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Dynamics of NO Motion in Solid-State [Co(tetraphenylporphinato)(NO)]

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The temperature dependence of the crystalline phase of (nitrosyl)(tetraphenylporphinato)cobalt(II), [Co(TPP)(NO)], has been explored over the temperature range of 100−250 K by X-ray diffraction experiments. The crystalline complex is found in the tetragonal crystal system at higher temperatures and in the triclinic crystal system at lower temperatures. In the tetragonal system, the axial ligand is strongly disordered, with the molecule having crystallographically required 4/m symmetry, leading to eight distinct positions of the single nitrosyl oxygen atom. The phase transition to the triclinic crystal system leads to a partial ordering with the molecule now having inversion symmetry and disorder of the axial nitrosyl ligand over only two positions. At an intermediate temperature near the transition point, a transition structure in which the ordering observed at lower temperatures is only partially complete has been characterized. The increase in ordering allows subtle molecular geometry features to be observed. The transition of the reversible phase change begins at about 195 K. This transition has been confirmed by both X-ray diffraction studies and a differential scanning calorimetry study.

Introduction

Nitrosyl metalloporphyrin systems are studied because of the known importance of NO as a sensor molecule[1] in functions such as cardiovascular regulation,[2,3] smooth muscle relaxation,[4] and neuromodulation.[5] Nitric oxide is produced in the body by oxidation of L-arginine to citrulline and NO by the hemoprotein nitric-oxide synthase.[6] A key step in many NO processes is the binding of NO to the heme protein and the subsequent formation of a five-coordinate species through loss of the ligand trans to the NO. Over the last three decades, many five-coordinate nitrosyl iron and cobalt porphyrinate compounds have been synthesized and characterized. In the iron(III) porphyrinates, the NO coordinates to the metal center in a linear fashion.[7,8] In iron(II) and cobalt(II) metalloporphyrins, however, NO is coordinated in a bent fashion. Such complexes are sometimes ordered,[9−12] sometimes have 2-fold disorder,[13−17] and sometimes have 8-fold disorder.[18−20] It is the last of these possibilities that is examined in this study. The analysis of these systems has led to insight into the dynamics of NO in crystalline porphyrin derivatives.

Recently, a temperature-dependent, crystallographic phase change was discovered in the five-coordinate nitrosyl metalloporphyrin, [Fe(TPP)(NO)].[20−22] At room temperature, this compound crystallizes in the tetragonal $I4/m$ space group, with 8-fold disorder of the nitrosyl group. It was found that upon cooling, the structure rearranges into a more ordered, lower symmetry $P\bar{1}$ space group. Upon cooling, the volume

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(21) The temperature of the phase change in [Fe(TPP)(NO)] was gauged to be close to 250 K by X-ray powder diffraction and DSC. However, the single crystal patterns show maxima for both phases from ∼190 to ∼260, and a single crystal data set was not collected.
(22) Abbreviations used in this paper. Por, generalized porphyrin dianion; TPP, dianion of tetraphenylporphyrin, T(p-OCH$_3$)PP, dianion of tetra-*para*-methoxyporphyrin; OEP, dianion of octaethylporphyrin; OC2OPor, dianion of 5,10,15,20-(benzene-1,2,4,5-tetrakis(2-phenyloxy)ethoxy)-2′,2′′,2′′′,2′′′′-tetrarylporphyrin.

of [Fe(TPP)(NO)] decreases similarly to that of several six-coordinate [Fe(Por)(NO)(L)] species that fail to undergo a phase change.[23] Study of the energetics of these six-coordinate species also shows that a lower barrier to rotation exists in these species at higher temperature than at low temperature.[24] This observation helps to explain why disorder is observed in some nitrosyl species at higher temperature.

[Co(TPP)(NO)], first synthesized in 1973,[18] exhibits the same disorder as the [Fe(TPP)(NO)] system at room temperature. Observed crystallographic disorder of the nitrosyl groups can be due to either a static disorder, in which one of the possible nitrosyl positions is occupied at each crystallographic site, or to dynamic movement of the nitrosyl group in the solid state. In 1992, Mason and co-workers found, through a solid-state nitrogen-15 NMR study of [Co(TPP)(NO)], that the nitrosyl disorder was most probably due to a swinging motion of the NO group.[25] This information, along with the results of the [Fe(TPP)(NO)] study, prompted a multiple-temperature crystallographic study of [Co(TPP)(NO)] to find details of the phase change in this species and whether the [Co(TPP)(NO)] crystallographic data supports dynamic NO motion in the crystalline solid.

