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Synthesis and Characterization of Iron(III) Complexes of 5-(8-Carboxy-1-naphthyl)-10,15,20-tritolyl Porphyrin

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Abstract. 5-(8-Carboxy-1-naphthyl)-10,15,20-tritolyl porphyrin (H₃CNTTP) and its iron(III) complexes, $[Fe(CNTTP)]_2$ and $[Fe(CNTTP)(N-MeIm)_2]$, were synthesized and characterized. X-ray crystallography revealed that the carboxylate group is "hanging" over the porphyrin plane. The rigid framework makes the distance between the carboxylate oxygen and iron in the same porphyrin too long to form a coordination bond. On the other hand, the carboxylate group is not bulky enough to block the axial binding site. In the presence of OH⁻, the carboxylate oxygen is coordinated to iron in the symmetry-

Introduction

Iron porphyrin is the common prosthetic group in many biological systems, such as globins, whose biological function is the reversible transport and storage of dioxygen, the peroxidases, enzymes that catalyze the conversion of hydrogen peroxide to water and/or the oxidation of substrates. In these biological systems, the first coordination sphere for the central metal (iron) atom is comprised by iron and a variety of axial ligands, such as histidines, tyrosines, thiolates, water etc. The functions of these systems are not only related to their first coordination spheres, but also their second coordination spheres. The second coordination sphere interactions, such as hydrogen bonds, π – π stacking, cation– π interactions, CH•••O interactions etc., are commonly noncovalent interactions between surrounding molecules and the ligands.^[1]

For example, globins and peroxidases have different biological functions even they both have the histidines as axial ligands. Structures suggest in the globins a weak hydrogen bond is formed between the coordinated histidine and a nearby carbonyl group,^[2] whereas in the peroxidases the coordinated histidine is strongly hydrogen-bonded to a conserved aspartate.^[3] The role of the hydrogen bond is still one of the unresolved issues concerning peroxidases. It has been postulated

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related unit, which led to the dimeric structure, $[Fe(CNTTP)]_2$. In the presence of excess N-methylimidazole, a six-coordinate species, $[Fe(CNTTP)(N-MeIm)_2]$, was obtained. In such a structure, CH···O interactions between the carboxylate group and imidazole probably play an important role to determine the orientation of imidazole plane. Two imidazole planes have relative parallel orientation. For $[Fe(CNTTP)(N-MeIm)_2]$, ¹H NMR shows pyrrole protons at the region –10 to –25 ppm. EPR shows rhombic spectrum. Those suggest $[Fe(CNTTP)(N-MeIm)_2]$ is a type II low-spin iron(III) porphyrinate.

that this strong hydrogen bond increases the basicity of the His170 proximal ligand, thus helping to stabilize the high oxidation state intermediates.^[3,4]

Besides hydrogen bonding, other non-covalent interactions are also common in biological systems. For examples, π - π interactions have been recognized to play an important role in the folding^[5] and the thermal stability of proteins,^[6] in mRNAcap recognition by proteins (in combination with cation– π interactions).^[7] It is also admitted that the weak interactions termed unconventional CH···O interactions contribute to the structural stability of proteins.^[8]

Model complexes have been invaluable as a means of understanding some general structure-function relationships. Many model systems have been intensively investigated in the last decades. For example, Collman and co-workers have recently developed an efficient synthetic model of cytochrome c oxidases.^[9] Such a model can perform the selective four-electron reduction of oxygen to water using cytochrome c. In their studies, they also suggest, there is an axial water ligand in the distal pocket. Such water further forms hydrogen bonds to other H₂O molecules. This slows down O2 binding as those reported for the actual Cco enzyme.^[10] Nocera and co-workers have developed a "Hangman" porphyrin, which is composed of porphyrin and distal hydrogen bond groups. Such model can orient exogenous water in a controlled fashion by hydrogen bonds. Their studies provide a useful minimalist model for the heme water channel assembly found in the cytochrome P450 enzymes.[11] Biotrel's group have recently developed a porphyrin system with both intramolecular axial carboxylic acid and pyridine.^[12] Their studies suggested the hydrogen bond might be the driving force that causes coordinated oxygen close to the iron, therefore to form unprecedented six-coordinate high-spin iron(II) complex. In other model systems, hydrogen bonds

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Scheme 1. Synthetic route to H₃CNTTP and its iron complexes.

have also been shown to adjust the microenvironment around metal ions, and even change the electron configuration of metal ion.^[13]

