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Coordination Behavior of Amine Bases to the Axial Site of a (Dibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(II)

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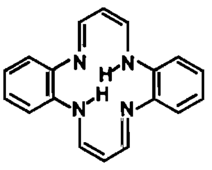
Abstract

The mutual interaction of various amine bases with the (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (Co(II)–1) was investigated by measuring electronic spectra in methyl benzoate. The Co(II)–1 became the pentacoordinated complex by taking up an amine base in the axial site: Co(II)–1 + B $\rightleftharpoons$ B–Co(II)–1. For the mutual interaction of substituted pyridines with the Co(II)–1, the general behavior of the equilibrium constants was explained on the basis of the amine basicity and the Hammett equation by reference to the corresponding behavior of the porphyrin, corrin and corrole complexes. Moreover, there exists a systematic correlation between log K and the chemical shift of the corresponding 4-position in the ^{13}C-NMR spectra of substituted pyridines. The isoequilibrium temperature obtained from a plot of ΔH against ΔS was 260 K. The equilibrium is primarily controlled by entropy at the usual temperature. The weaker coordination tendency of some hindered pyridine such as 2-methyl- and 2,6-dimethylpyridine toward Co(II)–1 was attributable to the steric effect between the in-plane ligand of Co(II)–1 and the 2- and/or 6-methyl groups of substituted pyridines in the coordination process.

Introduction

Axial-ligation equilibria for the porphyrin [1], corrin and corrole [2] complexes have been widely studied, on account of their interest biochemically. However, work has not been carried out on the structural variations associated with the macrocyclic framework such as ring size, charge and degree of unsaturation. We have investigated oxovanadium(IV), isothiocyanatomanganese(III), nickel(II), copper(II) and palladium(II) complexes of unsaturated N$_4$-macrocycles from the viewpoint of their spectral properties [3, 4]. On the other hand, a 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (1) with a diversity of structural types has an inner ring which is smaller than that of a porphyrin, 14 *vs.* 16 members. The cobalt(II) complex is of particular interest since this is a model compound of the cobalt(II)porphyrin type to obtain some information with a molecular oxygen complex. Greenaway *et al.* only studied the ESR spectra of the cobalt(II) complexes of 1 and a 5,14-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine, without providing any data with respect to axial-ligation equilibrium constants [5, 6].



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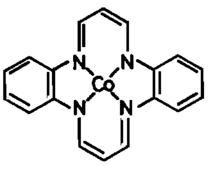

Co(II)-1

In the present study we employed the cobalt(II) complex of 1. The number of π-electrons in the interior molecular skeleton of this type extends from none for the completely saturated system to 16 for complete conjugation. Kinetic data for this cobalt(II) complex are lacking, even though such information is of importance for characterizing its catalytic functions. Consequently, axial-ligation constants and thermodynamic parameters for the reaction of Co(II)–1 with some pyridines and alicyclic amines were evaluated in methyl benzoate, and the coordination behavior of the Co(II)–1 discussed in referring to those of the porphyrin, corrin and corrole complexes.

Experimental

Preparation of Macrocycle and Its Cobalt(II) Complex

The synthetic procedure for 5,14-dihydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine (1) has been reported previously [3].

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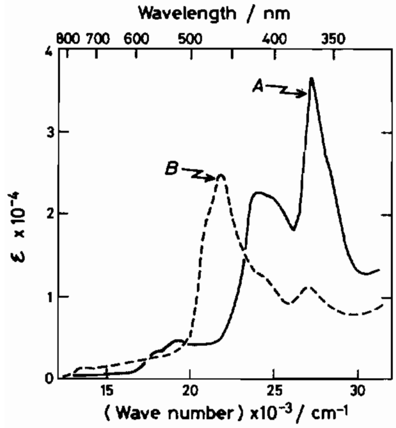

Fig. 1. Electronic spectra of (dibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinato)cobalt(II) (Co(II)–1) complex at room temperature: A, in methyl benzoate; B, in pyridine.

(Dibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinato)cobalt(II) (Co(II)–1)

This complex was prepared from 1 (1.0 g), cobalt(II) acetate tetrahydrate (1.0 g) and N,N-dimethylformamide (100 ml) after Hiller *et al.*, [7] and recrystallized from N,N-dimethylformamide to give glittering, dark-violet plates; yield 1.0 g (82%). Anal. Found: C, 62.41; H, 4.19; N, 16.56%; M^+, 345*. Calcd. for $C_{18}H_{14}N_4Co$: C, 62.61; H, 4.10; N, 16.23%; M, 345.27.

