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Journal of Porphyrins and Phthalocyanines

Article Title:	Temperature Effects on Structure: Five-Coordinate (Nitrosyl)(tetratolylporphinato)iron(II)		
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DOI:	10.1142/S1088424619501517		

To be cited as:

Nathan J. Silvernail, Allen G. Oliver, W. Robert Scheidt, Temperature Effects on Structure: Five-Coordinate (Nitrosyl)(tetratolylporphinato)iron(II), *Journal of Porphyrins and Phthalocyanines*, doi: 10.1142/S1088424619501517

Received: 20 August, 2019 Accepted: 4 October, 2019

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Temperature Effects on Structure: Five-Coordinate (Nitrosyl)(tetratolylporphinato)iron(II)

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Dedicated to Professor Roberto Paolese on the occasion of his 60th birthday

October 2, 2019

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[†]University of Notre Dame ^{*}To whom correspondence should be addressed **ABSTRACT:** We have prepared crystals of [Fe(TTP)(NO)] (TTP = tetratolylporphyrin), a five-coordinate nitrosyl complex and determined its crystal and molecular structure at two temperatures. The crystal structure at 100 K reveals two independent molecules in the asymmetric unit of structure. One molecule is completely ordered and the second molecule has a moderately disordered nitrosyl ligand. Both molecules show similar structural features: a substantial off-axis tilt of the Fe–N(NO) bond and an asymmetry of the equatorial Fe–N_p bonds that is correlated with the tilt. The axial Fe–N(NO) bond distances are 1.7230 (9) and 1.7210 (10) Å; the Fe–N–O bond angles are 141.62 (8) and 140.04 (10)°. Determination of the structure at ambient temperature (293 K) showed an unexpected phase change, a crystal structure with one molecule per asymmetric unit containing the superposition of the two molecules at lower temperature. However, there was an increase in the NO disorder.

KEYWORDS: Crystal structure, tetratolylporphyrin, iron(II), nitric oxide coordination, crystalline disorder, temperature effects.

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Introduction

Recent advances in X-ray instrumentation have led to substantially improved crystal structure determinations. Area detector technology leads to both rapid and precise x-ray intensity measurements. This data collection enhancement also led to an enhanced capability of easy data measurements at temperatures other than ambient and possibly at a number of different temperatures. Intensity data collection at lowered temperatures leads to molecular structures with reduced thermal motion, frequently reduced crystalline disorder and, in addition, generally improved structural data.

In this paper, we report the molecular structure of a five-coordinate nitrosyl derivative, (nitrosyl)(tetratolylporphinato)iron(II), a member of a class of species that has suffered from disorder involving the axial nitric oxide ligand. In general, there are two distinct geometries of the M–N–O group: linear and bent. In the systems with bent nitrosyls, for iron derivatives, the Fe–N–O angle is in the range of 140–150°. Apparent rotation of the nitrosyl group around the Fe–N(NO) bond leads to two or more positions of the nitrosyl oxygen atom. An early calculation by Hoffman et al. concluded that the rotation around the Fe–N(NO) bond was a relatively low energy process [1].

The early crystal structure determinations of iron porphyrinate nitrosyls all exhibited disorder with multiple positions of the coordinated NO. The first example was that of five-coordinate [Fe(TPP)(NO)] [2] with disorder that reflected both mirror and rotational disorder leading to eight equivalent oxygen atom positions. This disorder was so extreme that we called it the "hydra" [3]. Other five-coordinate systems also displayed substantial disordered FeNO fragments, i.e., $[Fe(TPPBr_8)(NO)]$ [4], [Fe(TpivPP)(NO)] [5] and $[Fe(TF_2PP)(NO)]$ [6].

The first characterized six-coordinate derivative, [Fe(TPP(1-MeIm)(NO)], also displayed a substantially disordered NO with two or three distinct oxygen atom locations [7, 8]. Subsequently, two crystalline forms of [Fe(TPP)(4-MePip)(NO)] were characterized; only one form had an ordered FeNO group [9]. Unfortunately, all of foregoing structures were limited in the detailed description of the FeNO group that could be provided. However, the six-coordinate

derivatives clearly showed that the NO group had a strong structural trans effect that led to long Fe–N bonds trans to the NO.

