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Carbonyl ligands in modified "picket fence" iron porphyrin complexes: Order and disorder

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ABSTRACT

A new modified "picket fence" porphyrin is synthesized and its six-coordinate iron(II) carbonyl derivatives [Fe(MmacTpivPP)(CO)(Py)] and [Fe(MmacTpivPP)(CO)(1-MeIm)] are characterized by single-crystal X-ray, UV-vis and IR spectroscopies. X-ray structural determinations revealed that both [Fe(MmacTpivPP)(CO)(Py)] and [Fe(MmacTpivPP)(CO)(1-MeIm)] are crystallized in the *C*2/*c* space group with 2-fold axes passing through the Fe atoms. The Fe—C—O angle of [Fe(MmacTpivPP)(CO)(Py)] is as small as 172.1°, contrasted to 180° of the same angle in [Fe(MmacTpivPP)(CO)(1-MeIm)]. Short intramolecular interactions are found between the terminal oxygen atom of CO and the carbon atoms of the pickets in [Fe(MmacTpivPP)(CO)(Py)]. The characteristic C—O stretching frequencies (ν_{CO}) of the two complexes are same at 1965 cm^{-1}.

1. Introduction

The carbon monoxide (CO) is one of the important diatomic ligands in the study of hemoglobin (Hb) and myoglobin (Mb). It shows high and reversible affinities for heme proteins and iron porphyrin model compounds [1–3], and plays a central role of the proteins' biological functions [4,5]. The characteristic absorbance of C—O vibration (ν_{CO}) can be detected by vibrational spectroscopic techniques such as infrared (IR) or Raman (rR) conveniently [6]. Consequently, CO has been widely used as a probe ligand to detect the nature of metal-ligand bonding and provide information on the environment of prosthetic groups in proteins [7]. It is usually assumed that the Fe—C—O group prefers a linear geometry in order to maximize the Fe $d\pi \rightarrow$ CO π^* back-bonding [8,9], which causes a reduction in the C—O bond order and a concomitant increase in the Fe—C bond order [7].

The origin of the molecular basis of the heme proteins' discrimination against CO has been an intensively studied problem for decades [10,11]. At first, it is believed that the principle of the heme proteins' discrimination against CO was mainly steric effect imposed by the protein ligand binding pocket that lower the CO affinity by deforming ("bending" and "tilting") the Fe—C—O group which prefers to a linear configuration, while not affecting the O_2 affinity, whereas the iron and O_2 combines in a "bent" fashion [9–11]. Although this hypothesis was supported by a series of structure studies of MbCO/HbCO [12–14] and some porphyrin model compounds [15–19]; many recent studies [3,20–22] suggested that there is no clear relationship between Fe—C—O group deformation and CO affinity to heme proteins [10]. The selective bonding of heme proteins between O_2 and CO is a complicated process and the hydrogen bond also play a very important role [10,23]. A study based on site-directed mutants of Mb shows that the H-bond between O_2 and the distal histidine side chain is stronger than that of CO, and this difference in H-bond strength attributes 3.5 kcal/mol to Mb's discrimination in favor of O_2; for comparison, the contribution of steric inhibition of CO binding is only about 0.5 kcal/mol [23].

The "picket fence" porphyrin is one of the successful models of oxyheme proteins, and its bulky pickets provide an efficient pocket for the reversible bonding of dioxygen (O_2) [24,25]. Although the study of this model has answered important questions about oxyheme proteins which had been debated for years, some problems remain partially due to the highly disordered axial ligands. The terminal oxygen atom of the dioxygen ligand always shows four positional disorder, which has been seen in the X-ray single crystal structures of [Fe(TpivPP)(O_2)(L)] (L = 1-MeIm, 1-EtIm and 2-MeHIm) complexes even at 80 K [26]. This phenomena prevented

