

**Registry No.** [Ru(bpy)<sub>2</sub>(NPP)]BF<sub>4</sub>, 98690-23-4; [Ru(bpy)<sub>2</sub>(NPP)]-BF<sub>4</sub>·<sup>1</sup>/<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub>·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O, 98690-24-5; [Ru(bpy)<sub>2</sub>(NPP)]<sup>+</sup>, 98690-22-3; [Ru(bpy)<sub>2</sub>(PP)]<sup>+</sup>, 98690-25-6; [Ru(bpy)<sub>2</sub>(BQ)]<sup>+</sup>, 98690-26-7; [Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, 20154-62-5; [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 15158-62-0.

**Supplementary Material Available:** Tables of bond distances, bond angles, coordinates for H atoms, anisotropic thermal parameters, and structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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## Crystal and Molecular Structure of a Six-Coordinate Zinc Porphyrin: Bis(tetrahydrofuran)(5,10,15,20-tetraphenylporphinato)zinc(II)

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The crystal and molecular structure of a six-coordinate zinc porphyrin, bis(tetrahydrofuran)(5,10,15,20-tetraphenylporphinato)zinc(II) (**1**), was determined. The compound crystallized in *P* $\bar{1}$  (*Z* = 1), with *a* = 9.572 (1) Å, *b* = 11.115 (2) Å, *c* = 11.720 (3) Å,  $\alpha$  = 102.71 (2)°,  $\beta$  = 103.78 (2)°, and  $\gamma$  = 115.01 (1)°. The structural model was refined to *R* = 0.040 (*R*<sub>w</sub> = 0.043) for 3178 reflections with *I* > 2σ(*I*). The zinc atom was found precisely in the mean porphyrin plane of the centrosymmetric molecule (Zn–N = 2.056 (2), 2.058 (2) Å) and was only weakly bound to the THF molecules (Zn–O = 2.380 (2) Å). Crystals of **1** have been used as hosts for single-crystal EPR studies of metalloporphyrins bearing nitroxyl radical substituents. An analysis of the "free space" in the lattice of **1** shows that to accommodate a nitroxyl-substituted metalloporphyrin, THF must be lost from a neighboring unsubstituted Zn(TPP)(THF)<sub>2</sub> moiety.

### Introduction

The relatively large size of the zinc(II) ion has been thought to preclude a zinc atom position in the mean porphyrin plane for zinc porphyrin complexes.<sup>2-5</sup> Spectroscopic<sup>3,5</sup> and binding constant<sup>4</sup> studies have supported this view and have not yielded any evidence for the existence of six-coordinate zinc porphyrins in solution. No six-coordinate zinc porphyrin has been structurally characterized, and the only zinc porphyrin in which the metal atom occupies a position in the porphyrin plane (as it would in a symmetric six-coordinate species) is the four-coordinate Zn(TPP) complex (TPP = 5,10,15,20-tetraphenylporphyrin) in [Zn(TPP)]·2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>.<sup>6</sup>

In a donor solvent such as THF, or in the presence of added ligands, zinc(II) porphyrins apparently exhibit a preference for a five-coordinate structure which is similar to that of high-spin iron(II) porphyrins.<sup>7</sup> High-spin iron(II) atoms were once thought to be too large to reside in the porphyrin plane, but the structural characterization of bis(tetrahydrofuran)(5,10,15,20-tetraphenylporphinato)iron(II) altered that belief.<sup>8</sup> The crystal and molecular structure of the analogous six-coordinate zinc compound bis(tetrahydrofuran)(5,10,15,20-tetraphenylporphinato)zinc(II) (hereafter **1**), which is reported herein, demonstrates the capability of a zinc atom to bind two axial ligands and to occupy a position in the mean plane of a porphyrin ligand.

Crystals of **1** have found recent use as hosts in a series of EPR studies of spin-labeled metallotetraphenylporphyrins.<sup>9</sup> The

**Table I.** Crystallographic Parameters and Refinement Results for Zn(TPP)(THF)<sub>2</sub>

mol formula	C <sub>52</sub> H <sub>44</sub> N <sub>4</sub> O <sub>2</sub> Zn
mol wt	822.33
space group	<i>P</i> $\bar{1}$
data collen temp, °C	-130
<i>a</i> , Å	9.572 (1)
<i>b</i> , Å	11.115 (2)
<i>c</i> , Å	11.720 (3)
$\alpha$ , deg	102.71 (2)
$\beta$ , deg	103.78 (2)
$\gamma$ , deg	115.01 (1)
<i>V</i> , Å <sup>3</sup>	1022
<i>Z</i>	1
<i>D</i> (calcd), g cm <sup>-3</sup>	1.34
cryst dimens, mm	0.48 (100- $\bar{1}$ 00) × 0.11 (010-0 $\bar{1}$ 0) × 0.20 (001-00 $\bar{1}$ )
radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073 Å), graphite monochromator
$\mu$ , cm <sup>-1</sup>	6.58
scan type	$\theta$ -2 $\theta$
2 $\theta$ range, deg	3.5-50
reflens	$\pm h, \pm k, l \geq 0$ ; 3613 (3178 with <i>I</i> > 2σ( <i>I</i> ))
scan speed, deg min <sup>-1</sup>	variable (3-30)
data:parameter ratio	11.4
<i>R</i>	0.040
<i>R</i> <sub>w</sub>	0.043
GOF	1.60
<i>g</i>	8.7 × 10 <sup>-4</sup>
slope of normal prob plot	1.18

spin-labeled complexes incorporated bulky nitroxyl-bearing substituents that were attached to a pyrrole carbon atom of the porphyrin ring. EPR spectra indicated that in all cases the *z* axes of the transition metal **g** and **A** tensors adopted similar orientations relative to the faces of the host crystal. Since these *z* axes are known to be normal to the porphyrin plane in metalloporphyrins, these results suggested that the porphyrin planes of host molecules and dopant molecules were parallel.