The impasse of limited and disordered NO structures was broken by the highly precise structures of [Fe(OEP)(NO)] [10]. Fortuitously, two crystalline polymorphs of the complex were obtained; both illustrated the same two striking features. The Fe–N(NO) axial bond was found to be tilted off-axis along with a concomitant asymmetry in the equatorial Fe– N_p bonds that tracked the off-axis tilt. These structural features were confirmed in other well-ordered structures: [Fe(0x0OEC)(NO)] [11] and three forms of $[Fe(TPPBr_4)(NO)]$ [11] and [Fe(OETAP)(NO)] [12]. The off-axis tilt appears to be an intrinsic feature of nitrosyl hemes. Similar structural features were seen for two naturally occurring nitrosyl porphyrinate derivatives: [Fe(DPIX-DME)(NO)] [13] and [Fe(PPIX-DME)(NO)] [14], although the latter species had a disordered NO group.

Later structural studies included variable temperature structure determinations that showed controlling crystal temperature provided much insight into NO disorder issues. Multiple temperature studies for [Fe(TPP)(NO)] showed that the crystals underwent a phase change that decreased, but did not eliminate, NO disorder [15]. More informative still, were temperature dependent studies on several six-coordinate derivatives Fe(Porph)(1-MeIm)(NO)] [16, 17].

Two crystalline forms of [Fe(TpFPP)(1-MeIm)(NO)] and $[Fe(TpOCH_3PP)(1-MeIm)(NO)]$ were found to have a single orientation of the FeNO group at 100 K, $[Fe(TpOCH_3PP)(1-MeIm)(NO)]$ meIm)(NO)] was almost completely ordered at 100 K, whereas [Fe(TPP)(1-MeIm)(NO)] and $[Fe(TpNO_2PP)(1-MeIm)(NO)]$ were found to have substantial disordered FeNO groups even at 100 K. ALL however became more disordered when the temperatures were raised to ambient. Some remained ordered up to a critical temperature below ambient. For systems where the structure was determined at several temperatures, the disorder increase was linear in temperature after a certain critical temperature was reached. The papers cited [16, 17] concluded that the temperature dependent NO orientation effects were the result of temperature-dependent crystal packing. Analysis of the structural data suggested that in, at least some derivatives, there was a controlled precise pathway for NO movement. Finally, a van't Hoff analysis of the temperature-dependent data allowed for an approximation to the energy difference between the most stable state (orientation) and a less energetically stable minor orientation; the free energy differences were between 2 and 4 kJ/mol.

A study of the Mössbauer spectral differences between five- and six-coordinate iron nitrosyls [18] led us to measure temperature-dependent Mössbauer spectra for several five-coordinate nitrosyl derivatives. The area under the Mössbauer absorption curve was found to have, unexpectedly, a very strong temperature dependence for the three different tetraarylporphyrin derivatives measured: [Fe(TPP)(NO)], [Fe(TTP)(NO)], and [Fe(TMP)(NO)] [19]. These results led to our initial investigation of the nuclear resonance vibrational spectra (NRVS) of [Fe(TPP)(NO)] [20, 21] and to a subsequent study of the combined use of temperature-dependent Mössbauer and NRVS to examine the dynamics of disorder of the [Fe(TPP)(NO)] and [Fe(OEP)(NO)] systems [22].

To further assist in these studies, we have attempted to determine the molecular structures of additional five-coordinate nitrosyls, especially those with tetraaryl peripheral substituents in order to better understand any disorder and its possible relation to the dynamics of the systems. Obtaining adequate crystalline material has turned out to be more challenging than might have been expected. In this paper, we report the molecular structure of the one such species we have obtained, that of [Fe(TTP)(NO)], at 100 K. The system was found to crystallize in the triclinic crystal system (*P*1) with two molecules in the asymmetric unit, one molecule exhibited nitrosyl disorder while the other was ordered. We explored a possible increase in disorder by studying the crystalline derivative at ambient temperature that revealed an unexpected result. There is an apparent increase in crystalline disorder with the two independent low temperature molecules merged into an apparent single entity. The disorder in the nitrosyl ligand is indeed increased at the higher temperature.

