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Structural Characterization of the Picket Fence (TpivPP) Porphyrins Co(TpivPP), Co(TpivPP)(NO_2)(1-MeIm), and Co(TpivPP)(NO_2)(1,2-Me_2Im)

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The compounds Co(TpivPP) (**1**), Co(TpivPP)(NO_2)(1-MeIm) (**2**), and Co(TpivPP)(NO_2)(1,2-Me_2Im) (**3**) have been synthesized (TpivPP = meso-tetrakis(α,α,α,α-*o*-pivalamidophenyl)porphyrinato dianion), and their structures have been determined with single-crystal X-ray diffraction methods. **1**: $a = 17.578(1)$ Å, $b = 17.596(1)$ Å, $c = 20.639(1)$ Å, $\beta = 115.03(1)°$, $P2_1/c$, $Z = 4$, $T = -120$ °C. **2**: $a = 18.522(4)$ Å, $b = 18.942(4)$ Å, $c = 18.177(4)$ Å, $\beta = 90.68(3)°$, $C2/c$, $Z = 4$, $T = -70$ °C. **3**: $a = 18.998(4)$ Å, $b = 19.187(4)$ Å, $c = 18.000(4)$ Å, $\beta = 90.96(3)°$, $C2/c$, $Z = 4$, $T = -120$ °C. Compounds **2** and **3** have crystallographically imposed 2-fold axes. In **2** and **3**, which represent R-state (relaxed) and T-state (tense) models, respectively, for hemoglobin, the NO_2 ligand is bound on the "picket" side to the Co atom, and either 1-MeIm (for **2**) or 1,2-Me_2Im (for **3**) is bound to the Co atom at the sixth coordination site on the sterically unhindered side of the molecule. The average deviations of atoms from the 24-atom porphyrin core are 0.031, 0.129, and 0.117 Å for **1**, **2**, and **3**, respectively. The Co atom is −0.043(1) Å out of the mean 24-atom porphyrin plane toward the 1-MeIm ligand in **2** and −0.089(1) Å out of the plane toward the 1,2-Me_2Im ligand in **3**. The bonds of both axial ligands in the R-state model **2**, 1.898(4) Å for Co−N(O_2) and 1.995(4) Å for Co−N(base), are shorter than the corresponding bonds in the T-state model **3**, 1.917(4) Å for Co−N(O_2) and 2.091(4) Å for Co−N(base).

Introduction

For several decades, porphyrin-based model systems of the heme active site have been used in attempts to understand the structure−function relationships in myoglobin (Mb) and hemoglobin (Hb).[1−6] A number of strategies have been employed to generate models that do not undergo irreversible oxidation and that mimic five-coordinate heme precursors. A plethora of elaborated porphyrins have been prepared, including "strapped",[7−13] "picnic basket",[14−18] "picket fence",[19−22] "pocket",[21,23,24] and "capped".[25−41]

Many hemoglobins and hemerythrins and all hemocyanins actually comprise two or more subunits. The binding of O_2 to one subunit affects the binding of O_2 to remaining subunits—a phenomenon of great physiological importance known as cooperativity. Cooperative ligand binding to Hb requires that the structural changes of ligand binding to the heme are communicated to the interfaces between subunits. A simple model for analyzing cooperative ligand binding was proposed by Monod, Wyman, and Changeux in 1965[42] and is usually referred to as the MWC two-state concerted model. Molecules

