgBF_2)_2(N\text{-meim})_2$ formed in a solution of $Co(dpgBF_2)_2\cdot 2CH_3OH$ containing N-methylimidazole (N-meim) is stable under aerobic conditions. The discoloration by introduction of BF_2-group (Eq. 1) and the high stability of resulting $Co(dpgBF_2)_2(N\text{-meim})_2$ complex against molecular oxygen suggest that the electronic state of the complexes is affected by the introduction of BF_2-group. Then, the substitution of BF_2-group for the bridging hydrogen may bring about change in the ring size and/or the electron density on the nitrogen atoms.

In this study, we have systematically prepared cobalt(II), nickel(II), and copper(II) complexes with BF_2- or $B(C_2H_5)_2$-substituted macrocyclic ligands as shown in Fig. 1, in order to elucidate the effects of these substituents on the electronic state of the complexes, coordination geometry, the reactivity of cobalt(II) complexes with molecular oxygen, and the equilibrium of cobalt(II) complexes with some organic bases, such as pyridine, in DMF solution.

Experimental

Synthesis. Triethylborane was prepared by the procedure of Meerwein and Mitab.[4] This material ignites spontaneously in air and hence it was used for subsequent reactions as a diethyl ether solution (*ca.* 30%).

$Cu(dmgBF_2)_2\cdot 2dioxane$: To a suspension of $Cu(dmgH)_2$ (4.5 g) in dioxane (90 cm^3) was added dropwise a dioxane solution (50 cm^3) containing boron trifluoride etherate (10 cm^3) at 60 °C. Reaction mixture was stirred at 80 °C for 1 h. On standing overnight, fine dark purple crystals were separated. These were recrystalized from acetone–dioxane (1 : 1).

Found: C, 33.84; H, 4.97; N, 9.93%. Calcd for $C_{16}H_{28}N_4O_8B_2F_4Cu$: C, 33.98; H, 4.99; N, 9.91%.

$Cu(dpgBF_2)_2\cdot 2dioxane$: This was prepared in a procedure similar to that for $Cu(dmgBF_2)_2\cdot 2dioxane$ by using $Cu(dpgH)_2$ (5.5 g) instead of $Cu(dmgH)_2$.

Found: C, 53.24; H, 4.53; N, 6.88%. Calcd for $C_{36}H_{36}N_4O_8B_2F_4Cu$: C, 53.13; H, 4.46; N, 6.88%.

$Cu\{dmgB(et)_2\}_2$: To a suspension of $Cu(dmgH)_2$ (4.5 g) in dioxane (100 cm^3) was added dropwise at room temperature 40 cm^3 of a diethyl ether solution of triethylborane. Reaction mixture was stirred at 80 °C for 1 h and concentrated to *ca.* 70 cm^3. After being left to stand overnight, the product was collected and recrystallized from dichloromethane-benzene (1 : 1) to give brown fine crystals.

Found: C, 44.73; H, 7.51; N, 13.04%. Calcd for $C_{16}H_{32}N_4O_4B_2Cu$: C, 44.31; H, 7.41; N, 13.25%.

$Cu\{dpgB(et)_2\}_2\cdot dioxane\cdot H_2O$: This was obtained in a procedure similar to that for $Cu\{dmgB(et)_2\}_2$ by using $Cu(dpgH)_2$ (5.5 g) instead of $Cu(dmgH)_2$. Recrystallization was carried out from chloroform–dioxane (1 : 1).

Found: C, 60.78; H, 6.15; N, 6.94%. Calcd for $C_{40}H_{50}N_4O_7B_2Cu$: C, 61.28; H, 6.43; N, 7.14%.

$Ni(dmgBF_2)_2$ and $Ni(dpgBF_2)_2$: These were prepared by the procedure of Schrauzer.[1]

$Ni\{dmgB(et)_2\}_2$: To a suspension of $Ni(dmgH)_2$ (4.3 g) in

dichloromethane (80 cm^3) was added dropwise 40 cm^3 of a diethyl ether solution of triethylborane at 40 °C. The solid dissolved gradually forming a red solution. The solution was evaporated to *ca.* 60 cm^3 and left stand overnight to give reddish orange fine crystals. These were recrystallized from benzene–chloroform (1 : 1).

