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Nitrosylmetalloporphyrins. II. Synthesis and Molecular Stereochemistry of Nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II)[1]

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Abstract: Nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II), ONFeTPP, is obtained by reductive nitrosylation of ClFeTPP. With a square-pyramidal coordination group, but with a bent Fe–N–O group, the ONFeTPP molecule has statistically required C_{4h} symmetry in an eightfold-disordered variant of a well-known structural type based on the tetragonal space group, $I4/m$. Cell data: a = 13.468 (9), c = 9.755 (8) Å; Z = 2; ρ_{calcd} = 1.31, ρ_{exptl} = 1.31 g/cm^3 at 20°. Intensity data for 951 independent reflections having $(\sin\theta)/\lambda \leq 0.725$ Å^{-1}, collected with graphite-monochromated Mo Kα radiation on a computer-controlled four-circle diffractometer, were used in the refinement of the statistically averaged structure. The final discrepancy indices were R_1 = 0.044 and R_2 = 0.061. Bond parameters in the porphinato core agree well with those observed in the other low-spin iron porphyrins. The displacement of the iron atom from the porphinato core (Ct ··· Fe) is 0.211 (5) Å; the displacement of the nitrosyl nitrogen atom (N_2) from the porphinato core is 1.928 (6) Å. The equatorial Fe–N_p bond length is 2.001 (3) Å, Fe–NO = 1.717 (7) Å. The FeN_2O angle is 149.2 (6)°.

Questions concerning the structure and bonding of the small molecules dioxygen, nitric oxide, and carbon monoxide coordinated to metalloporphyrins have been intensively investigated.[2] These compounds are of obvious interest in understanding the stereochemistry of iron porphyrins as it pertains to the biologically important hemoproteins. We have been investigating the reactions of nitric oxide with several metalloporphyrins and we report herein the preparation and structural characterization of one derivative, five-coordinate nitrosyl-α,β,γ,δ-tetraphenylporphinatoiron(II), to be written as ONFeTPP. This molecule has been independently synthesized by Wayland and coworkers.[2d] The magnetic data are consistent with the formal description of low-spin iron(II) and neutral NO.

Salient features of the stereochemistry of this complex include the mode of nitrosyl coordination (a linear or bent FeNO moiety) and the magnitude of the out-of-plane displacement of the *low-spin* iron(II) atom from the mean porphinato plane. In contrast to the high-spin five-coordinate iron(II) and iron(III) porphyrins in which the requisite Fe–N_p (N_p = porphinato nitrogen) distance (≥2.07 Å) is too long to permit centering of the iron in the porphinato mean plane,[3] low-spin iron(II) porphyrins are expected to have Fe–N_p bond distances sufficiently short to allow centering of the metal in the porphyrin plane. Any observed out-of-plane displacement is then rationally attributed to minimizing the nonbonded contacts between the single axial ligand and atoms of the porphinato core. A comparison of the stereochemical parameters of ONFeTPP with those of ONCoTPP[1] and ONFeTPP(NMeIm)[4] (NMeIm = 1-methylimidazole) should allow the evaluation of changes in stereochemistry caused by the addition of one additional d electron or the coordination of a second axial ligand, respectively.

Experimental Section

Preparation of ONFeTPP. All reactions were carried out under argon using modified Schlenk tubes. ClFeTPP was prepared as previously described.[5] A solution of 0.2 g of ClFeTPP in 60 ml of chloroform was carefully degassed and 1 ml of dry pyridine was added to it. Nitric oxide, purified by passing through a KOH column, was bubbled into the solution for 20 min. Methanol, distilled from Mg, was added until crystals of ONFeTPP appeared. Filtration, under argon, gave lustrous purple crystals of ONFeTPP. *Anal.* Calcd for $FeC_{44}H_{28}N_5O$: C, 75.65; H, 4.04; N, 10.02. Found: C, 75.14; H, 4.10; N, 9.90.