Spectroscopic Measurements

A JEOL JNM-FX 60 spectrometer was used to obtain ^{13}C-NMR spectra in chloroform-d (99.8 atom%D, Aldrich Chemical Co.) at room temperature and chemical shifts were given in ppm from internal TMS. Electronic absorption spectra were recorded on a Shimadzu UV-200S double beam spectrophotometer. Methyl benzoate for spectroscopic measurements was prepared by the standard procedure [8].

Commercial liquid amines (pyridine, 2-methyl-, 3-methyl- and 4-methylpyridine, 2,6-dimethylpyridine, piperidine and morpholine) were refluxed with potassium hydroxide and then fractionally distilled. Commercially available 4-cyanopyridine was recrystallized from aqueous ethanol. Other solid amines (4-amino- and 4-dimethylaminopyridine) were recrystallized from benzene. The purity of these organic amines was checked by gas chromatographic analysis.

TABLE I. Characteristic Absorption Bands due to $\pi \rightarrow \pi^*$ and Charge-transfer Transitions for the (Dibenzo[b,i] [1,4,8,11]-tetraazacyclotetradecinato)cobalt(II) Complex.[a]

	Transition energy in cm^{-1} (ε)	
Solvent	Methyl benzoate	Pyridine
	19200(4800)	13700(1300)
	23900(22500)	21800(24900)
	27200(36500)	27000(11500)

[a] The most intense band observed for metal-free ligand (1): 27200 cm^{-1} (ε 36500).

Determination of Equilibrium Constants for the Complex Formation Between Co(II)–1 and Amine Bases

The interaction of Co(II)–1 in methyl benzoate with an amine base was investigated by measuring the visible spectral change of a series of solutions in which the concentration of an amine was varied in a 20-fold range on one side and that of Co(II)–1 maintained constant (3×10^{-5} mol dm^{-3}) on the other. Upon addition of pyridines and alicyclic amines the visible peak at 365 nm decreased in intensity and clear isosbestic points were observed. Equilibrium constants were calculated by the Benesi-Hildebrand relationship. The values of log K, measured at three or four different temperatures over the 15–35 °C range, were used to evaluate ΔH and ΔS values.

Results and Discussion

Electronic Spectra

The electronic absorption spectrum for the (dibenzo[b,i] [1,4,8,11] tetraazacyclotetradecinato)cobalt(II) (Co(II)–1) complex is shown in Fig. 1, covering the 12500–34000 cm^{-1} range. The absorption bands lying above 18000 cm^{-1} are attributable to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and charge-transfer transitions from metal to ligand. General features of the spectrum in methyl benzoate for the Co(II)–1 are similar to those for previously studied oxovanadium(IV), nickel(II), copper(II) and palladium(II) complexes [3]. This result seems to indicate that the structure of the cobalt(II) complex is compatible with the square-planar coordination. As shown in Fig. 1 and Table I, the electronic spectrum of the Co(II)–1 shows an appreciable solvent-dependence. This spectral behavior seems to indicate a further coordination of one pyridine molecule at the axial position of the complex, which is consistent with the corresponding ESR data [5, 6].

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*Measurement of the mass spectrum was carried out by a JEOL JMS-DX 300 gas chromatograph-mass spectrometer.

TABLE II. Thermodynamic Parameters for Axial-ligation of Co(II)–1 with Various Amines.

Amine Base[a]	pK_a (BH^+)[b]	log K[c,d]	$-\Delta G$ kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	$-\Delta S$ J K^{-1} mol^{-1}	δ_C(ppm)[e]
4-CNPy	1.90	0.307	1.75	26.8	84	120.4
Py	5.19	1.26	7.18	45.2	126	135.8
3-CH_3Py	5.68	1.26	7.16	37.2	78	136.2
4-CH_3Py	6.02	1.65	9.42	37.0	93	146.6
4-NH_2Py	9.11	2.60	14.84	33.6	63	152.6
4-$(CH_3)_2$NPy	9.70	2.87	16.39	36.9	68	153.5
2-CH_3Py	5.97	0.225	1.29	24.4	84	136.0
2,6-$(CH_3)_2$Py	6.75	−0.044	−0.25	25.8	88	136.4
Morph	8.49	2.08	11.87			
Piperi	11.12	2.39	13.66			