[Co(TPP)(NO)] behaves similarly to [Fe(TPP)(NO)] and undergoes a crystallographic phase change from a disordered structure at high temperature to a more ordered structure at low temperature. Unlike [Fe(TPP)(NO)], the transition in the cobalt porphyrin system occurs over a relatively narrow temperature range and it was possible to solve the structure of this complex while it is trapped in a configuration intermediate to the low and high temperature forms. The three distinct structures for this system at multiple temperatures are reported herein. Additionally, whether the nature of the disorder in high temperature structures is static or dynamic is discussed. The possible cause of the crystallographic phase change was also studied through analysis of another *I*4/*m* metalloporphyrin, [Fe(TPP)Cl], whose molecular structure at 100 K is reported.

Experimental Section

General Information. All reactions were carried out under argon atmosphere using standard Schlenk line techniques. Nitric oxide (Mittler Specialty Gases) was purified by fractional distillation through a trap containing 4 Å molecular sieves bathed in a dry-ice/ethanol slurry.[26] Reagents and solvents were purchased from Aldrich or Fisher and used without further purification. Free-base porphyrin, H_2TPP, was synthesized according to the method of Adler.[27] Infrared spectroscopy measurements were performed using a Nicolet Nexus 670 FT-IR spectrometer equipped with a Specac variable temperature cell and an Omega-Engineering CN310 solid state temperature controller for multiple-temperature measurements. Samples were prepared using single crystals ground with KBr in an approximate 50:1 KBr/[Co(TPP)(NO)] ratio. Differential Scanning Calorimetry (DSC) measurements were obtained using a Mettler-Toledo model DSC822^e calorimeter equipped with STAR^e software. Data were collected against a blank sample. The experimental program ramped the temperature from 298 to 138 K at a rate of 10 K/min, held the temperature at 138 K for five minutes, and then ramped from 138 to 298 K at a rate of 5 K/min. The transition on cooling was centered at 191.3 K whereas the transition on warming was observed at 195.7 K.

Synthesis of [Co(TPP)(NO)]. [Co(TPP)(NO)] was prepared as previously reported.[18] Purple, tetragonal bipyramidal crystals of [Co(TPP)(NO)] appropriate for X-ray crystallographic studies were grown by liquid diffusion of methanol into a chloroform solution of the porphyrin. The identity of the crystals as [Co(TPP)(NO)] was verified by the presence of the NO infrared stretch at 1681 cm^{-1}.

Synthesis of [Fe(TPP)Cl]. [Fe(TPP)Cl] was synthesized according to the previously reported metalation procedure of Adler et al.[28] Crystals suitable for X-ray diffraction were obtained by vapor diffusion of methanol into a methylene chloride solution of the porphyrin.

X-ray Crystallographic Studies. Collection and integration of X-ray diffraction data was performed using a Bruker X8 or D8 Apex II diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation.

X-ray intensity data were collected on a [Co(TPP)(NO)] crystal at temperatures ranging from 100 to 250 K (700 Series Oxford Cryostream).[29] [Co(TPP)(NO)] was in the triclinic crystal system at 100, 180, and 190 K and was found to undergo a reversible phase change into the tetragonal crystal system at the higher temperatures, 195, 200, and 250 K. The phase change was further studied by performing unit cell determinations on two additional [Co(TPP)(NO)] crystals between the temperatures of 180 and 200 K.

The triclinic crystals were twinned and analyzed using the program cell_now.[31] The 100 and 180 K primitive systems had a primary domain and three additional twin domains related to the primary domain by ~90° or ~180° rotations about the triclinic [1, 0, 0] axis, which is similar to the tetragonal *c*-axis. At 190 K, near the transition temperature for this crystal, only two domains in addition to the primary domain were found, related by rotations of ~180° or ~4° about the [1, 0, 0] axis. No twinning was observed in the tetragonal systems.

Intensity data for [Fe(TPP)Cl] were collected at 100 K, and a unit cell was determined at 80 K. A tetragonal I-centered lattice was observed at both temperatures.