Found: C, 45.15; H, 7.62; N, 13.18%. Calcd for $C_{16}H_{32}N_4O_4B_2Ni$: C, 45.24; H, 7.59; N, 13.19%.

Ni{dpgB(et)$_2$}$_2$·1/2CH$_2$Cl$_2$: This was prepared in a procedure similar to that for Ni{dmgB(et)$_2$}$_2$ by using Ni(dpgH)$_2$ (5.5 g) instead of Ni(dmgH)$_2$. Recrystallization was carried out from dichloromethane–diethyl ether (2 : 1).

Found: C, 61.01; H, 6.08; N, 7.57%. Calcd for $C_{36.5}H_{41}N_4O_4B_2ClNi$: C, 61.27; H, 5.78; N, 7.83%.

Co(dmgBF$_2$)$_2$·2H$_2$O: This was prepared in a procedure similar to that for Cu(dmgBF$_2$)$_2$·2dioxane by using Co(dmgH)$_2$·2H$_2$O (4.2 g) instead of Cu(dmgH)$_2$. The operations were carried out under nitrogen atmosphere and then brown fine crystals were obtained. These were dried at 80 °C for several hours under a reduced pressure over P_2O_5.

Found: C, 23.05; H, 3.87; N, 12.98%. Calcd for $C_8H_{16}N_4O_6B_2F_4Co$: C, 22.84; H, 3.83; N, 13.31%.

Co(dpgBF$_2$)$_2$·2H$_2$O·dioxane: This was prepared in the procedure similar to that by Tovrog *et al.*[5] Recrystallization was carried out from acetone–dioxane (1 : 1) under nitrogen atmosphere to give marron fine crystals.

Found: C, 50.19; H, 4.35; N, 7.40%. Calcd for $C_{32}H_{32}N_4O_8B_2F_4Co$: C, 50.76; H, 4.26; N, 7.40%.

Physical Measurements. Electronic spectra were measured at 25.0±0.2 °C with a Shimadzu Multipurpose Spectrophotometer Model MPS-5000. ESR spectra were measured with a JES-ME-3X Spectrometer using an X-band at room and liquid nitrogen temperatures. DPPH and Mn/MgO were used as standard markers. Thermogravimetric analyses were carried out with a Rigaku-denki Thermogavimetric and Differential Thermal Analyzer Model 8075E-1. All polarographic measurements were made at 25.0±0.2 °C in *N,N*-dimethylformamide (DMF), which was dried over molecular sieves (4A—1/16 type) and was distilled under nitrogen atmosphere. Tetraethylammonium perchlorate (TEAP) was used as a supporting electrolyte (0.1 mol/dm^3). The concentration of complexes was maintained constant (5×10^{-4} mol/dm^3) except for Ni(dmgH)$_2$. In the case of Ni(dmgH)$_2$, the saturated solution was used. All solutions were deoxygenated by bubbling pure nitrogen gas. A Fuso Polarographic Analyzer Model 312 was used for sampled d. c. polarography.

A three-electrode system[6] consisting of the droping mercury, the platinum wire and the saturated calomel electrodes as a working, a counter and a reference electrodes, respectively, was adopted. The saturated calomel electrode was connected to the sample solution through a salt bridge.[7]

Determination of Adduct Formation Constant. Deoxygenated DMF solution (100 cm^3) of Co(dmgBF$_2$)$_2$·2H$_2$O, Co(dpgBF$_2$)$_2$·2H$_2$O·dioxane, or Co(dpgH)$_2$·2H$_2$O was placed into a three necked flask (200 cm^3, filled with dry nitrogen) fitted with a tube connected to the cell for spectral measurement, and another neck being fitted with a buret to drop DMF solution of an organic base. After an organic base had been added to as olution of the complex, the solution was stirred for 10 min with a magnetic stirrer. The reaction mixture was led to the cell for spectral measurements. Equilibrium constants were determined at 25.0±0.2 °C by the method of Marzilli *et al.*[8]

Results and Discussion

Results of the elemental analyses and the infrared spectra suggested that the molecules of dioxane and/or water are contained in crystals of some compounds obtained. These were confirmed by thermogravimetric analyses.