EXPERIMENTAL SECTION

Synthesis and Crystallization of [Fe(TTP)(NO]]. All reactions and manipulations were carried out under argon using a double manifold vacuum line, Schlenkware, and cannula techniques. [Fe(TTP)Cl] was prepared using the metallation method described by Adler [23]. A mixture of H₂TTP (1.51 g, 2.4 mmol) and FeCl₂ (0.7g, 5.5 mmol) in DMF (75 mL) was refluxed, the reaction was monitored using UV-visible spectroscopy. After the reaction was finished, the solution was cooled to room temperature and methanol was added to the residue upon removal of the solvent under vacuum and then filtered. The obtained solid was washed with warm methanol until the filtrate was colorless and dried under vacuum. [Fe(TTP)(NO]] was then prepared using the reported reductive nitrosylation procedure of Scheidt and Frisse for [Fe(TPP)(NO)] [3]. The reaction solution was purged with NO for 30 min. The solution was then cannula-transferred into 8 mm glass tubes, carefully layered with methanol, and the tubes were flame sealed. X-ray quality crystals of [Fe(TTP)(NO)] were isolated after several days. IR $(Nujol) \nu(NO)$ 1670 cm⁻¹.

Structure Determinations. A crystal of [Fe(TTP)(NO)] was glued to the end of a glass fiber and intensity data collected at 100 K. The structure was solved in the space group $P\overline{1}$ by direct methods with the SHELXS program [24]. There are two independent molecules in the asymmetric unit of structure. One molecule was completely ordered whereas the second molecule was disordered, displaying two positions of the nitrosyl oxygen atom, separated by about 0.8 Å. We then determined the structure at ambient temperature, in order to explore issues of further disorder of the nitrosyl group. Quite unexpectedly, the crystals were found to undergo a phase change with a single molecule in the asymmetric unit. All structures were refined against F² by the SHELXL program [24]. A summary of crystal data and data collection parameters are shown in Table 1.

	[Fe(TPP)(NO)]-100K	[Fe(TPP)(NO)]-293K		
formula				
FW	754.67		754.67	
$a, \mathrm{\AA}$	10.6302(3)		10.7259(3)	
b, Å	13.0675(4)		13.1609(4)	
$c, \mathrm{\AA}$	27.3903(8)		14.2790(4)	
α	80.473(2)		107.197(2)	
β , deg	80.3610(10)		94.252(2)	
γ	81.629(2)		96.362(2)	
$V, Å^3$	3672.06(19)		1901.52(10)	
Z	4		2	
space group	$P\bar{1}$		$P\bar{1}$	
$D_c, \mathrm{g/cm^3}$	1.365		1.318	
F(000)	1572		786	
μ , mm ⁻¹	0.457		0.441	
crystal dimens, mm		$0.466 \times 0.302 \times 0.302$	0.299	
absorption correction		multiscan		
radiation, MoK α , $\bar{\lambda}$		0.71073 Å		
T, K	100(2)		293(2)	
total data collected	159016		157104	
unique data	$35954 \ (R_{\rm int} = 0.0310)$		13186 ($R_{\rm int} = 0.0232$)	
unique obsd data[I > 2 σ (I)]	26371		10689	
refinement method		on F^2 (SHELX	L)	
final R indices $[I > 2 \sigma(I)]$	$R_1 = 0.0409, wR_2 = 0.0$)994	$R_1 = 0.0389, wR_2 = 0.1004$	
final R indices [for all data]	$R_1 = 0.0.0674, wR_2 = 0$).1148	$R_1 = 0.0565, wR_2 = 0.1205$	

 Table 1. Brief Crystallographic Data and Data Collection Parameters

RESULTS

The crystal and molecular structure of the nitrosyl complex [Fe(TTP)(NO]] is reported at low (100 K) and ambient temperatures. The two independent molecules characterized at 100 K are shown in Figures 1 and 2. The disorder in the NO group in molecule 2 is clearly apparent. The refined values for the occupancies of the two oxygen atoms are 0.823 (4) and 0.177 (4), so that one oxygen atom position is dominant; the two oxygen atoms are separated by ~0.8 Å.



Figure 1. Thermal ellipsoid plot of [Fe(TTP)(NO] (molecule 1) at 100 K showing atomic labels. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Figure 2. Thermal ellipsoid plot of $[Fe(TTP)(NO] \pmod{2} at 100 \text{ K}$ showing atomic labels. Ellipsoids are drawn at the the 50% probability level. Hydrogen atoms have been omitted for clarity.