Physical Data. The infrared spectrum of ONFeTPP was recorded on a Perkin-Elmer 457 spectrometer using a KBr pellet; the strong absorption at 1670 cm^{-1} was assigned as the NO stretching frequency. The mass spectrum, obtained on an AEI MS-9902 spectrometer, had prominent peaks at m/e 668 ($FeTPP^+$) and 30 (NO^+); the parent ion (m/e 698) was not observed. A sensitive test for piezoelectricity in the crystals, using a Geibe–Schiebe detector, was negative. The visible absorption spectrum of ONFeTPP in chloroform has peaks at 4050, 5370, and 6060 Å and a shoulder at 4750 Å. The extinction coefficients are 100 × 10^3, 8.7 × 10^3, 2.8 × 10^3, and 15 × 10^3 M^{-1} cm^{-1}, respectively. The visible absorption spectrum changes slowly on exposure to the atmosphere. The magnetic susceptibility, determined by the Evans method,[6] is 2.3 BM.

Crystallographic and X-Ray Data. Crystals of ONFeTPP suitable for X-ray study were grown by allowing anhydrous methanol to diffuse slowly into a chloroform solution of the porphyrin under argon–nitric oxide. Preliminary photographic study of a crystal of tetragonal bipyramidal habit displayed the Laue symmetry of $4/m\text{-}C_{4h}$. The systematic extinctions of $h + k + l = 2n + 1$ leave only $I4$, $I\bar{4}$, and $I4/m$ as the possible space groups.[7] Lattice constants, $a = 13.468$ (9) and $c = 9.755$ (8) Å (λ 0.71069 Å), came from a least-squares refinement that utilized the setting angles of 22 reflections, each collected at $\pm 2\theta$. All measurements were made on a computer-controlled four-circle diffractometer at the ambient laboratory temperature of 20 ± 1°. These constants led to a calculated density of 1.31 g/cm^3 for a cell content of two molecules of ONFeTPP; the experimentally determined density (by flotation) was 1.31 g/cm^3.

X-Ray intensity data were collected using graphite-monochromated Mo Kα radiation on a computer-controlled four-circle diffractometer. The crystals specimen was a tetragonal bipyramid with edge lengths of 0.43, 0.43, and 0.23 mm. All independent reflections for which $(\sin \theta)/\lambda \leq 0.725$ Å^{-1} were measured by θ–2θ scanning; a variable scan rate algorithm was applied with the slowest scan rate being 0.50 deg/min and the fastest being 6.0 deg/min.[8] Background counts of a duration equal to the time required for the scan itself were taken at the extremes of the scan. Four standard reflections, measured every 50 reflections during data collection, showed no trend with exposure to the X-ray beam. With a linear absorption coefficient of 0.53 mm^{-1} no absorption corrections were deemed necessary. Intensity data were reduced and standard deviations calculated as described previously.[8] Data were retained as objectively observed for $|F_o| > 3\sigma F_o$, 951 data were retained as observed, some 68% of the total number possible in the range of $(\sin \theta)/\lambda$ examined.

Determination and Refinement of Structure. The point group symmetry (real or statistically effective) required of the ONFeTPP molecule in the three possible space groups was seen to be C_4 in $I4$, S_4 in $I\bar{4}$, or C_{4h} in $I4/m$. Only in the space group $I4$ (and then only if the Fe–N–O bond system were linear) is it possible to place the molecules in a fully ordered crystalline structure, but a structure based upon $I4$ would require that all the molecular dipoles be in parallel alignment along the c axis and, thus, in disagreement with observation, to give rise to rather pronounced piezoelectricity.