All attempts to isolate a BF$_2$-linked metal free ligand or its alkali metal salt were unsuccessful to obtain dimethylglyoxime.

Electronic Spectra of Copper(II) Complexes. The electronic spectra of Cu(dmgH)$_2$ in various solvents[9,10] seem to consist of a number of bands overlapping each other. The d-d band[9] observed at about 22.0×10^3 cm^{-1} as a shoulder is almost concealed by an intense CT band. A methanol solution of Cu(dmgBF$_2$)$_2$ exhibits a peak at 21.5×10^3 cm^{-1} with a shoulder at 20.0×10^3 cm^{-1}. These bands regarded as d-d bands

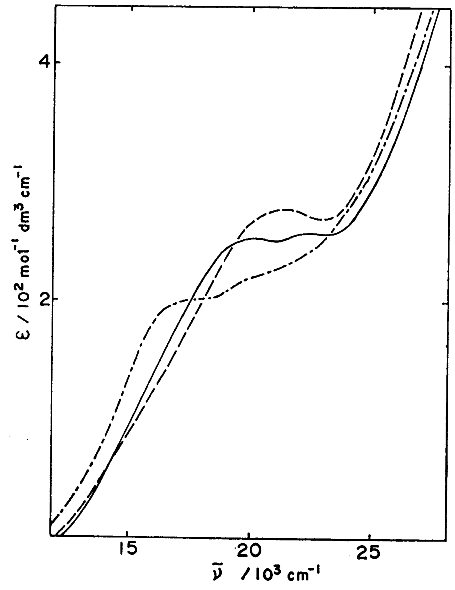


Fig. 2. Electronic spectra of Cu(dmgBF$_2$)$_2$ in methanol (----), acetone (——), and DMF (–––).

TABLE 1. ELECTRONIC AND ESR SPECTRAL DATA OF COPPER(II) COMPLEXES

Compound	Solvent	$\tilde{\nu}$/10^{3}cm^{-1}	(ε/mol^{-1} dm^3 cm^{-1})	$g_{//}$	$A_{//}$/10^{-4} cm^{-1}
Cu(dmgH)$_2$	DMF	21.0*(1350)	29.0(5400)	2.148	197.8
Cu(dmgBF$_2$)$_2$	DMF	17.0*(200) 19.5(215)	32.0(2900)	2.170	196.2
Cu{dmgB(et)$_2$}$_2$	DMF	21.0*(660)	29.0(4100)	2.147	202.4
Cu(dpgH)$_2$	CHCl$_3$	21.0*(1220)	24.0*(1780)	2.146	188.8
Cu(dpgBF$_2$)$_2$	CHCl$_3$	19.0*(490) 20.8(540)	25.5*(950)	2.167	194.4
Cu{dpgB(et)$_2$}$_2$	CHCl$_3$	21.5*(1540)	25.5*(3280)	2.149	193.6

*: Shoulder.

were shifted to lower energy side in a DMF solution (Fig. 2). On the other hand, the spectrum of methanol solution of $Cu\{dmgB(et)_2\}_2$ is similar to that of $Cu(dmgH)_2$ (Table 1). Therefore, it can be concluded that no drastic change due to the substitution of BF_2- and $B(C_2H_5)_2$-groups for bridging hydrogen occurs in the geometric structure and that the equatorial ligand field around the copper ion is weakened on account of the electron-withdrawing effect of BF_2-group, bringing about the subsequent axial ligation of solvent molecules.