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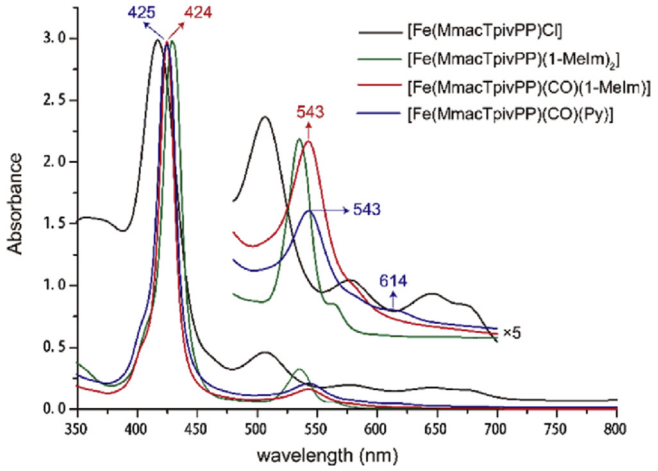

Fig. 1. The UV-vis spectra of [Fe(MmacTpivPP)Cl] (black, $CHCl_3$), [Fe(MmacTpivPP)(1-MeIm)$_2$] (green, C_6H_6), [Fe(MmacTpivPP)(CO)(1-MeIm)] (red, C_6H_6) and [Fe(MmacTpivPP)(CO)(Py)] (blue, C_6H_6) taken under argon atmosphere. The spectra from 480 to 700 nm are enlarged by 5 times. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

accurate analysis of the "structure-function" relationship and the electronic structure study of Mössbauer spectra [9,26]. With the aim to change the pocket polarity [27,28] and/or introduce H-bond interactions [29] which may stabilize the dioxygen dynamics, researchers have designed and synthesized some modified "picket fence" analogues that possess an "asymmetric pocket". Recently, we reported the synthesis and characterization of a modified "picket fence" porphyrin and its bis-imidazole derivative [Fe(MbenTpivPP)(1-MeIm)$_2$] [30]. The study suggested that the iron dπ → imidazole pπ back-bonding is sensitive to the mutual ligand orientation such that more perpendicular ligand orientations correspond to stronger π-bonding interactions (shorter axial bond distances). Here, we present the synthesis and characterization of a new modified "picket fence" porphyrin: *meso*-mono[α-*o*-(2-methylacrylamido)phenyl]tris(α,α,α-*o*-pivalamidophenyl) porphyrin (H_2MmacTpivPP) and two six-coordinate iron(II) carbonyl derivatives: [Fe(MmacTpivPP)(CO)(Py)] and [Fe(MmacTpivPP)(CO)(1-MeIm)].

2. Experimental section

2.1. Materials and techniques

All reactions were carried out using standard Schlenk line techniques under argon atmosphere unless otherwise noted. ^{1}H NMR spectrum was obtained on a BRUKER AV400 system. UV-vis spectra were obtained on a Perkin-Elmer Lambda-25 spectrometer, IR spectra were obtained on a Nicolet 6700 FT-IR spectrometer. Solid-state infrared samples were prepared by gently mulling microcrystals between two KBr plates.

Benzene and hexanes were distilled from sodium and benzophenone ketyl; dichloromethane was distilled from CaH_2; chlorobenzene was distilled twice over P_2O_5 under argon. All solvents were freeze/pump/thaw (thrice) prior to use. Pivaloyl chloride, methacryloyl chloride, 2,6-lutidine, pyridine and 1-methylimidazole were distilled under argon before use. Zinc and mercury were used as received. *Meso*-tetrakis(*o*-aminophenyl) porphyrin [31] and *meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl) porphyrin (H_2TamPP, **1**) [32] were prepared according to a local modification of the reported synthesis.

2.2. Synthesis of [Fe(MmacTpivPP)(CO)(L)] (L = 1-MeIm, Py)

2.2.1. Synthesis of H_2MmacTamPP (**2**)

H_2TamPP (**1**) (0.50 g, 0.74 mmol) and 2,6-lutidine (0.25 mL) were dissolved in 100 mL dry CH_2Cl_2. Freshly distilled methacryloyl chloride (0.0853 g, 0.81 mmol) and 2,6-lutidine (0.25 mL) in 15 mL dry CH_2Cl_2 was added dropwise to the H_2TamPP solution over 3 h in ice bath under Ar atmosphere. After additional 8 h stirring, the reaction solution was evaporated to dryness. The resulting solid was dissolved in small amount of eluent and purified by chromatography on a silica gel column (300–400 mesh, 15 cm; trichloromethane: acetone = 4:1). The second main band was collected, evaporated to dryness and followed by recrystallization (dichloromethane-hexane) to give a purple solid product (**2**) 186 mg (0.25 mmol, ~33%).