The EPR spectra indicated, however, that the spin-labeled substituents adopted several different positions in the lattice.<sup>9</sup> It therefore appeared that there was more than one way that the nitroxyl-labeled porphyrin could pack into the host crystal and that the steric effects of the host on the dopant were different in different orientations. The correlation between the metal-nitroxyl distance and the angle between the normal to the porphyrin and

- (1) (a) Colorado State University. (b) University of Colorado at Denver. (c) University of Denver.
- (2) Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761.
- (3) (a) Storm, C. B.; Turner, A. H.; Swann, M. B. *Inorg. Chem.* **1984**, *23*, 2743. (b) Storm, C. B. *J. Am. Chem. Soc.* **1970**, *92*, 1423.
- (4) See, for example: (a) Vogel, G. C.; Searby, L. A. *Inorg. Chem.* **1973**, *12*, 936. (b) Vogel, G. C.; Stahlbush, J. R. *Inorg. Chem.* **1977**, *16*, 950. (c) McDermott, G. A.; Walker, F. A. *Inorg. Chim. Acta* **1984**, *91*, 95. (d) Lambert, P. *Chem. Commun.* **1967**, 470.
- (5) Gust, D.; Neal, D. N. *J. Chem. Soc., Chem. Commun.* **1978**, 681.
- (6) Scheidt, W. R.; Kastner, M. E.; Hatano, K. *Inorg. Chem.* **1978**, *17*, 706.
- (7) Braut, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4591.
- (8) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartaian, K.; Lang, G. J. *Am. Chem. Soc.* **1980**, *102*, 2302.
- (9) (a) Damoder, R.; More, K. M.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 2147. (b) Damoder, R.; More, K. M.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1983**, *22*, 2836. (c) Damoder, R.; More, K. M.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1983**, *22*, 3738. (d) Damoder, R.; More, K. M.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1984**, *23*, 1320. (e) Damoder, R.; More, K. M.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1984**, *23*, 1326.

**Table II.** Atomic Coordinates ( $\times 10^4$ ) and Temperature Factors ( $\text{\AA}^2 \times 10^3$ ) for Zn(TPP)(THF)<sub>2</sub><sup>a</sup>

atom	x	y	z	$U_{iso}^b$
Zn	0	0	0	16 (1)
N1	-1061 (3)	186 (2)	-1648 (2)	15 (1)
N2	2315 (3)	1023 (2)	-85 (2)	15 (1)
O1	467 (2)	2302 (2)	1064 (2)	26 (1)
C <sub>a</sub> 1	-2698 (3)	-201 (3)	-2208 (2)	16 (1)
C <sub>b</sub> 1	-2871 (3)	380 (3)	-3185 (3)	20 (1)
C <sub>b</sub> 2	-1343 (3)	1107 (3)	-3209 (3)	20 (1)
C <sub>a</sub> 2	-202 (3)	984 (3)	-2244 (2)	16 (1)
C <sub>m</sub> 1	1517 (3)	1638 (3)	-1942 (2)	15 (1)
C <sub>a</sub> 3	2673 (3)	1672 (3)	-926 (2)	16 (1)
C <sub>b</sub> 3	4445 (3)	2453 (3)	-582 (3)	18 (1)
C <sub>b</sub> 4	5142 (3)	2299 (3)	479 (3)	18 (1)
C <sub>a</sub> 4	3803 (3)	1394 (3)	797 (2)	16 (1)
C <sub>m</sub> 2	4003 (3)	1003 (3)	1859 (4)	16 (1)
C1	2093 (4)	3477 (4)	1879 (3)	47 (2)
C2	1961 (8)	4836 (6)	1897 (15)	61 (4)
C2 <sup>c</sup>	1980 (22)	4644 (23)	2550 (23)	20 (8)
C3	157 (5)	4325 (4)	1507 (4)	43 (2)
C4	-553 (4)	2843 (4)	531 (3)	33 (2)
P1a <sup>d</sup>	2184 (3)	2420 (3)	-2753 (2)	17 (1)
P2a	2144 (4)	1693 (3)	-3897 (3)	24 (1)
P3a	2754 (4)	2414 (3)	-4649 (3)	28 (1)
P4a	3433 (4)	3878 (3)	-4252 (3)	25 (1)
P5a	3490 (4)	4612 (3)	-3117 (3)	27 (1)
P6a	2870 (4)	3886 (3)	-2371 (3)	24 (1)
P1b	5737 (3)	1534 (3)	2721 (3)	17 (1)
P2b	6796 (3)	1171 (3)	2304 (3)	20 (1)
P3b	8434 (4)	1745 (3)	3098 (3)	25 (1)
P4b	9028 (4)	2694 (3)	4310 (3)	28 (1)
P5b	7975 (4)	3048 (3)	4742 (3)	28 (1)
P6b	6336 (4)	2460 (3)	3953 (3)	21 (1)

<sup>a</sup>Estimated standard deviations in the least significant digits are given in parentheses. <sup>b</sup>Equivalent isotropic  $U$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>c</sup>The second resolved position for C2. <sup>d</sup>The atoms P<sub>n</sub> are the carbon atoms of phenyl groups a and b.

the interspin vector suggested that the spin-label substituent was pushed toward the porphyrin plane to different extents when located at different sites in the crystal. It was therefore of interest to determine whether there were sufficiently large voids in the host lattice to accommodate the substituted porphyrins without strain and whether incorporation of the substituted porphyrins with different orientations of the substituent required distortion of the host and/or substituent.

