Stereochemistry of a Porphyrin Atropisomer. The Molecular and Crystal Structure of Six-Coordinate [5α,10β-bis(o-nicotinamidophenyl)-15,20-diphenylporphinato]zinc(II)

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(Received May 12, 1987)

The synthesis and molecular structure of the title complex was investigated as part of our work into the chemical significance of atropisomerism in porphyrin compounds. The complex crystallizes in the triclinic system, space group $P\bar{1}$, a=11.707 (2) Å, b=12.744 (5) Å, c=9.521 (2) Å, α=102.60 (3)°, β=101.31 (2)°, and γ=100.29 (2)°, Z=1. A total of 3737 reflections (average of two forms) were considered observed and used in the solution and refinement of the structure. The structure was refined to a final R=0.081. The molecule, with a crystallographically imposed inversion center, has disordered nicotinamide side chains. This disorder leads to some ambiguity in defining the relative substitution pattern of the phenyl rings. Independent of the assumptions used to define the disorder, the nicotinamide side chains are found to coordinate the zinc ions of adjacent molecules to form a polymeric, linear chain containing six-coordinate zinc ions. The average equatorial Zn-N bond distance is 2.052 (3) Å and the unique axial bond distance is 2.432 (5) Å.

We and others[1-3] have been exploring strategies for introducing asymmetry in porphyrin species by appropriate substitution of tetraarylporphyrin derivatives. Such asymmetric species could, under appropriate circumstances, be utilized to control reactivity. One such series of asymmetric molecules are *o*-substituted tetraphenylporphyrin complexes in which an adjacent pair of phenyl groups are substituted on opposite sides of the porphyrin plane. The synthesis of one such example, 5α,10β-bis(*o*-aminophenyl)-15,20-diphenylporphyrin has been recently reported.[4] Measurements of the atropisomerization rates of tetrakis(*o*-aminophenyl)porphyrin[5] suggested that such a disubstituted derivative could be manipulated without significant loss of chirality. However, a crystal structure determination[6] of the above diamino derivative showed that the material was profoundly disordered, and suggested that substituents larger than amino groups are required for lattice (solid state) discrimination.

We report in this paper the preparation of a porphyrin derivative bearing much larger *o*-substituents on adjacent phenyls, a bis(nicotinamidophenyl) derivative. We also report the crystal structure of the zinc(II) complex of this porphyrin. Much to our surprise, this derivative also suffers from disorder. However, the disordered porphyrinate species has an interesting structural feature, namely, a six-coordinate zinc(II) ion that results from extended interaction in the solid state. The present complex, like the earlier reported [Zn(TPP)(THF)$_2$],[7] appears to achieve six-coordination purely as a result of solid-state effects. There remain no credible reports for six-coordinate zinc porphyrinates in solution.

Experimental

Syntheses. The preparation and isolation of 5α,10β-bis(*o*-aminophenyl)-15,20-diphenylporphyrin (H_2BADPP) has been described previously.[4] Nicotinoyl chloride hydrochloride (0.3 g, Tokyo Kasei Chem. Co.) was added to a H_2BADPP solution (0.5 g, 50 cm^3 of CH_2Cl_2 and 1 cm^3 pyridine) at room temperature. The resulting green solution was magnetically stirred for 1 h. Aqueous ammonia (8%, 25 cm^3) was poured into the solution and vigorously stirred for 30 min. The solution was then transferred to a separatory funnel and the CH_2Cl_2 layer was washed several times with water and then evaporated to dryness. The resulting solid porphyrin was dissolved in 15 cm^3 of $CHCl_3$ and crystallized by addition of petroleum ether. Yield 520 mg (78%). The product 5α,10β-bis(*o*-nicotinamidophenyl)-15,20-diphenylporphyrin(H_2BNDPP) (250 mg) was reacted with 0.5 g zinc acetate in 25 cm^3 of DMF in a temperature-controlled oil bath (35 °C) for 16 h. TLC of the reaction products confirmed that these conditions led to complete metallation and minimal rotational isomerization.[5] Zn(BNDPP) was obtained by addition of 50 cm^3 of water, followed by filtration of the resulting precipitate. Crystals of Zn(BNDPP) suitable for X-ray analysis were obtained by diffusing pentane into a pyridine-chloroform solution. Found: C, 72.88; H, 3.68; N, 12.06%. Calcd for $C_{66}H_{44}N_{10}O_2Zn$: C, 73.78; H, 4.13; N, 13.04%.

