Axial Ligation Constants of [5,10,15,20-Tetraphenylporphyrinato(2−)]cobalt

KENICHI YAMAMOTO

Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Received September 24, 1985

Abstract

Axial ligation constants ($\log K^B$) of bases for [5,10,15,20-tetraphenylporphyrinato(2−)]cobalt ([Co^{II}(tpp)]) are reported. The $\log K^B$ values of pyridine derivatives except for 4-cyanopyridine show a good linear relationship in a plot of $\log K^B$ vs. pK_a of the axial ligand. 4-Cyanopyridine gives a larger $\log K^B$ than expected. The $\log K^B$ value of 1-methylimidazole for [Co^{II}(tpp)] is almost the same as that for tetrakis(p-methoxyphenyl)porphyrinatocobalt(II) ([Co((p-CH$_3$O)tpp)]), althoug the other $\log K^B$ values for [Co^{II}(tpp)] are always slightly larger than those for [Co((p-CH$_3$O)tpp)]. These results are discussed on the basis of the σ- and π-bonding abilities of the bases, and the solvent effects on the $\log K^B$ values. The lower base affinities of cobalt(II) capped porphyrins are also discussed.

Introduction

Bases such as pyridine, imidazole, and their derivatives coordinate to the axial sites of [porphyrinato(2−)]cobalts, and five-coordinate complexes are formed in solution (eqn. (1); por and B represent porphyrin dianion and base, respectively) [1, 2].

$$[Co(por)] + B \underset{}{\overset{K^B}{\rightleftharpoons}} [Co(por)(B)] \qquad (1)$$
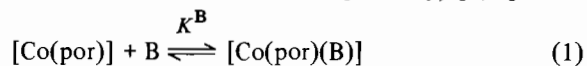
These five-coordinate [porphyrinato(2−)]cobalts react with an oxygen molecule to produce the dioxygen and μ-peroxo complexes. The reactivity of the five-coordinate [porphyrinato(2−)]cobalts towards dioxygen largely depends on the fifth axial ligand [1]. So the fifth ligand binding is an important factor for [porphyrinato(2−)]cobalt reactivity. Previous works have dealt with the fifth ligand binding of tetrakis(p-methoxyphenyl)porphyrin [3], protoporphyrin IX dimethyl ester [4], mesoporphyrin IX dimethyl ester [5], and *para*-substituted tetraphenylporphyrin [6] cobalt(II) compounds. Basolo and co-workers reported on the axial ligand binding of capped porphyrin systems [7, 8]. We now report on the axial ligation constants of bases for [Co^{II}(tpp)], measured under mostly the same conditions as Basolo

and co-workers*; there has been no systematic study of the axial ligation of [Co^{II}(tpp)], though some data have been reported in the previous study [6].

Experimental

5,10,15,20-Tetraphenylporphyrin (H$_2$tpp) and tetraphenylporphyrinatocobalt(II) ([Co^{II}(tpp)]) were synthesized by the literature methods [9, 10], respectively. The synthetic [Co^{II}(tpp)] was dissolved in the deoxygenated toluene. Three milliliter aliquots of this toluene solution of [Co^{II}(tpp)] were added to a UV and visible spectrum cell (1 × 1 × 4.5 cm) equipped with a glass tube (8 mmϕ × 5 cm) and a serum stopper, by use of a gastight syringe under nitrogen gas. Deoxygenated toluene solutions of bases were prepared in 50 ml flasks closed with serum stoppers. The optical cell was mounted on a Hitachi 557 type (double wavelength, and double beam) spectrophotometer. The initial spectrum was recorded, and then an aliquot of base toluene solution was added to the toluene solution of [Co^{II}(tpp)] by a gastight syringe under N$_2$. The cell was removed once from the spectrophotometer and the solution was mixed by shaking. After mixing, the spectrum was recorded in the 650–450 nm range. The addition of base toluene solution was repeated until the spectral change did not occur. From the spectral change, we obtained the equilibrium constants for each base according to the literature method [8]. Bases used were 1-methylimidazole, 1,2-dimethylimidazole, pyridine, 4-cyanopyridine, 3,5-dichloropyridine, 4-methylpyridine, 4-(dimethylamino)pyridine, quinoline, isoquinoline, and piperidine. All bases were reagent grade and used without further purification. The solvent effects on the $\log K^B$ values were studied using chlorobenzene, 1,2-dichloroethane, dichloromethane, chloroform, and N,N-dimethylformamide. These solvents were reagent grade and distilled under N$_2$ prior to use. Throughout