Earlier structure determinations for tetragonal crystals of the chloroiron(III),[9] aquozinc(II),[10] and aquomagnesium(II)[11] derivatives of tetraphenylporphine had shown that these metalloporphyrins crystallize in a disordered variant of the structural type, based upon $I4/m$, for which crystals of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatodichlorotin(IV),[12] Cl$_2$SnTPP, are the ordered prototype. The disordered variant is characterized by the statistically equal probability for parallel and antiparallel orientation of the unique molecular axis relative to the c axis of the crystal. Moreover, it was found for tetragonal crystals of *ONCoTPP*[1] that no less than eight equally probable orientations of the ONCoTPP molecule contribute to the crystalline disorder and to the structure of the statistically averaged molecule of C_{4h} symmetry. This result is the direct consequence of the markedly nonlinear geometry of the Co–N–O bond system which leads to eight distinctive orientations of the coordination group. A similar nonlinear geometry for the Fe–N–O bond system was found in ONFeTPP; the eight distinctive orientations of the coordination group are illustrated in Figure 1. The nitrosyl oxygen atom appears as eight equivalent fractions, each carrying only one-eighth of the charge density of the oxygen atom. Consequently, the presence of the oxygen atom was not detected in the initial Fourier synthesis[13] with phases determined by the contribution from the iron atom. The positions of all carbon and nitrogen atoms in the asymmetric unit of structure (one-eighth of the statistically averaged molecule) were found in this synthesis, the nitrosyl nitrogen atoms as half-atoms on the fourfold axis at $00z$ and $00\bar{z}$. Full-matrix least-squares refinement[14] of this trial structure, followed by a difference Fourier synthesis, then gave the coordinates of the eighth atom of oxygen in the asymmetric unit as a peak ~1.1 Å from the half-atom of nitrosyl nitrogen to which it is bonded.

Further refinement of the structure was continued with anisotropic thermal parameters (isotropic for oxygen) and with intermittent difference syntheses until all hydrogen atoms were located. The hydrogen atoms were included in the subsequent refinements using fixed coordinates and isotropic thermal parameters fixed one unit higher than their associated carbon atom. It was now clear that a displacement of the iron atom from the plane of the porphine nitrogen atoms was a physically real property of the individual ONFeTPP molecule. The out-of-plane displacement of the iron atom was successfully evaluated by the procedure that had been employed in several previous studies of this class of disordered structures; namely, the least-squares refinement of the variable z coordinate of half-atoms of the metal positioned at $00z$ and $00\bar{z}$. This refinement was then carried to convergence; the empirical weighting scheme described earlier was employed.[15] The final values for the discrepancy indices were

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.044$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2} = 0.061$$

The estimated standard deviation of an observation of unit weight was 1.10. A final difference Fourier synthesis was judged to be significantly free of features with no peaks greater than 0.3 e Å^{-3}.

The atomic coordinates and the associated anisotropic thermal parameters for the asymmetric unit of structure are listed in Tables I and II, respectively.[16] The numbering of the atoms given in Figure 2 is maintained in all tables.

Discussion of Results

Preparation of the ONFeTPP Molecule. We have found that the reaction of ClFeTPP with nitric oxide, in the presence of a hydroxylic solvent, leads to a reduced nitrosyl iron porphyrin, ONFeTPP. The reaction has been termed "reductive nitrosylation" [17] and can be written as

$$\text{ClFeTPP} + 2\text{NO} + \text{MeOH} \longrightarrow \text{ONFeTPP} + \text{MeONO} + \text{HCl}$$

Similar reductions of iron(III) are observed in methemoglobin;[18] both methemoglobin and hemoglobin (Fe^{2+}) react with NO to yield the same nitrosylhemoglobin. Indeed, reductive nitrosylation is a very versatile method for preparing various nitrosyl metalloporphyrins.[2d,4,19] We were therefore surprised to see the report[20] of the preparation of a compound claimed to be ClFeTPP(NO) from CHCl$_3$ and C$_2$H$_5$OH; in our hands, the procedure yields ONFeTPP.