Structure Determination. A single crystal of Zn(BNDPP) with approximate dimensions of 0.35×0.35×0.45 mm was mounted in a thin-walled glass capillary. Preliminary examination on a CAD4 diffractometer established a one-molecule triclinic unit cell. Refined cell constants, a=11.707(2) Å, b=12.744(5) Å, c=9.521(2) Å, α=102.60(3)°, β=101.31(2)°, and γ=100.29(2)°, came from the least-squares refinement of the setting angles of 25 reflections. For a cell content of Zn(BNDPP)·2py (or $ZnO_2N_{10}C_{66}H_{44}$) (F.W.=1074.5), the calculated density is 1.35 g cm^{-3} and the observed density of freshly prepared crystals is 1.36 g cm^{-3}. Intensity data were measured with graphite-monochromated Mo $K\alpha$ radiation at 21±1 °C. Since a completely ordered structure would require that the correct space group be $P1$, the entire triclinic sphere (to 2θ=52.9°) was measured. A total of 10833 reflections were measured. The linear absorption coefficient is 0.52 mm^{-1} and an empirical absorption correction was applied to the entire data set. Relative transmission coefficients ranged from 0.761 to 1.000.

The structure was solved by direct methods (MULTAN):[8] A total of 46 atoms (out of 79) were found in the initially chosen noncentrosymmetric space group $P1$. A few cycles of difference Fourier syntheses located the remaining atoms (except for the solvent molecules). Despite this initial success in the noncentrosymmetric space group, isotropic least-squares refinement led to a number of unsatisfactory interatomic distances and other features more consistent with the presence of inversion centers. Refinement was thus shifted into the centrosymmetric space group $P\bar{1}$. The triclinic data were first averaged assuming Friedel's Law, yielding 3737 observed[9] and averaged reflections (R_{int}=0.019). A certain amount of crystallographic disorder is required in order to describe the Zn(BNDPP) molecule in space group $P\bar{1}$ with Z=1. The zinc atom of the complex was shifted to the inversion center at 0,0,0; this necessarily leads to disorder for the two phenyl substituents. This disorder unfortunately leads to some ambiguity in defining the relative orientations for the two nicotinamide residues. Our analysis assumed the basic molecular structure shown in Fig. 1. The complete structure analysis shows that the terminal pyridine ring of each nicotinamide group coordinates to the zinc atom of an adjacent molecule translated along the c axis. One phenyl ring, C(7)—C(12), had rather large anisotropic thermal parameters and was described by two overlapping rigid groups, a and b. The two rigid groups are almost coplanar but with a C(7a)-C(m2)-C(7b) angle of 17.6°. The occupancy factors of individual atoms of the rigid phenyl groups and amide arms were held fixed at 0.5. The two pyridine solvates (per cell) were found near two separate inversion centers at 1/2,1/2,1/2 and 0,1/2,1/2. Each pyridine ring was close to but disordered around the inversion center. The pyridine near 0,1/2,1/2 was described in terms of two rigid groups. The nitrogen atoms were not conclusively identified and thus the pyridine rings were included in the refinement as three separate, partial occupancy (uniform occupancy factors of 0.25 for each atom) C_6 rigid groups with D_{6h} symmetry. All rigid group refinements were carried out with a locally modified version of ORFLS following the rigid-group description of Scheringer.[10] The hydrogen atoms of the porphyrin ligand were found in difference Fourier maps and were included in fixed idealized positions in the final cycles of least-squares refinement. The final model utilized anisotropic thermal parameters for all non-hydrogen atoms except those of rigid groups. Final values for the discrepancy indices were R_1=0.081 and R_2=0.111.[11] A final differ-

