Porphyrin Sponges. Inversion Disorder and Inversion Twinning in Lattice Clathrates Based on Five-Coordinate Metallotetraarylporphyrin Complexes

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Received June 27, 1990

Abstract: X-ray structural characterization has played a key role in revealing the potential of metalloporhyrin complexes as lattice clathrates, and further structural work is essential to the development of many applications of these "porphyrin sponges". Clathrates based on five-coordinate tetraphenylporphyrin (TPP) complexes, however, often exhibiit an incomplete inversion disorder that precludes accurate structure determination by standard methods. This report describes a refinement procedure that models the inversion disorder and twinning and allows the extraction of accurate structural information. Multiple-temperature structural data are provided for $Fe^{III}TPP$(benzenethiolate) as the toluene and chlorobenzene solvates, as well as for $Fe^{III}TPP$(*p*-bromobenzenethiolate) as the toluene solvate. Structural data are also provided for an unsolvated and completely ordered form of $Fe^{III}TPP$(benzenethiolate). Observation of some highly disordered but untwinned specimens of the solvates suggests that the residual order is created at the crystal/solution interface during crystal growth. Structural variations among the ten determinations carried out are consistent with admixed $S = {}^3/_2{:}S = {}^5/_2$ ground states for these materials.

Investigations in this laboratory[1] have explored structural systematics and applications of a large class of tetraphenylporphyrin- (TPP) based lattice clathrates that have been referred to as "porphyrin sponges". This designation alludes to the microporous structure of these materials and also to the "softness" of a host structure in which there are no covalent interactions among host molecules. Extended channels in these crystalline materials distort to accommodate guest species of diverse size and shape.

Materials in this series exhibit a common centrosymmetric arrangement of TPP molecules and have two centrosymmetrically related guest sites juxtaposed with the axial coordination sites of the porphyrin metal atom.[2] In materials based on four-coordinate metalloporphyrins, these sites are usually occupied by solvate molecules, while in materials based on six-coordinate metalloporphyrins the guest sites contain the axial ligands. It is possible to "program" a sponge to preferentially accommodate guest species of a predetermined size, shape, and handedness. This is accomplished by construction of a host lattice based on a five-coordinate TPP complex in which the axial ligand has the same size and shape as the desired guest but the opposite handedness.

Because of the many potential applications of clathrates based on these five-coordinate hosts, a substantial number of crystal structure determinations have been undertaken in this laboratory. These investigations have revealed a structural complexity that is not amenable to standard crystallographic refinement. This report outlines a refinement procedure that successfully models this complexity and describes the application of this procedure to a number of TPP-based clathrates.

The Problem. A recent report[1] from this laboratory described 65 "isostructural" TPP-based compounds. These compounds contain a wide range of metal atoms and metal atom oxidation states and incorporate from 0 to 80 "guest" atoms per porphyrin. The guest species consist of combinations of ligands, counterions, and solvate molecules.

The fact that these diverse materials adopt a common structure demonstrates the degree to which the molecular packing is controlled by the large and relatively rigid porphyrin. The common packing motif of the porphyrin ligands is centrosymmetric. In almost all cases where the porphyrin atoms are four- or six-coordinate, crystal structures exhibit rigorous inversion symmetry; the porphyrin metal atom is located on a crystallographic inversion center that also relates the two guest sites.

It is not surprising that when five-coordinate porphyrin complexes adopt this packing arrangement (with the axial ligand in one guest site and a solvate molecule in the other) they often exhibit an inversion disorder. This disorder involves the interchange of the ligand and solvate species and a displacement of the metal atom from one side of the porphyrin plane to the other. In some cases this disorder appears to be completely random, and a centrosymmetric refinement produces a good fit to the X-ray observations. In other cases, however, the fit of a centrosymmetric model is poor, with difference maps suggesting errors in the model associated with the disordered portion of the structure. Refinement of an ordered noncentrosymmetric model usually produces similarly poor fits, again with indications that the errors are associated with the metal atom, axial ligand, and solvate molecule.

