June, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1581—1585 (1971)

The Effect of Axial Pyridine Ligands on the Charge Transfer Bands of *trans*-Bis(dimethylglyoximato)Cobalt(III) and -Iron(II) Complexes

Yukio Yamano, Isao Masuda, and Koichiro Shinra

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka

(Received November 16, 1970)

The electronic absorption spectra of $[Co^{III}(dmgH)_2B_2]^+$ and $[Fe^{II}(dmgH)_2B_2]$ (dmgH=dimethylglyoximate monoanion and B=pyridine derivatives) are inspected with respect to the effect of the axial pyridine ligands on the charge-transfer bands of the complexes. The characteristic bands observed in the 275—305 mμ region for the Co(III) complexes and in the 485—555 mμ region for the Fe(II) complexes, which have been assigned to a metal→oxime charge-transfer band, are shifted to shorter wavelengths with a decrease in the basicity of the pyridine derivatives. The results have been discussed by taking into account the π-interaction of the $d_\pi(d_{xz}, d_{yz})$ orbital of the central metal ion with the empty π-orbitals of both the dimethylglyoximate and the pyridine derivatives. It is suggested that the π-interaction is stronger in the Fe(II) complexes than in the Co(III) complexes, while the σ-bond is stronger in the latter. The infrared spectral evidence that the C=N stretching frequency is dependent on the axial pyridine derivatives, and that it is observed at a lower frequency in the Fe(II) than in the Co(III) complexes, is consistent with the above results.

It was thought to be informative to investigate the nature of the bonding between axial ligands and planar transition metal complexes in order to understand the transmission of the electronic effect of the axial ligands in the complexes. When ligands such as pyridine are coordinated axially to the planar complexes, a d_π-(metal)-π^*(py) bonding may be either taken into account[1–3)] or may be omitted.[4,5)] In previous works, the present authors postulated a π-interaction between the central cobalt ion and the pyridine ring in the *trans*-bis(1,2-dioximato)cobalt(III) complexes on the basis of the anomalous behavior of the pyridine ligands, extensively facilitating the deprotonation reaction of the intramolecular hydrogen bridges of the complexes.[6)]

In earlier publications,[7)] it was reported that the electronic absorption spectra of the *trans*-bis(1,2-dioximato)cobalt(III) complexes with aniline derivatives show characteristic C-I(340—400 mμ) and C-II(300—375 mμ) bands, which can be ascribed to the charge-transfer transitions from the axial aniline derivatives to the cobalt ion, and from the cobalt ion to the dioximate ligand, respectively. It seemed that it would be interesting to elucidate the effects of the axial pyridine analogues on the charge-transfer spectra of the complexes.

In this paper, the electronic spectra of *trans*-$[Co(dmgH)_2B_2]^+$ (dmgH=dimethylglyoximate monoanion and B=pyridine derivatives) have been inspected and compared with the spectra of $[Fe(dmgH)_2B_2]$, and the data have been discussed by taking into account the π-interaction between the axial ligands and the central metal ion.

Experimental

Preparations. The cobalt(III)-dimethylglyoxime complexes with the $[Co(dmgH)_2B_2]Cl$ formula, listed in Table 2, were prepared by a method described elsewhere.[6)]

The iron(II)-dimethylglyoxime complexes with the $[Fe(dmgH)_2B_2]$ formula were prepared according to the method of Miwa *et al.*[8)] The procedure was carried out under a nitrogen atmosphere. To an ethanol solution of $dmgH_2$ (1.5 g, 0.013 mol), $FeSO_4\cdot 7H_2O$ (1.5 g, 0.0065 mol) in an aqueous solution was added at room temperature; this was followed by the stirring in of pyridine or its derivatives (3—4 g, 0.03—0.04 mol) in an ethanol solution. The pH value of the solution was adjusted to about 7 by adding aqueous HCl or NaOH. Fine crystals precipitated; they were collected on a filter and washed with water, ethanol, and then ether. The analytical data are summarized in Table 1.