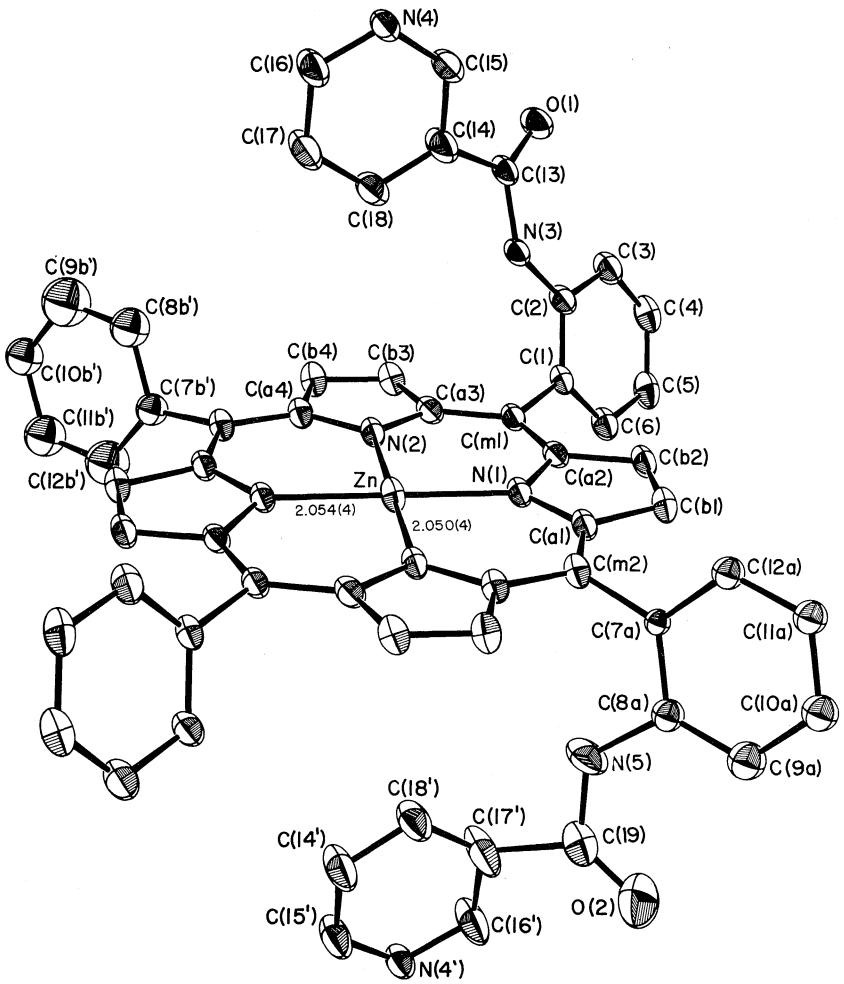

Fig. 1. ORTEP plot (50% ellipsoids) of the Zn(BNDPP) molecule as it exists in the crystal. The atom-labeling scheme for the crystallographically unique atoms are given. Primed (′) atoms are related to unprimed atoms by the inversion center located at the zinc atom.