Then, the lowering of π(2p)-orbitals of nitrogen atoms should be larger than that of d_{xy}-orbital with an unpaired electron, *i.e.*, the energy separation between metal d_{xy}- and ligand π(2p)-orbitals is expected to increase. In fact, the charge transfer band at 28.5×10^3 cm^{-1} in $Cu(dmgH)_2$[9] is shifted by $2.5\times10^3\ cm^{-1}$ to higher energy side in $Cu(dmgBF_2)_2$.

ESR Spectra of Copper(II) Complexes. The ESR spectra of BF_2- or $B(C_2H_5)_2$-substituted copper(II) complexes were measured in DMF solution at room and liquid nitrogen temperatures. All these spectra are similar to those of $Cu(dmgH)_2$[11] at both temperatures and essentially axial. The characteristic feature is that the $g_{//}$-value of $Cu(dmgBF_2)_2$ is appreciably large compared with those of $Cu(dmgH)_2$ and $Cu\{dmgB(et)_2\}_2$ which are comparable to each other (Table 1). The $g_{//}$-value for copper(II) complexes with axial symmetry is approximated[12] by

$$g_{//} = 2.0 - \frac{8\lambda\alpha^2}{\Delta}, \tag{2}$$

where λ is the spin-orbit coupling constant of the copper ion, α is the coefficient of d_{xy} in the molecular orbitals,[12,13] and Δ is the energy separation between d_{xy} and $d_{x^2-y^2}$. This shows that $g_{//}$-value increases with the decrease of energy separation Δ, because λ is negative. Therefore, the order of $g_{//}$-value is reasonable in view of that of the d-d band; $Cu(dmgH)_2 \approx Cu\{dmg(et)_2\}_2 > Cu(dmgBF_2)_2$. Such tendency is recognized in dpg-derivatives. These results support the conclusion mentioned above.

Polarography of Nickel(II) Complexes. The sampled d.c. polarograms of $Ni(dmgH)_2$, $Ni(dmgBF_2)_2$, and $Ni\{dmgB(et)_2\}_2$ were obtained in DMF solution containing TEAP (0.1 mol/dm^3). These complexes exhibited two reduction waves (Fig. 3). All these reduction waves are reversible one-electron reduction, judging from the results of coulometry. Olson and Vasilevskis[14] reported that a reduction wave corresponding to the electrode reaction, Ni(II)(14-diene)→Ni(I)(14-diene), was observed at −1.57 V *vs.* Ag–0.1 M $AgNO_3$ (1 M=1 mol/dm^3; −1.28 V *vs.* SCE) in the cyclic voltammetry of $Ni(14\text{-diene})(ClO_4)_2$ in acetonitrile. In view of this result, the first and the second waves should correspond to the following electrode processes,

$$\mathrm{Ni(II)L} \xrightarrow{e^-} \mathrm{Ni(I)L}$$
$$\mathrm{Ni(I)L} \xrightarrow{e^-} \mathrm{Ni(O)L}, \tag{3}$$

where L denotes $(dmgH)_2$, $(dmgBF_2)_2$, and $\{dmgB(et)_2\}_2$.

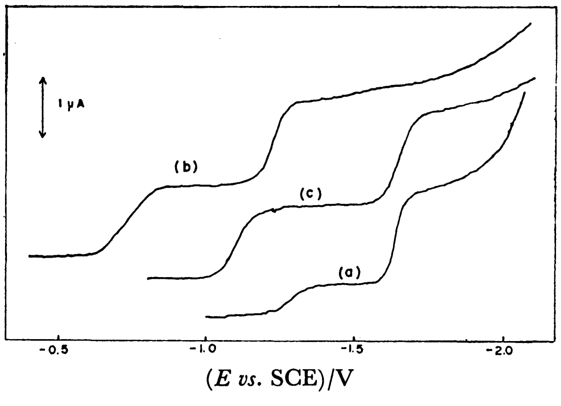


Fig. 3. Sampled d.c. polarograms of (a) $Ni(dmgH)_2$, (b) $Ni(dmgBF_2)_2$, and (c) $Ni\{dmgB(et)_2\}_2$ in DMF containing TEAP (0.1 mol/dm^3).