Measurements. The electronic absorption spectra of $[Co(dmgH)_2B_2]Cl$ were measured in an aqueous-ethanol (1 : 1) solution. As to $[Fe(dmgH)_2B_2]$, the electronic absorption spectra were measured in an ethanol solution containing an excess of the free axial ligand under a nitrogen atmosphere, since the complexes in solution are known to change upon standing in the air due to the dissociation of the axial ligand and the concomitant oxidation of the central iron ion.[9)] The complexes showed little spectral change under the above conditions, and they gave a spectrum quite close to that obtained for the solid sample. A Hitachi Spectrophotometer, Model EPS-3, and a Hitachi Infrared Spectrometer, Model EPI-2G, were used for recording the spectra.

Results and Discussion

Cobalt(III) Complexes. As may be seen in Fig. 1, the electronic absorption spectra of $[Co(dmgH)_2B_2]^+$ (B=pyridine derivatives) show three intense bands in the 250—400 mμ region, the band around 250 mμ may be assigned to the intraligand(dmgH) $\pi\rightarrow\pi^*$ transition.[10)] The bands at 315—370 mμ and 275—305 mμ, which will hereafter be referred to as the α- and β-bands respectively, are not well defined and

---

1) R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

2) B. C. Claude and G. Alain, *Tetrahedron Lett.*, **1969**, 4189.

3) S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **92**, 2991 (1970).

4) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *ibid.*, **86**, 3031 (1964).

5) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

6) Y. Yamano, I. Masuda and K. Shinra, *Inorg. Nucl. Chem. Lett.*, **4**, 581 (1968); *J. Inorg. Núcl. Chem.*, **33**, 521 (1971); I. Masuda, M. Sakano, and K. Shinra, This Bulletin, **42**, 2296 (1969).

7) C. Matsumoto, T. Kato, and K. Shinra, *Nippon Kagaku Zasshi*, **86**, 1266 (1965); C. Matsumoto, I. Masuda, and K. Shinra, *ibid.*, **88**, 46 (1967).

8) M. Miwa, Y. Kubota, and Y. Inamura, The 16th Symposium on Coordination Chemistry in Japan, p. 40 (1966).

9) B. A. Jillot and R. J. P. Williams, *J. Chem. Soc.*, **1958**, 462.

10) B. Roos, *Acta. Chem. Scand.*, **19**, 1715 (1965).

Table 1. Elemental analyses of the complexes

Complex[a]	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
$[Co(dmgH)_2(3\text{-}CH_3Py)_2]Cl\cdot 2H_2O$	43.90	5.84	15.39	43.69	5.84	16.14
$[Fe(dmgH)_2(4\text{-}NH_2Py)_2]\cdot H_2O$	43.90	5.73	22.75	43.74	5.53	21.40
$[Fe(dmgH)_2(3\text{-}NH_2Py)_2]$	45.58	5.53	23.63	45.36	5.65	23.25
$[Fe(dmgH)_2(4\text{-}CH_3Py)_2]\cdot H_2O$	49.00	6.17	17.13	49.15	6.07	17.66
$[Fe(dmgH)_2(3\text{-}CH_3Py)_2]\cdot H_2O$	49.00	6.17	17.13	48.82	6.08	18.96
$[Fe(dmgH)_2(Py)_2]\cdot H_2O$	46.77	5.67	18.18	46.28	5.44	18.80
$[Fe(dmgH)_2(3\text{-}CNPy)_2]\cdot 4H_2O$	42.38	5.29	19.78	41.96	4.32	19.78

a) dmgH = dimethylglyoximate monoanion and Py = pyridine.