In this paper, we have designed a ligand, 5-(8-carboxy-1naphthyl)-10,15,20-tritolyl-porphyrin (H₃CNTTP), as shown in Scheme 1. The 8-position substituent, carboxylate group, is "hanging" over the porphyrin plane. Because of the rigid framework, carboxylate oxygen could not coordinate directly to the central iron atom in the same porphyrin, also leave some spaces for axial ligands, such as water, imidazole etc., to coordinate to central iron atom. We are interested in the interactions between such carboxylate group and axial ligands. The two iron species, $[Fe(CNTTP)]_2$ and $[Fe(CNTTP)(N-MeIm)_2]$, were also characterized by X-ray crystallography. The structure of $[Fe(CNTTP)(N-MeIm)_2]$ has revealed some interactions between the carboxylate group and the imidazole ligand.

Results and Discussion

The iron complexes, $[Fe(CNTTP)]_2$ and $[Fe(CNTTP)-(N-MeIm)_2]$, were synthesized as shown in Scheme 1. 5-(8-Ethoxycarbonyl-1-naphthyl)-10,15,20-tritolyl-porphyrin (H₂ENTTP) and H₃CNTTP were prepared according to our previous method.^[14,15] The resulting (H₃CNTTP) was further metalated according to the literature^[16] and the formed iron(II) complex is eventually converted into iron(III) species [Fe(HCNTTP)Cl]. In the presence of OH⁻, a dimer $[Fe(CNTTP)]_2$ was obtained. When [Fe(HCNTTP)Cl] was treated with excess N-methylimidazole, a bis(imidazole) ligated species, $[Fe(CNTTP)(N-MeIm)_2]$ was obtained. Both $[Fe(CNTTP)]_2$ and $[Fe(CNTTP)(N-MeIm)_2]$ were measured by X-ray crystallography.

Molecular Structures

The crystal structure of $[Fe(CNTTP)]_2$ was solved in $P\overline{1}$. The ORTEP diagram of $[Fe(CNTTP)]_2$ is presented in Figure 1. It is a dimeric structure formed by two symmetry-related



Figure 1. ORTEP view for $[Fe(CNTTP)]_2$ at 50% probability thermal ellipsoids. The hydrogen atoms and tolyl groups are omitted for clarity. Symmetry operator a: -x + 2, -y + 2, -z + 1.

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iron(III) porphyrinates. In the porphyrin unit, there are three tolyl groups and one naphthyl at *meso* positions. The carboxylate group at the 8-position of naphthyl is hanging over the porphyrin plane. One of the carboxylate oxygen is coordinated to iron in the symmetry-related unit. So the overall arrangement for iron is square pyramidal. The average Fe–N_p distance is 2.060(12) Å, which is similar to those in five-coordinate iron(III) porphyrinates.^[17] Iron is not in the porphyrin plane, but out of 24 atom plane with displacement 0.63 Å. The large iron displacement and the long Fe–N_p distance suggest iron(III) is in the high-spin state. Related distances are listed in Table 1. The Fe–O distance is 1.886(4) Å, which is similar to those in carboxylate linked dimeric structures.^[18] The Fe···Fe distance in the dimer is 6.045 Å.

Table 1. Selected bond lengths /Å and angles /° for $[Fe(CNTTP)]_2$ and $[Fe(CNTTP)(N-MeIm)_2]$.