The Solution. In an effort to better model the inversion disorder in these systems, an order parameter has been introduced in the refinement procedure that, in the absence of anomalous dispersion, scales the imaginary part of the structure factor. This parameter makes it possible to model systems in which the inversion disorder is incomplete.

Figure 1 shows the scattering vectors, $\mathbf{v}'$ and $\mathbf{v}''$, for two inversion-related atoms with anomalous dispersion included. Inversion disorder results in a scattering vector that is a weighted average of these two.

$$\mathbf{v} = (1 - w)\mathbf{v}' + w\mathbf{v}''$$

The real and imaginary parts of this vector are given by

$$a = f \cos \phi - (1 - 2w)f'' \sin \phi$$

$$b = f'' \cos \phi + (1 - 2w)f \sin \phi$$

where $\phi = 2\pi\mathbf{hx}$ and where f and f'' are the real and imaginary parts of the scattering factor. Summation over all atoms gives the following expression for the structure factor

$$A(\mathbf{h}) = \textstyle\sum_k[f_k \cos (2\pi\mathbf{hx}_k) - \mathrm{OP}f''_k \sin (2\pi\mathbf{hx}_k)]$$

$$B(\mathbf{h}) = \textstyle\sum_k[f''_k \cos (2\pi\mathbf{hx}_k) + \mathrm{OP}f_k \sin (2\pi\mathbf{hx}_k)]$$

$$F(\mathbf{h}) = A(\mathbf{h}) + iB(\mathbf{h})$$

where the order parameter, $\mathrm{OP} = (1 - 2w)$, takes on a value of 1.0 for a completely ordered structure (space group $P1$) and a value of 0.0 in the case of complete disorder (space group $P\bar{1}$).

In cases where the order parameter is significantly less than one, it seemed likely that these materials would be inversion twinned, i.e., that independently scattering regions in the crystal would not all exhibit the same handedness. For this reason, a twinning parameter, TP, was included in the refinement procedure

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[1] Byrn, M. P.; Curtis, C. J.; Khan, S. I.; Sawin, P. A.; Tsurumi, R.; Strouse, C. E. *J. Am. Chem. Soc.* **1990**, *112*, 1865-74.

[2] In a few cases,[1] two adjacent sites are occupied by a single guest molecule.

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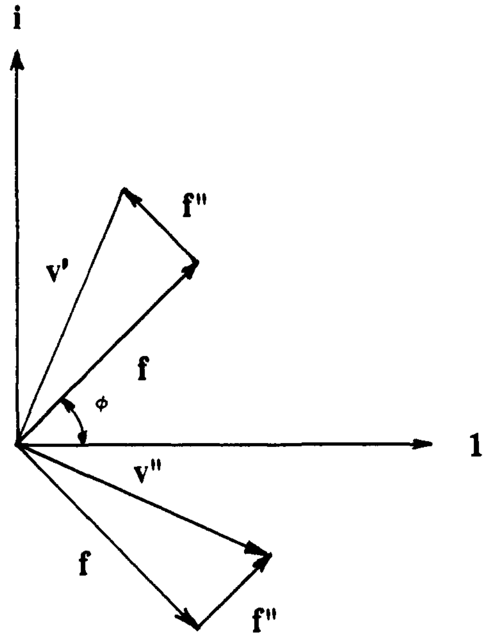

Figure 1. Scattering vectors for two inversion-related atoms.

to assure proper treatment of the anomalous scattering. This parameter corresponds to the fraction of the alternate enantiomer, with extreme values of 0 and 1 corresponding to untwinned enantiomeric crystals and a value of 0.5 corresponding to a 1:1 mixture. The expression for $F_{\text{calc}}(\mathbf{h})^2$ takes the following form:

$$F_{\text{calc}}(\mathbf{h})^2 = (1 - \text{TP})|F(\mathbf{h})|^2 + \text{TP}|F(-\mathbf{h})|^2$$

Flack[3] has used the same parameter for enantiomer-polarity estimation.

A provision was also made in the refinement code to allow constraint of the porphyrin ligand to inversion symmetry. This constraint could certainly introduce some error into the refinement of five-coordinate species, in which the porphyrin ligand has been found to exhibit a variety of distortions from D_{4h} symmetry, but in the refinement of nearly centrosymmetric structures this constraint is often a practical necessity. The potential effects of this constraint, particularly on the metal–nitrogen distances, must be considered in any analysis of the structural parameters obtained from these refinements.