The programs SADABS and TWINABS were used to determine absorption corrections for the crystallographic data. In the triclinic crystal system, the centrosymmetric space group $P\bar{1}$ was chosen, while in the tetragonal crystal system, the *I*4/*m* space group was assumed. The structures were solved in SHELXS and refined in SHELXL.[31] All non hydrogen atoms in the molecule were refined anisotropically, except the cobalt atom.

Structure Refinement. The required inversion symmetry of the triclinic $P\bar{1}$ space group leads to disorder in the nitrosyl group, and, consequently, the presence of two symmetry-related, equally occupied positions of the nitrogen and oxygen atoms at 100 and 180 K. At 190 K two equally occupied nitrogen positions and four disordered oxygen positions exist. There are two oxygen positions separated by a 79(3)° angle on each side of the porphyrin plane. They are related by an inversion center, with relative occupancies of ~3:1. The tetragonal *I*4/*m* systems at 195, 200, and 250 K have 4-fold rotational symmetry and

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mirror plane constraints that cause greater nitrosyl disorder. These systems have eight equally occupied oxygen positions, two equally occupied nitrogen positions, and a Co$-$N$_{\mathrm{NO}}$ bond that is exactly along the *z*-axis.

The Co atom was expected to be displaced from the porphyrin plane in two equally occupied positions in both the tetragonal and the triclinic systems, but displaced by too small a distance to be defined by least-squares refinement. This was confirmed by the refinement of the data with cobalt centered in the porphyrin plane, which led to an unrealistic, elongated temperature factor normal to the porphyrin plane. The out-of-plane location of the Co was assumed to be along the N$_{\mathrm{NO}}$$-N'_{\mathrm{NO}}$ vector because of the slight off-axis tilt of the Co$-$N$_{\mathrm{NO}}$ bond in the triclinic systems. The Co$-$N$_{\mathrm{NO}}$ distance was set equal to the average of the literature values of the Co$-$N$_{\mathrm{NO}}$ bond lengths, 1.842 Å.[10,18,32,33] On the basis of this assumption, idealized fractional coordinates for the Co position were obtained using a locally written program for geometry calculations. Least-squares refinement was continued with the Co position fixed, which allowed for slight changes in the Co$-$N$_{\mathrm{NO}}$ distances. The out-of-plane distance in the tetragonal case was solved in a similar way; however, the necessary 4-fold symmetry requires that the Co position lie on the *z*-axis.

[Fe(TPP)Cl] was found to have two, equally occupied positions for the Fe atom required by the symmetry of the *I*4/*m* space group. These two positions, separated by 0.781(2) Å, were far enough removed from one another that the Fe could be refined anisotropically.

Results and Discussion

The room temperature crystal structure of [Co(TPP)(NO)] was first described in 1973.[18] This structure has similar features to the 195, 200, and 250 K structures in this study, as it crystallizes in the *I*4/*m* space group and requires disorder of the five-coordinate cobalt center and the nitrosyl group (Figure 1).[18] A number of additional tetraphenylporphyrin derivatives of the general form [M(TPP)X], where X is a mono- or diatomic ligand, are known to crystallize in this tetragonal system.[18−20,34−39] One of these, [Fe(TPP)(NO)] shows the same disorder as the cobalt complex.[19,20] A low temperature study of [Fe(TPP)(NO)] showed this complex undergoes a reversible phase change from the tetragonal crystal system to a more ordered triclinic crystal system, $P\bar{1}$. To the best of our knowledge, [Fe(TPP)(NO)] is the only [M(TPP)X] reported to date to undergo a phase change. We report additional multi-temperature studies of [Co(TPP)(NO)] and [Fe(TPP)Cl] to further explore possible phase changes in *I*4/*m* metalloporphyrins.