---

TABLE I. Axial Ligation Constants of Bases for $[Co^{II}(tpp)]$ in Toluene

B (base)[a]	$\log K^{B}$ [b]	$\log K^{B}$ in literature		Reference
1-Meim	3.38	[Co(cap)]	2.32 ± 0.05	8
		[Co(hmcap)]	2.28 ± 0.05	8
		[Co((p-CH_3O)tpp)]	3.26^{c}	11
1,2-Me_2im	2.91	[Co(cap)]	1.84 ± 0.05	8
		[Co(hmcap)	1.93 ± 0.05	8
py	2.90	[Co((p-CH_3O)tpp)]	2.83^{d}	11
4-CNpy	2.76			
3,5-Cl_2py	2.34			
4-Mepy	3.04			
4-Me_2Npy	3.80			
isoq	2.96			
quin	1.52			
pip	3.51	[Co((p-CH_3O)tpp)]	3.41^{e}	12

[a] Abbreviations: 1-Meim, 1-methylimidazole; 1,2-Me_2im, 1,2-dimethylimidazole; py, pyridine; 4-CNpy, 4-cyanopyridine; 3,5-Cl_2py, 3,5-dichloropyridine; 4-Mepy, 4-methylpyridine; 4-Me_2Npy, 4-(dimethylamino)pyridine; isoq, isoquinoline; quin, quinoline; pip, piperidine.   [b] The values of $\log K^{B}$ were obtained in toluene at 23 ± 0.1 °C spectrophotometrically unless otherwise noted, and reproducible within 10%.   [c] At 22.8 °C.   [d] At 25 °C.   [e] At 23.6 °C.

the base titration, the temperature of the solution was kept at 23 ± 0.1 °C by circulating water into the cell holder using a refrigerated circulating bath (Neslab Instruments Inc., Portsmouth, U.S.A.).

Results and Discussion

The spectral change in the titration with 1-methylimidazole is shown in Fig. 1. The spectra obtained in the 500–600 nm range showed two isosbestic points at 512 and 539 nm; for bases other than 1-methylimidazole, the spectra changed in similar patterns. So it is clear that the reaction between $[Co^{II}(tpp)]$ and the bases proceeded according to eqn. (1). The data
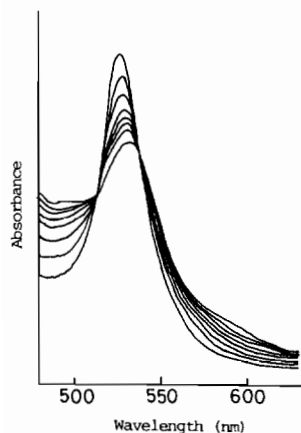

Fig. 1. Spectral changes by 1-methylimidazole titration. A 2.98×10^{-5} M toluene solution of $[Co^{II}(tpp)]$ is titrated with a 0.609 M toluene solution of 1-methylimidazole at 23 °C. The final base concentration is 2.30×10^{-2} M.

were fitted to eqn. (2) (the Hill equation) using a nonweighted linear least-squares method

$$\log y/(1 - y) = \log [B] + \log K^{B} \qquad (2)$$

where $y = (A_{obs} - A_0)/(A_\infty - A_0)$, A_{obs} = absorbance at a specific [B], A_0 = initial absorbance, and A_∞ = final absorbance. Values of $\log K^{B}$ were obtained from the y-intercept of the regression line for a plot of $\log y/(1 - y)$ vs. $\log [B]$.