### Experimental Section

**Preparation of 1.** 1 was prepared and purified as previously described.<sup>10</sup> Crystals of suitable quality for study by X-ray diffraction were grown by slow evaporation of a THF solution and were taken from the mother liquor immediately prior to the diffraction experiment to avoid desolvation. The crystal used for the X-ray structure determination had dimensions substantially smaller (see Table I) than the crystals used for the EPR studies (typically  $2 \times 3 \times 1$  mm<sup>3</sup>), but the crystal morphology was similar to that of the larger crystals. The morphology of the doped crystals obtained previously under similar conditions was identical with that of crystals of 1.

**NMR Spectra of 1.** A <sup>1</sup>H NMR spectrum of a solution of freshly grown crystals of 1 in CDCl<sub>3</sub> was recorded on a Chemagnetics A200 NMR spectrometer. Peaks due to THF occurred at 3.10 and 1.53 ppm downfield from Me<sub>4</sub>Si. Upfield ring current shifts are expected for axial ligands on metalloporphyrins.<sup>11</sup> The small upfield shifts of these THF peaks relative to those for free THF in CDCl<sub>3</sub> ( $\delta = 3.60, 1.73$  ppm) are consistent with rapid exchange between a small amount of coordinated THF and free THF. Integration of the spectrum established a 2:1 ratio of THF to Zn(TPP). After exposure of crystals to the atmosphere for 1 week, integration of an NMR spectrum of a solution prepared from

**Table III.** Bond Lengths ( $\text{\AA}$ ) Describing the Zinc Atom Coordination, the Porphyrin Core, and the THF Ligand<sup>a</sup>

Zn-N1	2.056 (2)	Zn-N2	2.058 (2)
Zn-O1	2.380 (2)	N1-C <sub>a</sub> 1	1.374 (4)
N1-C <sub>a</sub> 2	1.370 (4)	N2-C <sub>a</sub> 3	1.368 (4)
N2-C <sub>a</sub> 4	1.373 (3)	C <sub>a</sub> 1-C <sub>b</sub> 1	1.442 (5)
C <sub>b</sub> 1-C <sub>b</sub> 2	1.351 (4)	C <sub>b</sub> 2-C <sub>a</sub> 2	1.448 (5)
C <sub>a</sub> 2-C <sub>m</sub> 1	1.399 (4)	C <sub>m</sub> 1-P1a	1.500 (4)
C <sub>m</sub> 1-C <sub>a</sub> 3	1.401 (4)	C <sub>a</sub> 3-C <sub>b</sub> 3	1.439 (4)
C <sub>b</sub> 3-C <sub>b</sub> 4	1.347 (4)	C <sub>b</sub> 4-C <sub>a</sub> 4	1.448 (4)
C <sub>a</sub> 4-C <sub>m</sub> 2	1.404 (4)	C <sub>m</sub> 2-P1b	1.494 (4)
C <sub>m</sub> 2-C <sub>a</sub> 1'	1.409 (4)	O1-C1	1.437 (2)
O1-C4	1.440 (5)	C1-C2	1.565 (10)
C2-C3	1.481 (9)	C3-C4	1.529 (5)

<sup>a</sup>Estimated standard deviations in the least significant digits are given in parentheses.

**Table IV.** Bond Angles (deg) Describing the Zinc Atom Coordination, the Porphyrin Core, and the THF Ligand<sup>a</sup>

N1-Zn-N2	90.6 (1)	N1-Zn-O1	86.9 (1)
N2-Zn-O1	87.0 (1)	C <sub>a</sub> 1-N1-C <sub>a</sub> 1	126.8 (2)
Zn-N1-C <sub>a</sub> 2	125.2 (1)	C <sub>a</sub> 1-N1-C <sub>a</sub> 2	106.8 (3)
Zn-N2-C <sub>a</sub> 3	125.3 (2)	Zn-N2-C <sub>a</sub> 4	126.7 (2)
C <sub>a</sub> 3-N2-C <sub>a</sub> 4	107.1 (2)	Zn-O1-C1	122.5 (2)
Zn-O1-C4	121.8 (1)	C1-O1-C4	109.2 (3)
N1-C <sub>a</sub> 1-C <sub>b</sub> 1	109.6 (3)	N1-C <sub>a</sub> 1-C <sub>m</sub> 2'	125.4 (3)
C <sub>b</sub> 1-C <sub>a</sub> 1-C <sub>m</sub> 2'	125.0 (3)	C <sub>b</sub> 1-C <sub>b</sub> 2-C <sub>a</sub> 2	107.2 (3)
C <sub>a</sub> 1-C <sub>b</sub> 1-C <sub>b</sub> 2	107.1 (3)	N1-C <sub>a</sub> 2-C <sub>b</sub> 2	109.3 (2)
N1-C <sub>a</sub> 2-C <sub>m</sub> 1	126.0 (3)	C <sub>b</sub> 2-C <sub>a</sub> 2-C <sub>m</sub> 1	124.6 (3)
C <sub>a</sub> 2-C <sub>m</sub> 1-C <sub>a</sub> 3	125.9 (3)	C <sub>a</sub> 2-C <sub>m</sub> 1-P1a	116.9 (3)
C <sub>a</sub> 3-C <sub>m</sub> 1-P1a	117.2 (2)	N2-C <sub>a</sub> 3-C <sub>m</sub> 1	126.1 (3)
N2-C <sub>a</sub> 3-C <sub>b</sub> 3	109.5 (2)	C <sub>m</sub> 1-C <sub>a</sub> 3-C <sub>b</sub> 3	124.4 (3)
C <sub>a</sub> 3-C <sub>b</sub> 3-C <sub>b</sub> 4	107.2 (3)	C <sub>b</sub> 3-C <sub>b</sub> 4-C <sub>a</sub> 4	107.3 (2)
N2-C <sub>a</sub> 4-C <sub>b</sub> 4	108.8 (3)	N2-C <sub>a</sub> 4-C <sub>m</sub> 2	125.8 (3)
C <sub>b</sub> 4-C <sub>a</sub> 4-C <sub>m</sub> 2	125.4 (2)	C <sub>a</sub> 4-C <sub>m</sub> 2-P1b	117.6 (3)
C <sub>a</sub> 4-C <sub>m</sub> 2-C <sub>a</sub> 1'	125.0 (3)	P1b-C <sub>m</sub> 2-C <sub>a</sub> 1'	117.3 (3)
O1-C1-C2	104.6 (4)	C2-C3-C4	100.5 (5)
C1-C2-C3	104.3 (4)	O1-C4-C3	104.8 (3)