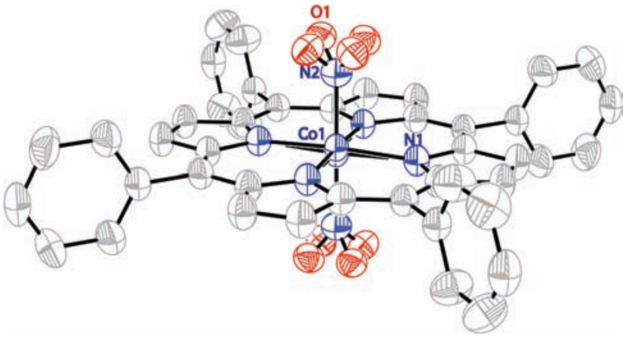

Figure 1. Thermal ellipsoid plot of [Co(TPP)(NO)] at 195 K in the *I*4/*m* space group (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. One-eighth of the molecule is crystallographically unique.

Indeed, [Co(TPP)(NO)] does undergo a reversible phase transition to the triclinic, $P\bar{1}$ space group, which was observed by cooling this system to 100 K and performing a structure determination. However, in crystal structure determinations at 200 and 250 K, the tetragonal *I*4/*m* lattice was observed. In an attempt to find the exact temperature of this phase transition, three additional structure determinations were performed at 180, 190, and 195 K. At 180 K, the crystal was similar to that observed at 100 K triclinic system. At 195 K a structure similar to the 200 and 250 K tetragonal systems was observed. At 190 K, the crystal could be indexed in the triclinic $P\bar{1}$ crystal system; however, it was found to be structurally distinct from both the low and the high temperature systems and is very close to the transition temperature for this system. The important structural features of the tetragonal and triclinic crystal systems are discussed below. We saw no evidence that the phase change is not completely reversible from measurements taken when crystals were either warmed or cooled.

Molecular Structures. All structures contain a five-coordinate, square-pyramidal [Co(TPP)(NO)] group with disorder of the nitrosyl positions. The structure undergoes small, but real changes with temperature that cause the amount of disorder within the system to vary depending on the temperature. At 195 K and above, there are eight discrete nitrosyl positions, four above the porphyrin plane and four symmetry-related positions below. At low temperature, only two nitrosyl positions exist, related by an inversion center. The complex disorder is the result of static disorder in which the axial ligand is on opposite sides of the porphyrin plane, whereas the 4-fold disorder on either side of the porphyrin plane is dynamic. Additionally, the cobalt is displaced from the porphyrin plane and, therefore, also displays 2-fold disorder in all structures, because of the symmetry requirements in both the *I*4/*m* and $P\bar{1}$ space groups.

As might have been expected, least-squares refinement difficulties were encountered when trying to find exact nitrosyl orientations in the tetragonal systems because of the increased disorder. The oxygen electron density is shared between the eight positions, which leads to shorter than expected N$-$O bond lengths in the tetragonal system. Table 1 shows that all of the structures with 8-fold disorder of the nitrosyl have average nitrosyl bond lengths of ~1.00 Å, which is shorter than the typical 1.167(1) Å N$-$O bond lengths in comparable porphyrin systems that have no disorder.[10,32,33] Perhaps surprisingly, the quality and resolution of the tetragonal structures does not improve with decreasing temperature. The apparent Co$-$N$-$O angle in the tetragonal structures, 133(2)°, is also larger than has been seen for more ordered nitrosyl structures, 123(2)°.[10,32,33] Other results of the *I*4/*m* symmetry

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Table 1. Notable Bonding Parameters for [Co(TPP)(NO)] and Related Compounds

complex, temp.	Co–NO[a]	Co–N[a]	N–O[a]	Co–N–O[b]	ΔCo[a,c]	ref
[Co(TPP)(NO)], 100 K	1.8301(5)	1.9672(6)	1.1492(7)	123.39(5)	0.070	tw
[Co(TPP)(NO)], 180 K	1.837(3)	1.975(6)	1.137(5)	124.8(4)	0.063	tw
[Co(TPP)(NO)], 190 K	1.842(7)	1.98(4)	1.093(12)[d]	125.0(8)[e]	0.085	tw
[Co(TPP)(NO)], 195 K	1.848(7)	1.9744(18)	1.00(1)	131.6(7)	0.070	tw
[Co(TPP)(NO)], 200 K	1.842(5)	1.9658(15)	0.994(8)	131.3(5)	0.070	tw
[Co(TPP)(NO)], 250 K	1.839(5)	1.9667(15)	0.999(8)	132.1(6)	0.070	tw
[Co(TPP)(NO)], 298 K	1.833(53)	1.978(4)	1.01(2)	135.2(8)	0.094(52)	18
[Co(OEP)(NO)], 298 K	1.8444(9)	1.9845(1)	1.1642(13)	122.70(8)	0.16	10
[Co(OC$_2$OPor)(NO)·0.46CHCl$_3$], 153 K	1.837(4)	1.972(7)	1.174(4)	121.8(3)	0.16	32
[Co(T(*p*-OCH$_3$)PP)(NO)], 228 K	1.855(6)	1.99(3)	1.159(8)	120.6(5)	0.20	33