[a] Abbreviations: 4-CNPy, 4-cyanopyridine; Py, pyridine; 3-CH_3Py, 3-methylpyridine; 4-CH_3Py, 4-methylpyridine; 4-NH_2Py, 4-aminopyridine; 4-$(CH_3)_2$NPy, 4-dimethylaminopyridine; 2-CH_3Py, 2-methylpyridine; 2,6-$(CH_3)_2$Py, 2,6-dimethylpyridine; Morph, morpholine; Piperi, piperidine. [b] G. D. Fasman, 'Handbook of Biochemistry and Molecular Biology. Physical and Chemical Data', vol. 1, 3rd ed., CRC Press, Inc., Cleveland, Ohio, 1976; S. Cabanl, V. Mollica, L. Lepori and S. T. Lobo, *J. Phys. Chem.*, *81*, 982 (1977). [c] Evaluated at 298.2 K. [d] K in mol^{-1} dm^3. [e] Measured in chloroform-d_1 at room temperature with TMS as an internal reference; δ_C, a chemical shift of a corresponding 4-position in a ^{13}C-NMR spectra of substitued pyridines.

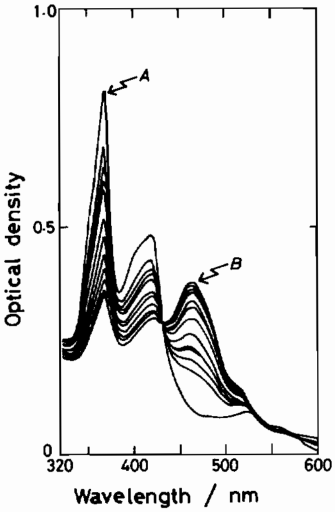

Fig. 2. Spectral change at 25.0 ± 0.1 °C for the reaction of Co(II)–1 complex in methyl benzoate with pyridine at various concentrations: 0, 2.47×10^{-2}, 3.71×10^{-2}, 6.18×10^{-2}, 9.30×10^{-2}, 1.24×10^{-1}, 1.86×10^{-1}, 2.47×10^{-1}, 3.09×10^{-1}, 3.71×10^{-1} and 4.33×10^{-1} mol dm^{-3} (read from A to B).

Interaction of Co(II)–1 with Amine Bases

The electronic absorption spectrum of Co(II)–1 dissolved in methyl benzoate underwent a marked change with succeeding amine bases: substituted pyridines (4-$(CH_3)_2$N, 4-NH_2, 4-CH_3, 3-CH_3, 4-CN, 2-CH_3 and 2,6-$(CH_3)_2$) and alicyclic amines (piperidine and morpholine). Since the spectral characteristic is nearly identical with that for the pyridine adduct shown in Fig. 2, the cobalt(II) ion in the Co(II)–1 complex leads to a pentacoordination by means of having an amine base at the axial site as the fifth ligand. The spectral variation upon addition of pyridine to Co(II)–1 is shown in Fig. 2. This spectral behaviour is in accord with the following solution equilibrium:

$$\mathrm{Co(II)–1} + \mathrm{B} \overset{K}{\rightleftharpoons} \mathrm{B–Co(II)–1} \qquad (1)$$

where B stands for an amine base. Isosbestic points are observed at 315, 425 and 575 nm, and a graph on the basis of log {[B–Co(II)–1]/[Co(II)–1]} against log [B] is a straight line with slope equal to unity. This indicates that only one molecule of the amine base is coordinated to one molecule of the Co(II)–1 complex, being in agreement with the ESR data [5, 6]. The formation constants (K) were determined with the intensity change at 365 nm by employing the Benesi-Hildebrand-type relationship (Eqn. (2)) [9].

$$\frac{[\mathrm{Co(II)–1}]\,[\mathrm{B}]}{\Delta A} = \frac{1}{\Delta\epsilon K} + \frac{[\mathrm{B}]}{\Delta\epsilon} \qquad (2)$$

Here, [Co(II)–1] and [B] represent the total concentrations of Co(II)–1 and amine, respectively, $\Delta\epsilon$ is the distinction in molar extinction coefficient between Co(II)–1 and B–Co(II)–1, and ΔA stands for the magnitude of the optical density change upon addition of amine bases. A good linear relationship based on Eqn. (2) is observed, as exemplified in Fig. 3 for the Co(II)–1–pyridine system at 298.2 K: $K = 1.81 \times 10$ mol^{-1} dm^3 and $\Delta\epsilon = 1.75 \times 10^4$. This $\Delta\epsilon$ value agrees with that obtained by use of a large

TABLE III. Brønsted[a] and Hammett[b] Parameters for the Coordination of Substituted Pyridine Bases.

