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Molecular interactions of dimethyl methylphosphonate (DMMP) with metalloporphyrins: Determination of the binding mechanism by spectroscopic methods

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ABSTRACT

The molecular interactions of 5,10,15,20-tetraphenylporphine zinc (ZnTPP) and 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) (CoTPP) with dimethyl methylphosphonate (DMMP) have been investigated by absorption/absorption difference spectroscopy. The interactions between the metalloporphyrins and DMMP change the absorbance characteristics of the porphyrins resulted from the formation of the metalloporphyrin–DMMP complexes. According to the Benesi–Hildebrand (B–H) equation, the equilibrium constants and stoichiometries of the binding systems at four different temperatures (288, 293, 298 and 303 K) were obtained. Experimental results showed that both ZnTPP and CoTPP bind to DMMP via axial coordination, resulting in the formation of 1:1 metalloporphyrin–DMMP complexes. However, it was found that ZnTPP showed stronger binding capacity with the equilibrium constant (K) of 83.864 M^{-1} at room temperature, while CoTPP exhibited weaker binding with K of 24.904 M^{-1}. The thermodynamic parameters, enthalpy change ($\Delta_r H_m^\theta$), entropy change ($\Delta_r S_m^\theta$) and free energy changes ($\Delta_r G_m^\theta$) were also studied for the interactions, indicating that the formation of the metalloporphyrins–DMMP complex was an exothermic reaction.

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1. Introduction

Using chemical warfare agents (CWAs) as a weapon of terrorism has become a real existing threat. The large-scale repeated uses of nerve gases during Iran-Iraq war in the 1980s against civilians by Iraqi troops and during terrorist attacks in the 1990s by the Aum Shinrikyo sect in Japan emphasize the constant danger [1]. Since the CWAs, especially the nerve agents, are highly toxic, early alert and sensitive detection of these agents in trace level is of great importance. Accordingly, the study on the detection of nerve agents has become a most active field. Due to the toxicity of nerve agents and usage restrictions, research on the detection of CWAs is often conducted using compounds with similar chemical structures but being non-toxic, named simulants [2]. Dimethyl methylphosphonate (DMMP) is usually used as a simulant in the lab for the detection of nerve agents. The research about the detection of DMMP lays a foundation for the detection of nerve agents. Such an endeavor is important for homeland security and environment monitoring.

Porphyrins are a type of macrocyclic organic molecule, which play an important role in our world. The rich chemistry of porphyrins, especially metalloporphyrins, results in a large variety of interaction mechanisms that can be utilized for chemical sensing [3]. The porphyrin molecular framework offers a wide range of interaction mechanisms for analyte binding, spanning from Van der Waals forces, hydrogen bond, π interactions and finally to the coordination to the central metal ion [4]. Generally, the role of the coordination in a metalloporphyrin is considered of primary importance to determine the sensitivity and selectivity properties by axial binding of the analyte molecule [5]. However, low energy mechanisms, such as hydrogen bonding, polarization and polar interactions, may simultaneously be present and cooperate in the total guest molecule binding [6]. Because of this extensive richness of interactions, metalloporphyrins have been widely used for the detection of hazardous [7,8], toxic gases [9–11], environment pollutant nitro-aromatic compounds [12], insecticides and pesticides [13,14].

Porphyrins can be modified by connecting different peripheral substitutes, changing the central metal or expanding the size of the macrocycle. 5,10,15,20-Tetraphenylporphine zinc (ZnTPP) and 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) (CoTPP) studied in this paper are metallo-tetraphenylporphyrins, whose

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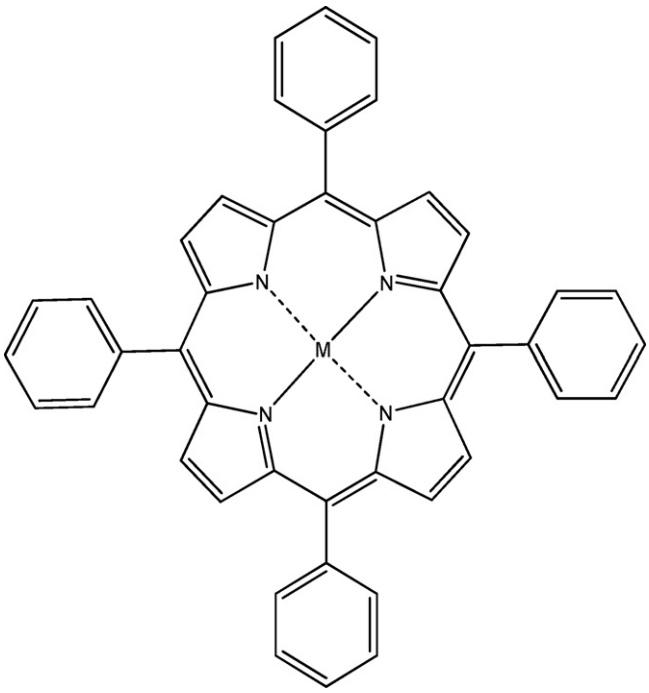

Fig. 1. Chemical structures of metalloporphyrins (M = Zn, Co).

structural sketches are shown in Fig. 1. The two compounds have similar chemical structures, with the difference only in the central metal ion. Our previous reports indicated that both ZnTPP and CoTPP can be used to detect DMMP due to the spectral changes associated with the interactions between porphyrins and DMMP. However, CoTPP could detect 10 ppm DMMP in solution, and ZnTPP has a superior DMMP detection sensitivity of 0.1 ppm. The sensitivity to DMMP is increased by 100 times. Because of these differences in sensing performance, a detailed knowledge about the interactions of ZnTPP and CoTPP with DMMP is essential for understanding the mechanisms involved in the detection process. In this work, we present the results of spectroscopic study to evaluate the mechanism in DMMP detection with ZnTPP or CoTPP. These studies are important for the development of preventive measures against CWAs.