DISCUSSION

We first consider the coordination features of the iron and the FeNO group for the structural results obtained at 100 K for [Fe(TPP)(NO)]. The two molecules clearly show the structural features of a low-spin state. Although the second molecule has a disordered nitrosyl ligand, the occupancy of the minor oxygen atom is relatively small at 0.177 (4). Accordingly, we will use the major oxygen atom position for describing the geometrical parameters of molecule 2. Table 2 summarizes a number of stereochemical parameters of five-coordinate nitrosyls. These include bond angle (Fe–N–O), bond distances (Fe–N(NO) and N–O), iron displacements from 24-atom plane (Δ Fe(Ct)), and four nitrogen plane (Δ Fe(N₄)), the orientation of NO (dihedral angle between FeNO and the closest Fe–N_p vector) and the tilt of the Fe–N(NO) bond vector from the normal to the porphyrin plane. The values for the 100 K structure of [Fe(TPP)(NO)] are seen to be similar to all others in Table 2 with one possible significant difference. The iron displacements in [Fe(TPP)(NO)] from the 24-atom plane are slightly larger and suggest that this is a feature of the tetraaryl derivatives.

Table 2. Bonding parameters for [Fe(Porph)(NO)] complexes.

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Complex	${\rm Fe-N-O}^a$	$\Delta \mathrm{Fe}(\mathrm{Ct})^{b,c}$	$\Delta \mathrm{Fe}(\mathrm{N}_4)^{b,d}$	$Fe-N(NO)^b$	$\mathrm{N-}\mathrm{O}^{b}$	$\operatorname{orientation}^{a,e}$	$\operatorname{tilt}^{a,f}$	$\Delta N(NO)^{b,g}$	ref.
$[Fe(TTP)(NO)](mol 1)^h$	141.62(8)	0.33	0.29	1.7247(9)	1.1730(13)	43.8	9.6	0.34	tw
$[Fe(TTP)(NO)](mol 2)^h$	140.04(10)	0.35	0.29	1.7210(10)	1.1817(16)	45.0	9.1	0.33	tw
$[Fe(TTP)(NO)]^i$	141.6(5)	0.35	0.29	1.7160(13)	1.158(8)	28.9	8.3	0.25	tw
[Fe(OEP)(NO)] (A)	144.4(2)	0.29	0.28	1.722(2)	1.167(3)	37.9	6.5	0.19	11
[Fe(OEP)(NO)] (B)	142.74(8)	0.27	0.28	1.7307(7)	1.1677(11)	40.2	8.2	0.25	11
$[Fe(TPPBr_4)(NO)](\mathbf{A'})$	147.9(8)	0.37	0.31	1.734(8)	1.119(11)	0.0	5.6	0.17	11
$[\mathrm{Fe}(\mathrm{TPPBr}_4)(\mathrm{NO})]~(\mathbf{A}'')$	146.9(9)	0.32	0.30	1.726(9)	1.144(12)	0.0	7.1	0.21	11
$[Fe(TPPBr_4)(NO)]$ (B)	145(1)	0.29	0.28	1.691(11)	1.145(16)	18.4	_	_	11
[Fe(TPP)(NO)]	145.6(4)	0.20	-	1.740(5)	1.153(4)	$_k$	5.8	_	15
[Fe(DPIX-DME)(NO)]	143.1(3)	0.26	0.26	1.723(3)	1.187(4)	35.0	6.2	—	13
[Fe(PPIX-DME)(NO)]	143.4(6)	0.29	0.26	1.719(4)	1.140(8)	36	$_k$	—	14
[Fe(3,5-MeBAFP)(NO)] (A)	146.3(4)	0.35	—	1.713(4)	1.149(5)	~ 0	$_k$		25
[Fe(3,5-MeBAFP)(NO)] (B)	146.6(5)	0.37	—	1.714(4)	1.142(5)	~ 0	$_k$		25
[Fe(oxoOEC)(NO)]	143.11(15)	0.26	0.26	1.7320(13)	1.1696(19)	40.9	7.1	0.22	11
[Fe(OETAP)(NO)]	143.7(4)	0.31	-	1.721(4)	1.155(5)	39.6	7.6	0.23	12

^aValue in degrees. ^bValue in A. ^cIron atom displacement from 24-atom mean plane. ^dIron atom displacement from four nitrogen atom plane. ^eMinimum dihedral angle between Fe–N–O and N_p–Fe–N(NO) planes. ^fDeviation from normal to 24-atom mean plane. ^gTranslation of the nitrosyl nitrogen atom off the heme normal. ^h100 K. ⁱ293 K. ^j90 K. ^kNot reported.