Stereochemistry of the ONFeTPP Molecule. Figure 2 is a computer-drawn model in perspective of one of the eight equivalent orientations of the Fe–N–O bond system; apart from the axial bond system, the molecule must conform to C_{4h} symmetry. Using C$_a$ and C$_b$ to denote the α- and β-carbon atoms of a pyrrole ring and C$_m$ for methine carbon, there are two structurally independent bonds of the N$_1$–C$_a$, C$_a$–C$_b$, and C$_a$–C$_m$ chemical classes for a molecule conforming to C_{4h} symmetry. The largest dimensional variation between two bonds of a chemical type is observed for C$_1$–C$_2$ and C$_3$–C$_4$ of the C$_a$–C$_b$ class; these bonds differ by 0.008 Å or two estimated standard deviations.

The Fe–N$_1$ distance of 2.001 (3) Å is comparable to the average Fe–N$_p$ distance of 2.004 Å found for low-spin bis(piperidine)tetraphenylporphinatoiron(II),[21] longer than the 1.989 Å distance found for low-spin bis(imidazole)tetraphenylporphinatoiron(III),[22] and shorter than the 2.086 Å distance found for high-spin (2-methylimidazole)tetraphenylporphinatoiron(II).[23] Thus, the Fe–N$_1$ distance observed for ONFeTPP is seen to be consistent with the value anticipated for a low-spin iron(II) porphyrin. The Fe–N$_1$ distance is also consistent with the formal description of ONFeTPP as low-spin iron(III) coordinated by NO$^-$.

As can be seen from Figures 1 and 2, the Fe–N$_2$–O group of the axial bond system in ONFeTPP is decidedly nonlinear. The geometry of the axial bond system is similar to that of the isomorphous derivative ONCoTPP,[1] and we shall compare some aspects of the molecular packing of the two derivatives.[24] The nonlinear Fe–N$_2$–O geometry is not attributable to the packing of the molecules in the crystal. If the Fe–N$_2$–O system were to have a linear geometry, the

Table I. Atomic Coordinates in the Unit Cell

Atom type[a]	Coordinates with standard deviations[b] 10^4x	10^4y	10^4z
Fe	0	0	217 (5)
N_2	0	0	1973 (6)
O	350 (13)	244 (17)	2959 (13)
N_1	370 (2)	1430 (2)	0
C_1	−264 (2)	2236 (2)	0
C_2	293 (2)	3140 (2)	0
C_3	1261 (2)	2893 (2)	0
C_4	1312 (2)	1827 (2)	0
C_5	2193 (2)	1295 (2)	0
C_6	3153 (2)	1863 (2)	0
C_7	4916 (2)	2935 (2)	0
C_8	3598 (2)	2124 (2)	1208 (3)
C_9	4483 (2)	2663 (2)	1199 (3)
H_2	3828	0	0
H_3	1852	3337	0
H_7	3326	4453	0
H_8	3299	1953	2225
H_9	4780	2839	2135

[a] Each hydrogen atom carries the same subscript as the carbon atom to which it is attached. [b] Numbers in parentheses are the estimated standard deviations.

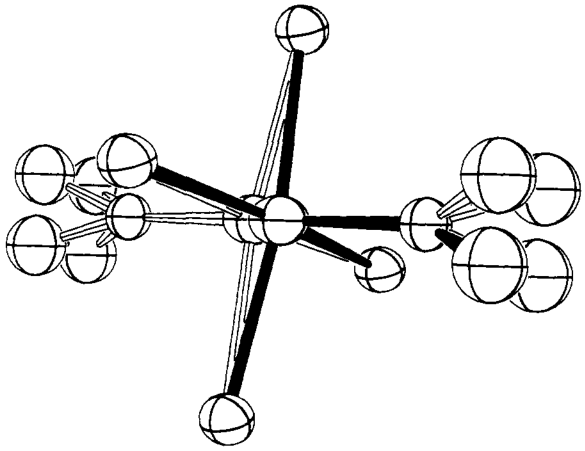

Figure 1. Computer-drawn diagram of the statistically disordered coordination group of the ONFeTPP molecule in the tetragonal crystal. The heavy solid lines show the bonding pattern for one orientation of the molecule.

oxygen atom on the fourfold axis would have as nearest and next nearest neighbors the four H_7 and four H_9 hydrogen atoms. However, for any credible value of the Ct · · · O distance, 2.90–3.20 Å, both O · · · H_7 and O · · · H_9 would always be substantially larger than the normal van der Waals separation of 2.60 Å.