Steric Effects of Base

The values of $\log K^{B}$ at 23 °C in toluene for each base are summarized in Table I. The data of Table 1 show that 1,2-dimethylimidazole bound about three times more weakly than 1-methylimidazole, despite the fact that the basicity of 1,2-dimethylimidazole (pK_a of conjugated acid (BH⁺), 7.85) is greater than that of 1-methylimidazole (pK_a of conjugated acid, 7.25)*. Quinoline (pK_a, 4.94) coordinated about 28 times more weakly compared with isoquinoline (pK_a, 5.14), although the K_a value is only 1.6 times smaller. These results show the same trend as that reported earlier by Walker for $[Co((p-CH_3O)-tpp)]$ [3]. There would be steric hindrance in the coordination of 1,2-dimethylimidazole and quinoline due to the 2-methyl group and 8-hydrogen, respectively. The ratios of the K^{B} values, (the K^{B} of 1-methylimidazole)/(the K^{B} of 1,2-dimethylimidazole) (abbreviated as R_1) and (the K^{B} of isoquinoline)/

*The values of pK_a: 5.27(pyridine), 1.86(4-cyanopyridine), <2.84(3,5-dichloropyridine), 5.98(4-methylpyridine), 9.70-(4-(dimethylamino)pyridine), 4.94(quinoline), 5.14(isoquinoline), 7.25(1-methylimidazole), 7.85(1,2-dimethylimidazole), 11.12(piperidine). These values were cited from refs. 3 and 4, and refs. therein.

TABLE II. The Ratios of K^B Values of the Porphyrinato-cobalt(II)

Co porphyrin	Approximate ratio of K^B values	
	R_1 [a]	R_2 [a]
[Co^{II}(tpp)]	3	28
[Co((p-CH$_3$O)tpp)] [b]	4	41
[Co(cap)] [c]	3	—
[Co(hmcap)] [c]	2.2	—

[a] R_1 and R_2 represent the ratios, (K^B of 1-Meim)/(K^B of 1,2-Me$_2$im) and (K^B of isoq)/(K^B of quin), respectively. [b] The K^B values were cited from ref. 3. [c] The K^B values were cited from ref. 8.
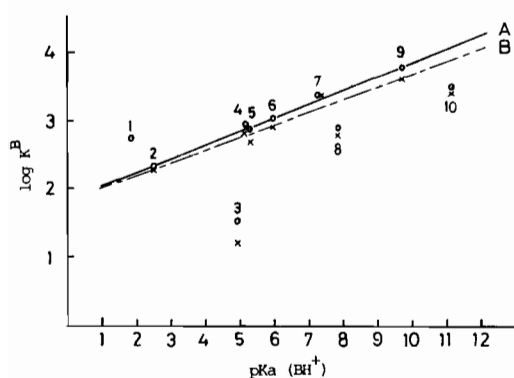

Fig. 2. Correlation between pK_a and log K^B in toluene. (A) For [Co^{II}(tpp)]. (B) For [Co((p-CH$_3$O)tpp)], the values of log K^B (at 25 °C) and the straight line were cited from ref. 3. Bases are 1: 4-CNpy; 2: 3,5-Cl$_2$py; 3: quin; 4: isoq; 5: py; 6: 4-Mepy; 7: 1-Meim; 8: 1,2-Me$_2$im; 9: 4-Me$_2$Npy; and 10: pip. The straight lines represent the least-squares regression lines for points 2, 4, 5, 6, and 9.

