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Axial Ligation of some Lewis Bases to Oxo-metalloporphyrins

TOSHIHIKO OZAWA* and AKIRA HANAKI

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

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Abstract

Axial ligation of some Lewis base ligands to three oxo-metalloporphyrins, oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV) [Cr(IV)O(TPP)], oxo(5,10,15,20-tetraphenylporphyrinato)vanadium(IV) [V(IV)O(TPP)] and oxo(5,10,15,20-tetraphenylporphyrinato)titanium(IV) [Ti(IV)O(TPP)] were investigated spectroscopically. The order of the ligand binding affinity of the Lewis bases was Cr(IV)O(TPP) > V(IV)O(TPP) > Ti(IV)O(TPP). It was also found that steric constraints influence the ligand binding affinity of Lewis bases to oxo-metalloporphyrins. These results could be explained by the size of the cavity which is made of the plane of the four pyrrole nitrogens and the oxo-metal ions in the oxo-metalloporphyrins.

Introduction

In a previous paper [1], we reported that the formation constants (K_f) for the coordination of Lewis base ligands to oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV) [Cr(IV)O(TPP)]** had been determined for 11 Lewis bases with nitrogen, oxygen and sulfur donors. We also reported that steric constraints influence the ligand binding affinity of the Lewis bases to Cr(IV)O(TPP). That is, in oxo-metalloporphyrins a ligand has to enter a small cavity, which is made of the oxo-metal ion and the plane of the four pyrrole nitrogens, in order to effect coordination [2]. In order to ascertain this suggestion, it is necessary to compare the formation constant for the coordination of the same Lewis ligands to different oxo-metalloporphyrins with the different sizes of the cavity. However, the axial coordination of Lewis base ligands to oxo-metalloporphyrins have not hitherto been investigated comparatively. Therefore, in order to compare the formation constant of the axial ligation of Lewis base ligands to the different oxo-metalloporphyrins, we have synthesized some oxo-metalloporphyrins such as Cr(IV)O(TPP), V(IV)O(TPP) and Ti(IV)O(TPP) and studied the axial ligation of some Lewis base ligands to these oxo-metalloporphyrins. We report these results in this paper.

Experimental

Materials

meso-Tetraphenylporphyrin (TPP) was synthesized as described previously [3] and freed of *meso*-tetraphenylchlorine by oxidation with 2,3-dichloro-5,6-dicyanoquinone (DDQ) [4]. Chloro-*meso*-tetraphenylporphyrinatochromium(III) [Cr(III)(TPP)Cl] was synthesized and purified as described previously [5–8]. 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.* [9]. Oxo(5,10,15,20-tetraphenylporphyrinato)vanadium(IV) [V(IV)O(TPP)] was prepared by the method described by Bencosme *et al.* [10]. Oxo(5,10,15,20-tetraphenylporphyrinato)-titanium(IV) [Ti(IV)O(TPP)] was synthesized by modification of the method described by literature [11] as follows: TPP (200 mg) was suspended in diethylene glycol (100 ml) with 1 g of dicyclopentadienyltitanium dichloride [$TiCl_2(C_2H_5)_2$] and then the reaction mixture was refluxed for 30 min. Completion of the reaction was checked by spectrophotometry. The reaction mixture was cooled to room temperature, mixed with dichloromethane (CH_2Cl_2), washed with dilute HCl, then saturated $NaHCO_3$ solution and water several times. The CH_2Cl_2 phase was dried by $MgSO_4$ and then the solvent was evaporated to dryness. The residue was chromatographed on a dry column of alumina (Woelm, neutral) and eluted with CH_2Cl_2 to remove the unreacted TPP and then the desired compound

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*Author to whom correspondence should be addressed.

**Abbreviations used here: TPP, *meso*-tetraphenylporphyrin; Cr(III)(TPP)Cl, chloro-*meso*-tetraphenylporphyrinatochromium(III); Cr(IV)O(TPP), oxo(5,10,15,20-tetraphenylporphyrinato)chromium(IV); V(IV)O(TPP), oxo(5,10,15,20-tetraphenylporphyrinato)vanadium(IV); Ti(IV)O(TPP), oxo-(5,10,15,20-tetraphenylporphyrinato)titanium(IV); $TiO(OEPMe_2)_2$, oxo(5,15-dimethyl-5,15-dihydrooctaethylporphyrinato)titanium; CH_2Cl_2, dichloromethane; DMSO, dimethyl sulfoxide; M, metal; B, base.

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was eluted by CH_2Cl_2–MeOH (19:1). After evaporation of the solvent, recrystallization from CH_2Cl_2–MeOH gave 180.4 mg (82.9%) of crystals. The structure of these oxo-metalloporphyrins is shown in Fig. 1.

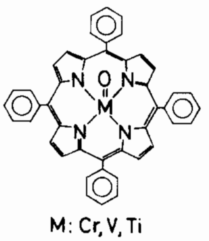

Fig. 1. Structure of oxo-metalloporphyrins studied.