Applications. Development of the refinement technique described herein was prompted by severe difficulties encountered in the refinement of some complex mixed crystals. The toluene and chlorobenzene solvates of Fe$^{\text{III}}$TPP(benzenethiolate) were synthesized to provide relatively simple systems with which the refinement procedure could be tested. Multiple-temperature data sets were obtained for both solvates. To assess the accuracy of the structural data obtained from these refinements, a structure determination was also carried out on an unsolvated form of Fe$^{\text{III}}$TPP(benzenethiolate). To provide a more critical test of the procedure, multiple-temperature data sets (full sphere) were collected for Fe$^{\text{III}}$TPP(*p*-bromobenzenethiolate) as the toluene solvate. The large scattering factor of bromine and its large anomalous scattering cross section provide order and twinning parameters with smaller uncertainties than those for the unbrominated analogues. A final application reported herein is to the structure of Fe$^{\text{III}}$TPP(benzoate) as the toluene solvate. In all cases the refinement gave a satisfactory fit to the observed data and chemically reasonable structural parameters.

Experimental Section

Preparation of Fe$^{\text{III}}$TPP(benzenethiolate) Toluene Solvate. Twenty milligrams of (μ-oxo)(Fe$^{\text{III}}$TPP)$_2$ and 21 mg of diphenyl disulfide were weighed into a 5-mL Mininert vial that had been flushed with nitrogen. Nitrogen-flushed toluene, 2.5 mL, and benzenethiol, 0.1 mL, were added via syringe. (The diphenyl disulfide and the benzenethiol were added to the solutions to provide a redox buffer of fixed potential. The benzenethiol also served as the source of the benzenethiolate ligand.) The vial was heated to 80 °C overnight and then allowed to cool slowly. After 1 week large black crystals were collected. The total yield from four such vials was 68 mg. Anal. Calcd for $\text{FeSN}_4\text{C}_{57}\text{H}_{41}$: C, 78.69; H, 4.76; N, 6.44; S, 3.69; Fe, 6.42. Found: C, 78.47; H, 4.82; N, 6.50; S, 3.76; Fe, 6.35, corresponding to a S/Fe mole ratio of 1.07. The mother liquor from the four vials was transferred via syringe to another vial, which had been flushed with nitrogen and contained 10 mL of heptane. The heptane diffused into the mother liquor over several days and yielded single crystals suitable for X-ray analysis.

Preparation of Fe$^{\text{III}}$TPP(benzenethiolate) Chlorobenzene/Benzenethiol Solvate. Twenty milligrams of (μ-oxo)(Fe$^{\text{III}}$TPP)$_2$ and 21 mg of diphenyl disulfide were weighed into a 5-mL Mininert vial that had been flushed with nitrogen. Nitrogen-purged chlorobenzene, 1 mL, and benzenethiol, 0.1 mL, were added to the vial via syringe. The vial was heated to 80 °C overnight and then allowed to cool slowly. Large platelets were obtained in 66–75% yield. Anal. Calcd for $\text{FeSClC}_{56}\text{H}_{38}\text{N}_4$: C, 75.54; H, 4.31; N, 6.29; S, 3.60; Fe, 6.27; Cl, 3.98. Found: C, 75.35; H, 4.28; N, 6.36; S, 4.04; Fe, 6.06; Cl, 3.49, corresponding to an S/Fe mole ratio of 1.16 and a Cl/Fe mole ratio of 0.91.

Preparation of Fe$^{\text{III}}$TPP(*p*-bromobenzenethiolate) Toluene Solvate. (μ-oxo)(Fe$^{\text{III}}$TPP)$_2$, 19.4 mg, and 104 mg of *p*-bromobenzenethiol were placed in a Mininert vial flushed with nitrogen. Toluene, 0.75 mL, flushed with nitrogen was added to the vial via syringe. The vial was then heated overnight to 80 °C and allowed to cool slowly. Several large crystals and a few smaller ones were obtained after several months. The crystals used in the X-ray study were cut from larger specimens.