(the K^B of quinoline) (R_2) are shown in Table II. The ratios in [Co^{II}(tpp)] are obviously smaller than in [Co((p-CH$_3$O)tpp)]. As is shown in Fig. 2, the log K^B in [Co^{II}(tpp)] is always slightly larger than that of [Co((p-CH$_3$O)tpp)], and suggests that the out-of-plane displacement of the cobalt(II) in the former is larger than the latter. This is consistent with the fact that the R_1 and R_2 become the smaller as the displacement of cobalt(II) is larger.

Electronic Effects of Base

The relationship of log K^B to pK_a of the ligand was investigated for pyridine derivatives. The plot of log K^B vs. pK_a of the conjugated acid of the base showed a good linear relationship, except for 4-cyanopyridine (Fig. 2). The log K^B of 4-cyanopyridine was larger than expected. The reason for this is not clear because there has been no evidence that 4-cyanopyridine is a better π-acceptor than other pyridine derivatives. But the π-electron density on the nitrogen atom or the pyridine ring of 4-cyanopyridine would be lower, as compared to 4-(dimethylamino)-pyridine and pyridine with higher pK_a. So it seems possible that the π-back donation from the cobalt(II) to the axial ligand is likely to increase in the 4-cyanopyridine adduct. In addition, the lower electron density of the cobalt(II) would prompt the solvation of an aromatic solvent such as toluene to the sixth coordination site of the cobalt(II) to form a more stable base adduct than expected. The log K^B value of 3-chloropyridine (pK_a, 2.84), 2.88 at 23 °C in toluene, supports the above speculation. In fact, the log K^B values of the lower pK_a bases such as 4-cyanopyridine, 3-chloropyridine, isoquinoline, and pyridine lie on another line, as shown in Fig. 4,B.

As the value of pK_a only measures the σ-donor ability of base ligand, there is not necessarily a correlation between the pK_a of a base and its binding ability (log K^B) among different types of amines with different π-bonding properties. Sometimes imidazoles are better π-acceptors than pyridines; piperidine, with no π-accepting ability, binds to metal more weakly than pyridines, for example, for [Co((p-CH$_3$O)tpp)] [3] and [Fe(cap)] [8]. In the present results, 1-methylimidazole and piperidine also showed the same trends (Fig. 2). It should be noted, however, that the values of 1-methylimidazole were equal for both [Co^{II}(tpp)] and [Co((p-CH$_3$O)tpp)], as shown in Table III. This result provides evidence that 1-methyl-imidazole is a good π-acceptor. The electron donating effect of p-methoxyl groups on the 5,10,15,20-phenyl rings increases the electron density on the cobalt(II) and strengthens the π-back bonding, although it weakens the σ-donation of the base [6]. Thus, the log K^B of 1-methylimidazole for [Co((p-

TABLE III. Axial Ligation Constants of Bases for [Co^{II}(tpp)] and [Co((p-CH$_3$O)tpp)] in Toluene

Co porphyrin	log K^B			Reference
	pip	py	1-Meim	
[Co^{II}(tpp)]	3.51(23) [a]	2.90(23)	3.38(23)	this work
	3.62(25)	2.88(25)	—	6
[Co((p-CH$_3$O)tpp)]	3.39(25)	2.69(25)	3.37(25)	3
	3.41(23.6)	2.83(25)	3.26(22.8)	11

[a] Numbers in parentheses show the temperatures at which log K^B values were measured.

TABLE IV. Values of log K^B for [Co^{II}(tpp)] in Various Solvents

Solvent	log $K^{B\ a}$		
	4-CNpy	py	4-Me$_2$Npy
1,2-dichloroethane (10.36)[b]	2.57	2.92	3.59
dichloromethane (9.08)	2.60	2.90	3.40
chloroform (4.81)	2.42	2.48	2.82
chlorobenzene (5.67)	2.73	2.87	3.72
toluene (2.38)	2.76	2.90	3.80
N,N-dimethylformamide (36.71)	1.95	2.40	3.20

[a] The values of log K^B were obtained at 23 ± 0.1 °C and reproducible within 10%.   [b] Dielectric constants.