Earlier studies had shown that the nitric oxide ligand led to intrinsic structural distortions in nitrosyl iron porphyrinates [10, 11]. Typically these features include a substantial off-axis Fe–N(NO) tilt (tabulated in Table 2) and an asymmetry in the equatorial Fe–N_p bond distances that is correlated with the Fe–N–O orientation. The difference in the bond distances are statistically significant in all of the structures tabulated in Table 3. The pattern of correlated "long" and "short" Fe-N_p bond distances is seen to hold even though there is substantial variation in bond distances amongst the several complexes of Table 3.

Table 3 . Equatorial Fe–N _p Bond Distances	(Å	r)	a
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-	1				
Complex	${ m Fe-N(1)}$	$\rm Fe-N(2)$	Fe-N(3)	Fe-N(4)	ref.
$[Fe(TTP)(NO)](mol 1)^b$	1.9647(8)	1.9580(9)	1.9885(9)	1.9871(9)	tw
$[\mathrm{Fe}(\mathrm{TTP})(\mathrm{NO})](\mathrm{mol}\ 2)^b$	1.9683(8)	1.9650(8)	1.9881(9)	1.9878(9)	tw
$[Fe(TTP)(NO)]^c$	1.9669(11)	1.9654(11)	1.9872(12)	1.9820(11)	tw
$[\mathrm{Fe}(\mathrm{OEP})(\mathrm{NO})]~(\mathbf{A})$	2.016(2)	1.989(2)	1.993(2)	2.017(2)	11
$[\mathrm{Fe}(\mathrm{OEP})(\mathrm{NO})]~(\mathbf{B})$	2.0226(6)	2.0000(6)	1.9985(6)	2.0167(6)	11
[Fe(oxoOEC)(NO)]	2.0174(13)	2.0141(12)	2.0082(13)	1.9974(12)	11
$[\mathrm{Fe}(\mathrm{TPPBr}_4)(\mathrm{NO})]~(\mathbf{A}')$	2.031(8)	1.976(5)	2.041(9)	$_d$	11
$[\mathrm{Fe}(\mathrm{TPPBr}_4)(\mathrm{NO})]~(\mathbf{A}'')$	2.004(7)	1.977(6)	2.027(7)	$_d$	11
$[Fe(TPPBr_4)(NO)]$ (B)	1.976(6)	1.926(7)	_e	$_d$	11
[Fe(DPIX-DME)(NO)]	1.991(3)	2.005(3)	2.034(3)	1.987(3)	13
[Fe(OETAP)(NO)]	1.938	1.922	1.925	1.941	12

^aEstimated standard deviations of least significant digits are given in parentheses. The effects of NO tilt on the Fe–N_p bond distances are indicated as follows: those expected to be "long" are indicated in bold type, those expected to be "short" are given in italic type and those that are not expected to be affected are given in Roman type. ^b100 K. ^c293 K. ^dEqual to Fe–N(2) by symmetry. ^eEqual to Fe–N(1) by symmetry. The two independent porphyrin planes are nearly coplanar; the dihedral angle between the mean planes of molecule 1 and molecule 2 is $3.44(1)^{\circ}$. Strikingly, the two cores are both strongly ruffled. Even more striking is the quantitative similarity. The displacements of the core atoms from the mean plane of the 24-atom core in the two molecules are shown in Figures 3 and 4. The two diagrams are oriented with respect to the position of the bent axial FeNO group and the quantitative similarity is apparent. The largest difference between the two molecules is the nitrosyl ligands, one ordered and the other disordered.



Figure 3. Formal diagram of the porphinato core in molecule 1 of [Fe(TTP)(NO)] displaying the displacement of each atom, in units of 0.01 Å, from the 24-atom mean plane. The position of the NO ligand is shown by the solid line. Averaged bond distances and angles for the core atoms are also displayed, the numbers in parentheses are the estimated standard uncertainties calculated on the assumption that all values are drawn from the same population.



Figure 4. Formal diagram of the porphinato core in molecule 2 of [Fe(TTP)(NO)] displaying the displacement of each atom, in units of 0.01 Å. from the 24-atom mean plane. The position of the NO ligand is shown by the solid line. Averaged bond distances and angles for the core atoms are also displayed, the numbers in parentheses are the estimated standard uncertainties calculated on the assumption that all values are drawn from the same population.