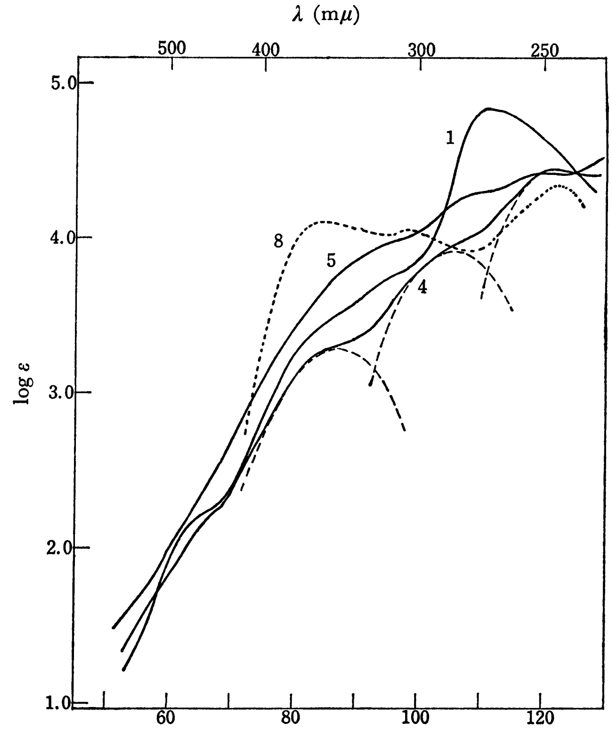


Fig. 1. Electronic absorption spectra of $[Co(dmgH)_2B_2]^+$ in aqueous-ethanol (1 : 1) solution.
1: B=4-NH_2Py, 4: B=Py, 5: B=4-CNPy, 8: B=aniline.

have lower intensities than the C-I and C-II bands of $[Co(dmgH)_2A_2]^+$ (A=aniline derivatives). The lower intense band at about 450 mμ might be due to a *d*—*d* transition. The complexes of the same type with ammonia, benzylamine, and imidazole as axial ligands show a spectral pattern similar to that of the pyridine species.[7] The absorption maxima of the α- and β-bands have been determined by the method of parabolic approximation.[11] The results obtained for $[Co(dmgH)_2Py_2]^+$ are represented in Fig. 1, while the numerical data are given in Table 2.

By plotting the frequencies (ν_{max}) of the α- and β-bands against the basicities of the free pyridine derivatives,[12–14] linear correlations have been found, as is shown in Fig. 2-α and -β. The α- and β-bands are shifted to a longer wavelength with an increase in the basicity of the pyridine derivatives. The degree of the shifts for the α-band is 1.5 times larger than that for the β-band. These shifts for the α- and β-bands caused by the nature of the axial ligands seem to be qualitatively similar to those observed for the C-I and C-II bands of $[Co(dmgH)_2A_2]^+$. In the case of this complex, the C-I band has been assigned to the charge-transfer band from the axial aniline derivatives to the cobalt ion on the basis of the fact that, with an increase in the basicity of the aniline derivatives, this band is