<sup>a</sup>Estimated standard deviations in the least significant digits are given in parentheses.

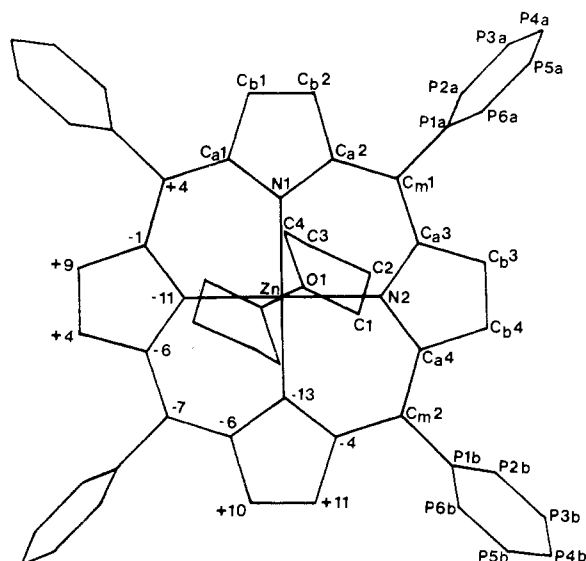
these crystals yielded an approximately 1:1 ratio of THF to Zn(TPP). Apparently, one molecule of THF is readily lost from 1 on standing in the solid state.

**X-ray Structure Determination.** Crystal data for 1, together with details of the X-ray diffraction experiment, are reported in Table I. Cell constants were obtained by a least-squares refinement procedure<sup>12</sup> based on the setting angles for 24 reflections ( $2\theta(\text{av}) = 16.3^\circ$ ) on the Nicolet R3m diffractometer. The stability of the crystal was monitored during data collection by measurement of the intensities of three standard reflections (300, 040, 004) every 150 data points. Over the course of data collection, no significant change in the intensity of any of these reflections was noted. Lorentz and polarization corrections were applied to the raw data. No absorption correction was performed (due to the small average value of  $\mu$ ).

The space group chosen was  $P\bar{1}$  (thus assuming the structure to be isomorphous with that of Fe(TPP)(THF)<sub>2</sub>), and the zinc atom was positioned at the origin (as required by  $Z = 1$ ). Neutral-atom scattering factors were taken from ref 13, and anomalous scattering contributions<sup>13</sup> were included for all atoms. A difference Fourier electron density calculation revealed all unique porphyrin core atoms, the atoms of the two unique phenyl groups, and all the atoms but one in the unique tetrahydrofuran molecule. The remaining atom was found to be disordered between two positions that corresponded to two different conformations of the coordinated THF molecule. This disorder was modeled by placing partial carbon atoms at each site. Refinement of site occupancy factors ( $x$  and  $1-x$ ) for these two carbon atoms yielded a value of  $x = 0.75$  for

- (10) (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (b) Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, 4251. (c) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.  
 (11) (a) Abraham, R. J.; Bedford, G. R.; McNeillie, D.; Wright, B. *Org. Magn. Res.* **1980**, *14*, 418. (b) Abraham, R. J. *J. Magn. Res.* **1981**, *43*, 491.

- (12) Software used for diffractometer manipulations and data collection was provided with the Nicolet R3m diffractometer. All crystallographic computations were carried out with the SHELXTL program package written by G. M. Sheldrick and supplied by Nicolet XRD for the Data General Eclipse S140 computer in the crystallographic laboratory at Colorado State University.  
 (13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974, Vol. IV.



**Figure 1.** Projection of the molecular structure in the porphyrin plane. The numbering scheme for all unique atoms is given, as well as deviations of the atoms (in units of 0.01 Å) from the best least-squares plane through the atoms of the porphyrin core.

**Table V.** Comparative Structural Analysis of Zinc Porphyrins<sup>a</sup>

zinc-porphyrin complex	(Zn-N) <sub>av.</sub> , Å	Ct <sub>N</sub> ...N, Å	ref
Zn(TPP)(THF) <sub>2</sub>	2.057 (1)	2.057	this work
Zn(TPyP)(py)	2.073 (8)	2.047	2
Zn(OEP)(py)	2.067 (6)	2.043	15
Zn(TPP)(ClO <sub>4</sub> ) <sup>b</sup>	2.076 (9)	2.045	16
Zn(TPP)·2C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	2.036 (6)	2.036	6
Zn(TPP-NHC(O)(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N)·C <sub>6</sub> H <sub>6</sub> ·0.50CH <sub>3</sub> CH <sub>2</sub> OH	2.059 (10)	2.033	14