2. Experimental and computational methods

2.1. Experimental method

2.1.1. Materials and apparatus

5,10,15,20-Tetraphenylporphine zinc (ZnTPP) and 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) (CoTPP) were all obtained from the Sigma (St. Louis, MO, USA) and used without further purification. DMMP was purchased from the Sigma (St. Louis, MO, USA). Absorbance spectra were recorded with a LAMBDA 500 spectrophotometer (CT, USA). Fluorescence spectra were measured on a RF-5301 fluorescence spectrophotometer (Shimadzu, Japan).

2.1.2. Absorbance measurements

In a typical absorbance measurement, 0.5 ml of ZnTPP (40.178 μM in methylene chloride)/CoTPP (40.541 μM in methylene chloride) was transferred into a 5 ml volumetric flask, then different amounts of DMMP were added to yield final concentrations of 1.36–13.6 mM. The mixture was diluted to 5 ml with methylene chloride and mixed thoroughly. The fluorescence intensities were determined after letting it standing for 15 min.

The absorbance spectra were measured at 288, 293, 298 and 303 K using a thermostat bath to maintain the temperatures. Additionally, if DMMP interacts with ZnTPP/CoTPP and causes a change in the absorbance spectra, the largest change in the spectra will likely be observed in the Soret region and, for this reason, we have chosen the wavelength region from 350 to 500 nm to study the interaction of ZnTPP/CoTPP with DMMP.

2.2. Computational methods

2.2.1. Computational method for binding parameters

Benesi–Hildebrand (B–H) method [15] was used to determine the association constants and stoichiometries of the hydrogen bonding interactions in the porphyrin–DMMP systems. If we assume a porphyrin molecule S interacts with ligand L to form a 1:1 complex SL, that is

$$S + L \overset{K}{\longleftrightarrow} SL \tag{1}$$

Then 1:1 B–H equation is as follows:

$$\frac{b}{\Delta A} = \frac{1}{S_t K \Delta\varepsilon_{11}[L]} + \frac{1}{S_t \Delta\varepsilon_{11}} \tag{2}$$

where b is the length of absorption cell (b = 1.0 cm), ΔA is the absorbance change during complexation; $\Delta\varepsilon_{11} = \varepsilon_{11} - \varepsilon_S - \varepsilon_L$, where ε_{11}, ε_S and ε_L are the extinction coefficient of the complex, substrate (porphyrin) and ligand (DMMP), respectively; total substrate concentration = $S_t = [S] + [SL]$ and $K = [SL]/[S][L]$ = equilibrium constant, where $[SL]$ is the concentration of the complex, $[S]$ is the concentration of the unbound substrate and $[L]$ is the concentration of unbound ligand. In our system L_t (total DMMP concentration) was much larger than S_t, and we can assume $[L] = L_t$.

By plotting $b/\Delta A$ versus $1/[L]$, a linear relationship can be obtained. The parameters can then be calculated from the intercept and slope as follows:

$$K = \frac{y - \text{intercept}}{slope} \tag{3}$$

$$\Delta\varepsilon_{11} = \frac{1}{S_t(y - \text{intercept})} \tag{4}$$

If the one-step 1:2 interaction between porphyrin and DMMP takes place, there will be a interaction in the form of $S + 2L \overset{K}{\longleftrightarrow} SL_2$, then, we can obtain 1:2 B–H equation:

$$\frac{b}{\Delta A} = \frac{1}{S_t K \Delta\varepsilon_{11}[L]^2} + \frac{1}{S_t \Delta\varepsilon_{11}} \tag{5}$$

It is generally believed that the $b/\Delta A$ versus $(1/[L])^2$ plot would assure a straight line for a 1:2 complex.

But if it is a two-step interaction, there will be two ways. Firstly, S interacts with L gradually:

$$S + L \overset{K_1}{\longleftrightarrow} SL \tag{6}$$

$$SL + L \overset{K_2}{\longleftrightarrow} SL_2 \tag{7}$$

Then the K_1 and K_2 can be expressed as follows:

$$K_1 = \frac{[SL]}{(S_t - [SL] - [SI_2])(L_t - [SL] - 2[SL_2])} \tag{8}$$

$$K_2 = \frac{[SL_2]}{[SL](L_t - [SL] - 2[SL_2])} \tag{9}$$

Thus, the 1:1 and 1:2 B–H methods can help us to obtain the equilibrium constants and stoichiometries of the interactions in porphyrin systems.

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