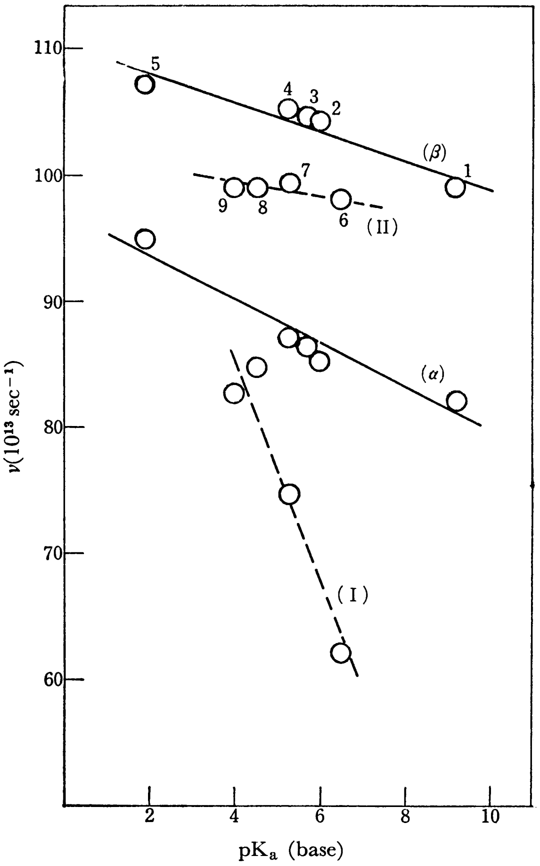


Fig. 2. Plots of the $\nu_{max.}$ of $[Co(dmgH)_2B_2]^+$ and $[Co(dmgH)_2A_2]^+$ against the pK$_a$ values of the conjugate acids of free bases.
(α): α-band, and (β): β-band of axial pyridine complexes.
(I): C-I band, and (II): C-II band of axial aniline complexes.

---

11) W. Kuhn and E. Braun, *Z. Phys. Chem.* (Leipzig), **B8**, 281 (1930).

12) H. H. Jaffe and G. O. Doak, *J. Amer. Chem. Soc.*, **77**, 4441 (1955).

13) P. T. T. Wong and D. G. Brewer, *Can. J. Chem.*, **46**, 131 (1968).

14) N. F. Hall, *J. Amer. Chem. Soc.*, **52**, 5124 (1930).

TABLE 2. ELECTRONIC ABSORPTION SPECTRA OF $[Co(dmgH)_2B_2]^+$ IN AQUEOUS-ETHANOL SOLUTION

Number[a]	B	α-Band		β-Band		π→π* (dmgH) Band	
		ν_{max}	log ε_{max}	ν_{max}	log ε_{max}	ν_{max}	log ε_{max}
1	4-NH_2Py	82.00	3.30	99.00	3.80	110.65[b]	4.80
2	4-CH_3Py	85.15	3.27	104.20	3.89	121.85	4.50
3	3-CH_3Py	86.25	3.30	104.50	3.90	123.20	4.50
4	Py	87.00	3.30	105.20	3.95	121.20	4.40
5	4-CNPy	94.80	3.98	107.20	4.23	119.10	4.40
	A	C-I band[c]		C-II band		π→π* (dmgH) band	
6	*p*-$N(CH_3)_2$An[d]	62.11	3.99	98.04	3.94	121.46	4.59
7	*p*-CH_3OAn	74.63	4.09	99.34	3.88	120.19	4.36
8	An	84.63	4.12	99.01	4.02	120.48	4.33
9	*p*-ClAn	82.64	4.18	99.01	4.00	120.09	4.36

The frequency is given in 10^{13} sec^{-1}.

a) These numbers are referred in Figs. 1 and 2.

b) This band includes the π→π* bands of both dmgH and 4-NH_2Py.

c) In Ref. 7.

d) An=aniline.

shifted to a longer wavelength, although the C-II band is shifted only a little.[7] As to the C-II band, it has been assigned to the charge-transfer band from the cobalt ion to the dioximate ligand, since it is shifted to a longer wavelength with an increase in the electron-withdrawing property of the dioximate ligands for $[Co(DH)_2(p\text{-}CH_3OAn)_2]^+$ (DH=1,2-dioximate monoanion and An=aniline).[7] Judging from the above observations and the frequencies of these bands, it is reasonable to ascribe the α- and β-bands for $[Co(dmgH)_2B_2]^+$ to the charge-transfer bands from the axial pyridine derivatives to the cobalt ion, and from the cobalt ion to the dimethylglyoximate ligand, respectively.