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(6) Abbreviations: TpivPP, meso-tetrakis(α,α,α,α-*o*-pivalamidophenyl)-porphyrinato dianion (picket fence porphyrin); TPP, 5,10,15,20-tetraphenylporphyrinato dianion; OC_3O, 5,10,15,20-(benzene-1,2,4,5-tetrakis(2-phenyloxy)propoxy)-2′,2″,2‴,2⁗-tetrayl)porphyrinato dianion; Im, imidazole; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; SC_6HF_4, 2,3,5,6-tetrafluorothiophenolate; Hb, hemoglobin; Mb, myogoblin; pip, piperidine; lut, 3,5-lutidine; Py, pyridine; C_n-cap ($n = 2-3$), TPP with linkages of the type $-OC_nO(CO)-$ connecting an ortho position on each of the phenyl rings to the 1, 2, 4, and 5 positions of the benzene cap; Deut, deuterioporphyrinato dianion; Piv_2C_n ($n = 6-10$), porphyrin with a strap of the type $-NH(CO)(CH_2)_n(CO)NH-$ linking the ortho positions on the same side of the porphyrin plane of opposite phenyl groups of TPP and pivalamido groups extending from the ortho positions of the remaining two phenyl groups of TPP in the α direction; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; TMP, 5,10,15,-20-tetramesitylporphyrinato dianion; C_6-PBP, picnic basket porphyrin with handle of the type $-OC_6O-$; PocPivP, porphyrin with three $-CH_2(CO)NH-$ linkages connecting the 1, 3, and 5 positions of a benzene cap to an ortho position on each of three phenyl rings of TPP and a pivalamido arm extending from an ortho position of the fourth phenyl group in either the α (toward the cap) or β (away from the cap) direction.

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Table 1. Selected Crystallographic Data

compound	Co(TpivPP) (**1**)	Co(TpivPP)(NO_2)(1-MeIm) (**2**)	Co(TpivPP)(NO_2)(1,2-Me_2Im) (**3**)
formula	$C_{64}H_{64}CoN_8O_4$	$C_{68}H_{70}CoN_{11}O_6$	$C_{69}H_{72}CoN_{11}O_6$
fw	1068.2	1196.3	1210.3
space group	C^5_{2h}-$P2_1/c$	C^6_{2h}-$C2/c$	C^6_{2h}-$C2/c$
a (Å)	17.578(1)	18.522(4)	18.998(4)
b (Å)	17.596(1)	18.942(4)	19.187(4)
c (Å)	20.639(1)	18.177(4)	18.000(4)
β (deg)	115.030(1)	90.68(3)	90.96(3)
Z	4	4	4
density (g/cm^3)	1.227	1.246	1.225
radiation (λ, Å)	MoKα, 0.71073 Å	MoKα, 0.71073 Å	MoKα, 0.71073 Å
μ (cm^{-1})	3.5	3.3	3.2
T (°C)	−120	−70	−120
R^a	0.050	0.055	0.076
Rw^b	0.122	0.120	0.203

[a] $R = (\sum|F_o|) - |F_c|)/\sum|F_o|$ [b] $Rw(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 1$.

are assumed to be in equilibrium between two conformations or quaternary structures, one that has a low ligand affinity and a second that has a high ligand affinity. The low-affinity conformation is often designated the "T" or tense state and the high-affinity conformation the "R" or relaxed state. All mammalian Hbs that have been structurally characterized can be categorized as being in either the T- or R-state quaternary conformation.

The Fe atom in deoxyHb is five-coordinate and displaced from the porphyrin plane in the direction of the proximal histidine residue. Upon ligation, the Fe atom moves toward and into the porphyrin plane. One way to mimic T-state Hb in model systems is to restrict the movement of the Fe atom into the porphyrin plane, for example, by attaching as a ligand to the Fe atom a bulky base instead of the imidazole group of the histidine residue.[43] Thus, comparative studies of model systems, in which the base does not restrict movement of the Fe atom (R-state) but a bulkier base does restrict movement (T-state), provide valuable metrical data at a level unobtainable in macromolecular structure determinations. To date, there appear to be three such comparative studies: Fe(TpivPP)(O_2)(1-MeIm)[44] vs Fe(TpivPP)(O_2)(2-MeIm),[45] Fe(OC_3OPor)(CO)(1-MeIm) vs Fe(OC_3OPor)(CO)(1,2-Me_2Im),[39] and Fe(TPP)(N_3)(1-MeIm) vs Fe(TPP)(N_3)(1,2-Me_2Im).[46] The present study of Co(TpivPP) (**1**), Co(TpivPP)(NO_2)(1-MeIm) (**2**), and Co(TpivPP)(NO_2)(1,2-Me_2Im) (**3**) examines another such system. Whereas Fe is the central atom in the porphyrins of Hb and Mb, Co-substituted Hb does exhibit cooperativity.[47] Moreover, Co model systems offer advantages of stability over Fe model systems. Only two other cobalt porphyrin nitrite structures are known.[48,49]

Experimental Details

Materials and Equipment. All solvents and reagents were used as purchased except $CHCl_3$, which was freshly distilled under N_2 from CaH_2, and NO, which was passed through a KOH column prior to use. IR spectra were taken on a Bio-Rad FTS infrared spectrophotometer. Mass spectra were taken on a QUATTRO II electrospray mass spectrometer from Micromass, Altringham, England.