[Fe(CNTTP)] ₂			
Fe(1)–O(1a)	1.886(4)	C(1)–O(1)	1.307(7)
Fe(1) - N(1)	2.052(5)	C(1) - O(2)	1.227(8)
Fe(1) - N(2)	2.060(5)	O(1a) - Fe(1) - N(1)	105.87(19)
Fe(1) - N(3)	2.052(5)	O(1a) - Fe(1) - N(2)	111.10(2)
Fe(1) - N(4)	2.077(5)	O(1a) - Fe(1) - N(3)	103.94(19)
C(M1)-C(10)	1.510(8)	O(1a) - Fe(1) - N(4)	95.80(2)
C(1)–C(17)	1.520(8)		
[Fe(CNTTP)(N	I-MeIm) ₂]	-	
Fe(1)–N(1)	1.982(4)	N(5)-Fe(1)-N(1)	88.64(15)
Fe(1) - N(2)	1.997(3)	N(5)-Fe(1)-N(2)	92.07(14)
Fe(1) - N(3)	1.994(4)	N(5)-Fe(1)-N(3)	91.25(15)
Fe(1) - N(4)	2.001(3)	N(5)-Fe(1)-N(4)	87.59(14)
Fe(1) - N(5)	1.970(3)	N(7)-Fe(1)-N(1)	89.86(15)
Fe(1) - N(7)	1.998(3)	N(7)-Fe(1)-N(2)	89.34(14)
C(1) - O(1)	1.191(11)	N(7)-Fe(1)-N(3)	90.25(15)
C(1)–O(2)	1.259(10)	N(7)-Fe(1)-N(4)	91.00(14)
C(1)–C(17)	1.518(9)	N(5)-Fe(1)-N(7)	177.94(16)
C(M1)-C(10)	1.501(6)	N(1)-Fe(1)-N(2)	89.60(15)
C(2)•••O(1)	3.35	N(1)-Fe(1)-N(3)	179.81(15)
C(2)•••O(2)	3.35	N(1)-Fe(1)-N(4)	90.42(15)
		N(2)-Fe(1)-N(3)	90.26(15)
		N(2)-Fe(1)-N(4)	179.66(15)
		N(3)-Fe(1)-N(4)	89.73(15)

Symmetry operator a: -x + 2, -y + 2, -z + 1

The displacement diagram in Figure 2 shows clearly that the porphyrin core is nonplanar. It shows large displacements for *meso* carbons with alternate sign, which is typical for the ruffled core conformation.^[19] Such ruffled conformation could be due to the crowded dimeric structure. The closest nonbonding distance between O(2) and C(M1) is 2.90 Å, which is much smaller than the corresponding distance in H₂ENTTP (3.17 Å).^[14] The repulsion interactions could be the driving force to make C(M1) away from porphyrin plane to form ruffled conformation.

The crystal structure of $[Fe(CNTTP)(N-MeIm)_2]$ is shown in Figure 3. In order to verify the formula, we measured molar conductivity on $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ solution of $[Fe(CNTTP)(N-MeIm)_2]$ and $N(Bu)_4Br$ in CH₃CN. For $[Fe(CNTTP)(N-MeIm)_2]$, the molar conductivity is 37 S·cm²·mol⁻¹, which is much smaller than 166 S·cm²·mol⁻¹ for N(Bu)_4Br and also smaller than those 1,1-electrolytes



Figure 2. Formal diagram of the porphyrinato core of $[Fe(CNTTP)]_2$. Illustrated are the displacements of each atom from the mean plane of the 24 atom in units of 0.01 Å. Positive values of displacement are toward the carboxylate group.

reported by *Barthel* et al.^[20] It suggests the $[Fe(CNTTP)-(N-MeIm)_2]$ is a neutral species rather than an ionic compound. The following NMR and EPR studies suggest the iron's oxidation state is +3. So the porphyrin ligand should be -3 charged, which means three protons of H₃CNTTP (two from NH and one from COOH group) were deprotonated during the reaction. Obviously, the excess of the imidazole removes one equivalent of HCl, and deprotonates the carboxylic acid.



Figure 3. ORTEP view for $[Fe(CNTTP)(N-MeIm)_2]$ at 50% probability thermal ellipsoids. The hydrogen atoms [except H(2)] and tolyl groups are omitted for clarity.

In the structure of $[Fe(CNTTP)(N-MeIm)_2]$, the iron atom is six-coordinate and in the center of porphyrin plane with displacement 0.04 Å. The porphyrin core has slightly ruffling conformation with maxium displacements on *meso* carbon atoms as shown in Figure 4. The average Fe–N_p distance is 1.994(8) Å, such distance is similar to those six-coordinate

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low-spin iron(III) porphyrinates, which have effectively planar porphyrin core conformations.^[21] Related distances and angles are also listed in Table 1.



Figure 4. Formal diagram of the porphyrinato core of [Fe(CNTTP)(N-MeIm)₂]. Illustrated are the displacements of each atom from the mean plane of 24 atom in units of 0.01 Å. Positive values of displacement are toward the carboxylate group. The diagram also shows the orientation of the imidazole ligands with respect to the atoms of the porphyrin core. The location of the methyl group is represented by the circle.