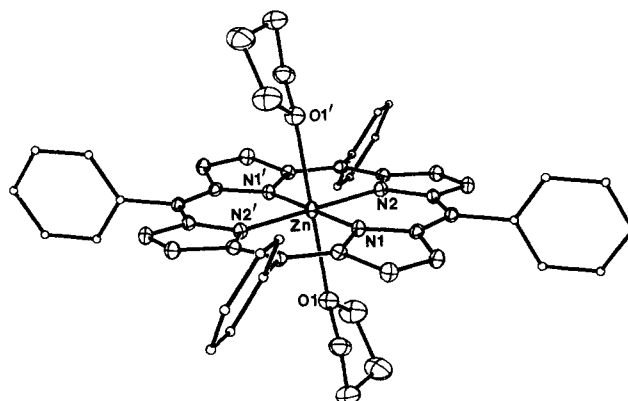
<sup>a</sup> Root-mean-square standard deviations are specified in parentheses for the least significant digits. <sup>b</sup> A porphyrin radical cation complex.

C2. In the final structural model, hydrogen atoms were included in idealized positions (C-H = 0.96 Å) where appropriate (not on the disordered THF) with thermal parameters 20% higher than the equivalent isotropic thermal parameters of the carbon atoms to which the hydrogen atoms were bonded. All non-hydrogen atoms were given anisotropic thermal parameters. The refinement converged ((shift/esd)<sub>av</sub> < 0.015 over the last three cycles) to yield the discrepancy factors shown in Table I. In the final difference electron density map, the highest peaks (~0.7 e Å<sup>-3</sup>) occurred in the vicinity of the disordered THF molecule, while the minimum in the map was -0.3 e Å<sup>-3</sup>. The site occupancy factor for the atoms of the THF molecule was refined and found to equal 1.

The final fractional atomic coordinates for all non-hydrogen atoms may be found in Table II. Bond lengths and angles involving the porphyrin core, the zinc atom, and the coordinated THF molecule may be found in Tables III and IV. Tables of bond lengths and angles for the phenyl groups (Table VII), anisotropic thermal parameters (Table VIII), calculated hydrogen atom positions (Table IX), selected least-squares planes (Table X), and structure factors (calculated and observed, Table XI) have been included as supplementary material.

## Results and Discussion

**Molecular Structure.** A projection of the structure of Zn(TPP)(THF)<sub>2</sub> (**1**) is shown in Figure 1, and a thermal ellipsoid plot of **1** is depicted in Figure 2. The coincidence of the inversion center and the zinc atom requires that atom to be precisely in the mean plane of the porphyrin. This results in the most expanded porphyrin core thus far observed for a zinc porphyrin complex (see Table V). At the same time, **1** exhibits compressed metal-nitrogen bonds (Zn-N1 = 2.056 (2) Å, Zn-N2 = 2.058 (2) Å) that are shorter than similar bonds in five-coordinate zinc complexes (Zn-N = 2.059 (6)–2.076 (9) Å)<sup>2,14–16</sup> but are longer



**Figure 2.** Thermal ellipsoid plot (40% probability) of **1**. Carbon atoms in phenyl rings are drawn with arbitrary radii for clarity. Hydrogen atoms have been omitted.

than the Zn-N distance (2.036 (6) Å)<sup>6</sup> in four-coordinate Zn(TPP) (see Table V).

The enlargement of the porphyrin core is accomplished by means of an imperfect C<sub>2h</sub> distortion, in which the two unique pyrrole rings are canted by 6.3° (for the pyrrole containing N1) and 4.6° (for the pyrrole containing N2) relative to the mean porphyrin plane. The results of this distortion are evident in the displacements of the unique atoms from the porphyrin plane (see Figure 1). The average porphyrin structural parameters (see Table VI) are also indicative of an expanded core.<sup>17</sup> Sn(TPP)Cl<sub>2</sub>, which exhibits the most highly expanded porphyrin core known,<sup>18</sup> and the reference porphyrin core of least strain<sup>17</sup> are also included in Table VI.

The THF molecules are bound quite weakly to the zinc atom (Zn-O = 2.380 (2) Å), as is demonstrated by comparison with the much shorter Zn-H<sub>2</sub>O distance of 2.20 Å estimated in the disordered Zn(TPP)(OH<sub>2</sub>) structure.<sup>19</sup> The oxygen atom of the THF ligand does not lie along the normal to the porphyrin plane. Instead the Zn-O vector is tilted by 9.2° with respect to that normal (see Figure 2). This tilt may arise from a repulsive van der Waals interaction of the THF oxygen atom with the pair of nitrogen atoms that are on the same side of the porphyrin plane. The average N...O distance to this pair of nitrogen atoms (N1 and N2 for O1') is 3.061 (3) Å compared to 3.228 (3) Å for the nitrogen atoms (N1' and N2') that are on the opposite side of the porphyrin plane. The coordinated THF molecule exhibits the commonly observed envelope conformation.<sup>8</sup>

The dihedral angles between the phenyl rings and the mean porphyrin plane are not correlated with the tilt of the Zn-O vector. Instead, the orientations of the phenyl groups appear to depend upon interactions with the α-hydrogen atoms on the THF molecule (see Figure 1). The phenyl group that is most influenced by these interactions (group b) exhibits a smaller dihedral angle (63.2°) with respect to the porphyrin plane than does group a (80.8°). All individual phenyl rings and pyrrole rings of **1** are planar to within 0.01 Å.

The results summarized in Table VI allow a comparison of the average bonding parameters (assuming fourfold symmetry) for **1** and the analogous iron compound, Fe(TPP)(THF)<sub>2</sub>. As can be seen, the structures of these six-coordinate porphyrin complexes of zinc(II) and high-spin iron(II) are quite similar. The same C<sub>2h</sub> distortion of the porphyrin core is seen in the two structures, the dihedral angles between the phenyl rings and the porphyrin core are very similar (65.9 and 83.5° in the iron compound), and even the tilts of the metal-oxygen vector relative to the mean porphyrin plane are nearly identical (8.3° for Fe and 9.2° for Zn).