Table 1. Final Fractional Coordinates and Equivalent Isotropic Temperature Factors for Zn(BNDPP)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Zn[a]	0.0	0.0	0.0	4.1	C(7a)[a]	−0.2357	−0.3663	−0.0069	2.9
O(1)[a]	−0.3326(7)	0.1452(9)	−0.6490(9)	5.3	C(8a)[a]	−0.2463	−0.3823	0.1313	4.5
O(2)[a]	−0.2259(13)	−0.3502(12)	0.4528(17)	10.0	C(9a)[a]	−0.3142	−0.4807	0.1415	6.0
N(1)	−0.1790(3)	−0.0751(4)	−0.0666(4)	3.6	C(10a)[a]	−0.3727	−0.5647	0.0134	5.3
N(2)	−0.0371(3)	0.1413(4)	−0.0479(5)	3.7	C(11a)[a]	−0.3628	−0.5497	−0.1248	4.6
N(3)[a]	−0.2786(7)	0.1101(8)	−0.4210(9)	3.7	C(12a)[a]	−0.2949	−0.4513	−0.1348	4.3
N(4)	−0.0171(4)	0.0721(4)	−0.7483(5)	4.8	C(7b)[a]	−0.2418	−0.3661	−0.0561	5.2
N(5)[a]	−0.1707(12)	−0.2893(11)	0.2582(12)	6.6	C(8b)[a]	−0.2675	−0.3926	0.0713	8.1
C(a1)	−0.2285(4)	−0.1816(5)	−0.0698(6)	3.8	C(9b)[a]	−0.3373	−0.4955	0.0624	13.0
C(a2)	−0.2709(4)	−0.0307(4)	−0.1247(5)	3.5	C(10b)[a]	−0.3826	−0.5738	−0.0743	7.7
C(a3)	−0.1489(4)	0.1584(5)	−0.0991(6)	3.9	C(11b)[a]	−0.3576	−0.5484	−0.2019	9.4
C(a4)	0.0414(4)	0.2385(4)	−0.0260(6)	4.0	C(12b)[a]	−0.2878	−0.4454	−0.1928	10.5
C(b1)	−0.3571(5)	−0.2063(5)	−0.1331(7)	4.5	C(g1)[b]	0.0881	−0.4707	0.5517	13.4
C(b2)	−0.3811(4)	−0.1139(5)	−0.1678(6)	4.2	C(g2)[b]	0.0529	−0.5212	0.3990	13.4
C(b3)	−0.1367(5)	0.2699(5)	−0.1053(7)	4.7	C(g3)[b]	−0.0603	−0.5904	0.3345	13.4
C(b4)	−0.0203(5)	0.3207(5)	−0.0622(7)	4.6	C(g4)[b]	−0.1403	−0.6101	0.4218	13.4
C(m1)	−0.2570(4)	0.0772(4)	−0.1399(5)	3.6	C(g5)[b]	−0.1062	−0.5603	0.5740	13.4
C(m2)	−0.1674(4)	−0.2588(4)	−0.0245(6)	4.0	C(g6)[b]	0.0071	−0.4911	0.6383	13.4
C(1)	−0.3682(4)	0.1089(4)	−0.2127(6)	3.9	C(g7)[b]	0.2466	−0.3175	0.6983	15.9
C(2)	−0.3774(5)	0.1261(5)	−0.3517(6)	4.4	C(g8)[b]	0.2636	−0.3421	0.5543	15.9
C(3)	−0.4824(5)	0.1509(6)	−0.4216(7)	5.4	C(g9)[b]	0.1672	−0.3940	0.4327	15.9
C(4)	−0.5717(5)	0.1600(6)	−0.3520(8)	5.6	C(g10)[b]	0.0521	−0.4222	0.4532	15.9
C(5)	−0.5624(5)	0.1428(6)	−0.2147(8)	5.6	C(g11)[b]	0.0341	−0.3982	0.5961	15.9
C(6)	−0.4603(5)	0.1172(5)	−0.1456(7)	5.0	C(g12)[b]	0.1306	−0.3463	0.7175	15.9
C(13)[a]	−0.2630(9)	0.1268(10)	−0.5546(12)	3.9	C(g13)[b]	−0.3833	0.3931	0.4011	11.8
C(14)	−0.1340(6)	0.1034(10)	−0.5730(8)	6.8	C(g14)[b]	−0.4774	0.4272	0.4552	11.8
C(15)	−0.1209(6)	0.0638(9)	−0.7136(7)	6.4	C(g15)[b]	−0.4740	0.5390	0.5059	11.8
C(16)	0.0748(6)	0.1291(9)	−0.6393(8)	6.6	C(g16)[b]	−0.3765	0.6187	0.5034	11.8
C(17)	0.0681(7)	0.1680(10)	−0.4953(8)	6.9	C(g17)[b]	−0.2823	0.5858	0.4498	11.8
C(18)	−0.0374(6)	0.1499(8)	−0.4613(7)	6.3	C(g18)[b]	−0.2858	0.4739	0.3992	11.8
C(19)[a]	−0.1632(13)	−0.2868(14)	0.4029(19)	6.8					