The half-wave potential of $Ni(dmgBF_2)_2$ is more positive in both processes than those of $Ni(dmgH)_2$ and $Ni\{dmgB(et)_2\}_2$ which are approximatly comparable. The same tendency was found in dpg-derivatives. The BF_2-linked complexes are more facile to be reduced compared with corresponding hydrogen bridged or $B(C_2H_5)_2$-linked complexes, due to the electron-withdrawing effect of BF_2-group. Therefore, the electron-withdrawing effect of BF_2-group considerably exerts on the electronic states of the nikel(II) complexes, although Schrauzer[1] claimed that the BF_2-group little affects the ligand field around the nickel(II) ion.

The reduction potentials of $Ni(dpgX)_2$ (X denotes H, BF_2, and $B(et)_2$) are more positive than those of the corresponding $Ni(dmgX)_2$. This suggests that the electron density on nickel ion of $Ni(dpgX)_2$ decreases because of the rather weak electron-donating effect of phenyl group compared with that of methyl group.

Electronic Spectra of Nickel(II) Complexes. Schrauzer[1] reported that in the spectra of $Ni(dmgX)_2$ (X denotes H, BF_2, and BR_2) in chloroform the bands at 21.1 and $24.4\times10^3\ cm^{-1}$ of $Ni(dmgH)_2$ are little shifted by the substitution of BF_2- or BR_2-groups for bridging hydrogen atoms. We measured the spectra of these complexes in DMF and in pyridine (Fig. 4). These spectra suffer little solvent effect in these solvents except for increase of intensity, although some of these solvents are capable of coordinating to a metal ion. On the other hand, it was shown from our polarographic results that the electron density on nickel ion of $Ni(dmgBF_2)_2$ decreases considerably compared with $Ni(dmgH)_2$ and $Ni\{(dmgB(et)_2\}_2$. Consequently, the resemblance in the spectra of $Ni(dmgX)_2$ reported by Schrauzer is attributed to the fact that the axial coordination of solvents is not promoted by the substitution of BF_2-group for bridging hydrogen atom.

Formation Constants of $Co(dmgBF_2)_2(base)_n$ and $Co(dpgBF_2)_2(base)_n$ (n=1 or 2). A solution of $Co(dmgBF_2)_2$ in DMF exhibits an absorption band at $21.7\times10^3\ cm^{-1}$ (ε=2700) at 25 °C. When pyridine is added to this solution, the band diminished and a new band appeared at $23.5\times10^3\ cm^{-1}$ with an isosbestic point at $22.7\times10^3\ cm^{-1}$ (Fig. 5). The spectrum converged to one curve when pyridine concentration exceeded 0.1 mol/dm^3 (400 times of the complex

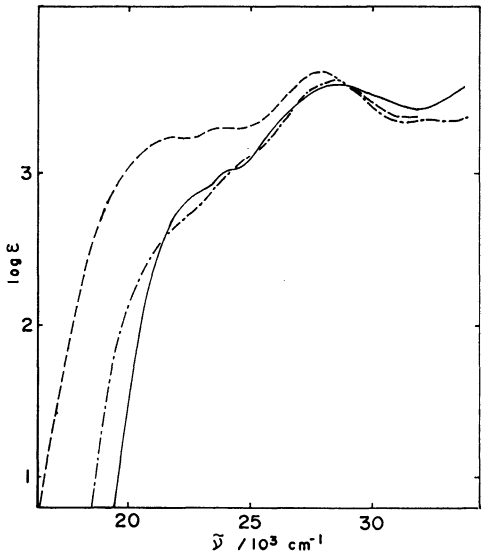


Fig. 4. Electronic spectra of $Ni(dmgBF_2)_2$ in chloroform (——), DMF (-·-·-·-), and pyridine (-----).