We now note that the observed Fe–N_2O configuration (Tables I and III) requires two short O · · · H_9 separations of 2.52 and 2.59 Å; the O · · · H_7 separation is also rather short at 2.71 Å. The corresponding separations in ONCoTPP are 2.51, 2.58, and 2.86 Å. The observed atomic positions in the two complexes correspond to a FeN_2O angle of 149.2 (6)° and a N_2–O bond of 1.12 (1) Å,[25] and a CoN_2O angle of 135° and a N_2–O bond length of 1.03 Å. However, it is readily seen that the severity of the O · · · H_9 contacts can be diminished by allowing the MN_2O angle to decrease while allowing a reasonable N_2O length of at least 1.15 Å.

The thermal parameters of the N_2 atom in ONCoTPP, wherein the parameter for vibration normal to the fourfold axis, $B_{11} = B_{22} = 5.5$ Å^2, is nearly as large as the isotropic thermal parameter of the oxygen atom (5.7 Å^2), provide indirect evidence that the (N_2) nitrogen atom is not precisely centered on the fourfold axis. With the observed ON_2CoN_1 dihedral angle of 39.7°, intramolecular contacts of the O · · · N_1 type in ONCoTPP are 3.04 and 3.09 Å; these distances should be compared to the sum, 3.10 Å, of the van der Waals radii for oxygen and aromatic nitrogen. Thus the tight O · · · N_1 contacts within an individual molecule force the N_2 atom off the fourfold axis and give rise, in the statistically averaged molecule, to distorted values for the CoN_2O angle and the N_2–O bond distance. An analysis[1] of the likely displacement off axis leads to a CoN_2O angle of ≤128.5°, near the ~120° value anticipated.[26-28]

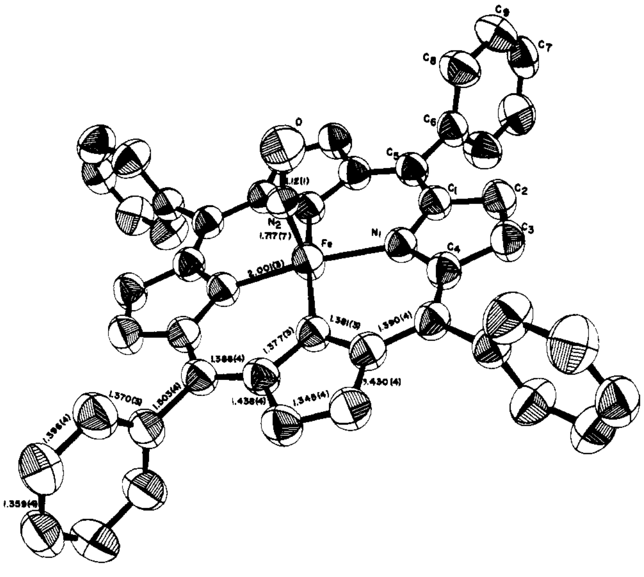

Figure 2. Computer-drawn model in perspective of the ONFeTPP molecule. Each atom is represented by an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table II. The bond parameters are from Table III.

By contrast, for ONFeTPP, the O · · · N_1 contacts are 3.30 and 3.34 Å, and the ON_2FeN_1 dihedral angle is 40.6°. The thermal parameters for N_2, which are nearly isotropic with $B_{11} = B_{22} = 3.7$ and $B_{33} = 3.8$ Å^2, are substantially smaller than the isotropic temperature factor for oxygen, 6.9 Å^2, and consistent with the N_2 atom being centered on the fourfold axis.