The estimated standard deviations of the least significant digits are given in parentheses. a) Site occupancies set to 0.5, see text. b) Site occupancies set to 0.25, see text.

ence Fourier synthesis had its highest peak (0.9 e Å^{-3}) near one of the solvate rigid groups. The atomic coordinates are given in Table 1. Final values for the fixed atoms, rigid group descriptions and anisotropic thermal parameters are available.[12]

Results and Discussion

The molecular structure of Zn(BNDPP) is displayed in Fig. 1 along with the atom labeling scheme. Each nicotinamide pyridine ring is coordinated to a zinc ion above or below its porphyrin plane to create a linear chain along the c axis. Three molecules of the resulting chain of six-coordinate zinc porphyrinates is illustrated in Fig. 2. Bond distances and angles (with estimated standard deviations) in the unique half of the porphinato core are given in Fig. 3. Complete tables of individual bond distances and angles are available.[12] Figure 3 also displays the deviations (in units of 0.01 Å) of each atom from the least-squares plane of the porphinato core. Deviations from exact planarity are unremarkable. The zinc(II) ion is precisely centered in the porphinato plane, as required by the molecular (and crystallographic) inversion center.

The two unique Zn-N_p bond distances are 2.050 (4) and 2.054 (4) Å. This 2.052 (3) Å-average value is larger than the 2.037 Å-average value found for three[13-15] different four-coordinate zinc porphyrinates and significantly shorter than the 2.059 (10) to 2.079 (8) Å range observed in a variety[16-21] of five-coordinate zinc porphyrinates. The 2.052 Å distance is comparable to the 2.057 (1) Å-value observed[7] in the only other known six-coordinate porphinatozinc(II) derivative. In both species, the six-coordinate zinc(II) ion is accommodated by substantial radial expansion of the porphinato central hole.

The axial Zn-N(py) bond distance in Zn(BNDPP) is 2.432 (5) Å. This distance is substantially longer than the Zn-N(ax) distance observed[16-23] in any of the five-coordinate species where the axial distances vary from 2.106 (4) to 2.200 (3) Å. The axial distance is even longer than the 2.380 (2) Å Zn-O distance found in [Zn(TPP)(THF)$_2$].[7] This long distance is consistent with quite weak axial bonding, although the observed porphinate core expansion makes evident that a real axial interaction exists. The coordinated pyridine ring plane makes an 88.2° dihedral angle with the porphinato plane. The dihedral angle between the N(1)-Zn-N(4)′ coordinate plane and the pyridine plane is 5.9°.