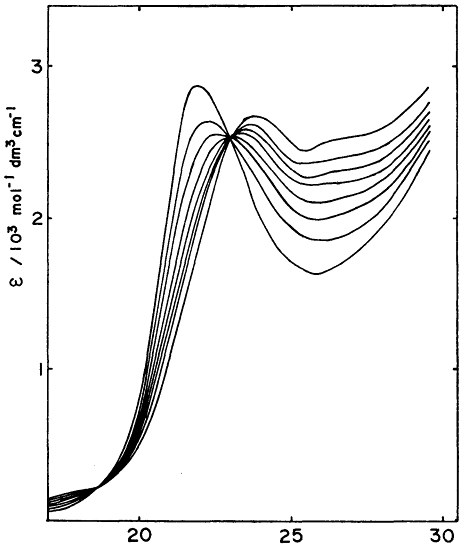


Fig. 5. Electronic spectra of $Co(dmgBF_2)_2$ in DMF with various contents of pyridine: 1), 0; 2), 1.4×10^{-3}; 3), 2.7×10^{-3}; 4), 5.9×10^{-3}; 5), 9.4×10^{-3}; 6), 1.5×10^{-2}; 7), 3.0×10^{-2}; 8), 1.0×10^{-1} mol/dm³. The concentration of $Co(dmgBF_2)_2$ is maintained constant (2.5×10^{-4} mol/dm³).

concentration). This spectral variation should correspond to the equilibrium,

$$Co(dmgBF_2)_2 + n\cdot py \rightleftharpoons Co(dmgBF_2)_2(py)_n (n=1 \text{ or } 2). \quad (4)$$

The equilibrium constant of this equation is given by the relation,

$$\beta = [Co(dmgBF_2)_2(py)_n]/[Co(dmgBF_2)_2][py]^n. \quad (5)$$

When A_0, A, and A_∞ denote the absorbances of $Co(dmgBF_2)_2$ at 21.7×10^3 cm⁻¹ in the absence of pyridine, in the presence of pyridine and in the presence of large excess of pyridine, respectively, the equilibrium constant is given by

$$\log\beta = \log[(A_0-A)/(A-A_\infty)] - n\log[py]. \quad (6)$$

The free pyridine concentration [py] is corrected by

$$[py] = [py]_t - [(A_0-A)/(A_0-A_\infty)]\ [M], \quad (7)$$

where $[py]_t$ and [M] denote total concentrations of pyridine and the metal complex, respectively. Then, $\log[(A_0-A)/(A-A_\infty)]$ was plotted against log [py] which was calculated by Eq. 7 for both cases of $n=1$ and 2 (Hill-plot). The plot for $n=1$ gives a straight line with a slope nearly equal to 1, and that for $n=2$ gives no straight line. Then, it became evident that one molecule of pyridine is bound to a cobalt ion. The equilibrium constant ($\log\beta$) was evaluated by extrapolating log [py] to zero. In the cases that the other organic base was used instead of pyridine, the equilibrium constants and n-values were evaluated in a similar manner as above (Table 2). For all the reactions between $Co(dmgBF_2)_2$ and organic bases, $n=1$ was

TABLE 2. FORMATION CONSTANTS OF $Co(dmgBF_2)_2(base)_n$, $Co(dpgBF_2)_2(base)_n$, AND THEIR RELATED COMPLEXES

Compound	Base[c] (pK_a)	n	$\log\beta$ (Temp/°C)	n^*[d]	Solvent	Reference
$Co(dmgBF_2)_2$	im (7.03)	1	4.04(25)	2	DMF	This work
$Co(dmgBF_2)_2$	py (5.27)	1	2.25(25)	2	DMF	This work
$Co(dmgBF_2)_2$	2-etim (7.99)	1	2.50(25)	1	DMF	This work
$Co(dmgBF_2)_2$	α-pic (5.97)	1	0.16(25)	2	DMF	This work
$Co(dpgBF_2)_2$	im (7.03)	2	7.19(25)	2	DMF	This work
$Co(dpgBF_2)_2$	γ-pic (6.02)	2	4.46(25)	2	DMF	This work
$Co(dpgBF_2)_2$	py (5.27)	2	4.20(25)	2	DMF	This work
$Co(dpgBF_2)_2$	2-etim (7.99)	1	3.18(25)	1	DMF	This work
$Co(dpgBF_2)_2$	α-pic (5.97)	2	0.97(25)	2	DMF	This work
$Co(dpgH)_2$	py (5.27)	1	2.94(25)	2[e]	DMF	This work
$Co(dmgH)_2$	py (5.27)	1	2.11(r.t.)	2[e]	CH_3OH	Ref. 15
Co(J-en)[a]	py (5.27)	1	2.18(20)	2	DCE[f]	Ref. 16
Co(ppIXdme)[b]	py (5.27)	1	3.27(20)	—	Toluene	Ref. 17
Co(ppIXdme)	py (5.27)	1	3.78(23)	—	Toluene	Ref. 18