CH$_3$O)tpp)] becomes comparable to [Co^{II}(tpp)]; in contrast, the log K^B values of pyridine derivatives and piperidine are smaller than those for [Co^{II}(tpp)].

Solvent Effects

The values of log K^B of 4-cyanopyridine, pyridine, and 4-(dimethylamino)pyridine were obtained at 23 °C in various solvents with different dielectric constants (ϵ) to study the solvent effects. The results are summarized in Table IV. The plots of log K^B vs. pK_a are shown in Fig. 3.
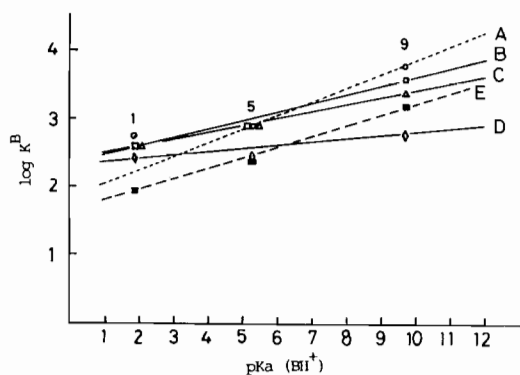

Fig. 3. Correlation between pK_a and log K^B in various solvents. Solvents are (A) toluene, (B) 1,2-dichloroethane, (C) dichloromethane, (D) chloroform, and (E) N,N-dimethylformamide. Bases are 1: 4-CNpy; 5: py; and 9: 4-Me$_2$Npy.

The log K^B of 4-(dimethylamino)pyridine was the highest in toluene (ϵ = 2.38, log K^B = 3.80) and the lowest in chloroform (ϵ = 4.81, log K^B = 2.82). The difference was about one order of magnitude. As was reported by Rillema [11], the base adduct of Co((p-CH$_3$O)tpp) is more stabile in the higher dielectric medium because the out-of-plane displacement of the cobalt(II) increases its dipole character. This reason is applicable to the present results for 4-(dimethylamino)pyridine, except in toluene and N,N-dimethylformamide (DMF). The higher log K^B could not be obtained in the highest dielectric medium of DMF (ϵ = 36.71, log K^B = 3.20), probably because the initial [Co^{II}(tpp)] was also stabilized by DMF. The

highest log K^B in toluene can not be explained by the above dipole–dipole interaction. Another type of solvation, such as π-interaction, might stabilize the base adduct, as in [Co((p-CH$_3$O)tpp)] [11].

The log K^B values of pyridine were comparable in toluene (log K^B = 2.90), 1,2-dichloroethane (ϵ = 10.36, log K^B = 2.92), and dichloromethane (ϵ = 9.08, log K^B = 2.90), and the lowest in DMF (log K^B = 2.40). The out-of-plane displacement of the pyridine adduct may be smaller than the 4-(dimethylamino)pyridine adduct. For this reason, a greater decrease in the solvation of toluene and DMF might give the present results.

4-Cyanopyridine gave the highest log K^B in toluene (2.76) and the lowest in DMF (1.95). The log K^B values decreased by the following sequence: toluene > chlorobenzene > 1,2-dichloroethane $\sim$ dichloromethane > chloroform > DMF. This sequence is in the reverse order of the dielectric constants of the solvents. There would be two possible reasons to account for the results, as follows: (a) toluene solvated to the initial [Co^{II}(tpp)] most weakly and was substituted by the base most easily; (b) the lower electron density of the cobalt(II) in the adduct is preferable for the solvation of [Co^{II}(tpp)(4-CNpy)] by the π-donor type of toluene. Only reason (a) can explain the present results. But reason (b) may also contribute to the higher log K^B of 4-CNpy in toluene, as described above, to explain the results shown in Fig. 2.