According to the nomenclature introduced by Walker,^[22] there are three types of low-spin iron(III) porphyrin centers: type I, which have $(d_{xy})^2(d_{xz},d_{yz})^3$ electronic ground states with axial ligands aligned in perpendicular planes; type II, which also have $(d_{xy})^2(d_{xz},d_{yz})^3$ electronic ground states, but with axial ligands aligned in parallel planes; and type III, which have $(d_{xz}, d_{yz})^4 (d_{xy})^1$ electronic ground states with axial ligands in any orientation. In [Fe(CNTTP)(N-MeIm)2], the relative orientation between two imidazole planes is relative parallel with a dihedral angle 17.3° . Fe–N_{Im} distances are 1.970(3)and 1.998(3) Å, which are also in the range of the corresponding distances observed in other bis(imidazole-ligated) iron(III) porphyrinates with unhindered imidazoles [1.975 and 1.965 Å in Fe(TMP)(N-MeIm)₂]ClO₄,^[23] 1.977 and 1.964 Å in [Fe(TPP)(HIm)₂]Cl·CHCl₃,^[24] 1.975 and 1.987 Å in [Fe(TPP)(4-MeHIm)₂]Cl,^[25] 1.974 and 1.995 Å in [Fe(TPP)(N-MeIm)₂]ClO₄,^[26] 1.970 and 1.982 Å in para-[Fe(TMP)(5-MeHIm)₂]ClO₄^[27]], where these iron(III) species have been confirmed as type II species with a relative parallel orientation of the two imidazole planes. The above structural feature also suggests [Fe(CNTTP)(N-MeIm)₂] is a type II species. ¹H NMR and EPR studies have further confirmed such point. (vide infra)

For such a structure, we are more interested in the influence of the carboxylate group on the coordination and orientation of the imidazole ligands. The existence of two axial ligands indicates the carboxylate is not bulky enough to block the sixth coordination site. On the carboxylate side, the imidazole plane is towards the carboxylate group and nearly bisecting the O–C–O angle. In this arrangement, the closest C···O distance is 3.35 Å. Such a distance is within the range for common CH···O interactions.^[28] It suggests the existence of CH···O interactions between the carboxylate group and imidazole ligand. But because we can not get accurate hydrogen positions from X-ray data, it is hard to tell its strength. Such interactions are common in biological systems,^[8] and could contribute to stabilize the orientation of this imidazole ligands could be related to the porphyrin core conformation. *Patra* et al. have recently reported porphyrin nonplanarity may have some influence on the stabilization of parallel axial orientations.^[29] In our case, the porphyrin core has slightly ruffling conformation, which may contribute to the parallel axial orientation.

¹H NMR Spectroscopy

¹H NMR spectra were measured and are shown in Figure 5. For H₂ENTTP and H₃CNTTP, the signals of eight protons are located at around 8.6-8.8 ppm, which are similar to the corresponding values for meso-5,10,15,20-tetraphenylporphyrin. So they are assigned to pyrrole protons. The 2:1:1 ratio of pyrrole protons is consistent with the low symmetry related to the 1:3 ratio of naphthyl to phenyl substituents on the meso-positions. For H₂ENTTP, there are two resonances at 0.48 and -0.68 ppm, which are similar to those for 5-(8-ethoxycarbonyl-1-naphthyl)-10,15,20-triphenyl-porphyrin.^[4] So they are assigned to the ethyl protons, which are shifted upfield by 3.98 and 2.12 ppm comparing with naphthalene-1-carboxylic acid ethyl ester.^[30] It suggests the ethyl group is located above the porphyrin plane in solution, the shielding effect of the ring current causes such upfield shifts. When it is hydrolyzed, the resonances of ethyl group disappeared, instead a signal at $\delta = 10.35$ ppm appeared, which is assigned to the COOH proton.

For the paramagnetic Fe^{III} species, the signals are broader and expanded. For typical five-coordinate high-spin (tetraphenyl-porphyrinato)iron(III) complex, the pyrrole protons signals are around 80 ppm.^[31] In our case for both [Fe(HCNTTP)Cl] and [Fe(CNTTP)]₂, the spectra show resonances in the far-downfield region at 79.49 or 78.91 ppm, which are assigned to the pyrrole protons.

