Inorganica Chimica Acta, *127* (1987) 147–150

Spectroscopic Studies for the Coordination of Lewis Bases to Oxochromium(IV) Porphyrin

TOSHIHIKO OZAWA and AKIRA HANAKI

National Institute of Radiological Sciences, 9-1, Anagawa-4-chome, Chiba-shi 260, Japan

(Received July 25, 1986)

Abstract

Formation constants (K_f) for the coordination of Lewis base ligands to oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV) [Cr(IV)O(TPP)] have been determined for 11 Lewis bases with nitrogen donor, oxygen donor and sulfur donor. The coordinating ability of those Lewis bases to Cr(IV)O(TPP) was found to follow the sequence in decreasing order; oxygen donor > nitrogen donor > sulfur donor. It was also found that steric constraints influence the ligand binding affinity of Lewis bases to Cr(IV)O(TPP).

Introduction

It is known that transition-metal oxo complexes are useful reagents for the oxidation of organic molecules [1]. However oxo-metalloporphyrin complexes of titanium(IV) [2], vanadium(IV) [3], molybdenum(IV) [4], molybdenum(V) [5] and chromium(IV) [6] have not been shown to be effective oxidizing agents. On the other hand, oxoiron(IV) porphyrin complexes are extremely reactive species and have only been detected spectroscopically in solution at low temperature when iron(II) porphyrin reacts with oxygen in the presence of a Lewis base [7]. Similarly, the coordination of *N*-methylimidazole was a necessary requirement in stabilizing an Fe(IV)O(P) (P: porphyrin) complex at low temperatures [7]. Recently, related to the coordination of Lewis bases to oxoiron(IV), the coordination of Lewis bases to oxo-metalloporphyrins has been studied for V(IV)O(TPP) [8, 9] (TPP: *meso*-tetraphenylporphyrin)* and Mo(V)O(TPP)X (X = F, Cl, Br, NCS) [10]. However, there have been no reports concerning the coordination of oxochromium(IV) porphyrins, although recently it has been briefly reported that a large excess of pyridine (py) can react with several Cr(IV)O(P) complexes to form labile monopyridine adducts, Cr(IV)O(P)(py) [11]. However, in this reaction the formation constant was not determined. Therefore, we have examined the interaction of Cr(IV)O(TPP) with many kinds of Lewis bases.

In this paper we first report on the relative affinities of a large number of Lewis bases to oxo(*meso*-tetraphenylporphyrinato)chromium(IV) [Cr(IV)O(TPP)] and briefly discuss the difference of the affinities to Lewis bases between Cr(IV)O(TPP) and other oxo-metalloporphyrins such as V(IV)O(TPP).

Experimental

Materials

meso-Tetraphenylporphyrin (TPP) was synthesized as described previously [12]. Chlorine impurities were removed by refluxing the free base with 2,3-dichloro-5,6-dicyanoquinone (DDQ) in benzene following the procedure of Smith *et al.* [13]. Chloro-*meso*-tetraphenylporphyrinatochromium(III) [Cr(III)(TPP)Cl] was synthesized and purified as previously described [14–17]. Cr(IV)O(TPP) was synthesized by the oxidation of Cr(III)(TPP)Cl with iodosylbenzene or sodium hypochlorite according to the method described by Groves *et al.* [6].

All reagents and solvents were of analytically high grade or spectroscopic grade. Lewis bases (except imidazole) were distilled and dried over 4 Å molecular sieves. Dichloromethane (CH_2Cl_2) was distilled and passed through a neutral alumina column prior to use.

Methods

Using a microsyringe, aliquots of ligand solutions (neat or dissolved in CH_2Cl_2) were successively added to 2 ml of CH_2Cl_2 solution of Cr(IV)O(TPP) ($\sim 10^{-6}$ M) in a capped quartz cell with a light path of 10 mm, as mentioned previously [18, 19]. UV–Vis absorption spectra were measured with a Union Giken SM-401 spectrometer at 25 °C.

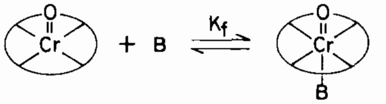
---

*Abbreviations used here: TPP, *meso*-tetraphenylporphyrin; TMP, tetrakis(*p*-methoxyphenyl)porphyrin; TFMP, tetrakis[(*p*-trifluoromethyl)phenyl]porphyrin; Cr(III) (TPP)-Cl, chloro-*meso*-tetraphenylporphyrinatochromium(III); Cr-(IV)O(TPP), oxo(*meso*-tetraphenylporphyrinato)chromium-(IV); V(IV)O(TPP), oxo(*meso*-tetraphenylporphyrinato)-vanadium(IV); P, porphyrin; B, Lewis base; UV, ultraviolet; CH_2Cl_2, dichloromethane; py, pyridine; DMSO, dimethyl sulfoxide; EtOH, ethyl alcohol; THT, tetrahydrothiophen; DMF, dimethyl formamide; Im, imidazole; pip, piperidine.