(16) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 982.

(17) Hoard, J. L. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 18.

(18) Collins, D. M.; Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6689.

(19) Glick, M. D.; Cohen, G. H.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 1996.

(14) Bobrik, M. A.; Walker, F. A. *Inorg. Chem.* **1980**, *19*, 3383.

(15) Cullen, D. L.; Meyer, E. F., Jr. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 2259.

Table VI. Comparative Average Porphyrin Structural Parameters<sup>a</sup>

parameter	ref core of least strain	Zn(TPP)	Zn(TPP)(THF) <sub>2</sub>	Fe(TPP)(THF) <sub>2</sub>	Sn(TPP)Cl <sub>2</sub> <sup>b</sup>
N...Ct <sub>N</sub> (=M-N <sub>av</sub> )	2.010	2.036 (6)	2.057 (1)	2.057 (4)	2.098 (2)
N-C <sub>a</sub>	1.384	1.375 (4)	1.371 (3)	1.374 (6)	1.370 (2)
C <sub>a</sub> -C <sub>b</sub>	1.446	1.443 (4)	1.444 (5)	1.438 (8)	1.446 (1)
C <sub>b</sub> -C <sub>c</sub>	1.355	1.351 (5)	1.349 (3)	1.342 (9)	1.380 (3)
C <sub>a</sub> -C <sub>m</sub>	1.395	1.399 (4)	1.403 (4)	1.406 (9)	1.407 (1)
M-O			2.380 (2)	2.351 (3)	
C <sub>a</sub> -N-C <sub>a</sub>	105.4	106.5 (1)	107.0 (2)	106.7 (4)	109.2 (2)
N-C <sub>a</sub> -C <sub>b</sub>	110.3	109.6 (2)	109.3 (4)	109.2 (4)	108.2 (2)
N-C <sub>a</sub> -C <sub>m</sub>	125.4	125.7 (1)	125.8 (3)	125.5 (4)	126.3 (2)
C <sub>a</sub> -C <sub>b</sub> -C <sub>c</sub>	107.0	107.2 (1)	107.2 (1)	107.5 (4)	107.2 (1)
C <sub>a</sub> -C <sub>m</sub> -C <sub>a</sub>	124.6	125.0 (2)	125.0 (2)	125.8 (12)	126.3 (2)
ref	17	6	this work	8	18

<sup>a</sup>The porphyrin structural parameters are averaged on the basis of fourfold symmetry. For all averaged quantities, root-mean-square standard deviations are specified in parentheses for the least significant digits. <sup>b</sup>This molecule has crystallographically required fourfold symmetry.

This structural similarity also extends to five-coordinate porphyrin complexes of these two metals. For example, the structure of Zn(TpyP)(py)<sup>2</sup> (Zn-N(porph) = 2.073 (3) Å, Zn-N(py) = 2.143 (4) Å, N...Ct<sub>N</sub> = 2.047 Å) is very similar to that of the high-spin Fe(II) complex Fe(TPP)(2-MeIm)<sup>20</sup> (Fe-N(porph) = 2.086 (8) Å, Fe-N(Im) = 2.161 (5) Å, N...Ct<sub>N</sub> = 2.044 Å).

The zinc(II) porphyrins contains two  $\sigma^*$  electrons that are not present in high-spin iron(II) porphyrin complexes. These electrons, located in  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals, would be expected to have a strong influence on metal-ligand bonding parameters. Since the metal-ligand bonding parameters in the two complexes are so similar, zinc(II) must be a sufficiently stronger Lewis acid than iron(II) to offset the effects expected from the two additional antibonding electrons. As in the case of Fe(TPP)(THF)<sub>2</sub>, the fact that the six-coordinate zinc porphyrin species crystallizes from solutions in which the five-coordinate species is predominant<sup>2-5</sup> must be the result of more favorable interactions in the crystal lattice for the six-coordinate complex than for the five-coordinate complex. This conclusion is also supported by the fact that bis(piperidine) complexes of Fe(TPP)<sup>21</sup> and Co(TPP)<sup>22</sup> also crystallize isomorphously with **1**.

**Lattice Structure.** Crystals of **1** have been found to provide an exceptionally good host lattice for metalloporphyrins containing a paramagnetic metal atom and bearing a peripheral spin-labeled substituent (see the Introduction). A number of observations are pertinent with regard to how crystals of **1** function in this manner. The triclinic space group  $P\bar{1}$  ( $Z = 1$ ) demands only that the complex be centrosymmetric. The porphyrin plane and the normal to that plane are not parallel to or aligned with the crystal faces. The normal to the porphyrin plane makes a smallest angle of 36° with respect to the (010) face, a value that compares well with the value of 33° determined by EPR for the angle between the dopant metal  $z$  axis and the 010 crystal face.<sup>9c</sup> The EPR spectra of the spin-labeled metalloporphyrins doped into **1** indicated that the nitroxyl substituent was located at different pyrrole positions in the lattice. Although only three or four positions were identified for any particular combination of metal ion and nitroxyl substituent, the combined data for all of the complexes examined indicated a nearly random distribution of the substituents over the possible pyrrole positions. For each of the substituents the values of  $r$  (the distance between the unpaired electron on the paramagnetic metal and the unpaired electron on the nitroxyl radical),  $\epsilon$  (the angle between the normal to the porphyrin plane and the vector between the two unpaired electrons), and  $J$  (the exchange interaction between the two unpaired electrons) were different for different locations of the substituent in the crystal. For the cis isomers the values of  $r$  were found from 9.2 to 12.5 Å, while  $\epsilon$  ranged from 25 to 63°. For the trans isomer the values of  $r$  and  $\epsilon$  spanned 11.5–15.5 Å and 60–85°, respectively. These variations indicated different conformations of the substituent at