It is significant to note that: i) the β-band in $[Co(dmgH)_2B_2]^+$ is considerably affected by the nature of the axial pyridine derivatives, whereas the C-II band in $[Co(dmgH)_2A_2]^+$ is only slightly affected, and ii) the β-band for the axial pyridine complexes is observed at a higher energy than the C-II band for the axial aniline complexes (the difference in the energies between these two bands becomes larger as the basicity of the bases decreases) (Fig. 2). In order to explain these facts, it will be necessary to consider the d_π(Co)-π*(Py) interaction in addition to the d_π(Co)-π*(dmgH) bonding,[15] and the σ-bonding. As is shown in Fig. 5, it seems that the $d_\pi(d_{xz}, d_{yz})$-π*(Py) interaction stabilizes the d_π-levels, thus weakening the $d_\pi(d_{xz}, d_{yz})$-π*(dmgH) bonding and stabilizing the π*(dmgH) level. The extent of the stabilization of the π*(dmgH) level would, in this case, be smaller than that of the d_π-levels. Therefore, the d_π(Co)→π*(dmgH) charge-transfer band is observed in a shorter wavelength region for the axial pyridine complexes than for the axial aniline complexes. The empty π-level of the pyridine derivatives is expected to be lowered in the order: 4-NH_2Py>Py>4-CNPy.[16,17] Therefore, the π-interaction described above will become stronger and the d_π(Co)→π*(dmgH) charge-transfer band will be shifted to a higher energy in the order; 4-NH_2Py<Py<4-CNPy. The intraligand-(dmgH)π→π* band tends to shift to a longer wavelength as the π-acceptor property of the pyridine derivatives increases. This seems to be consistent with the above considerations.

Iron(II) Complexes. $[Fe(dmgH)_2B_2]$ (B=pyridine derivatives) has often been characterized by two intense absorption bands at about 500 and 400 mμ (Fig. 3).[8,9,18,19] In this paper we will designate them as the γ- and δ-bands respectively. In the case of the complexes with axial ammine or hydrazine ligands, no absorption band corresponding to the above δ-band has been observed. The γ-band has been assigned to the d_π(Fe)→π*(dmgH) transition on

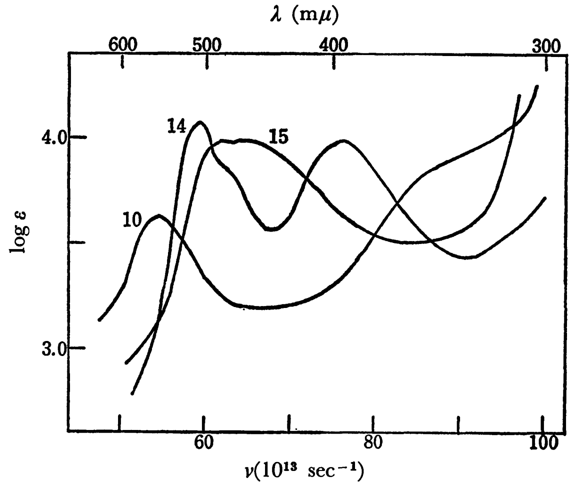


Fig. 3. Electronic absorption spectra of $[Fe(dmgH)_2B_2]$ in ethanol solution.
10: B=4-NH_2Py, 14: B=Py, 15: B=3-CNPy.

---

15) K. Burger and I. Ruff, *Talanta*, **10**, 329 (1963); K. Burger' I. Ruff, and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).

16) H. Tsubomura, *Nippon Kagaku Zasshi*, **78**, 293 (1957).

17) M. R. Basica and D. J. Clancy, *J. Phys. Chem.*, **67**, 1551 (1963).

18) K. Sone, This Bulletin, **25**, 1 (1952).

19) C. Matsumoto, Y. Yamano, and K. Shinra, *Nippon Kagaku Zasshi*, **89**, 46 (1968).