Dimethyl sulfoxide (DMSO) was distilled at reduced pressure and dried over 4 Å molecular sieves. Other Lewis base ligands were distilled prior to use. CH_2Cl_2 was distilled and passed through a neutral alumina (Woelm) column prior to use. Other reagents were of analytically high grade.

Methods

Using a microsyringe, aliquots of ligand solutions (neat or dissolved in CH_2Cl_2) were successively added to 2 ml CH_2Cl_2 solutions of the oxo-metalloporphyrins (~10^{-6} M) in a capped quartz cell with a light path of 10 mm, as mentioned previously [12, 13]. UV–Vis absorption spectra were measured by a Union Giken SM-401 spectrometer at 25 °C.

Determination of the Formation Constant

The formation constant (K_f) was calculated from spectrophotometric data using a modified Drago's method [14, 15]. In this method, the following eqn. (1) was used [1].

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

where K_f = the formation constant of the adduct, $\Delta\epsilon$ = the extinction coefficient difference between metalloporphyrin and the adduct, ΔA = the absorbance difference between metalloporphyrin and the adduct, A_T = the initial concentration of metalloporphyrin and B_T = the initial concentration of base. From eqn. (1), a linear least-squares 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 of the interaction of different Lewis bases with VO(TPP) [2]. It has been found that this modified method is very useful for evaluating the formation constant for the 1:1 adducts of Cr(IV)O(TPP) with some Lewis bases [1]. We then used this modified method to calculate the formation constant for the adducts, M(IV)O(TPP)(B) [M: metal; B: base], as shown in eqn. (2).

$$\text{M(IV)O(TPP)} + \text{B} \rightleftharpoons \text{M(IV)O(TPP)(B)} \qquad (2)$$

Table I shows the visible spectral parameters for the synthesized oxo-metalloporphyrins in CH_2Cl_2 which is known as a non-coordinating solvent. When DMSO was stepwise added to these oxo-metalloporphyrins, a red shift (*i.e.* to higher wavelength) is seen for all bands in the electronic absorption spectrum of both CrO(TPP) and VO(TPP), but no such shift is seen for TiO(TPP). Similar results were obtained for other amine ligands. The formation constants for the axial ligations to oxo-metalloporphyrins are summarized in Table II. From Table II, it is apparent that axial ligation to oxo-metalloporphyrins such as CrO(TPP) and VO(TPP) is sensitive to the steric bulkiness of the ligands, *i.e.* the order of K_f is n-butylamine > tert-butylamine > diethylamine = triethylamine. It is thought that the ligand has to enter a small cavity (Fig. 2), which is made of the oxo-metal ion and the plane of the four pyrrole nitrogens in the porphyrin skeleton, in order to effect coordination, while hindered nucleophiles cannot reach the metal.

It is also shown in Table II that K_f values for CrO(TPP)(B) are larger than those for VO(TPP)(B)

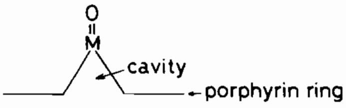

Fig. 2. Cavity which is made of the oxo-metal ion and the plane of four pyrrole nitrogens in the porphyrin macrocycle.

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

Oxo-metalloporphyrin	λ_{max} (log ϵ)				
CrO(TPP)	381(4.51)	430(5.26)		547(4.24)	
VO(TPP)		423(5.62)	513(3.65)	548(4.29)	587(3.49)
TiO(TPP)		422(5.63)	511(3.65)	552(4.32)	590(4.00)

TABLE II. Formation Constants (K_f) for the Reaction M(IV)O(TPP) + B ⇌ M(IV)O(TPP)(B)

Lewis base	K_f (M^{-1})		
	CrO(TPP)[a]	VO(TPP)[b]	TiO(TPP)[b]
DMSO	51.8	0.05	[d]
n-Butylamine	12.2	1.20	[c]
t-Butylamine	7.50	0.08	[c]
Diethylamine	1.10	[c]	[c]
Triethylamine	1.10	[d]	[d]

[a] Ref. 1. [b] This work. [c] Weak coordination. [d] No coordination.

and that TiO(TPP) does not react with almost all the Lewis bases examined here. These results may reflect the size of the cavity, that is, the difference of the distance between the metal and the plane formed by the nitrogen group of the porphyrin macrocycle. Fortunately, such distances for three of the oxo-metalloporphyrins examined here have been reported from X-ray structural studies, although instead of TiO(TPP) oxo(5,15-dimethyl-5,15-dihydro-octaethylporphyrinato)titanium(IV) [Ti(OEPMe$_2$)$_2$], the size of which is thought to be almost same as that of TiO(TPP), has been reported. That is, the distances are 0.469 Å for CrO(TPP) [16], 0.53 Å for VO(TPP) [17] and 0.58 Å for TiO(OEPMe$_2$)$_2$ [18]. From these results, it is suggested that CrO-(TPP) which has the smallest cavity can easily ligate with the Lewis bases, whereas TiO(TPP) which has the largest cavity cannot.

The present study has therefore shown that axial ligations of Lewis bases to oxo-metalloporphyrins such as CrO(TPP), VO(TPP) and TiO(TPP) are affected by the size of the cavity which is made of the plane of the porphyrin ring and the oxo-metal ions.

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