0020-1693/87/$3.50

Determination of Formation Constant

Formation constant (K_f) presented in eqn. (1) was calculated from spectrophotometric data by use of a



(1)

modified Drago's method [20, 21]. In this method, the following approximate eqn. (2) was used.

$$A_T/\Delta A = [1/K_f \Delta\epsilon \times 1/B_T] + 1/\Delta\epsilon \qquad (2)$$

where K_f = the formation constant of the adduct, $\Delta\epsilon$ = the extinction coefficient difference between metalloporphyrin and the adducts, ΔA = the absorbance difference between metalloporphyrin and the adducts, A_T = the initial concentration of metalloporphyrin and B_T = the initial concentration of base. From eqn. (2), a linear least square fit to the experimental data for $A_T/\Delta A$ *versus* $1/B_T$ was obtained. $\Delta\epsilon$ and K_f were then calculated from the intercept of the ordinate and slope, respectively, of a straight line.

Results and Discussion

Recently, Bencosme *et al.* modified Drago's method in order to calculate the formation constant for the 1:1 adducts by interaction of different Lewis bases with the oxo(*meso*-tetraphenylporphyrinato)-vanadium(IV) [V(IV)O(TPP)] [9]. This modified method is very useful for evaluating the formation constant for the 1:1 adducts of the metalloporphyrins with some Lewis bases. Thus, we used this modified method to calculate the formation constant for the adducts, Cr(IV)O(TPP)(B).

Dichloromethane solutions of pure Cr(IV)O(TPP) were bright red and showed absorption bands at 380 (log ϵ = 4.51), 430 (log ϵ = 5.26) and 547 nm (log ϵ = 4.24), as shown in Fig. 1. Upon addition of Lewis

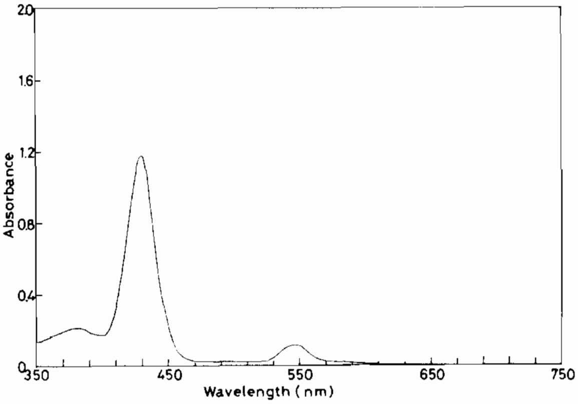


Fig. 1. Visible spectrum of Cr(IV)O(TPP) in CH_2Cl_2. Porphyrin concentration is 6.50×10^{-5} M.

TABLE I. Visible Spectra of Cr(IV)O(TPP)(B) in CH_2Cl_2

Cr(IV) Complexes	λ_{max} (nm) (log ϵ)		
Cr(IV)O(TPP)	381(4.51)	430(5.26)	547(4.24)
Cr(IV)O(TPP)(DMSO)	364(4.44) 565(3.99)	397(4.58) 603(3.87)	445(5.38)
Cr(IV)O(TPP)(EtOH)	364(4.44) 566(4.02)	397(4.58) 603(3.89)	448(5.38)
Cr(IV)O(TPP)(THT)	366(4.35) 572(3.94)	401(4.62) 610(3.99)	454(5.27)
Cr(IV)O(TPP)(DMF)	393(4.49) 603(3.66)	443(5.32)	565(3.99)
Cr(IV)O(TPP)(Im)	366(4.52) 573(3.94)	406(4.72) 613(4.00)	456(5.39)
Cr(IV)O(TPP)(pip)	366(4.52) 572(3.94)	401(4.66) 609(4.00)	454(5.36)
Cr(IV)O(TPP)(aniline)	400(4.47) 607(3.95)	440(5.19)	570(3.94)
Cr(IV)O(TPP)(n-butylamine)	364(4.52) 572(3.97)	402(4.65) 610(4.03)	454(5.37)
Cr(IV)O(TPP)(t-butylamine)	365(4.43) 572(3.96)	400(4.62) 610(3.99)	451(5.32)
Cr(IV)O(TPP)(diethylamine)	361(4.42) 572(3.97)	400(4.61) 612(4.07)	451(5.34)
Cr(IV)O(TPP)(triethylamine)	397(4.37) 610(3.88)	446(5.00)	570(3.84)