TABLE 3. ELECTRONIC ABSORPTION SPECTRA OF $[Fe(dmgH)_2B_2]$ IN ETHANOL SOLUTION AND IN POWDER REFLECTION ($\nu_{p.r.}$)

Number[a]	B	$d\rightarrow d$ Band[b]		γ-Band			δ-Band		
		$\nu_{p.r.}$	$\nu_{p.r.}$	ν_{max}	$\log \varepsilon_{max}$	$\nu_{p.r.}$	ν_{max}	$\log \varepsilon_{max}$	$\nu_{p.r.}$
10	$4\text{-}NH_2Py$	40.68	43.50	54.15	3.62	53.86	89.85	3.86	85.47
11	$4\text{-}CH_3Py$	41.70	45.90	57.70	3.95	57.80	79.20	3.90	74.63
12	$3\text{-}NH_2Py$	41.70	45.04	57.30	3.95	57.63	79.00	3.89	74.47
13	$3\text{-}CH_3Py$	42.25	46.00	58.25	3.98	58.10	75.80	3.87	73.44
14	Py	42.87	46.50	59.06	4.07	58.59	75.80	3.99	73.17
15	3-CNPy	43.30	48.50	61.65	3.98	61.48	64.65	3.99	64.79

The frequency is given in 10^{13} sec^{-1}.

a) These numbers are referred in Figs. 3 and 4.

b) In the spectra of $[Fe(dmgH)_2(3\text{-}CH_3Py)_2]$ in ethanol solution, two $d\rightarrow d$ bands with lower intensity ($\log \varepsilon = 2.16$ and 2.0) are observed at $\nu_{max} = 46.13$ and 42.13. In the spectra of the other complexes in ethanol solution, similar bands were unsuccessfully observed for their lower solubility.

the basis of the fact that, with an increase in the electron-withdrawing property of the dioximate ligand, it is shifted to a longer wavelength, although the δ-band is shifted only a little.[19] In a recent theoretical treatment,[20] the band at 526 mμ for $[Fe(dmgH)_2(NH_3)_2]$ has been indicated to be the $d_\pi(Fe)\rightarrow\pi^*(dmgH)$ charge-transfer band. As to the δ-band mentioned above, it has been proposed that it is due to the $d_\pi(Fe)\rightarrow\pi^*(Py)$ charge-transfer transition, since it is shifted to a longer wavelength in the 4-cyanopyridine complex than in the pyridine complex.[9]

Our interest led us to inspect the shifts of both the γ- and δ-bands for a series of axial pyridine derivatives in connection with the shifts of the α- and β-bands for $[Co(dmgH)_2B_2]^+$. As is shown in Fig. 4, the δ-band is considerably shifted to a longer wavelength with a decrease in the basicity of the pyridine derivatives; this indicates an increase in the derivatives' π-acceptor property. Therefore, the δ-band is ascribed to the $d_\pi(Fe)\rightarrow\pi^*(Py)$ charge-transfer transition. The γ-band is shifted to a shorter wavelength as the basicity of the pyridine derivatives decreases. The degree in the shift of the γ-band is almost the same as that of the β-band for $[Co(dmgH)_2B_2]^+$ (Figs. 2 and 4). This result is consistent with the above statement that the γ-band of the Fe(II) complexes, like the β-band of the Co(III) complexes, is due to the $d_\pi(metal)\rightarrow\pi^*(dmgH)$ charge-transfer transition.

Such an effect of the axial pyridine derivatives on the $d_\pi(Fe)\rightarrow\pi^*(dmgH)$ charge-transfer band may, as has been discussed for the Co(III) complexes, reflect a contribution of the $d_\pi(Fe)\text{-}\pi^*(Py)$ interaction to the bonding between the iron ion and the pyridine ring. That is, with an increase in the π-acceptor property of the pyridine derivatives, the $d_\pi(Fe)\text{-}\pi^*(Py)$ bonding becomes stronger and the d_π-orbitals are further stabilized. Therefore, the $d_\pi(Fe)\text{-}\pi^*(dmgH)$ bonding becomes weaker. The fact that the bands with lower intensities in the 610—740 mμ region, which may be attributed to $d\rightarrow d$ transitions, are shifted in the same way as the γ-band (Fig. 4) seems to support the above consideration.