[a] Å. [b] Degrees. [c] Displacement from 24-atom mean plane. [d] The second N–O bond length is 0.98(3) Å. [e] The second Co–N–O angle is 133(2)°.

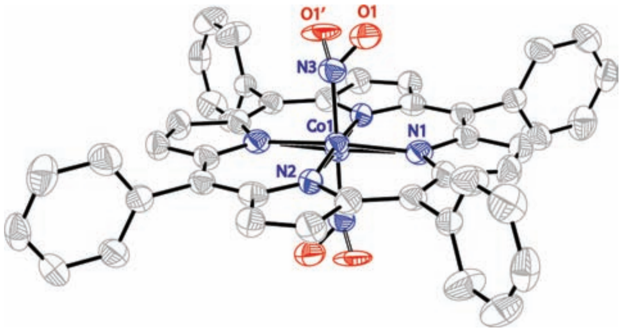

Figure 2. Thermal ellipsoid plot of [Co(TPP)(NO)] at 190 K in the $P\bar{1}$ space group (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. One-half of the molecule is crystallographically unique. The relative occupancy of O1:O1′ is 3:1.

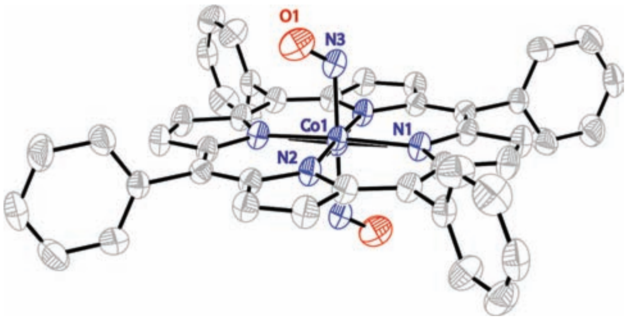

Figure 3. Thermal ellipsoid plot of [Co(TPP)(NO)] at 180 K in the $P\bar{1}$ space group (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. One half of the molecule is crystallographically unique.

are that the Co–N$_{NO}$ bond is normal to the porphyrin plane and the dihedral angle between the unique phenyl group and the porphyrin core is 90°. As described in the Experimental Section, the Co–N$_{NO}$ bond length was fixed during refinement as part of the model to determine the cobalt out-of-plane distance. With that constraint, the cobalt out-of-plane distance for all tetragonal structures was estimated to be ±0.070 Å.

At 190 K, the molecule has begun the transition into a more ordered structure, but has not yet achieved maximal ordering, apparently poised in the middle of the ordering transition. At this temperature, the complex has two unequally populated nitrosyl positions on each side of the porphyrin plane (Figure 2). The two positions with 3:1 relative occupancies are related to the symmetry equivalent nitrosyl groups through the inversion center. The dihedral angle between the two CoNO planes is ~90°. The Co–N–O angle (125.0(8)°) and the N–O bond length (1.093(12) Å) for the site of major occupancy of the nitrosyl are closer to literature values for ordered structures at this temperature; however, they are still slightly different than the average literature values. A Co–N–O angle (133.(2)°) and N–O bond length (0.98(3) Å) for the site of minor occupancy of the nitrosyl are, interestingly, similar to the values in the disordered, tetragonal system. This observation might be attributed to the system being trapped in an incomplete transition, and thus has not, at this temperature, achieved maximal ordering nor maximal symmetry.[10,32,33] Unlike the tetragonal case, the dihedral angle between the phenyl group and the porphyrin core is not required by symmetry to be exactly 90°. The angles in this system are 83.8° and 87.5°, and the cobalt out-of-plane distance is 0.085 Å. The out-of-plane distance of the cobalt atom was more difficult to define in the triclinic system because the Co–N$_{NO}$ bond is not required by symmetry to be perpendicular to the porphyrin plane. To place the cobalt atom in the triclinic systems, therefore, the assumption was made that the cobalt atom was along the N$_3$–N$_3$′ vector. This assumption allows a Co–N$_{NO}$ off-axis tilt; however, the magnitude of this tilt can not be reliably determined because of the assumptions made in placing the cobalt atom.