Synthesis of Co(TpivPP) (1). Co(TpivPP) was prepared following literature methods.[50,51] Low-resolution mass spectrum (ES): m/z 1068 $[Co(TpivPP)]^+$ (100%). IR (KBr, cm^{-1}): $\nu_{CO} = 1685$.

Synthesis of Co(TpivPP)(NO_2)(1-MeIm) (2). Co(TpivPP) (∼10 mg) was added to a Schlenk H-tube and degassed with three cycles of vacuum, followed by N_2 back filling. A 2 mL sample of $CHCl_3$ was added via syringe. A 0.1 mL sample of 1-MeIm was added via gastight

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syringe. Four milliliters of methanol was added to the other arm of the H-tube through gastight syringe. Gaseous NO was bubbled into the porphyrin solution for approximately 15 min. The tube was sealed under an atmosphere of N_2 and NO and stored at room temperature. Crystals of **2** formed in 2−3 weeks (6.0 mg, 5.0 mmol, ~60% isolated yield). They are air stable. Low-resolution mass spectrum (ES): m/z 1200 $[Co(TpivPP)(NO_2)(1\text{-}MeIm)]^+$ (40%), 1149 $[Co(TpivPP)(1\text{-}MeIm)]^+$ (30%), 1113 $[Co(TpivPP)(NO_2)]^+$ (10%), 1091 $\{(TpivPP)^{2-}[H(1\text{-}MeIm)^+]\}^+$ (100%), 1068 $[Co(TpivPP)]^+$ (60%). IR (KBr, cm^{-1}): ν_{CO} = 1685.

Synthesis of Co(TpivPP)(NO$_2$)(1,2-Me$_2$Im) (3). Co(TpivPP) (~10 mg) and a >10-fold excess of 1,2-Me$_2$Im were added to a Schlenk H-tube, and the procedures outlined in the preparation of **2** were followed. Crystals of **3** formed in 2−3 weeks (7.7 mg, 6.4 mmol, ~77% yield). They are air stable. Low-resolution mass spectrum (ES): m/z 1211 $[Co(TpivPP)(NO_2)(1,2\text{-}Me_2Im)]^+$ (5%), 1164 $[Co(TpivPP)(1,2\text{-}Me_2Im)]^+$ (8%), 1113 $[Co(TpivPP)(NO_2)]^+$ (5%), 1068 $[Co(TpivPP)]^+$ (100%). IR (KBr, cm^{-1}): ν_{CO} = 1685.

X-ray Crystal Structure Determinations. A chosen crystal was attached with silicone cement to the tip of a drawn glass fiber on a goniometer head and transferred to the cold stream of a Bruker Smart 1000 CCD diffractometer. The crystal was kept at low temperature for the length of the data collection. For all three structures, data were collected with 0.3° ω scans for 15, 40, and 60 s per frame for **1**, **2**, and **3**, respectively. Final unit cell parameters were determined from a global refinement of the positions of all reflections, as performed by the processing program SAINT+.[52] A face-indexed absorption correction was applied with the use of XPREP,[53] and the program SADABS,[52] which relies on redundancy in the data, was then used to apply semiempirical corrections for frame variations. The structures were solved with the use of the direct-methods program SHELXS of the SHELXTL PC suite of programs.[53] The structures were refined by full-matrix least-squares techniques with the program SHELXL.[53] For all three structures, non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed at calculated positions.

The refinement of **1** was straightforward. However, for **2** and **3**, there were difficulties in refining the solvents of crystallization, as these molecules could not be resolved. Electron density associated with the solvent regions was removed with the SQUEEZE[54] algorithm in the PLATON[55] suite of programs.