Thus, an analysis of the intermolecular and intramolecular packing of ONCoTPP suggests that the effect of packing is to force the N_2 atom off axis and thereby yield an apparently large CoN_2O angle. The same analysis for ONFeTPP leads to the conclusion that the only effect of packing on the FeN_2O angle could be a slight decrease in the angle, and hence the FeN_2O angle observed is probably close to the true value. The nonlinear FeN_2O geometry is conustent with the esr spectrum[2d] in frozen solution with three unique g values indicating nonaxial symmetry for the complex.

The iron atom is displaced 0.211 (5) Å from the center (Ct) of the mean porphinato plane; this value is a probable lower limit of the displacement.[29] The displacement of the iron out-of-plane appears to be attributable to minimizing the nonbonded contacts of the N_1 · · · N_2 type. With an Fe–N_2 distance of 1.717 (7) Å, the Ct · · · N_2 distance is 1.928 (6) Å and N_1 · · · N_2 is only 2.770 Å. The nonbonded contacts for the molecule with the FeN_2O group displaced by 0.21 Å parallel to the fourfold axis so that the iron is centered in the porphinato plane can be readily calculated. The only contact that is significantly changed for this hypothetical geometry is a decrease in N_1 · · · N_2 to 2.627 Å, thereby providing indirect evidence that the displacement of the iron is primarily the result of maximizing the N_1 · · · N_2 distance. It is interesting to note that for ONCoTPP, wherein the displacement of the cobalt is ~0.09 Å, the Ct · · · N_2 distance is 1.927 (10) Å and N_1 · · · N_2 is 2.760 Å.

Table II. Thermal Parameters of the Atoms in the Crystal

Atom type	Anisotropic parameters (Å²) with standard deviations[a]					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B^b
Fe	3.74 (5)	3.74 (5)	5.6 (2)	0	0	0	4.29
N_2	3.7 (2)	3.7 (2)	3.8 (3)	0	0	0	3.8
O							6.9 (3)
N_1	3.95 (8)	4.01 (8)	5.1 (1)	−0.03 (6)	0	0	4.3
C_1	4.5 (1)	3.9 (1)	5.2 (1)	0.15 (1)	0	0	4.6
C_2	5.0 (1)	4.1 (1)	7.2 (2)	−0.08 (9)	0	0	5.3
C_3	4.8 (1)	4.1 (1)	7.3 (2)	−0.49 (4)	0	0	5.2
C_4	4.2 (1)	4.1 (1)	5.4 (1)	−0.28 (8)	0	0	4.6
C_5	4.0 (1)	4.5 (1)	5.0 (1)	−0.52 (4)	0	0	4.5
C_6	3.8 (1)	4.4 (1)	6.0 (1)	−0.29 (4)	0	0	4.7
C_7	3.9 (1)	5.1 (1)	10.0 (3)	−0.35 (5)	0	0	5.9
C_8	5.7 (1)	8.0 (1)	6.2 (1)	−1.8 (1)	−0.5 (1)	0.1 (1)	6.4
C_9	5.8 (1)	8.0 (1)	8.1 (1)	−1.82 (7)	−1.5 (1)	−0.3 (1)	6.9

[a] Numbers in parentheses are the estimated standard deviations. The B_{ij} are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$. [b] Isotopic thermal parameter as calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Stereochemical Parameters of the ONFeTPP Molecule[a]