For [Fe(CNTTP)(N-MeIm)₂] as a low-spin iron(III) porphyrinates, the NMR spectrum is much different from the above high-spin species. The above mentioned three types of low-spin iron(III) porphyrinates have distinguished NMR properties. For type I, NMR spectra show pyrrole-H resonances in the -10 to -20 ppm range. In comparison, type II centers have NMR spectra including pyrrole-H resonances in the -15 to -30 ppm region. Type III centers have NMR spectra including pyrrole-H resonances in the 0 to 10 ppm region.^[22] In our case, the ¹H NMR spectrum of [Fe(CNTTP)(N-MeIm)₂] has shown four well resolved pyrrole-H resonances at -10.22, -11.98, -22.29, and -25.01 ppm (Figure 5), which is very similar to those signals of [(2,3-MoOL)(TTP)Fe^{III}(N-MeIm)₂]⁻ (a type II species).^[31,32] So their resonances are assigned to

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Figure 5. ¹H NMR spectra of (a) H_2ENTTP in CDCl₃, (b) H_3CNTTP in [D₆]DMSO, (c) [Fe(HCNTTP)Cl] in CDCl₃, (d) [Fe(CNTTP)]₂ in CDCl₃, (e) [Fe(CNTTP)(N-MeIm)₂] in CDCl₃ at 293 K. X: signal from impurity.

pyrrole protons. The experimental results from both the structural features and NMR spectroscopic data confirm [Fe(CNTTP)(N-MeIm)₂] is a type II species.(vide supra)

EPR Study

The above mentioned three types of low-spin iron(III) porphyrinates have also distinguished EPR properties. Type I centers are characterized by "large g_{max} " EPR spectra with g > 3.3 in most cases; type II centers have well-resolved rhombic EPR spectra; type III centers have axial EPR spectra with $g_{\perp} = 2.6$ (or smaller) and $g_{\parallel} = 0.9-1.95$ (but with g_{\parallel} often not resolved). As shown in Figure 6, in our case, the EPR spectrum of polycrystalline sample of [Fe(CNTTP)(N-MeIm)₂]

shown typical rhombic spectrum with $g_1 = 1.67$, $g_2 = 2.31$, $g_3 = 2.86$. Some small bumps could be caused by some impurities. The solution EPR in CH₂Cl₂ was measured (see Supporting Information), it also shows the rhombic spectrum. But there is an extra resonance at g = 6.20. It suggests that the dissociation occurs in the solution, which leads to high-spin iron(III) species. These g values for the rhombic spectrum are similar to those for [Fe(TPP)(HIm)₂]⁺ ($g_1 = 1.59$, $g_2 = 2.32$, $g_3 = 2.84$),^[33] [Fe(TPP)(4-MeHIm)₂]⁺ ($g_1 = 1.82$, $g_2 = 2.24$, $g_3 = 2.60$),^[34] [Fe(TFPPCl₈)(Im)₂]ClO₄ ($g_1 = 1.57$, $g_2 = 2.30$, $g_3 = 2.88$),^[29] and *para*-[Fe(TMP)(5-MeHIm)₂]ClO₄ ($g_1 = 1.66$, $g_2 = 2.38$, $g_3 = 2.72$).^[27] Those complexes are all type II species, it further confirms [Fe(CNTTP)(N-MeIm)₂] is a type II species.



Figure 6. X-band EPR spectrum of polycrystalline sample of [Fe(CNTTP)(N-MeIm)₂] at 77 K.

Conclusions

H₃CNTTP and its iron complexes were synthesized and characterized. The X-ray crystal structures of [Fe(CNTTP)]₂ and [Fe(CNTTP)(N-MeIm)₂] revealed that the carboxylate group is "hanging" over the porphyrin plane. Such group can not coordinate to iron in the same porphyrin, but can coordinate to iron in symmetry-related porphyrin, which is the case for [Fe(CNTTP)]2. When excess N-methylimidazole was used, six-coordinate species, [Fe(CNTTP)(N-MeIm)2], was obtained. In such structure, CH···O interactions between the carboxylate group and imidazole play an important role to determine the orientation of imidazole plane. One the other hand, the ruffling core conformation could contribute to the parallel axial orientation of two imidazole ligands. All the X-ray crystallography, ¹H NMR, and EPR spectroscopy confirm that [Fe(CNTTP)(N-MeIm)₂] is a type II low-spin iron(III) porphyrinate.

Experimental Section

The ¹H NMR spectra were recorded with a Bruker AVANCE 400 spectrometer in the solvents indicated with tetramethylsilane (TMS) as the internal standard at 293 K. Chemical shifts are expressed in ppm rela-

tive to chloroform (δ = 7.26 ppm) or dimethyl sulfoxide (δ = 2.50 ppm). UV/Vis spectra were measured with a Shimadzu UV-3150 spectrometer. FT-IR spectra were recorded with a Varian Scimitar 1000 spectrometer. Mass spectra were taken with a Agilent 6220 Accurate-Mass TOF LC/MS. EPR spectrum of polycrystalline sample of [Fe(CNTTP)(N-MeIm)₂] was obtained with a EMX 10/12 EPR spectrometer operating at X band at 77 K at Nanjing University. Molar conductivity was measured with a Mettler Toledo Conductivity Meter FE30 at 288 K. Methylene chloride was distilled over CaH₂, and THF was distilled over sodium. All other chemicals and solvents were of analytical grade available commercially and were used as received.