Crystallographic details may be found in Table 1. Additional information is available in Supporting Information. Drawings of the molecular structures of **1**, **2**, and **3** are presented in Figures 1, 2, and 3, respectively. Table 2 compares similar bond lengths and angles among these compounds.

Results and Discussion

Source of and Evidence for NO$_2^-$. The target compounds were Co(TpivPP)(NO)(1-MeIm) and Co(TpivPP)(NO)(1,2-Me$_2$-Im). But the results of the crystallographic studies indicate that NO_2^- rather than NO complexes have been prepared. In the presence of air, Co(porphyrin)(NO) complexes can be oxidized into their nitrite analogues.[48] As the present reactions were carried out on a small scale and the tubes left sealed for some time, trace oxygen is the likely cause of the nitrite products. Further evidence that the present compounds are not NO complexes comes from infrared data. Co−NO species typically exhibit a strong infrared absorption peak between 1600 and 1700 cm^{-1}. Compounds **1**, **2**, and **3** all exhibit a single peak in this region at 1685 cm^{-1}, which arises from the CO group of the pivalamido picket.

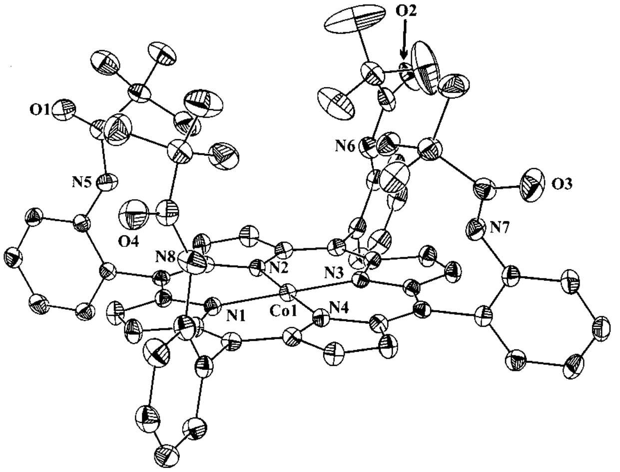

Figure 1. Co(TpivPP) (**1**) molecule. Displacement ellipsoids are shown at the 30% probability level, and H atoms have been omitted for clarity.

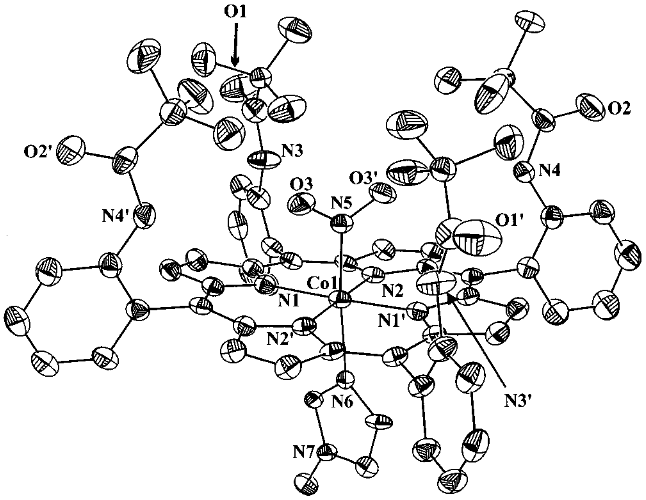

Figure 2. Co(TpivPP)(NO$_2$)(1-MeIm) (**2**) molecule. Displacement ellipsoids are shown at the 30% probability level, and H atoms have been omitted for clarity.