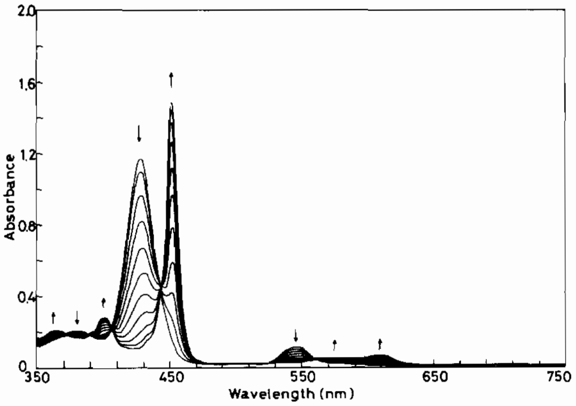


Fig. 2. Visible spectral changes occurring upon titration of a Cr(IV)O(TPP) solution with n-butylamine. Porphyrin concentration is 6.50×10^{-5} M. Spectrum recorded at 25 °C with CH_2Cl_2 as the solvent. 20 μl of neat n-butylamine was successively added to 2 ml solution of Cr(IV)O(TPP).

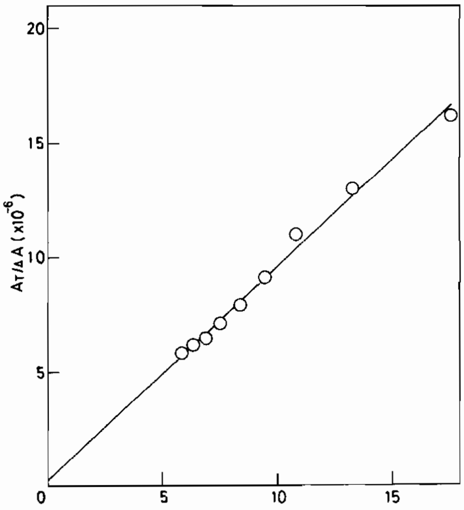


Fig. 3. Plot of $A_T/\Delta A$ *vs.* $1/B_T$ for the coordination of diethylamine to Cr(IV)O(TPP).

TABLE II. Formation Constants (K_f) for the Reaction Cr(IV)O(TPP) + B $\rightleftharpoons$ Cr(IV)O(TPP)(B) and K_f for the Coordination of Lewis Bases to V(IV)O(TPP) [9] for Comparison

Lewis base	K_f (M^{-1})	
	Cr(IV)O(TPP)	V(IV)O(TPP)
n-butylamine	12.2	1.24
t-butylamine	7.50	0.07
diethylamine	1.10	a
triethylamine	1.10	b
imidazole	90.9	1.33
piperidine	37.3	0.75
aniline	3.00	0.186
pyrrole	a	a
pyridine	c	0.148
DMF	16.4	d
DMSO	51.8	0.051
ethyl alcohol	56.5	d
n-butyl alcohol	d	a
t-butyl alcohol	b	d
acetone	b	b
acetonitrile	b	b
thiophene	d	b
tetrahydrothiophene	1.80	d
THF	a	b

[a] Weak coordination. [b] No coordination. [c] Different spectral change from others. [d] Not measured.

bases to Cr(IV)O(TPP), a red shift (*i.e.* to higher wavelength) is seen for all bands in the electron absorption spectrum, accompanied by the appearance of the beta (~568 nm) and the alpha (~600 nm) bands (Table I). In general, the spectral pattern observed upon axial coordination is the same regardless of the nature of the donor atom in the base (Table I). That is, the Soret band of Cr(IV)O(TPP) is red-shifted. The peak at 547 nm also undergoes a red shift to 565–573 nm, and a new band appears around 607 nm. These red shifts are also observed for the coordination of Lewis bases to oxovanadium porphyrin [8, 9]. A typical example is shown in Fig. 2 where the spectral changes following the stepwise addition of n-butylamine to a solution of Cr(IV)O(TPP) in CH_2Cl_2, which is often used as a non-coordinating solvent [10], are displayed. Distinct isosbestic points were observed during the formation of all Cr(IV)O(TPP)(B) complexes reported in this study.

A typical plot of $A_T/\Delta A$ *versus* $1/B_T$ is shown in Fig. 3 for the coordination of diethylamine to Cr(IV)O(TPP). Table II contains K_f values calculated from eqn. (2) for Cr(IV)O(TPP)(B), along with the K_f values for the coordination of Lewis bases to V(IV)O(TPP) for comparison. The K_f values range from 1.10 M^{-1} (low affinity) to 90.9 M^{-1} (moderate affinity). Pyrrole and tetrahydrofuran weakly coordinate to Cr(IV)O(TPP). They bring small shifts on the visible spectra but not enough to calculate K_f from spectrophotometric data. Acetonitrile, acetone and t-butanol do not coordinate to Cr(IV)O(TPP). Pyridine showed different spectral changes from those shown in Fig. 2. This may be caused by the formation of a labile intermediate, monopyridine adduct Cr(IV)O(TPP)(py) which had a half-life of 15 min [11]. Therefore, the formation constant was not calculated.