Preparation of Fe$^{\text{III}}$TPP(benzoate) Toluene Solvate. This material was prepared by Judith Burstyn.[4] A toluene solution of the complex was layered with heptane to produce X-ray quality crystals.

Preparation of Unsolvated Fe$^{\text{III}}$TPP(benzenethiolate). Twenty milligrams of (μ-oxo)(Fe$^{\text{III}}$TPP)$_2$, 0.208 g of diphenyl disulfide, 0.1 mL of benzenethiol (distilled and stored under nitrogen at low temperature), and 2 mL of benzene were mixed in a Mininert vial previously flushed with nitrogen. The vial was heated to 80 °C for 12 h and cooled slowly to room temperature. After 1 week there were no crystals, but after 8 months there was a collection of platelets. One crystal was suitable for X-ray analysis. Crystalline samples for other analyses were grown in more concentrated solutions and diffused with heptane under a nitrogen atmosphere. Anal. Calcd for $\text{FeSN}_4\text{C}_{50}\text{H}_{33}$: C, 77.11; H, 4.41; N, 7.20; S, 4.12; Fe, 7.17. Found: C, 77.07; H, 4.60; N, 7.12; S, 4.21; Fe, 7.29.

Magnetic Susceptibility Measurements. All magnetic susceptibility measurements made use of a SHE magnetometer maintained by the University of Southern California. All samples were imbedded in fast-setting epoxy and corrections were made for the diamagnetism of the epoxy and the sample.

Thermogravimetric and Mass Spectrometric Analyses. TGA analyses made use of a Du Pont 951 TGA, while mass spectrometric analyses made use of a Kratos MS-25.

Fe$^{\text{III}}$TPP(benzenethiolate) Toluene Solvate. A 3.75-mg crystalline sample of the material crystallized from the original mother liquor was analyzed over the range 20–500 °C under an argon stream with a 5 °C/min scan speed. A weight loss of 9.7% (theoretical = 10.6%) at 111 °C is attributed to the toluene solvate (bp = 110 °C). Mass spectrometric analysis at this temperature gave a molecular ion of 91 Da (Da = daltons). A second loss at 255 °C, corresponding to 12.7% (theoretical 12.5%), is attributed to conversion of benzenethiolate to diphenyl disulfide (bp = 310 °C) with concomitant reduction of Fe$^{\text{III}}$ to Fe$^{\text{II}}$. Mass spectrometric analysis at this temperature gave peaks at 109 and 218 Da corresponding to SC_6H_5 and $\text{S}_2\text{C}_{12}\text{H}_{10}$ and at 186 Da corresponding to $\text{SC}_{12}\text{H}_{10}$.

Fe$^{\text{III}}$TPP(benzenethiolate) Chlorobenzene/Benzenethiol Solvate. A 4.37-mg crystalline sample was analyzed over the range 20–500 °C under a nitrogen stream with a 5 °C/min scan speed. At 102 °C there was a 10.25% weight loss (theoretical = 12.6%) attributed to chlorobenzene solvate (bp = 131 °C). This TGA showed a small shoulder around 70 °C, but no evidence of benzenethiol (bp = 168 °C) was detected in a low-temperature mass spectrometric analysis. A second loss at 248 °C corresponding to 11.8% (theoretical = 12.2%) is attributed to conversion of the benzenethiolate ligand to diphenyl disulfide. Mass spectrometric analysis gave peaks at 109 and 218 Da corresponding to SC_6H_5 and $\text{S}_2\text{C}_{12}\text{H}_{10}$ and at 186 Da corresponding to $\text{SC}_{12}\text{H}_{10}$.

Fe$^{\text{III}}$TPP(*p*-bromobenzenethiolate) Toluene Solvate. This material did not give a clean TGA. The sample appeared to undergo a reaction at elevated temperature.

X-ray Measurements. All X-ray measurements made use of locally automated Huber and Picker diffractometers equipped with graphite

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[3] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.