Co(II)-Chelate System[c]	a	b	ρ	Ref.
Co(II)–1	0.32		1.8	This work
Co(II)–PP(IX)DME	0.09		0.6	1(f)
Co(II)-*p*-MeOTPP	0.19	1.7	1.0	1(e)
Co(III)–corrole	0.37	2.5	2.0	2(b)
Co(II)–TDHC	0.24	2.1	1.6	2(a)

[a] Refer to Eqn. (3). [b] Refer to Eqn. (4). [c] Ligand abbreviations: PP(IX)DME, 13,17-bis[2-(methoxycarbonyl)-ethyl]-3,8-divinyl-2,7,12,18-tetramethylporphine; *p*-MeO-TPP, 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphine; corrole, 2,3,7,8,12,13,17,18-octaethylcorrole; TDHC, 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin.

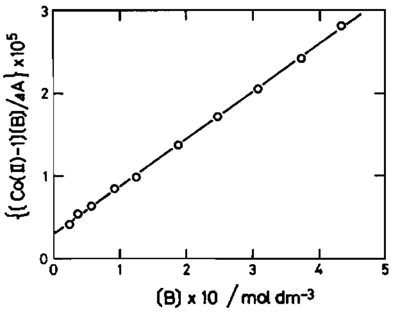

Fig. 3. Determination of K and $\Delta\epsilon$ values for the Co(II)–1–pyridine (B) system on the basis of Eqn. (2): [Co(II)–1] = 2.90×10^{-5} mol dm^{-3} in methyl benzoate at 25.0 ± 0.1 °C.

excess of pyridine base. The equilibrium constants for other amines were obtained in an analogous method, and are summarized in Table II.

The equilibrium constants for complexation of amine–Co(II)–1 system are smaller in magnitude than are those observed for the complexes derived from porphyrins [1(e)–1(f)] and Schiff bases [10, 11]. Seemingly there exists no linear relationship between log K and amine basicity, as shown in Fig. 4, taking no account of the structural characteristics of the amine bases. There is a single straight line correlation for each of the different types of amine bases; pyridines and alicyclic amines. In addition, the formation constant is very sensitive to the chemical shift (δ_C) of the corresponding 4-position in the ^{13}C-NMR spectra of substituted pyridines, listed in Table II. As seen in Fig. 5, there exists a systematic correlation between log K and ^{13}C-NMR spectral shifts (δ_C-value), except for 2-methylpyridine and 2,6-dimethylpyridine. The increasing order of log K is compatible with that of the δ_C-value of substituted pyridines, This tendency is analogous to the correlation between log K and the amine basicity (Fig. 4). Hence the equilibrium constant (K) can be correlated with the basicity of pyridine bases (pK_a) by Eqn. (3) for the axial coordination of pyridine bases to the Co(II)–1 but 2-methyl- and 2,6-dimethylpyridine, as shown in Fig. 4.

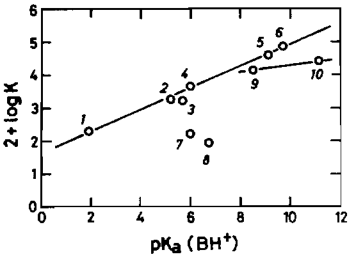

Fig. 4. Correlation between formation constant (log K) and amine basicity in methyl benzoate at 25.0 °C; K in mol^{-1} dm^3. Amines: 1, 4-CNPy; 2, Py; 3, 3-CH$_3$Py; 4, 4-CH$_3$Py; 5, 4-NH$_2$Py; 6, 4-(CH$_3$)$_2$NPy; 7, 2-CH$_3$Py; 8, 2,6-(CH$_3$)$_2$-Py; 9, Morph; 10, Piperi (see Table II for abbreviations).

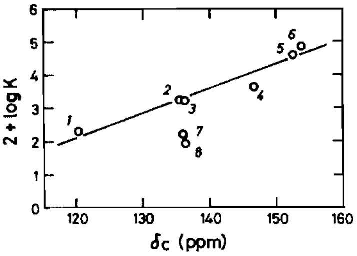

Fig. 5. Correlation between log K and ^{13}C-NMR spectral shifts (δ_C) for 4-position of substituted pyridine. Substituted pyridines; 1, 4-CNPy; 2, Py; 3, 3-CH$_3$Py; 4, 4-CH$_3$Py; 5, 4-NH$_2$Py; 6, 4-(CH$_3$)$_2$NPy; 7, 2-CH$_3$Py; 8, 2,6-(CH$_3$)$_2$-Py (see Table II for abbreviations).