H2ENTTP: The free-base porphyrin ligand 5-(8-ethoxycarbonyl-1naphthyl)-10,15,20-tritolyl porphyrin (H2ENTTP) were prepared according to our previous method.^[14] The reaction was carried out under anaerobic condition. Acenaphthenequinone (1.26 g, 6.9 mmol), pmethyl benzaldehyde (2.5 mL, 21 mmol) and pyrrole (1.9 mL, 28 mmol) were dissolved in a solution of ethanol in chloroform (7%, 500 mL). BF₃·OEt₂ (1.0 mL, 7.9 mmol) was added to the above solution and stirred for 1 h at room temperature, afterwards tetrachloro-1,4benzoquinone(6.81 g, 27.6 mmol) was added. After 2 h under reflux, triethylamine (4.0 mL) was added, and the mixture was stirred for another half hour. When it was cooled down to room temperature, it was filtered by sintered glass funnel. The filtrate was rotoevaporated to dryness. The black solid was further purified by column chromatography (silica, CH_2Cl_2 /petroleum ether = 1:1). The second purple band was collected, and the solvents evaporated to dryness. Purple product was obtained, yield 0.36 g (6.9%). ¹H NMR (400 MHz. CDCl₃; Me₄Si): $\delta_{\rm H}$ = 8.92 (s, 4 H, pyrr-H), 8.85 (s, 2 H, pyrr-H), 8.67 (s, 2 H, pyrr-H), 8.30-8.07 (m, 9 H), 7.86 (t, J = 7.5 Hz, 1 H), 7.59 -7.54 (m, 7 H), 7.38 (d, J = 6.7 Hz, 1 H), 2.74 (s, 3 H, phenyl-CH₃), 2.71 (s, 6 H, phenyl-CH₃), 0.48 (s, 2 H, CH₂CH₃), -0.68 (t, J = 7.1 Hz, 3 H, CH₂CH₃), -2.56 (s, 2 H, NH) ppm. **IR** (KBr): $\tilde{v} = 3437$ (m), 3319 (m), 2920 (m), 2850 (m), 1724(s), 1630 (m), 1559 (m), 1506 (m), 1473 (m), 1401 (m), 1347 (m), 1275 (m), 1195 (s), 1146 (m), 1105 (m), 1024 (m), 972 (s), 800 (s), 735 (s), 522 (w) cm $^{-1}$. UV/Vis (CH_2Cl_2) : λ_{max} , (M⁻¹·cm⁻¹): 422 (6.58 × 10⁵), 519 (2.74 × 10⁴), 554 (1.46 × 10⁴), 593 (1.04×10^4), 650 (7.78×10^3) nm. LC-ESI-MS: m/z calcd. for C₅₄H₄₂N₄O₂ 778.33 found 779.33 [M + H]⁺. C₅₄H₄₂N₄O₂•0.7CH₂Cl₂: calcd. C 78.36; H 5.22; N 6.68%; found C 78.28; H 5.40; N 6.38%.