Distances, Å		Angles, deg	
Fe–N_2	1.717 (7)	N_1FeN_2	96.1 (1)
Fe–N_1	2.001 (3)	N_1FeN_1'	89.4 (1)
O–N_2	1.122 (12)	FeN_2O	149.2 (6)
N_1–C_1	1.381 (3)	FeN_1C_1	127.1 (2)
N_1–C_4	1.377 (3)	FeN_1C_4	127.1 (2)
C_1–C_2	1.430 (4)	$N_1C_1C_5'$	125.8 (2)
C_4–C_3	1.438 (4)	$N_1C_4C_5$	126.1 (2)
C_2–C_3	1.345 (4)	$C_1'C_5C_4$	123.5 (2)
C_1–C_5'	1.390 (4)	$C_1N_1C_4$	105.3 (2)
C_4–C_5	1.386 (4)	$N_1C_1C_2$	110.1 (2)
C_5–C_6	1.503 (4)	$N_1C_4C_3$	110.1 (2)
C_6–C_8	1.370 (3)	$C_1C_2C_3$	107.4 (2)
C_8–C_9	1.396 (4)	$C_4C_3C_2$	107.0 (2)
C_9–C_7	1.359 (3)	$C_1'C_5C_6$	118.2 (2)
Ct···Fe[b]	0.211 (5)	$C_5C_6C_8$	120.5 (2)
Ct···N_2	1.928 (6)	$C_8C_6C_8'$	119.0 (3)
Ct···N_1	1.990 (2)	$C_6C_8C_9$	120.1 (3)
Ct···C_5	3.431 (3)	$C_8C_9C_7$	120.7 (3)
N_1···N_2	2.770	$C_9C_7C_9'$	119.2 (3)

[a] Figures in parentheses are the estimated standard deviations. [b] Ct denotes the center of the statistically averaged molecule of C_{4h} symmetry.

A comparison of the coordination group geometry of ONFeTPP with that of nitrosyltetraphenylporphinato(1-methylimidazole)iron[4] displays the stereochemical effects of adding a sixth ligand to the coordination sphere. Changes in the Fe–N_p lengths are minimal, increasing from 2.001 Å to an average value of 2.008 Å in the six-coordinate derivative. The Fe–N_{NO} distance of 1.717 Å for ONFeTPP increases to 1.743 Å upon addition of the sixth ligand; the Fe–N–O angle decreases by ~7°. As would be expected, the bonding of a sixth ligand trans to the nitrosyl decreases the displacement of the iron atom out of the plane of the porphinato nitrogens by ~0.14 to 0.07 Å.

One of the more interesting features of nitrosyl complexes is the variation in the geometry of the M–N–O moiety. Several recent theoretical studies[30-34] have attempted to predict the geometry of square-pyramidal nitrosyl complexes. All studies emphasize the importance of the number of electrons in the M–N–O group and the relative energies of d_{z^2} orbital and the (π^*(NO); d_{xz}, d_{yz}) degenerate orbitals. For the fragment denoted by $\{MNO\}^6$ (ref 35), the theories suggest a linear MNO group. For the $\{MNO\}^8$ complexes, a strongly bent M–N–O moiety with MNO approaching 120° is suggested. Bending the M–N–O group in the $\{MNO\}^8$ complexes lifts the degeneracy of the (π^*(NO); d_{xz}, d_{yz}) pair and mixes (π^*(NO), d_{xz}) and d_{z^2} to form a "stabilized" and a "destabilized" combination. The two additional electrons in the $\{MNO\}^8$ complexes occupy this "stabilized" combination.

ONFeTPP is an $\{FeNO\}^7$ complex, and thus has only one electron in an orbital which favors bending. It is therefore reasonable that the M–N–O angle is substantially larger in ONFeTPP than in ONCoTPP. The Fe–N–O angle in ONFeTPP is smaller than in most other square-pyramidal $\{FeNO\}^7$ complexes[36] consistent with the suggestion[33] that strong σ donors in the basal plane will cause greater bending of the nitrosyl.

The trends in the coordination geometry of ONFeTPP and ONCoTPP are in reasonable accord with the bonding theories dealing with nitrosyl complexes. Nonetheless, the structural characterization of five-coordinate nitrosyl cobalt and iron porphyrins with completely ordered axial groups is clearly desirable, and attempts to obtain the requisite ordered crystals are in progress.