Cooling the crystal to 180 K led to greater order in the system (Figure 3) with two inversion related nitrosyl positions. The average N–O bond length (1.143(8) Å) and Co–N–O angle (124.1(9)°) for these low-temperature systems are in good agreement with values of ordered nitrosyl porphyrins.[10,32,33] At 100 K, the two nonequivalent phenyl groups are rotated 83.0° and 84.1° from the porphyrin plane, and at 180 K, these rotations are 84.5° and 86.3°. One of the phenyl–porphyrin core dihedral angles at the 190 K transition temperature is smaller than all of the low temperature structure angles, while the other is higher. This suggests that the phenyl groups are twisting around at this temperature to find the position of maximal stability, but have not yet found it. The 87.5° angle at 190 K allows more room for a second NO orientation near the transition temperature.

As [Co(TPP)(NO)] changes from a disordered structure to a more ordered form with decreasing temperature, the cell volumes shown in Table 2 give insight into the structural changes. As the temperature decreases from room temperature to 250 and then to 200 K, the volume of the cell steadily decreases, as would be expected with a decrease in temperature. As the crystal approaches the transition temperature at 195 and 190 K, however, a spike in the volume is observed, which might be attributed to

Table 2. Summary of Crystallographic Data for [Co(TPP)(NO)] and [Fe(TPP)Cl] at Several Temperatures

temp., K	*a*, Å	*b*, Å	*c*, Å	α, deg	*β*, deg	*γ*, deg	V/Z, Å^3	final *R*	final wR_2
				[Co(TPP)(NO)]					
100^a	9.667(5)	9.932(4)	10.357(5)	81.93(3)	65.56(3)	68.86(3)	844.3(7)	0.0510	0.1346
180^a	9.7110(19)	10.170(2)	10.556(2)	80.31(3)	64.08(3)	67.57(3)	866.7(3)	0.0378	0.0968
190^a	9.785(2)	10.260(2)	10.622(2)	80.67(3)	64.64(3)	65.97(3)	880.0(3)	0.0975	0.2187
195^b	13.4106(19)	13.4106(19)	9.6824(19)	90	90	90	870.6(5)	0.0428	0.1183
200^b	13.3518(3)	13.3518(3)	9.6444(3)	90	90	90	859.65(5)	0.0384	0.1058
250^b	13.3719(5)	13.3719(5)	9.6786(4)	90	90	90	865.30(5)	0.0353	0.0977
298^{b,c}	13.434(1)	13.434(1)	9.754(1)	90	90	90	880.1	0.0600	N.A.
				[Fe(TPP)Cl]]					
100	13.4576	13. 4576	9.6853	90	90	90	877.04(8)	0.0583	0.1351
298^d	13.534(6)	13.534(6)	9.820(6)	90	90	90	899.3	0.073	N.A.

^{a} Triclinic, $P\bar{1}$. ^{b} Tetragonal, $I4/m$. ^{c} Reference 18. ^{d} Reference 40.