To summarize the solvent effects of toluene, we wish to present the following two concepts: (i) with the higher pK_a base of 4-(dimethylamino)pyridine, the adduct is stabilized by the solvation due to the larger out-of-plane displacement of the cobalt(II). (ii) With the lower pK_a base of 4-cyanopyridine, the adduct is also stabilized by the solvation due to the lower electron density of the cobalt(II). These two concepts are qualitative, but they explain the present results consistently, as shown in Fig. 4.

The Values of log K^B in [Co(cap)]

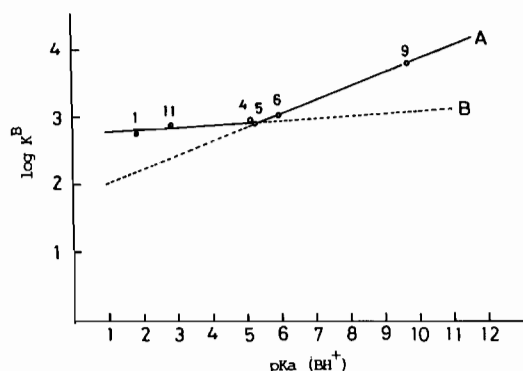Table I also shows that the log K^B values of [Co(cap)] systems are about one order less than the

Fig. 4. Correlation between pK_a and log K^B for pyridine derivatives in toluene. (A) For the higher pK_a bases, 5, 6, and 9. (B) For the lower pK_a bases, 1, 11, 4, and 5. The number 11 stands for 3-chloropyridine. The points 2, 3, 7, 8, and 10 were omitted.
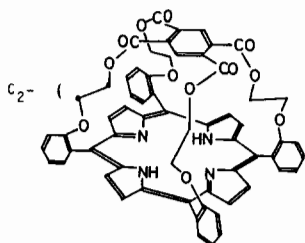

Fig. 5. 'Capped' porphyrin.

values for [Co^{II}(tpp)] systems (cap = 'capped' porphyrin dianion, C_2-cap; and hmcap = homologous 'capped' porphyrin dianion, C_3-cap; the 'capped' porphyrin [12, 13] is illustrated in Fig. 5). This lower base affinity of the capped system was already reported and discussed by Basolo *et al.* [7, 8]. It shows that the conformational restraints caused by the 'cap' in the five-coordinate base adduct of metal-capped porphyrins seem to be responsible for the lower base affinity.

We want to consider an other possibility on the basis of the present results on the log K^B in [Co^{II}(tpp)]. The largest difference in the log K^B of [Co^{II}(tpp)] in various solvents was about one order of magnitude. Study of the solvent effects on the log $K_B^{O_2}$ of the capped system has shown that the solvent can not enter the inside of the cap; therefore, the solvent effects are smaller compared with other flat-open porphyrin systems [14]. There would be a possibility that the lower log K^B in [Co(cap)] results from the same reason as above.

As the data on the out-of-plane displacement of the cobalt(II) in [Co(cap)(B)] has not been reported, the distance is unknown. As shown in Table II, the ratios, R_1, were 3, 3, and 2.2 for [Co^{II}(tpp)], [Co(cap)], and [Co(hmcap)], respectively. From these ratios, the displacement in [Co(cap)(B)] is expected to be comparable to [Co^{II}(tpp)(B)], and
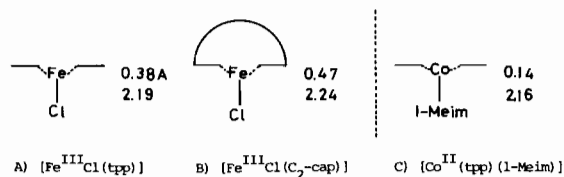

Fig. 6. Schematic representations of the five-coordinate metal porphyrin complexes. (A) [Fe^{III}Cl(tpp)]. (B) [Fe^{III}Cl(C$_2$-cap)]. (C) [Co^{II}(tpp)(1-Meim)]. The numbers show the displacements of the metal ion from the plane of 24 atoms of the porphyrin core and the bond lengths of the metal to axial ligand, respectively.