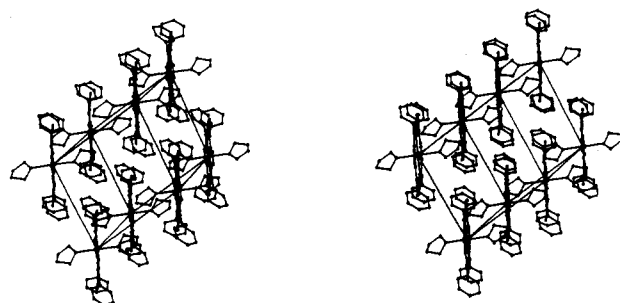


Figure 3. Packing diagram of **1** oriented perpendicular to the mean porphyrin plane.

different locations in the lattice and suggested that the changes might be due to steric interactions with the host lattice.

The crystallographic results were examined to explore the possibility of packing these rather large substituents into the lattice of **1** (see Figure 3). Two regions of the lattice were selected to sample the range of values of  $r$  and  $\epsilon$  that were obtained from the EPR data:  $r = 9$  Å,  $\epsilon = 45^\circ$ , and  $r = 14$  Å,  $\epsilon = 85^\circ$ . The "free space" available in the lattice for occupancy by such bulky substituents was explored by calculating the coordinates of a set of points 0.75 Å apart from each other on a circle described by these representative  $r$ ,  $\epsilon$  pairs. All contacts between any such points and an atom in the TPP, an atom in the THF, or the zinc atom that were less than the sum of the covalent radii plus 0.50 Å were considered to preclude the presence of nitroxyl substituent. In a "perfect" lattice, no points in either ( $r$ ,  $\epsilon$ ) configuration were free of such restrictive van der Waals contacts, thus implying that it is not possible to pack the nitroxyl substituents into a defect-free lattice.

One of the simplest possible lattice defects involves the absence of a THF molecule. If one ignores interactions involving atoms in the THF molecules and points in the generated set, voids in the lattice become apparent that appear sufficiently large to accommodate the porphyrin substituents. The voids generated in this fashion were of unequal size and occurred with approximate fourfold symmetry, as predicted by the EPR results. Although it is difficult to describe the "free space" precisely, the possible locations on the substituent are not crystallographically equivalent, so it is plausible that the steric interactions with the substituent would be different. Thus, substituents at these locations might adopt different conformations as proposed on the basis of the EPR data. All aspects of the behavior of the dopant species in the host lattice suggest that a nitroxyl-substituted metalloporphyrin simply takes the place of a Zn(TPP)(THF)<sub>2</sub> molecule. The only lattice defect that must occur to incorporate the large nitroxyl substituent is loss of a THF molecule from a neighboring Zn(TPP)(THF)<sub>2</sub> molecule. Such a defect may be occurring in the lattice of **1**. The observation that the principal axis of the thermal ellipsoid for the zinc atom is perpendicular to the porphyrin plane (see Figure 2) may indicate that a small amount of five-coordinate Zn(TPP)(THF) has been incorporated into the lattice. The fact that this defect may occur so readily for Zn(TPP)(THF)<sub>2</sub>, which is

(20) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 6769.

(21) Radonovich, L. J.; Bloom, A.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2073.

(22) Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84.

more stable in solution as five-coordinate Zn(TPP)(THF), explains why crystals of **1** function so nicely as a host lattice for the spin-labeled porphyrins.

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**Supplementary Material Available:** Listings of bond lengths and angles for the phenyl groups (Table VII), anisotropic thermal parameters (Table VIII), calculated hydrogen atom positions (Table IX), selected least-squares planes (Table X), and structure factors (calculated and observed; Table XI) (23 pages). Ordering information is given on any current masthead page.

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## Chelate and Steric Effects in the Aquation of the (Thiolato)chromium(III) Complexes $[(en)_2Cr(S-X-COO)]^+$ Where $X = -CH_2-$ , $-CH_2CH_2-$ , and $-C(CH_3)_2-$ : Anchimeric Assistance in Competitive Cr-S, Cr-N, and C-O Bond Fission<sup>1</sup>