$$\log K = a \times pK_a + b \qquad (3)$$

The a- and b-parameters thus evaluated are listed in Table III, together with those for Co(II)–porphyrin, Co(II)–TDHC and Co(III)–corrole. The equilibrium data for the present set of pyridine bases can be referred to the Hammett equation (Eqn. (4)):

$$-\log K/K^{\circ} = \rho \times \sigma \qquad (4)$$

where K is for a substituted pyridine and K° for pyridine, and σ is the Hammett substituent constant. The log (K/K°) for the substituted pyridines is listed in Table IV. The evaluated ρ value (Fig. 6) is listed in Table III, along with other reference data of relevant cobalt complexes. It is interesting to note that both a and ρ values for the present Co(II)–1 system are considerably larger than the corresponding values for the cobalt(II) complexes of 5,10,15,20-tetrakis-(*p*-methoxyphenyl)porphine [1(e)] and 13,17-bis[2-(methoxycarbonyl)ethyl]-3,8-divinyl-2,7,12,18-tetramethylporphine [1(f)]. Moreover, the values in this work are comparable to those obtained for the com-

TABLE IV. Log ($K/K°$) for the Substituted Pyridine Complexes of Co(II)–1.[a]

Substituted pyridine[b]	σ[c]	$-\log(K/K°)$
4-CNPy	0.66	0.95
$3\text{-}CH_3Py$	−0.07	0.24×10^{-2}
$4\text{-}CH_3Py$	−0.17	−0.39
$4\text{-}NH_2Py$	−0.66	−1.34
$4\text{-}(CH_3)_2NPy$	−0.83	−1.62

[a] Measured in methyl benzoate at 25.0 ± 0.1 °C. [b] See Table II for substituted pyridine abbreviations. [c] Cited from 'Advances in Linear Free Energy Relationship', N. B. Chapman and J. Shorter, Plenum, 1972.

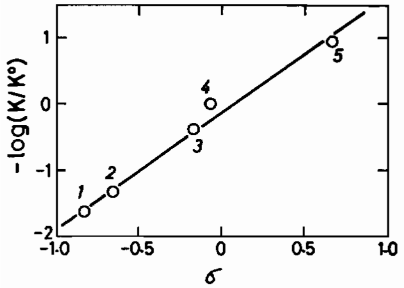

Fig. 6. Hammett plot for the substituted pyridine system. Substituted pyridines: 1, $4\text{-}(CH_3)_2NPy$; 2, $4\text{-}NH_2Py$; 3, $4\text{-}CH_3Py$; 4, $3\text{-}CH_3Py$; 5, 4-CNPy (see Table II for abbreviations).

plexes of Co(II)–TDHC [2(a)] and Co(III)–corrole [2(b)]. The a and ρ values suggest that the nuclear cobalt in Co(II)–1 is more electronegative than in cobalt(II)–porphyrins, and the pyridine nitrogen in $X\text{-}C_5H_4N\text{-}Co(II)\text{-}1$ is much more electron-deficient than in the corresponding cobalt(II)–porphyrin complexes.

As shown in Fig. 4, a large decrease in the K value was observed for some hindered pyridines, such as 2-methylpyridine and 2,6-dimethylpyridine. This may be attributed to the steric hindrance effect due to the interaction between the macrocyclic skeleton and the 2- and/or 6-methyl groups of the substituted pyridines in the coordination process. The coordination of pyridines to metalloporphyrins, cobalt(II)–TDHC and Co(III)–corrole is also subject to a similar steric effect [1(b), 1(c), 1(e), 2(a), 2(b)]. The free energy loss by the steric effect is estimated to be 7.78 J mol^{-1} (25 °C) for 2-methylpyridine, while 10.50 J mol^{-1} (25 °C) for 2,6-dimethylpyridine.

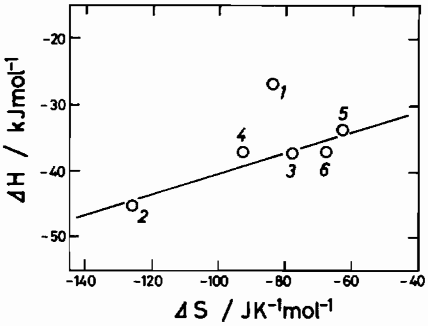

Fig. 7. A plot of ΔH against ΔS for the reaction of Co(II)–1 with amines in methyl benzoate. The solid line is based on the least squares calculation applied to all points. Amines: 1, 4-CNPy; 2, Py; 3, $3\text{-}CH_3Py$; 4, $4\text{-}CH_3Py$; 5, $4\text{-}NH_2Py$; 6, $4\text{-}(CH_3)_2NPy$ (see Table II for abbreviations).