Acknowledgments. We thank Professors B. Wayland, J. H. Enemark, R. Feltham, and R. Hoffmann for furnishing preprints of their work. This work was supported by National Institutes of Health Grant HL-15627 and the Research Corporation.

Supplementary Material Available. A listing of structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-17 ·

References and Notes

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Electronic Spectral and Magnetic Susceptibility Studies of Nickel(II) and Cobalt(II) Carboxypeptidase A Complexes

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Received April 11, 1974

Abstract: The electronic absorption spectrum of nickel(II) carboxypeptidase A exhibits weak bands at 9430, 14,600, and 24,250 cm^{-1}, which are assigned to the three spin-allowed d–d transitions ($^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$) of octahedrally coordinated nickel(II). Comparison of the ligand field parameters $Dq = 923$, $B = 755$ cm^{-1} for Ni^{II}CPA with those of a variety of octahedral Ni(II) complexes suggests either an N_2O_4 or NO_5 donor-atom set in the resting enzyme. Addition of fluoride ion or the model substrate glycyl-L-tyrosine does not change the octahedral nature of the Ni(II) center. The electronic spectrum of the complex between Ni^{II}CPA and the inhibitor β-phenylpropionate (βPP), however, is substantially different, as two visible bands of moderate intensity and a low-energy feature (<6500 cm^{-1}) are observed. The position and molar extinction coefficient of the principal peak (23,350 cm^{-1}; $\epsilon \sim 50$) are suggestive of five-coordinate Ni(II). A formation constant of $K_I = 0.37 \times 10^4$ M^{-1} was measured by spectroscopic methods for the Ni^{II}CPA·βPP complex. Magnetic susceptibility and electronic absorption spectral data for Co^{II}CPA are analyzed in detail. The $\mu_{eff} = 4.77$ BM and the intensity of the principal visible absorption band (18,000 cm^{-1}; $\epsilon \sim 150$) are more compatible with five coordination than with a distorted tetrahedral Co(II) center. The fact that substantially different coordination geometries are adopted by various fully active CPA derivatives demonstrates the considerable flexibility of the binding site for metal ions.

Carboxypeptidase A (CPA) is a zinc metalloenzyme of molecular weight 34,600.[1,2] The enzyme catalyzes the hydrolysis of the C-terminal amino acid of a polypeptide chain. Enhanced activity is observed for C-terminal residues that have aromatic or branched aliphatic side chains or are in the L configuration. Esterase activity subject to these criteria has also been observed.[3]

A combination of high resolution X-ray[4-6] and complete amino acid sequence[7] studies has provided structural explanations for the peptide substrate specificity of CPA. These studies have also established His 69, Glu 72, and His 196 as the protein ligands of the active-site zinc ion and that the probable coordination geometry is distorted tetrahedral, with the fourth ligand a water molecule in the resting enzyme. The zinc ion in CPA is thought to bind to the carbonyl oxygen of the peptide bond to be hydrolyzed, thereby withdrawing some electron density from the adjacent carbon and rendering it more susceptible to nucleophilic attack by other groups in the enzyme.[5,6,8] Dipositive first-row transition metal ions[9] such as Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, as well as the vanadyl ion,[10] VO^{2+}, can be substituted for the zinc ion in CPA with varying degrees of retention of activity. Only Co^{II}CPA and Ni^{II}CPA, however, retain full peptidase activity.[9]

The spectral properties of Co^{II}CPA have been extensively studied. The electronic absorption,[11] circular dichroism,[11] magneto circular dichroism,[12] and low temperature electron paramagnetic resonance[13] spectra of Co^{II}CPA have been interpreted as being consistent with distorted tetrahedral coordination about the metal center. However, except for the absorption spectra, extensive model system data are simply not available for Co(II) systems, making attempts to assign structure based on results from the various physical measurements subject to considerable uncertainty.