a) Jäger-type open-chain ligand. b) Protoporphyrin IX dimethyl ester. c) im: Imidazole, py: pyridine, 2-etim: 2-ethylimidazole, α-pic: α-picoline, γ-pic: γ-picoline. d) n^* was evaluated from ^{14}N-superhyperfine splitting of the ESR spectrum. e) See Ref. 20. f) 1,2-Dichloroethane.

obtained. This shows that one molecule of the organic base links to the metal complex to form a five-coordinate complex Co(dmgBF$_2$)$_2$(base).

The formation constants of Co(dmgH)$_2$(py),[15] Co-(J-en)(py),[16] and Co(ppIXdme)(py)[17,18] at room temperature were reported (Table 2). In all cases, the mono-base adducts are predominant in the solution. Accordingly, it seems that square planer cobalt(II) complexes tend to form five-coordinate complexes with an organic base in solution. Thus, the present result that a five-coordinate complex, Co(dmgBF$_2$)$_2$(base), is formed is consistent with this tendency.

On the other hand, two molecules of organic base coordinate to Co(dmgBF$_2$)$_2$ at apical sites at 77 K, judging from the five-lined ^{14}N-superhyperfine structure in ESR spectrum in DMF glass containing organic base (except for 2-ethylimidazole). Therefore, it was revealed that the coordination manner of the organic base to Co(dmgBF$_2$)$_2$ at room temperature is different from that at low temperature, as seen in Co(J-en)-pyridine system reported by Kubokura *et al.*[16]

The formation constants of Co(dpgBF$_2$)$_2$(base)$_n$ at 25 °C were evaluated by using the variation of absorbance at 20.0×10^3 cm^{-1} by a procedure similar to the case of Co(dmgBF$_2$)$_2$(py). When pyridine, imidazole, α- and γ-picoline were used, $n=2$ was obtained from the slope of Hill-plots, and then, six-coordinate complexes Co(dpgBF$_2$)$_2$(base)$_2$ were shown to be formed, in contrast to the general tendency as mentioned above.

The electron-withdrawing effect of BF$_2$-group is more effectively exerted on Co(dpgBF$_2$)$_2$ than Co(dmgBF$_2$)$_2$, because the electron-donating ability of phenyl group is negligibly weak compared with that of methyl group. Consequently, the electron density on the cobalt(II) ion decreases and the axial coordination of ligands is facilitated.

When 2-ethylimidazole was used, the five-coordinate complex Co(dpgBF$_2$)$_2$(2-etim) was formed at 25 °C. This is explained in terms of the steric hindrance of ethyl group adjacent to the donating nitrogen atom.

Reaction of Co(dmgBF$_2$)$_2$ and Co(dpgBF$_2$)$_2$ with Molecular Oxygen. The electronic spectra of Co(dmgBF$_2$)$_2$ in DMF solution were measured under N$_2$-, O$_2$-, and an open atmospheres. The spectrum obtained under O$_2$-atmosphere is practically same as those under an open and N$_2$-atmospheres. This indicates that Co(dmgBF$_2$)$_2$ in the solution hardly reacts with molecular oxygen at room temperature.