The remaining H_2TamPP (**1**) which did not react with the methacryloyl chloride was rest at the top of the silica gel column. These H_2TamPP was eluted (trichloromethane: acetone = 1.3:1), evaporated to dryness and followed by recrystallization (dichloromethane-hexane) to give a purple solid ~110 mg (0.16 mmol) which could be recycled.

2.2.2. Synthesis of H_2MmacTpivPP (**3**)

Freshly distilled pivaloyl chloride (3.01 g, 25 mmol) and 2,6-lutidine (0.5 mL) were dissolved in 20 mL dry dichloromethane. This solution was then added dropwise to a dichloromethane solution (50 mL) of H_2MmacTamPP (**2**) (186 mg, 0.25 mmol) and 2,6-lutidine (0.3 mL). The mixture was stirred at ambient temperature overnight under Ar atmosphere and concentrated by a rotary evaporator. The residue was added ~100 mL hexane, and then filtered to give a purple solid product. The crude product was chromatographed on a silica gel column (300–400 mesh, 20 cm; trichloromethane: ethyl acetate: hexane = 4:1:1). The main band was collected and recrystallized from dichloromethane-hexane to yield compound (**3**) 171 mg (0.17 mmol, 70%).

The ^{1}H NMR data of H_2MmacTpivPP (**3**) (400 MHz, $CDCl_3$, TMS): δ_H, ppm −2.60 (s, 2H, pyrrole-N*H*), 0.06–0.07 (s, 27H, $-CH_3$), 0.88 (s, 3H, $-CH_3$), 4.23–4.25 (d, J = 6.6 Hz, 2H, C$-CH_2$), 7.18–7.20 (s, 2H, Ph), 7.50–7.52 (d, J = 7.3 Hz, 4H, Ph), 7.84–7.92 (m, 10H, Ph), 8.68–8.72 (t, J = 7.2 Hz, 3H, −CON*H*− and pyrrole-*H*), 8.68–8.83 (d, J = 8.7 Hz, 9H, −CON*H*− and pyrrole-*H*).

2.2.3. Synthesis of [Fe(MmacTpivPP)Cl] (**4**)

Chlorobenzene solution of H_2MmacTpivPP (**3**) (250 mg, 0.251 mmol) and 2,6-lutidine (0.4 mL) was transferred to anhydrous $FeCl_2$ (0.31 g, 2.44 mmol) by cannula. The mixture was stirred at 65 °C for 10 h till the reaction was completed (monitored by TLC, trichloromethane: ethyl acetate: hexane = 4:1:1). After the solvent was evaporated, the residue was dissolved in $CHCl_3$ and washed with portions of diluted hydrochloric acid solution. The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The resulting solid was purified on a silica gel column (300–400 mesh; trichloromethane: ethyl acetate: hexane = 4:1:1) and the first main band was collected. After evaporation, the solid was recrystallized from trichloromethane-hexane to give the fine product [Fe(MmacTpivPP)Cl] (**4**) 200 mg (0.185 mmol, 73.4%). The UV-vis spectrum ($CHCl_3$): 417, 505, 578, 644, 676 nm.

2.2.4. Synthesis of [Fe(MmacTpivPP)(CO)(L)] (L = 1-MeIm, Py) (**6**)

[Fe(MmacTpivPP)Cl] (13 mg, 0.012 mmol) and zinc amalgam (10% zinc, 1 mL) were dried in vacuum for 2 h. Dry benzene (~8 mL) was transferred in and the mixture was stirred overnight. After 2 h standing, the red solution was filtered to a new Schlenk and 1-MeIm (0.1 mL, 1.2 mmol) or pyridine (0.1 mL, 1.2 mmol) was added. The solution was stirred for 20 min under argon