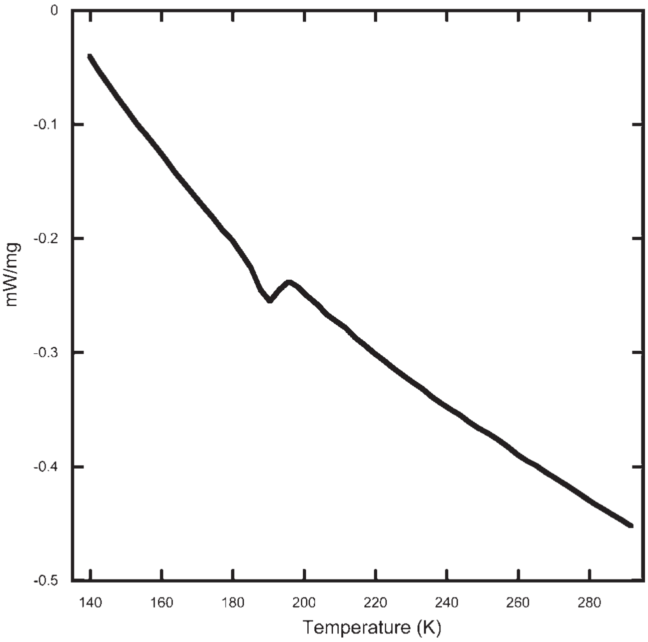

Figure 4. DSC measurement of ground single crystals of [Co(TPP)(NO)]. The measurement was recorded between 298 and 138 K. The endotherm is centered at 195.7 K.

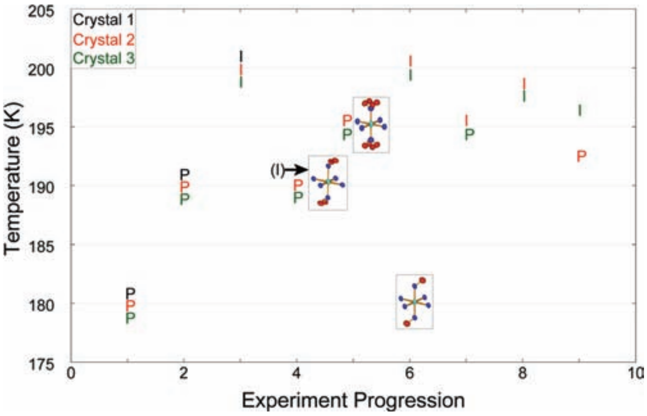

Figure 5. Plot showing the observed phase for [Co(TPP)(NO)] for temperature sequences between 180−200 K. The results from the crystal of the first crystallization experiment are shown in black. Results for crystals from the second crystal preparation are shown in red and green. Full data set collections are indicated by partial crystal structure icons. The observed unit cell is indicated by either "P" for the triclinic $P\bar{1}$ cell or "I" for the tetragonal $I4/m$ cell at that temperature. The heating or cooling protocol can be seen from the temperature progressions. Note the reversibility of the phase change. All full data collections were performed on the first crystal. As noted,[29] all temperatures are believed accurate to within 2 K. For the clusters with two or three points, the experimental temperature is that given at the midpoint of the cluster.

the rearrangement of the molecule in an attempt to reach its more ordered structure. Below the transition temperature, at 180 and 100 K, the volume again decreases. All of these structural observations support the idea of a dynamic phase change (See Phase Change Section).

Phase Change. The exact temperature of the phase change in [Co(TPP)(NO)] was studied through Differential Scanning Calorimetry (DSC) (Figure 4). An endotherm occurs at 195.7 K upon heating, indicating that this is the transition temperature. The DSC results agree well with the phase change temperature found crystallographically, between 190 and 196.5 K.

The reproducibility of the crystallographic phase change was studied through unit cell determinations on two crystals obtained from a crystallization experiment separate from that of crystal 1. Figure 5 shows the phases of crystals 1, 2, and 3 at different temperatures. In all three cases, [Co(TPP)(NO)] has undergone the transition from triclinic to tetragonal above 196.5 K. There was a small, but possibly significant deviation in the exact temperature of the phase transition in the three crystals. Cell determinations for crystal 1 found the phase change to be between 190 and 195 K. At 190 K, the crystal was indexed as triclinic when it was heated to this temperature, but remained tetragonal when cooled to this temperature. It converted back to a triclinic cell after waiting 10 min. Crystal 2 behaved similarly at 195 K, except that it had not converted into a triclinic cell after waiting for 25 min after cooling. The unit cell determinations show that the phase change in these systems is reproducible and sharp, although a small crystal-dependent variation of the exact temperature of the transition exists. In this way, [Co(TPP)(NO)] differs from [Fe(TPP)(NO)], which underwent the complete transition between the states over a very broad temperature range.[20]

Multiple-temperature infrared spectroscopic measurements of [Co(TPP)(NO)] show that the NO stretching

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(40) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992.

frequency does not change significantly as a function of temperature, changing only from 1679 cm^{-1} at 105 K to 1682 cm^{-1} at 318 K.