The ESR spectrum of Co(dpgBF$_2$)$_2$ measured in acetonitrile frozen solution under an open atmosphere exhibited an axial pattern characteristic of low-spin, d^7-tetragonal complexes of cobalt(II) with $(d_{xy})^2(d_{z^2})^1$-ground state[19] (Fig. 6).

These results are noteworthy in contrast to the fact that the solutions of Co(dmgH)$_2$ and Co(dpgH)$_2$ are oxidized immediately on exposure to air. The d_{z^2}-orbital of Co(dmgBF$_2$)$_2$ and Co(dpgBF$_2$)$_2$ is lowlying relative to that of Co(dmgH)$_2$ and Co(dpgH)$_2$ because of the electron-withdrawing effect of BF$_2$-group. Accordingly, in the cases of BF$_2$-linked complexes the donation from metal-d_{z^2}-orbital to oxygen-π^*-orbital is diminished. Drago and Gaul[3] found that six-coordinate complex, Co(dpgBF$_2$)$_2$(N-meim)$_2$, is prepared in the solution of Co(dpgBF$_2$)$_2$ containing N-methylimidazole (N-meim) and that no oxygenated complex is formed under aerobic conditions. The formation of the same type six-coordinate complexes is recognized in solutions of Co(dpgBF$_2$)$_2$ containing excess pyridine and γ-picoline under an open atmosphere (Fig. 6), although oxygenated complexes were found in a solution of Co(dpgH)$_2$ containing excess pyridine.[20] These facts suggest that decrease of the electron density on cobalt ion facilitates the formation of normal coordination bond between cobalt and organic base, and that the formation of such strong bond hinders the exchange an organic base for molecular oxygen.

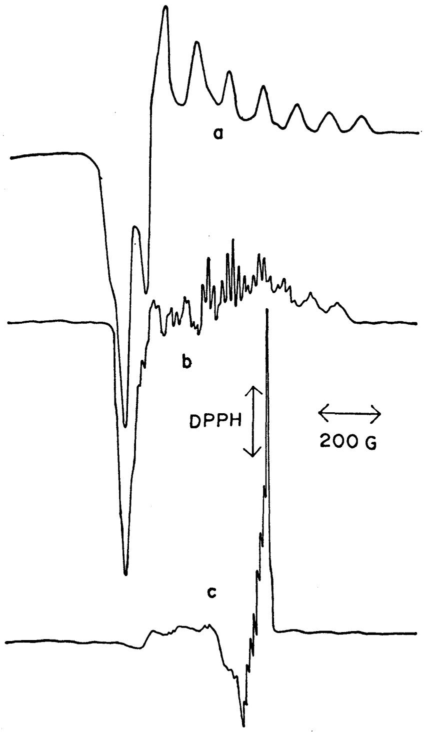


Fig. 6. ESR spectra of Co(dpgBF$_2$)$_2$ in (a) acetonitrile, (b) DMF–pyridine (19 : 1), and (c) DMF–2-etim (19 : 1) at liquid nitrogen temperature under aerobic conditions. (1G=10^{-4} T).

ESR spectrum of the DMF frozen solution of Co-(dmgBF$_2$)$_2$ containing excess pyridine under an open atmosphere exhibits a relatively weak, sharp signal at g=*ca.* 2, in addition to main signal due to the di-base adduct, Co(dmgBF$_2$)$_2$(py)$_2$. This shows the slight formation of an oxygenated complex. The reason may be that the electron-withdrawing effect of BF$_2$-group is partially canceled by the electron-donating ability of methyl group.

The ESR spectra of Co(dmgBF$_2$)$_2$ and Co(dpgBF$_2$)$_2$ in DMF frozen solution containing excess 2-ethylimidazole under an open atmosphere (Fig. 6) are drastically different from those of the di-base adducts such as Co(dmgBF$_2$)$_2$(py)$_2$ and are characteristic of oxygenated complexes formally described as a superoxide-cobalt(III) complex.[21] As mentioned above, the five-coordinate complex is formed under an unaerobic condition when 2-ethylimidazole was used. Thus, it becomes possible for a molecular oxygen to come close to a vacant sixth coordination site of cobalt ion.

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