H₃CNTTP: H₂ENTTP (0.30 g, 0.39 mmol) was dissolved in glacial acetic acid (16.8 mL), deionized water (6 mL) and concentrated sulfuric acid (6 mL) were added. The bright green solution was stirred at 388 K for 3 d. Afterwards, CHCl₃ (50 mL) was added to the mixture, and the solution was washed with water. The organic layer was collected, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was purified on silica gel with dichloromethane/ methanol (98:2) to give light purple solid. Yield 0.27 g (93.4%). ¹H **NMR** (400 MHz, [D₆]DMSO) : $\delta_{\rm H}$ = 10.35 (s, 1 H, COOH), 8.80 (s, 4 H, pyrr-H), 8.68 (s, 2 H, pyrr-H), 8.53 (s, 2 H, pyrr-H), 8.43 (d, J = 6.5 Hz, 1 H), 8.36 (d, J = 7.6 Hz, 1 H), 8.29 (d, J = 0.8 Hz, 1 H), 8.19-7.84 (m, 7 H), 7.73-7.43 (m, 7 H), 7.39 (s, 1 H), 2.60 (s, 9 H, phenyl-CH₃), -2.72 (s, 2 H, NH) ppm. **IR** (KBr): $\tilde{v} = 3429$ (m), 3317 (m), 3124 (w), 3044 (w), 3021 (w), 2921 (m), 2849 (w), 1709 (s), 1558 (m), 1507 (m), 1472 (m), 1346 (m), 1298 (m), 1223 (m), 1183 (m), 1151 (m), 1022 (m), 971 (m), 800 (s), 733 (s), 523 (m) cm⁻¹. UV/ **Vis** (CH₂Cl₂); λ_{max} , (M⁻¹·cm⁻¹): 422 (6.55×10⁵), 519 (2.54×10⁴), 555 (1.30×10^4) , 593 (8.64×10^3) , 650 (6.28×10^3) nm . LC-ESI-MS: m/z calcd. for C₅₂H₃₈N₄O₂ 750.30; found 751.30 [M + H]⁺. C₅₂H₃₈N₄O₂•0.6CH₂Cl₂: calcd. C 78.79; H 4.93; N 6.99%; found C 78.36; H 4.98; N 7.15%.

[Fe(HCNTTP)CI]: To the mixture of anhydrous FeCl₂ (1.74 g, 8.75 mmol) and H₃CNTTP (0.3 g, 0.4 mmol) in anhydrous tetrahydrofuran (150 mL), 380 uL of pyridine was added. The mixture was heated under reflux for overnight. It was filtered and the crude product was further purified by silica gel chromatography [CH₂Cl₂/EtOAc(2:1)]. Yield 0.29 g (86.4%). **UV/Vis**(CH₂Cl₂); λ_{max} (M⁻¹·cm⁻¹): 420 (7.29 × 10⁴), 515 (1.04 × 10⁴), 587 (2.71 × 10³), 702 (2.41 × 10³) nm. **IR** (KBr): $\tilde{v} = 3427$ (m), 3048 (w), 3020 (w), 2962 (m), 2918 (w), 2850 (w), 1736(m), 1695 (w), 1577 (w), 1496 (m), 1448 (w), 1404 (w), 1331 (m), 1261 (s), 1181 (m), 1108 (m), 1021 (w), 997 (w), 873 (w), 807 (s), 722 (m), 622 (m), 525 (m) cm⁻¹. C₅₂H₃₆ClFeN₄O₂: calcd. C 74.34; H 4.32; N 6.67%; found C 74.58; H 4.52; N 6.59%.

[Fe(CNTTP)]₂: [Fe(HCNTTP)Cl] (0.30 g, 0.36 mmol) was dissolved in CH₂Cl₂ (100 mL), further washed by 2 mol·L⁻¹ NaOH for 4–6 times. The organic layer was collected, dried with sodium sulfate, and concentrated under reduced pressure. The residue was purified on silica gel with CH₂Cl₂/ dimethylformamide (95:5) to give the final compound (0.19 g, yield 66%). **IR** (KBr): $\tilde{v} = 3338$ (m), 3048 (w), 3020 (m), 2962 (m), 2919 (m), 2858 (w), 1811 (w), 1701 (m), 1649 (m), 1609 (w), 1529 (w), 1496 (m), 1448 (w), 1331 (m), 1261 (m), 1204 (m), 1094 (m), 1000 (s), 799 (s), 720 (m), 559 (m), 5111 (m) cm⁻¹. **UV**/ **Vis** (CH₂Cl₂); λ_{max} , (M⁻¹·cm⁻¹): 421 (2.28 × 10⁵), 508 (2.05 × 10⁴), 571 (9.74 × 10³), 658 (6.31 × 10³) nm. C₁₀₅H₇₄Fe₂N₈O₄·DMF: calcd. C 76.47; H 4.62; N 7.50%; found C, 76.12; H 4.24; N 7.48%. X-ray quality crystals were obtained by liquid diffusion of *n*-hexane into the CH₂Cl₂ solution in 8 mm diameter glass tubes.