What is the possible nature of the disorder in the high temperature structures? There are two possibilities. The first is that all disorder is static, and the nitrosyl group sits in one of eight equally preferred positions at each site in the crystal lattice. The other, more likely, is that the nitrosyl group is moving dynamically between the four different positions on each side of the porphyrin plane. The nature of this disorder was first studied by Mason and co-workers in a ^{15}N solid-state NMR study.[25] CPMAS NMR data of [Co(TPP)(NO)] above 220 K led to the conclusion that some internal motion must be causing an averaging of the shielding tensor, which they attributed to a dynamic, swinging motion of the nitrosyl group. Below 200 K, however, the data indicated that the swinging motion had ceased. The NMR results agree strongly with the results of the present study. The occupancy factors of our structures, along with the increase in order with temperature change support the idea of dynamic NO motion, and the crystal structures show that the structure becomes more ordered after it undergoes a phase change between 190 and 195 K. The NMR study showed no detectable motion in the system below 200−220 K, only slightly higher than our crystallographic phase change was detected.

Mason and co-workers attribute the change of NO motion to crystal packing. In [Fe(TPP)(NO)], a second suggestion for the phase change was made: the stability of an off-axis distortion of the axial ligand lends to increasing order.[20] According to this second idea, the off-axis tilt of the axial ligand, frequently seen in nitrosyl porphyrin systems, becomes more favorable at lower temperatures, and, as a result, the rest of the molecule adjusts. This explains the four-domain twinning seen in this system at low temperatures, as each domain is separated 90 or 180° from one another and represents the Co$-$N$_{NO}$ bond tilted toward one of the four preferred positions above the porphyrin plane.

If indeed an increase in packing efficiency causes a phase change, it might be expected that a similar change might occur in other $I4/m$ porphyrin systems. To determine if an increase in the solid-state packing efficiency causes the phase change, [Fe(TPP)Cl] was synthesized and studied crystallographically (Figure 6). [Fe(TPP)Cl] was chosen because it is known to crystallize in the $I4/m$ space group at room temperature.[40] It also lacks the axial nitrosyl group, ensuring that if a phase change did occur in this system, it would be due to an increase in solid state packing efficiency. Both a unit cell and a crystal structure determination at 80 and 100 K, respectively, found the compound to be in the tetragonal $I4/m$ space group. This result seems to suggest that the occurrence of the transition as a result of increased solid-state packing efficiency can be ruled out; however, the transition could occur at a lower temperature than the 80 K available in our lab.

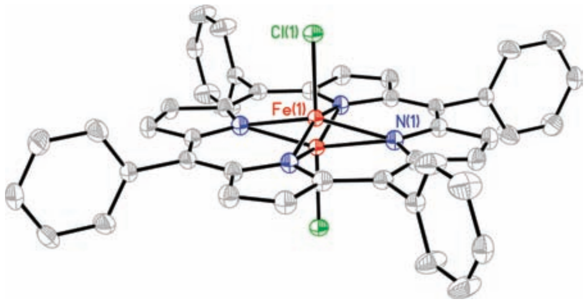

Figure 6. Thermal ellipsoid plot of [Fe(TPP)Cl] at 100 K (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Summary. A reversible, temperature-dependent phase change is observed in [Co(TPP)(NO)]. Three distinct structures have been observed for this system: a disordered, high-temperature structure in the $I4/m$ space group with eight nitrosyl positions, a low temperature structure in the $P\bar{1}$ space group with two nitrosyl orientations, and a transition structure in the $P\bar{1}$ space group that is close to complete ordering. The NO disorder observed in the high temperature phase is due to a dynamic movement of the nitrosyl ligand. The lack of an analogous low-temperature phase change in [Fe(TPP)Cl] suggests that the origin of the phase change in the cobalt and iron nitrosyls is a result of intrinsic molecular features of the nitrosyl complexes, probably the off-axis nitrosyl tilt.

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Supporting Information Available: Figures S1−S31: ORTEP diagrams of [Co(TPP)(NO)] at 100, 200, and 250 K. Tables S1−S36 give complete crystallographic details for [Co(TPP)(NO)] at 100, 180, 190, 195, 200, 250 K, including atomic coordinates, bond lengths and angles, and anisotropic displacement parameters. Tables S37−S42 give complete crystallographic details for [Fe(TPP)Cl]. Crystallographic data are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.