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Hydrolysis of the (thiolato)chromium(III) complexes  $[(en)_2Cr(S-X-COO)]^+$ , where  $X = -CH_2-$ ,  $-CH_2CH_2-$ , and  $-C(CH_3)_2-$ , is a complicated process. The initial step of this process involves acid-catalyzed Cr-S bond cleavage, but the  $[(en)_2Cr(OH_2)(OOC-X-SH)]^{2+}$  product of this step can then undergo three subsequent reactions based on the nucleophilicity of the pendant thiol moiety. (1) The pendant thiol can displace coordinated water to re-form the Cr-S linkage and regenerate the starting thiolato complex. (2) The pendant thiol can anchimerically assist C-O bond fission to eliminate the entire thiolato ligand and produce  $[(en)_2Cr(OH_2)_2]^{3+}$ . (3) The pendant thiol can anchimerically assist Cr-N bond fission to yield higher charged complexes that also contain pendant thiol moieties and can thus react further. The relative rates of these three subsequent reactions are dependent on the size of the ring formed upon attack by the pendant thiol. Formation of five-membered rings is favored over formation of six-membered rings. Thus, C-O bond fission is favored for  $X = -CH_2CH_2-$ , but Cr-S bond formation and Cr-N bond fission are favored for  $X = -CH_2-$  and  $-C(CH_3)_2-$ . C-O bond fission is especially unfavorable when  $X = -C(CH_3)_2-$ , because the extra methyl groups further hinder formation of the already sterically restricted four-membered ring required for this process. Anchimerically assisted Cr-N bond fission is at least 2 orders of magnitude faster than unassisted Cr-N bond fission and is competitive with Cr-S bond fission. This leads to the observation of complicated kinetic profiles for the rupture of the Cr-S bond, which can be monitored at the characteristic ligand-to-metal charge-transfer absorption band of these complexes. Some of these complexities can be resolved by the use of initial-rate techniques for the complex with  $X = -CH_2CH_2-$  and by analysis of the rate data for the complex with  $X = -C(CH_3)_2-$  within a consecutive first-order reaction scheme. Comparable rate parameters governing acid-catalyzed Cr-S bond fission at 25°C with  $\mu = 1.00$  M ( $HClO_4/LiClO_4$ ) are  $(19 \pm 3) \times 10^{-4}$ ,  $(11.1 \pm 0.2) \times 10^{-4}$ , and  $(8.0 \pm 0.3) \times 10^{-4} M^{-1} s^{-1}$  for  $X = -CH_2CH_2-$ ,  $-CH_2-$ , and  $-C(CH_3)_2-$ , respectively. The significantly larger rate for the complex with  $X = -CH_2CH_2-$  results at least in part from the greater basicity of the sulfur atom in the more flexible six-membered ring. At  $\mu = 4.00$  M and at 25°C, the  $K_a$  values for the protonated complexes are estimated to be 0.35 M for  $X = -CH_2CH_2-$ , 1.2 M for  $X = -CH_2-$ , and  $>4$  M for  $X = -C(CH_3)_2-$ . Overall, the rates of initial Cr-S bond fission in these complexes are remarkably similar and are not strongly influenced by the chelate and steric effects that dominate the subsequent reactions of  $[(en)_2Cr(OH_2)(OOC-X-SH)]^{2+}$ .

### Introduction

The chemistry of coordinated sulfur and the relevance of this chemistry to biological systems have been recently reviewed in detail.<sup>2</sup> The chemistry of thiolato complexes is of special relevance in this area because of the prevalence of thiol-metal interactions in many metalloenzymes.<sup>3</sup> In order to elucidate the general reactivity patterns of thiolato ligands, we have prepared several complexes of the general formula  $[(en)_2M(X)]^{n+}$ , where M represents Co(III) or Cr(III) and X represents one of several bidentate-N,S or bidentate-O,S ligands. An early investigation<sup>4</sup> into the lability of the M-S bond showed that the Co(III) complexes  $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$  and  $[(en)_2Co(SCH_2COO)]^+$  are remarkably resistant to hydrolysis and acid media but that the Cr(III) analogues  $[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$  and  $[(en)_2Cr(SCH_2COO)]^+$  undergo rapid acid-catalyzed Cr-S bond fission, as well as acid-independent Cr-S and Cr-N bond cleavage. The chemistry of the Cr-S bond fission process is complex, and more

than one hydrolysis product is observed. In order to further elucidate the chemistry and reactivity of the thiolato-chromium(III) linkage, the related complexes  $[(en)_2Cr(SCH_2CH_2COO)]^+$  and  $[(en)_2Cr(SC(CH_3)_2COO)]^+$  have been prepared. In this paper we report on the kinetics and mechanism of the acid-catalyzed hydrolysis of these two complexes, as well as on the nature of the products arising from hydrolysis of all three of the related complexes  $[(en)_2Cr(S-X-COO)]^+$ , where  $X = -CH_2-$ ,  $-CH_2CH_2-$ , and  $-C(CH_3)_2-$ .

### Experimental Section

**Materials.** Doubly distilled water was used in all work. Common laboratory chemicals were of reagent grade and were used without further purification. G. F. Smith doubly vacuum-distilled 70-72% perchloric acid was used in all kinetic experiments. Dowex 50W-X2, 200-400 mesh, cation-exchange resin was cleaned and converted to the lithium form before use.<sup>5</sup> Well-characterized, and purified, perchlorate salts of (2-mercaptoacetato-O,S)bis(ethylenediamine)chromium(III), (3-mercaptopropionato-O,S)bis(ethylenediamine)chromium(III), and (2-methyl-2-mercaptopropionato-O,S)bis(ethylenediamine)chromium(III) (i.e., the title complexes with  $X = -CH_2-$ ,  $-CH_2CH_2-$ , and  $-C(CH_3)_2-$ , respectively) were available from previous studies.<sup>4,6</sup>

**Product Analyses.** Approximately 50 mg of each complex was dissolved in 25 mL of aqueous reaction medium at room temperature, and the hydrolysis reaction was allowed to proceed for various periods of time.

(1) Abstracted in part from: Adzamlı, I. K. M.S. Thesis, University of Cincinnati, 1975.

(2) Deutsch, E.; Root, M. J.; Nosco, D. L. In "Advances in Inorganic and Bioinorganic Reaction Mechanisms"; Sykes, A. G., Ed.; Academic Press: London, 1982; Vol. 1, p 269.

(3) (a) Lovenberg, W. *Met. Ions Biol.* **1973**, *1*; **1973**, *2*; **1976**, *3*. (b) Timkovich, R.; Dickerson, R. E. *Enzymes (3rd Ed.)* **1976**, *11*, 347. (c) Spiro, T. G. *Met. Ions Biol.* **1982**, *4*. (d) Sigel, H. *Met. Ions Biol. Syst.* **1981**, *13*.

(4) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.

(5) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

(6) Adzamlı, I. K.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 1366.