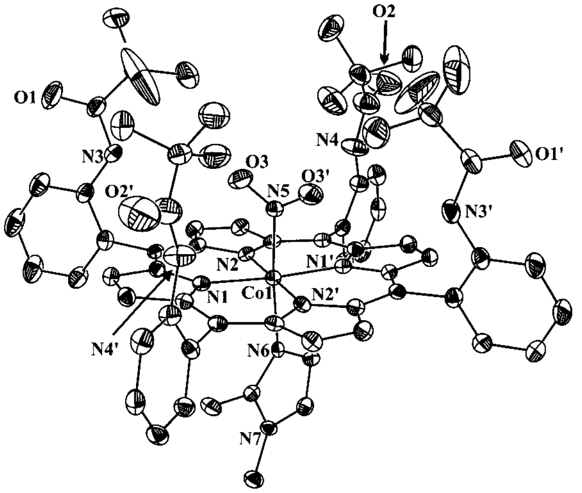

Figure 3. Co(TpivPP)(NO$_2$)(1,2-Me$_2$Im) (**3**) molecule. Displacement ellipsoids are shown at the 30% probability level, and H atoms have been omitted for clarity.

Description of the Structures. The sterically encumbered porphyrin TpivPP (meso-tetrakis(α,α,α,α-*o*-pivalamidophenyl)-porphyrinato dianion) consists of four pivalamido picket arms of the type $-(NH)(CO)(C(CH_3)_3)$, all oriented to the same side

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Co(TpivPP) (**1**), Co(TpivPP)(NO$_2$)(1-MeIm) (**2**), and Co(TpivPP)(NO$_2$)(1,2-Me$_2$Im) (**3**)

	Co(TpivPP) (**1**)	Co(TpivPP)(NO$_2$)-(1-MeIm) (**2**)	Co(TpivPP)NO$_2$)-(1,2-Me$_2$Im) (**3**)
Co−N(NO$_2$)		1.898(4)	1.917(4)
N−O(NO$_2$)		1.223(3)	1.227(3)
Co−L$_{ax}$[a]		1.995(4)	2.091(4)
Co−N1	1.963(2)	1.959(3)	1.984(3)
Co−N2	1.970(2)	1.969(3)	1.981(3)
Co−N3[b]	1.959(2)	1.959(3)	1.984(3)
Co−N4[b]	1.970(2)	1.969(3)	1.981(3)
av Co−N$_{eq}$[c]	1.966(4)	1.964(4)	1.983(4)
av N−C$_a$[c]	1.391(8)	1.371(8)	1.375(9)
av C$_a$−C$_b$[c]	1.434(10)	1.424(9)	1.439(10
av C$_b$−C$_b$	1.346(7)	1.332(7)	1.343(7)
av C$_a$−C$_m$[c]	1.386(10)	1.382(9)	1.392(10)
Co−N−O		120.1(2)	119.8(2)
O−N−O		119.8(4)	120.4(4)
N(NO$_2$)−Co−N1		88.86(8)	87.45(7)
N(NO$_2$)−Co−N2		90.31(8)	90.39(8)
N(NO$_2$)−Co−N3		88.86(8)	87.45(7)
N(NO$_2$)−Co−N4		90.31(8)	90.39(8)
N(NO$_2$)−Co−L$_{ax}$		174.2(2)	174.3(2)
L$_{ax}$−Co−N$_1$		96.9(3)	98.0(2)
L$_{ax}$−Co−N$_2$		90.5(3)	87.9(3)
L$_{ax}$−Co−N$_3$		85.4(3)	87.1(2)
L$_{ax}$−Co−N$_4$		88.9(3)	91.3(3)
N1−N3/Im[d]		69.3	111.4
NO$_2$/Im[e]		72.3	76.5
N1−N3/NO$_2$		141.6	34.9
N1−Co−N2	90.11(8)	90.3(1)	90.1(1)
N1−Co−N3	179.89(11)	177.7(2)	174.9(2)
N1−Co−N4	89.67(8)	89.8(1)	89.3(1)
N2−Co−N3	89.98(8)	89.8(1)	89.3(1)
N2−Co−N4	178.62(8)	179.4(2)	179.2(2)
N3−Co−N4	90.24(8)	90.3(1)	90.7(1)

[a] L$_{ax}$ = N(1-MeIm) for **2** and N(1,2-Me$_2$Im) for **3**. [b] For clarity, N3 in this table refers to N1′ and N4 refers to N2′ of porphyrins **2** and **3**. [c] C$_a$, C$_b$, and C$_m$ stand respectively for the α pyrrole, *β* pyrrole, and methine carbon atoms, and N$_{eq}$ stands for the porphyrinato nitrogen atoms N1, N2, N3, and N4. [d] Angle between the N1−N3 line and the normal to the Im (N6−N7−C33−C34−C35) plane. [e] Angle between the normal to the Im plane and the normal to the NO$_2$ (O3−N5−O3′) plane.