[Fe(CNTTP)(N-MeIm)₂]: In a 10 mL flask, [Fe(HCNTTP)Cl] (100 mg, 0.12 mmol) was dissolved in methylene dichloride (5 mL). N-methylimidazole (98 mg, 1.2 mmol) was added to it, and the mixture was stirred for 30 min at room temperature. The resulting solution was concentrated and dissolved in chlorobenzene solution, filtered to remove any solid residue and carefully layered with n-hexane. Upon standing for 7-8 d, dark red crystalline solid was formed, which was collected by filtration, washed with *n*-hexane, and dried under vacuum. Yield: 63 mg (55%). **UV/Vis** (CH₂Cl₂); λ_{max} , (M⁻¹·cm⁻¹): 422 (1.06×10^5) , 553 (6.84×10^3) , 588 (4.32×10^3) , 648 (1.45×10^3) , 700 (7.57×10^2) nm. C₆₀H₄₇FeN₈O₂·0.5C₆H₅Cl: calcd. C 73.88; H 4.87; N 10.94%; found C 73.45; H 5.04; N 10.55%. IR (KBr): $\tilde{v} = 3406$ (m), 3127 (m), 3021 (m), 2918 (m), 2849 (m), 1806 (m), 1686 (m), 1630 (w), 1581 (m), 1508 (m), 1450 (m), 1420 (m), 1340 (m), 1284 (m), 1237 (m), 1205 (m), 1181 (m), 1096 (s), 1002 (s), 959 (m), 917 (w), 799 (s), 714 (m), 662 (m), 615 (m), 526 (m) cm⁻¹.

X-ray Crystallography: X-ray data collections were made with a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo- K_{α} ($\lambda = 0.071073$ nm) at 293(2) K. Both structures were solved by direct methods and refined on F^2 using full-matrix leastsquares methods with SHELXTL version 97.[35] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were idealized with the standard SHELXL-97 idealization methods. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates are given in the cif file. Both structures have badly disordered solvate molecules. SQUEEZE^[36] was used to model disordered solvate molecules. The residue electron count in the interporphyrins voids amounted to 24 electrons per unit-cell for $[Fe(CNTTP)]_2$ (corresponding roughly to 0.6 molecule of CH_2Cl_2 per porphyrin), 116 electrons per unit-cell for [Fe(CNTTP)(N-MeIm)₂] (corresponding to 0.5 molecule of chlorobenzene per porphyrin) A summary of the key crystallographic information of the complexes are given in Table 2.

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Iron(III) Complexes of 5-(8-Carboxy-1-naphthyl)-10,15,20-tritolyl Porphyrin

Table 2. Crystallographic data for [Fe(CNTTP)]₂ and [Fe(CNTTP)(N-MeIm)₂].

	[Fe(CNTTP)] ₂	[Fe(CNTTP)(N-MeIm)2]
Empirical formula	C ₁₀₄ H ₇₀ Fe ₂ N ₈ O ₄	C ₆₀ H ₄₇ FeN ₈ O ₂
Formula weight /g•mol ⁻¹	1607.38	967.91
<i>Т /</i> К	293(2)	293(2)
λ/Å	0.71073	0.71073
Space group	$P\bar{1}$	$P2_{1}/c$
a /Å	12.688(3)	16.890(3)
b /Å	12.854(3)	15.524(3)
<i>c</i> /Å	12.861(3)	24.498(8)
$a /^{\circ}$	86.48(3)	90
β /°	82.67(3)	124.35(2)
y /°	82.51(3)	90
$V/Å^3$	2060.5(8)	5303(2)
Ζ	1	4
$\rho / \text{g} \cdot \text{cm}^{-3}$	1.295	1.212
F(000)	834	2020
μ /mm ⁻¹	0.413	0.334
Data / restraints / param-	7158 / 0 / 536	9292 / 0 / 645
eters		
GOF	1.097	1.037
$R_1 \left[I > 2\sigma(I) \right]^{a}$	0.0812	0.0781,
$wR_2 [I > 2\sigma(I)]^{a}$	0.2494	0.2154
R_1 (all data) ^{a)}	0.1160	0.1205
wR_2 (all data) ^{a)}	0.2692	0.2420
Largest diff. peak and hole $/e^{A^{-3}}$	0.917 and -0.461	0.477 and -0.303

a) $w = 1/[\sigma^2 (F_0^2) + (aP)^2 + bP]$, where $P = (F_0^2 + 2F_c^2)^3$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-926708 and CCDC-926709. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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Iron(III) Complexes of 5-(8-Carboxy-1-naphthyl)-10,15,20-tritolyl Porphyrin



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Synthesis and Characterization of Iron(III) Complexes of 5-(8-Carboxy-1-naphthyl)-10,15,20-tritolyl Porphyrin