Alicyclic amines form complexes with Co(II)–1 which are less stable than those derived from substituted pyridines, on the basis of the basicity scale given in Fig. 4. This trend is similar to those observed for the cobalt(II) complexes derived from porphyrin [1(e)] and TDHC [2(a)]. The extra stabilization observed for the pyridine complexes may result from the π-back bonding from the nuclear cobalt to the pyridine moiety.

Leffler pointed out that the enthalpy and entropy changes are linearly correlated by Eqn. (5) [12, 13].

$$\Delta H = \Delta H_0 + \beta \Delta S \qquad (5)$$

Here, ΔH_0 is the ΔH value corresponding to ΔS = 0, and β denotes the isoequilibrium temperature. Thermodynamic parameters for the reaction of Co(II)–1 with various amines in methyl benzoate are tabulated in Table II. A plot of ΔH against ΔS for determination of the isoequilibrium temperature is shown in Fig. 7. All points appear to lie along the same line, irrespective of the character of base except for the sterically hindered ones (2-methyl- and 2,6-dimethylpyridine): correlation coefficient, 0.96; β, 260 K. The β value is smaller in magnitude than those observed for the complexes derived from porphyrins [1(g), 2(c)]. As a consequence, in methyl benzoate which does not interact with Co(II)–1, the equilibrium constant is primarily controlled by entropy at ordinary temperatures and the log K value varies sensitively with the change in pK_a of amine.

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References

1 (a) C. B. Storm, A. H. Corwin, R. R. Arellano, M. Martz and R. Weintraub, *J. Am. Chem. Soc., 88,* 2525 (1966);

(b) C. H. Kirksey, P. Hambright and C. B. Storm, *Inorg. Chem., 8,* 2141 (1969);
(c) C. H. Kirksey and P. Hambright, *Inorg. Chem., 9,* 958 (1970);
(d) S. J. Cole, G. C. Curthoys and E. A. Magnusson, *J. Am. Chem. Soc., 92,* 2991 (1970);
(e) F. A. Walker, *J. Am. Chem. Soc., 95,* 1150 (1973);
(f) D. V. Stynes, H. C. Stynes, B. R. James and J. A. Ibers, *J. Am. Chem. Soc., 95,* 1796 (1973);
(g) D. P. Rillema, C. M. Wicker, Jr., R. D. Morgan, L. F. Barringer and L. A. Scism, *J. Am. Chem. Soc., 104,* 1276 (1982);
(h) G. A. McDermott and F. A. Walker, *Inorg. Chim. Acta, 91,* 95 (1984).

2 (a) Y. Murakami and Y. Aoyama, *Bull. Chem. Soc. Jpn., 49,* 683 (1976);
(b) Y. Murakami, S. Yamada, Y. Matsuda and K. Sakata, *Bull. Chem. Soc. Jpn., 51,* 123 (1978);
(c) Y. Murakami, Y. Hisaeda and A. Kajihara, *Bull. Chem. Soc. Jpn., 56,* 3642 (1983).

3 K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, *Bull. Chem. Soc. Jpn., 53,* 2262 (1980).

4 K. Sakata, H. Nakamura and M. Hashimoto, *Inorg. Chim. Acta, 83,* L67 (1984).

5 A. Pezeshk, F. T. Greenaway, J. C. Dabrowiak and G. Vincow, *Inorg. Chem., 17,* 1717 (1978).

6 A. Pezeshk, F. T. Greenaway and G. Vincow, *Inorg. Chem., 17,* 3421 (1978).

7 H. Hiller, P. Dimroth and H. Pfitzner, *Liebigs Ann. Chem., 717,* 137 (1968).

8 J. A. Riddick and W. B. Bunger, 'Organic Solvent', Wiley-Interscience, New York, 1970.

9 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc., 71,* 2703 (1949).

10 L. G. Marzilli, P. A. Marzilli and J. Halpern, *J. Am. Chem. Soc., 92,* 5752 (1970).

11 L. G. Marzilli, P. A. Marzilli and J. Halpern, *J. Am. Chem. Soc., 93,* 1374 (1971).

12 J. E. Leffler, *J. Org. Chem., 20,* 1202 (1955).

13 J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reaction', Wiley, New York, 1963.