Table 3. Displacements (Å) from the 24-Atom Porphyrin Mean Plane

atom	Co(TpivPP) (**1**)	Co(TpivPP)(NO$_2$)-(1-MeIm) (**2**)	Co(TpivPP)(NO$_2$)-(1,2-Me$_2$Im) (**3**)
N1	−0.026(2)[a]	−0.004(3)	−0.001(3)
N2	0.020(2)	−0.053(3)	−0.103(3)
N3, N1A[b]	−0.021(2)	−0.004(3)	−0.001(3)
N4, N2A	−0.018(2)	−0.053(3)	−0.103(3)
C1	−0.008(2)	0.150(3)	0.011(3)
C2	0.013(3)	0.212(3)	0.143(3)
C3	0.013(2)	0.068(3)	0.221(3)
C4	−0.023(2)	−0.059(3)	0.113(3)
C5	−0.053(2)	−0.203(3)	0.101(3)
C6	−0.027(2)	−0.170(3)	−0.012(3)
C7	−0.012(2)	−0.145(3)	−0.052(3)
C8	0.058(2)	−0.007(3)	−0.138(3)
C9	0.054(2)	0.047(3)	−0.153(3)
C10	0.039(2)	0.165(3)	−0.130(3)
C11, C1A	−0.003(2)	0.150(3)	0.011(3)
C12, C2A	−0.010(3)	0.212(3)	0.143(3)
C13, C3A	−0.029(3)	0.068(3)	0.221(3)
C14, C4A	−0.038(2)	−0.059(3)	0.113(3)
C15, C5A	−0.026(2)	−0.203(3)	0.101(3)
C16, C6A	−0.006(2)	−0.170(3)	−0.012(3)
C17, C7A	0.047(3)	−0.145(3)	−0.052(3)
C18, C8A	0.055(3)	−0.007(3)	−0.138(3)
C19, C9A	0.004(2)	0.047(3)	−0.153(3)
C20, C10A	−0.005(2)	0.165(3)	−0.130(3)
Co[c]	−0.023(1)	−0.043(1)	−0.089(1)
av deviation[b]	0.031	0.129	0.117

[a] Negative values indicate the direction away from the picket side of the molecule. [b] In compounds **2** and **3**, symmetry-generated atoms are reported with an "A′" appended. [c] Co was not included in the calculation of the mean plane or the average deviation from the plane.

of the 5,10,15,20-tetraphenylporphyrinato plane. Table 3 presents information on the least-squares planes through the 24-atom porphyrin core in these compounds. This core is essentially planar for compound **1**, whereas the cores for **2** and **3** are substantially distorted. The position of the Co atom relative to the mean plane varies as expected. In Co(TpivPP) (**1**), where there is no base, the Co atom deviates by −0.023(1) Å from the mean plane. In Co(TpivPP)(NO$_2$)(1-MeIm) (**2**), the Co atom is −0.043(1) Å out of the plane toward the 1-MeIm ligand. In Co(TpivPP)(NO$_2$)(1,2-Me$_2$Im) (**3**), where the base is bulky, the Co is −0.089(1) Å out of the plane toward the 1,2-Me$_2$Im ligand.

The dihedral angles of the phenyl rings in the 5, 10, 15, and 20 positions relative to the mean plane differ to some extent in these compounds, but as expected, they remain near 90°. The independent dihedral angles in these compounds are 75.66(7)°, 87.84(7)°, 89.22(7)°, and 77.32(6)° for **1**, 85.19(9)° and 80.33(10)° for **2**, and 82.35(11)° and 83.35(9)° for **3**. All four picket arms of **1**, **2**, and **3** are oriented with their amido H atoms toward the center of the porphryin and their carbonyl O atoms away from the center. In **1**, one methyl group on each *tert*-butyl group is oriented toward the center of the porphyrin, another is oriented toward the gap with a neighboring picket, and the third completes the tetrahedral geometry by pointing up and slightly away from the porphyrin. For **2** and **3**, the orientation of the *tert*-butyl groups is less regular.