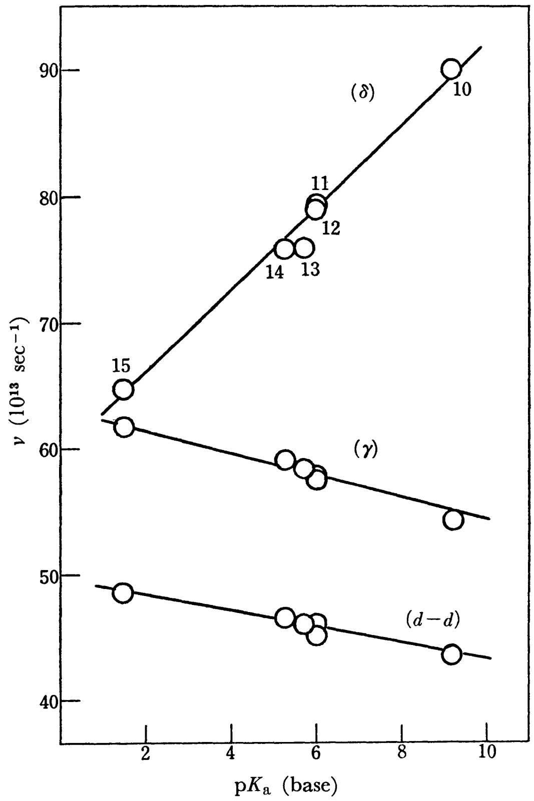


Fig. 4. Plots of the ν_{max} of $[Fe(dmgH)_2B_2]$ against the pK_a values of the conjugate acids of free bases. (γ): γ-band, (δ): δ-band, and (d—d): $d\rightarrow d$ band.

Comparison of the Cobalt(III) and Iron(II) Complexes. The $d_\pi(metal)\rightarrow\pi^*(dmgH)$ charge-transfer bands in the Co(III) complexes(β-band) and in the Fe(II) complexes(γ-band) are almost equally shifted to longer wavelengths as the basicity of the pyridine derivatives increases. The energy of the charge-transfer band for the Co(III) complexes is about twice that for the Fe(II) complexes (Figs. 2 and 4). One reason for this may be that, in these complexes, the ionization potential of the Fe(II) ion is lower than that of the Co(III) ion, as is shown in Fig. 5.[21] A lower ioni-

---

[20] G. De Alti, V. Galasso, A. Bigotto, and G. Costa, *Inorg. Chim. Acta*, **3**, 533 (1969).

[21] H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965); *J. Chem. Phys.*, **44**, 10 (1966).

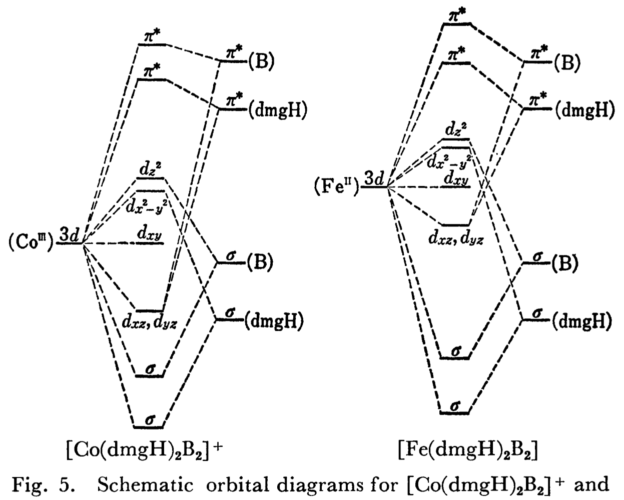
Table 4. IR spectra of the complexes,[a] cm^{-1}