The coordinating ability of Lewis bases to Cr(IV)O(TPP) was found to follow the sequence in decreasing order; oxygen donor > nitrogen donor > sulfur donor. It was also observed that axial ligation is sensitive to steric bulkiness of the ligand, *i.e.* n-butylamine > tert-butylamine > diethylamine = triethylamine. This order of sensitivity can be understood from the results of X-ray structural studies of Cr(IV)O(TPP). Since the oxochromium ion in Cr(IV)-O(TPP) is displaced 0.469 Å above the mean plane of the four pyrrole nitrogens [11], a ligand has to enter a small cavity in order to effect coordination while hindered nucleophiles cannot reach the metal. Bonnett *et al.* have qualitatively observed a similar trend in the interactions of several nitrogenated solvents with vanadyl octaethylporphyrin [22]. K_f values for Cr(IV)O(TPP)(B) are larger than those for V(IV)O(TPP)(B) [9], as shown in Table II. This result may reflect the difference of the distance between the metal and the plane formed by the nitrogen group of the porphyrin macrocycle. That is, the distances are 0.469 Å for Cr(IV)O(TPP) and 0.53 Å for V(IV)O(TPP) [23], respectively.

In conclusion, we have presented the first extensive equilibrium study of the interactions of Cr(IV)-O(TPP) with Lewis bases. We have established spectrophotometrically that there is coordination of Lewis bases to the chromium atom. It can also be shown that axial interactions of Lewis bases with the chromium are weak, but are stronger than those with the vanadium and the bulkiness of the ligands affects the coordination to Cr(IV)O(TPP).

References

1 J. T. Groves, in T. G. Spiro (ed.), 'Metal Ion Activation of Dioxygen', Wiley, New York, 1980, p. 125.
2 P. N. Dwyer, J. W. Buchler and W. R. Scheidt, *J. Am. Chem. Soc., 96,* 2789 (1974).
3 R. C. Pettersen and L. E. Alexander, *J. Am. Chem. Soc., 90,* 3873 (1968).
4 T. Diebold, B. Chevrier and R. Weis, *Inorg. Chem., 18,* 1193 (1979).
5 H. Ledon and B. Mentzen, *Inorg. Chim. Acta, 31,* L393 (1978).
6 J. T. Groves, W. J. Kruper, Jr., R. C. Haushalter and W. M. Butler, *Inorg. Chem., 21,* 1363 (1982).
7 D.-H. Chin, A. L. Balch and G. N. La Mar, *J. Am. Chem. Soc., 102,* 1446 (1980).
8 F. A. Walker, E. Hui and J. M. Walker, *J. Am. Chem. Soc., 97,* 2390 (1975).
9 C. S. Bencosme, C. Romero and S. Simoni, *Inorg. Chem., 24,* 1603 (1985).
10 T. Imamura, T. Tanaka and M. Fujimoto, *Inorg. Chem., 24,* 1038 (1985).
11 D. J. Liston and B. O. West, *Inorg. Chem., 24,* 1568 (1985).
12 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem., 32,* 476 (1967).
13 G. H. Barnett, M. F. Hudson and K. M. Smith, *Tetrahedron Lett.,* 2887 (1973).
14 D. A. Summerville, R. D. Jones, B. M. Hoffman and F. Basolo, *J. Am. Chem. Soc., 99,* 8195 (1977).
15 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem., 32,* 2443 (1970).
16 S. K. Cheung, C. J. Grimes, J. Wong and C. A. Reed, *J. Am. Chem. Soc., 98,* 5028 (1976).
17 T. Ozawa and A. Hanaki, *Inorg. Chim. Acta, 102,* 169 (1985).
18 T. Ozawa and A. Hanaki, *Inorg. Chim. Acta, 80,* 33 (1983).
19 T. Ozawa and A. Hanaki, *J. Chem. Soc., Dalton Trans.,* 1513 (1985).
20 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc., 81,* 6138 (1959).
21 R. M. Guirdy and R. S. Drago, *J. Am. Chem. Soc., 95,* 6645 (1973).
22 R. Bonnett, P. Brewer, K. Noro and T. Noro, *Tetrahedron, 34,* 379 (1978).
23 M. G. B. Drew, P. C. H. Mitchell and C. E. Scott, *Inorg. Chim. Acta, 82,* 63 (1984).