The determination of the structure at 293 K led to an additional surprise. Increasing the temperature for crystalline [Fe(TPP)(NO)] might have been expected to simply increase the nitrosyl disorder. This was not observed. Rather, the crystalline system undergoes a phase change, and the unit cell volume has decreased by slightly less than half that observed at 100 K. The new asymmetric unit contains a single molecule with two oxygen atom positions, one with a fairly large thermal parameter. Unexpectedly, the structure observed in the asymmetric unit is the superimposed pair of independent molecules observed at 100 K as illustrated in Figure 5. Although the issue is somewhat clouded by the new single-molecule asymmetric unit, the disorder of the NO group has increased. Previous iron porphyrinate nitrosyls studies show that a NO orientation approximately midway between two adjacent Fe–N_p bonds is the most favorable. At 100 K, one [Fe(TTP)(NO)] molecule has this orientation at 100% occupancy and

the second at 82% occupancy. For the merged molecule at 293 K, the preferred orientation has only a 43% occupancy.



Figure 5. Thermal ellipsoid plot of the molecule in the asymmetric unit of structure at 293 K. (50% probability ellipsoid s are shown.) Hydrogen atoms are omitted for clarity.

What has led to these differences? We note that the difference in crystal density at the two temperatures is larger than typical in our experience (see Table 1). This suggests that there is an increase in crystal packing efficiency at lower temperature, but without substantial change in the molecular structure. This may be borne out by examining the detailed differences in conformation at the two temperatures. Figure 6 displays the overlay of the two molecules at 100 K with the ambient structure. The very close overlap is clear, but with one peripheral phenyl group showing differences. The effects of the differing NO orientation are not expected to influence the packing.



Figure 6. An overlay of the two independent molecules at 100 K (light and dark blue) with the ambient temperature structure displayed in red. Illustration produced with MERCURY.

SUMMARY and CONCLUSIONS

The crystal and molecular structure of five-coordinate [Fe(TTP)(NO)] at two temperatures (100 and 293 K) reveals that the species show the unsupported off-axis tilt of the NO ligand and the concomitant asymmetry in the Fe–N_p bond distances of the equatorial plane. The two independent molecules observed at 100 K merge into a single molecule at 293 K with a phase change and increased NO disorder.

Acknowledgments

We thank the National Institutes of Health for support of this research under Grant GM–38401.

Supporting Information

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC 1947566 and 1947567. Copies can be obtained on request, free of charge, via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

References and Notes

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- 2. The following abbreviations are used in this paper: Porphyrins: Porph, generalized porphyrin dianion; TPP, dianion of dianion of 5,10,15,20-tetraphenylporphyrin; TTP, dianion of 5,10,15,20-tetratolylporphyrin; TpivPP, dianion of α,α,α,α-tetrakis(o-pivalamido-phenyl)porphyrin or picket fence porphyrin; TPPBr₈, ianion of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin; TpFPP), dianion of 5,10,15,20-tetrapfluorphenylporphyrin; TpOCH₃PP, dianion of 5,10,15,20-tetrap-methoxyphenylporphyrin; TMP, dianion of 5,10,15,20-tetramesitylporphyrin; 3,5-MeBAFP, dianion of 3,5-methyl-bis(aryloxy)-fence porphyrin; TF₂PP, dianion of 5,10,15,20-tetra-2,6-difluorophenylporphyrin; TPPBr₄, dianion of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin; PPIX-DME, dianion of protoporphyrin IX dimethylester; DPIX-DME, dianion of deuteroporphyrin IX dimethylester; OEP, dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraazaporphyrin; oxoOEC, dianion of 3,3,7,8,12,13,17,18-octaethyl-(3H)-porphin-2-onato(2-); 1-MeIm, 1-methylimidazole; 4-MePip, 4-methylpirperidine; N_p, porphyrinato nitrogen;
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Tables

Table 1. Crystallographic data.

Table 2. BD

Table 3. asymmetry

Captions for Figures

Figure 1. ORTEP Complete figure caption given in the text.

Figure 2. ORTEP Complete figure caption given in the text.

Figure 3. Complete figure caption given in the text.

Figure 4. Complete figure caption given in the text.

Figure 5. Packing figure caption given in the text.

Figure 6. ocwelay diagram

Captions for Supporting Information Figures

Figure S1. Figure of Alt ORTEP