A comparison of bond lengths and angles in Table 2 shows that the distortions of the cores in compounds **2** and **3** have only modest effects on similar bond lengths. The average Co−N$_{eq}$ bond varies from 1.966(4) to 1.964(4) to 1.983(4) Å among **1**, **2**, and **3**. Averages of N−C$_a$, C$_a$−C$_b$, C$_b$−C$_b$, and C$_a$−C$_m$ bonds show only minor variation among the compounds as well. The largest effect of the core distortions and the movement of the Co atom is on the N1−Co−N3 bond angle, which varies from 179.9(1)° in **1** to 177.7(2)° in **2** to 174.9(2)° in **3**. In general, the changes to the core structure are similar to those in the Fe(TpivPP)(base)(ligand) system.[56−62]

Table 4 summarizes M−NO$_2$ bond lengths in a number of metalloporphyrins. The bond lengths and angles for **2** and **3** are reasonable. Thus, among the four Co structures, Co(TpivPP)(NO$_2$)(1-MeIm) (**2**) and Co(TPP)(NO$_2$)(pip),[49] the two with the least sterically demanding bases show the shortest Co−N$_B$ distances. The Co−N(NO$_2$) distances are longer for Co(TpivPP)(NO$_2$)(1,2-Me$_2$Im) (**3**) and Co(TPP)(NO$_2$)(lut),[48] the species with the more sterically demanding bases. Given the possible effects of thermal motion and crystallographically imposed symmetry on the M−O$_2$ geometries, the metrical details on the nitrite groups in Table 2 are in surprising agreement.

Curiously, the nitrite ligands of **2** and **3** are not oriented between the picket arms. Instead, they point almost directly at the amido hydrogen atoms, which are oriented toward the center of the porphyrin. The closest contacts in this position are O3···H4B at 2.96 Å for **2** and O3···H3B at 2.96 Å for **3**. The resonance Raman spectra of dioxygen adducts in a series of Co picket fence porphyrins support the existence of N−H···O$_2$

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Table 4. Comparison of M−NO_2 Bond Lengths (Å) in Neutral Complexes

compound	M−N_B[a]	M−N_P[b]	M−N(NO_2)	N−O	O−N−O	ref
Co(TpivPP)(NO_2)(1-MeIm) (**2**)	1.995(4)	1.964(4)	1.898(4)	1.223(3)	119.8(4)	this work
Co(TPP)(NO_2)(pip)	2.034(10)	1.953(18)	1.897(11)	1.207(14) 1.182(14)	115.4(11)	49
Co(TPP)(NO_2)(lut)	2.036(4)	1.954(3)	1.948(4)	1.155(5) 1.35[c,d]	115.4(6)	48
Co(TpivPP)(NO_2)(1,2-Me_2Im) (**3**)	2.091(4)	1.983(4)	1.917(4)	1.227(3)	120.4(4)	this work
Fe(TpivPP)(NO_2)		1.970(4)	1.849(6)	1.241[d]	119.46[d]	59
Fe(TpivPP)(NO_2)(Py)	2.093(5)	1.985(3)	1.960(5)	1.233(4)	119.9(4)	65
Fe(TpivPP)(NO_2)(Im)	2.037(10)	1.970(8)	1.949(10)	1.191(8)	116.1(13)	65
Fe(TpivPP)(NO_2)(NO)	1.87[d]	1.991(2)	1.85[d,e]	1.20[d,e]	114[d,e]	62
Fe(TpivPP)(NO_2)(NO)	1.733[d]	2.000(2)	1.916[d,e]	1.246[d,e]	120.8(8)	62
Fe(TpivPP)(NO_2)(NO)	1.668(2)	2.000(5)	2.002(2)	1.2226(2)	120.8(8)	62
Fe(TpivPP)(NO_2)(NO)	1.671(2)	1.996(4)	1.998(2)	1.224(3) 1.222(3)	121.4(2)	62

[a] N_B corresponds to the coordinating base: 1-MeIm for **2** and 1,2-Me_2Im for 3. [b] Average of the four Co−N_{por} bonds. [c] Corrected for thermal motion. [d] Reported without errors. [e] Value obscured or likely affected by disorder.