B	$[Co(dmgH)_2B_2]^+$				$[Fe(dmgH)_2B_2]$			
	$\nu_{C=N}$	ν_{N-O}		ν_{Co-N}[b]	$\nu_{C=N}$	ν_{N-O}		ν_{Fe-N}[b]
4-NH_2Py	1529	1223	1089	518	1518	1219	1069	518
4-CH_3Py	1562	1236	1093	514	1540	1210	1078	517
3-NH_2Py					1536	1212	1068	516
3-CH_3Py	1560	1233	1093	514	1537	1206	1080	515
Py	1564	1238	1095	515	1532	1203	1081	515
4-CNPy	1568	1235	1092	514				
3-CNPy					1542	1209	1068	514
p-$N(CH_3)_2$An	1573	1242	1096	515				
p-CH_3OAn	1580	1236	1088	515				
An	1582	1236	1088	515				
p-ClAn	1578	1237	1093	512				

a) Measured in Nujol mull.
b) Metal-N(oxime) stretching frequency.

zation potential of the Fe(II) ion may also explain the different direction of the charge-transfer band between the axial ligands and the central metal ion for the Co(III) and Fe(II) complexes: from the pyridine derivatives to the cobalt ion, and from the iron ion to the pyridine derivatives, respectively.

The above facts suggest that the π-bonds between the central metal ion and the ligands are stronger in the Fe(II) complexes than in the Co(III) complexes and that the σ-bonds are stronger in the latter than in the former.



$[Co(dmgH)_2B_2]^+$ $[Fe(dmgH)_2B_2]$

Fig. 5. Schematic orbital diagrams for $[Co(dmgH)_2B_2]^+$ and $[Fe(dmgH)_2B_2]$. By using the approximation of C_{4v} symmetry for the planar metal chelate of the complexes the axes were determined as follows; the nitrogen atoms of the dimethylglyoximate ligands lie on the x and y axes, and the cobalt ion lies on the intersection. The z axis is perpendicular to the xy plane.

IR Spectra. As is shown in Table 4, the IR spectra of the Co(III) and Fe(II) complexes show characteristic bands in the 1700—1800, 1510—1590, and 1060—1240 cm^{-1} regions; these are assigned to the O–H–O, C=N, and N–O stretching frequencies respectively.[15,22] The band observed at about 515 cm^{-1} might be attributed to the metal-N(oxime) stretching frequency on the basis of the assignment for $[Ni(dmgH)_2]$.[23] The C=N stretching frequencies of the complexes are shifted to much lower frequencies than for the free dimethylglyoxime($\nu_{C=N}$=1750 cm^{-1})[23] because of the existence of a d_π(metal)-π^*(dmgH) bonding.[15] The C=N stretching frequencies are dependent on the axial pyridine derivatives.

In the Co(III) complexes, it is obvious from Tables 2 and 4 that the C=N stretching frequencies are shifted to longer wavelengths as the β-band(d_π(Co)$\rightarrow\pi^*$-(dmgH)) is shifted to a longer wavelength. These results seem to suggest that, as the d_π(Co)-π^*(Py) interaction becomes stronger, the d_π(Co)-π^*(dmgH) bonding is more weakened and the C=N double bonding character is increased. The C=N stretching frequencies are lower in the Fe(II) complexes than in the Co(III) complexes, indicating that the d_π(metal)-π^*(dmgH) bonding is stronger in the former. The stretching frequency of the Co–N(oxime) is slightly lower than that of the Fe–N(oxime). This may be due to the facts that the π-bond is stronger in the Fe(II) complexes and that the σ-bond is stronger in the Co(III) complexes, as has been suggested before.

---

22) A. Nakahara, J. Fujita, and R. Tsuchida, This Bulletin, **29**, 296 (1956).

23) K. Torii, I. Nakagawa, and T. Shimanouchi, The 14th Symposium on Coordination Chemistry in Japan, p. 269 (1964).