larger in [Co(hmcap)(B)]. The X-ray analysis data reported on the five-coordinate metal porphyrins show that the displacements of the metal ions are 0.47 Å for [FeF(tpp)] [15], 0.38 Å for [FeCl(tpp)] [16], 0.47 Å for [FECl(cap)] [17], 0.14 Å for [Co^{II}(tpp)(1-Meim)] [18] and 0.16 Å for [Co(oep)(1-Meim)] [19] (oep represents octaethylporphyrin dianion). Some schematic representations are shown in Fig. 6. These data suggest that the coordination geometry about Fe(III) is not influenced by the restraints caused by the cap [17]. Provided that the displacement in [Co(cap)(B)] is similar to [Co^{II}(tpp)(B)], the lower base affinity of [Co(cap)] system may also be attributable to a factor other than the restraints caused by the cap, such as the lesser solvent effects of toluene in [Co(cap)(B)]. The study of the solvent effects on log K^B in [Co(cap)] system is in progress.

References

1 K. Yamamoto and T. Kwan, *J. Catal.*, *18*, 354 (1970).
2 K. Yamamoto and T. Kwan, *Bull. Chem. Soc. Jpn.*, *45*, 664 (1972).
3 F. A. Walker, *J. Am. Chem. Soc.*, *95*, 1150 (1973).
4 D. V. Stynes, H. C. Stynes, J. A. Ibers and B. R. James, *J. Am. Chem. Soc.*, *95*, 1142 (1973); D. V. Stynes, H. C. Stynes, B. R. James and J. A. Ibers, *J. Am. Chem. Soc.*, *95*, 1796 (1973).
5 T. Takayanagi, H. Yamamoto and T. Kwan, *Bull. Chem. Soc. Jpn.*, *48*, 2618 (1975).
6 F. A. Walker, D. Beroiz and K. M. Kadish, *J. Am. Chem. Soc.*, *98*, 3484 (1976).
7 J. R. Budge, P. E. Ellis, Jr., R. D. Jones, J. E. Linard, T. Szymanski, F. Basolo, J. E. Baldwin and R. L. Dyer, *J. Am. Chem. Soc.*, *101*, 4762 (1979).
8 P. E. Ellis, Jr., J. E. Linard, T. Szymanski, R. D. Jones, J. R. Budge and F. Basolo, *J. Am. Chem. Soc.*, *102*, 1889 (1980).
9 A. D. Adler, F. A. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, *32*, 476 (1967).
10 P. Rothmund and A. R. Menotti, *J. Am. Chem. Soc.*, *70*, 1808 (1948).
11 D. P. Rillema, C. M. Wicker, Jr., R. D. Morgan, L. F. Barringer and L. A. Scism, *J. Am. Chem. Soc.*, *104*, 1276 (1982).
12 J. Almog, J. E. Baldwin, R. L. Dyer and M. Peters, *J. Am. Chem. Soc.*, *97*, 226 (1975).

13 J. Almog, J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.,* *97,* 227 (1975).

14 T. Hashimoto, R. L. Dyer, M. J. Crossley, J. E. Baldwin and F. Basolo, *J. Am. Chem. Soc., 104,* 2101 (1982).

15 K. Anzai, K. Hatano, Y. J. Lee and W. R. Scheidt, *Inorg. Chem., 20,* 2337 (1981).

16 J. L. Hoard, G. H. Cohen and M. D. Glick, *J. Am. Chem. Soc., 89,* 1992 (1967).

17 M. Sabat and J. A. Ibers, *J. Am. Chem. Soc., 104,* 3715 (1982).

18 W. R. Scheidt, *J. Am. Chem. Soc., 96,* 90 (1974).

19 R. G. Little and J. A. Ibers, *J. Am. Chem. Soc., 96,* 4452 (1974).