The structural analysis of this molecule is like the

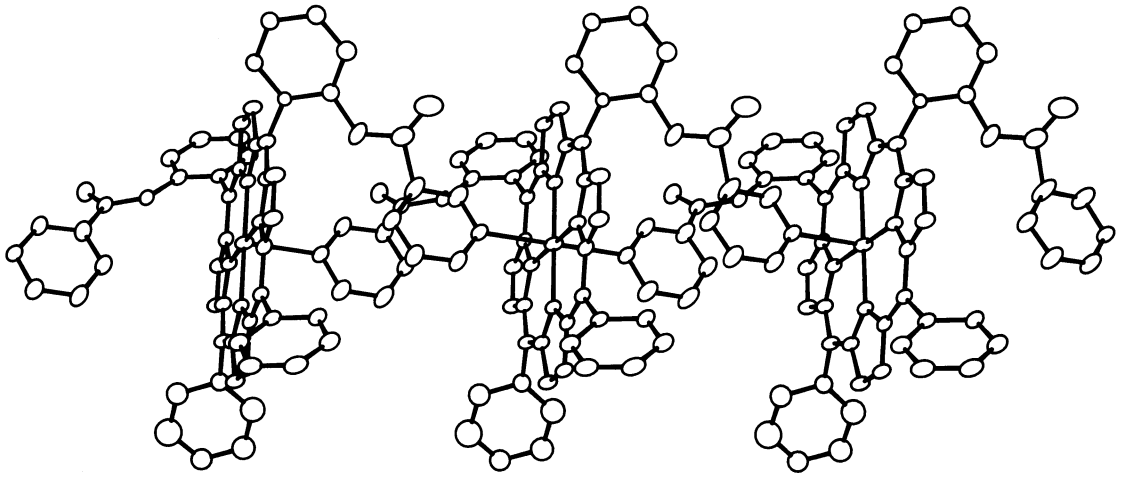

Fig. 2. Computer-drawn plot of the extended structure in crystals of Zn(BNDPP) showing the coordination of the pyridines of the nicotinamide residues on adjacent zinc atoms (*c*-axis). Only three molecules of the infinite chain are illustrated.

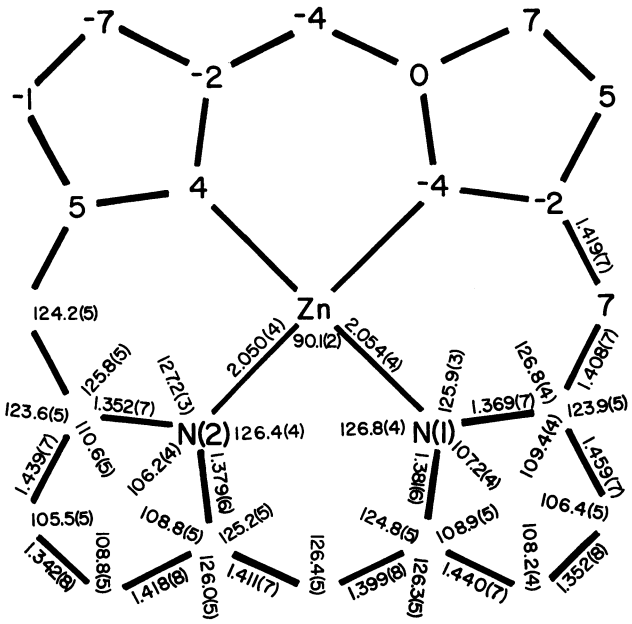

Fig. 3. Formal diagram of the porphinato core illustrating on the top half the displacement of the unique atoms from the mean plane of the 24-atom core. The centrosymmetrically related atoms in the lower half of the diagram have displacements of the same magnitude but opposite sign. All displacement values are in units of 0.01 Å. On the lower half of the diagram are entered the individual values of the bond distances (Å) and angles (°) in the core of the molecule.

resolution of a small puzzle ring. As noted in the Experimental section, the presence of inversion symmetry in the crystal requires a disordered solid-state structure. Unfortunately, this leads to some ambiguity in the complete definition of the molecular structure. However, unless the unlikely assumption—that both amido arms join the porphyrin core to the same pyridine ring—is allowed, the structure determination provides direct evidence that the phenyl substituents are on opposite sides of the porphyrin plane, i.e. the conformation is $\alpha\beta$. Further, unless the assumption that the disorder in the crystal includes two 90° rotational positions (i.e., relative right and left turns) of porphyrin core (in addition to the inversion required disorder), then the structural analysis leads to the conclusion that the substituted phenyl rings on a given molecule must be adjacent. Finally, the six-coordinate nature of the zinc ion is most consistent with this $\alpha\beta$-adjacent substitution of the porphyrin derivative. The disorder in the crystal lattice involves both the chains and the pyridine groups of the nicotinamides, and leads to the enantiomeric disorder. However, although the disorder in the crystal lattice is complex, the $\alpha\beta$-adjacent molecular structure seems to hold in the crystal.

The authors thank the U. S. National Institutes of Health (Grant HL-15627 to WRS) and the Ministry of Education, Science and Culture of Japan (Grant-in-Aid No. 60571024 to KH) for support of this work.

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12) Final tables of anisotropic thermal parameters, atomic coordinates of the fixed hydrogen atoms, rigid group parameters, bond distances and angles and a table (×10) of observed and calculated structure amplitudes are deposited as Document No. 8760 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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