Table 5. Metrical Data for Single-Porphyrin Heme Models

compound	M−N_p	M−N_{Im}	M−L	M−P_{core}	M−P_N	ref
Co(TpivPP) (**1**)	1.966(4)			0.0225(6)	0.011(1)	[a]
Co(TpivPP)(NO_2)(1-MeIm) (**2**)	1.964(4)	1.995(4)	1.898(4)	−0.043(1)	−0.014(2)	[a]
Co(TpivPP)(NO_2)(1,2-Me_2Im) (**3**)	1.983(4)	2.091(4)	1.917(4)	−0.089(1)	−0.037(2)	[a]
Fe(TpivPP)(O_2)(1-MeIm)	1.978(10)	2.068(18)	1.745(18)	0.015[b]	0.03[b]	44
Fe(TpivPP)(O_2)(2-MeIm)	1.997(4)	2.107(4)	1.898(7)	−0.110[b]	−0.086[b]	44
Fe(OC_3OPor)(CO)(1-MeIm)	1.996(12)	2.027(5)	1.748(7)	0.06[b]	0.06[b]	39
Fe(OC_3OPor)(CO)(1,2-Me_2Im)	2.00(2)	2.102(6)	1.713(8)	−0.10[b]	−0.10[b]	39
Fe(TPP)(N_3)(1-MeIm)	1.988(5)	1.987(5)	1.931(5)	0.067(6)	0.027(5)	46
Fe(TPP)(N_3)(1,2-Me_2Im)	1.983(8)	2.070(8)	1.934(8)	−0.008(8)	0.004(8)	46
R-oxy Hb	1.99(5)	1.94(9)	1.66(8)	−0.16(8)	−0.12(8)	46
T-α-oxy Hb	2.03(4)	2.2(1)	1.82(4)	−0.37(4)	−0.18(5)	46

[a] This work. [b] Reported without errors.

hydrogen bonds between the *o*-acetamido NH group of the pickets and the dioxygen molecule bound to the Co center.[63] It is possible that some weak electrostatic interaction with the *o*-amido NH group exists in compounds **2** and **3**. In the related Fe(TpivPP)(NO_2)[59] and Fe(TpivPP)(NO_2)(X) species (X = NO,[60,62] NO_2,[64] pyridine,[65] Im,[65] or SC_6HF_4[66]), the NO_2 groups show a similar preferred orientation; this has been ascribed to π-donation from the Fe atom to the nitrite group.[59, 60]

R-State and T-State Model Systems. Metrical details for the present compounds as well as for other R- and T-state model systems and oxyHb are presented in Table 5. The lengthening of the M−N_{Im} bond in the T-state models (base = 1,2-Me_2Im or 2-MeIm) versus R-state models (base = 1-MeIm) is surprisingly consistent, given various crystallographic problems that have plagued some of these structure determinations.[44,45] Thus, this difference is 0.096(6), 0.039(18), 0.075(8), and 0.083(9) Å in the Co(TPivPP)(NO_2), Fe(TpivPP)(O_2), Fe(OC_3OPor)(CO), and Fe(TPP)(N_3) systems, respectively. The difference is 0.26(13) Å in oxyHb,[46,67] which emphasizes the decrease in precision going from the model systems to the hemes. In all instances, the metal is further out of the mean porphyrin plane toward the base in the T-state than in the R-state. The effect of the change in base on the trans M−L distance is much smaller, except in the model and heme O_2 species. In the model Fe(TpivPP)(O_2)(base) system, at least, the M−O_2 distances are unreliable, owing to disorder.

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Supporting Information Available: Crystallographic files, in CIF format, for Co(TpivPP) (**1**), Co(TpivPP)(NO_2)(1-MeIm) (**2**), and Co(TpivPP)(NO_2)(1,2-Me_2Im) (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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