[4] Burstyn, J. N. Ph.D. Thesis, Department of Chemistry, UCLA, 1986.

monochromatized Mo sources. The Huber diffractometer is equipped with a closed cycle Air Products refrigerator, and the Picker diffractometer is equipped with a gas stream low-temperature device. All solvate crystals were coated with epoxy to prevent loss of solvate and mounted on glass fibers. No significant radiation damage was detected. All data (except those for the benzoate complex) were corrected for absorption, and the structures were solved by standard methods.

Crystallographic programs included in the UCLA Crystallographic Computing Package include modified versions of the following: REDUCE (Coppens, Becker, Blessing, and Broach), peak profile analysis, Lorentz and polarization corrections; MULTAN (Mains), direct methods, Fourier analysis, and map searching; ORFLS (Busing, Martin, and Levy), structure factor calculation and least-squares refinement; ORFFE (Busing, Martin, and Levy), distance, angle, and error calculations; ABSORB (Coppens, Edwards, and Hamilton), absorption correction; ABSCOR (Heinemann), empirical absorption correction; ORTEP (Johnson), Figure plotting; HYDROGEN (Trueblood), calculation of hydrogen atom positions. All calculations were performed on DEC VAX computers. Atomic scattering factors and anomalous dispersion corrections were taken from ref 5. Agreement factors were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$ where F_o and F_c are the observed and calculated structure factors, respectively, and $w = 1/(\sigma(F_o))^2$. The function minimized in final refinements was $\sum(w||F_o| - |F_c||)^2$.

Details of the Refinement Protocol. In all the refinements of the Fe^{III}TPP(benzenethiolate) solvates reported herein, the axial ligands and solvate molecules are treated as rigid groups with C–C and C–H distances of 1.39 and 1.00 Å, respectively. The C–S distance was refined as an independent parameter. In all these refinements the thermal motion of the phenyl group of the benzenethiolate ligand was modeled with six translational parameters, three librational parameters, and two screw motion parameters.[6] The origin of the group was located at the sulfur atom position. Independent anisotropic thermal parameters were assigned to the sulfur atom. In all cases the porphyrin hydrogen atom positions were calculated (C–H = 1.0 Å) late in the refinement process, and these positions were fixed; a single parameter was refined corresponding to the temperature factor of the porphyrin hydrogen atoms.

In the refinements of the toluene solvates, the thermal motion of the toluene molecules was modeled with six translational parameters. In the structures that exhibited end-for-end disorder of the toluene molecules, the sum of the toluene occupancies was constrained to unity. No toluene methyl hydrogen atoms were included in the final models.

In refinements of the chlorobenzene solvate, the thermal motion of the chlorobenzene molecule was modeled with six translational parameters, three librational parameters, and two screw motion parameters. The origin of the group was located at the para-carbon position (at 125 K) or the center of the phenyl group (at 294 K). The C–Cl distance of the chlorobenzene molecule was refined as an independent parameter. In the low-temperature refinement, the thermal motion of the axial ligand of the six-coordinate form was modeled with six translational parameters, and the sum of the five-coordinate and six-coordinate iron atom occupancies was constrained to unity.

In the refinements of Fe^{III}TPP(*p*-bromobenzenethiolate) toluene solvate, the ligand and solvate molecules were not constrained. The presence of the bromine atom and the large data sets available made such constraints unnecessary.

Results

Fe^{III}TPP(benzenethiolate) Toluene Solvate. Multiple-temperature X-ray examination of this material revealed that below about 175 K the diffraction peaks broadened drastically. The first sample of this material, prepared by heptane diffusion, was studied at 301 and 175 K. Since the order parameter reflects the order in the direction of the displacement of the iron atom and the thiolate ligand from the porphyrin plane and since there is no obvious mechanism whereby the thiolate ligand and the toluene solvate molecule can be exchanged, the order parameter and the twinning parameter are presumably established at the time of crystallization and not subject to change with temperature. Indeed, both the order parameter and the twinning parameter were found to be virtually independent of temperature (OP = 0.451 (4) at 175 K and OP = 0.476 (6) at 301 K; TP = 0.04 (7) at 175 K and TP = 0.03 (9) at 301 K).

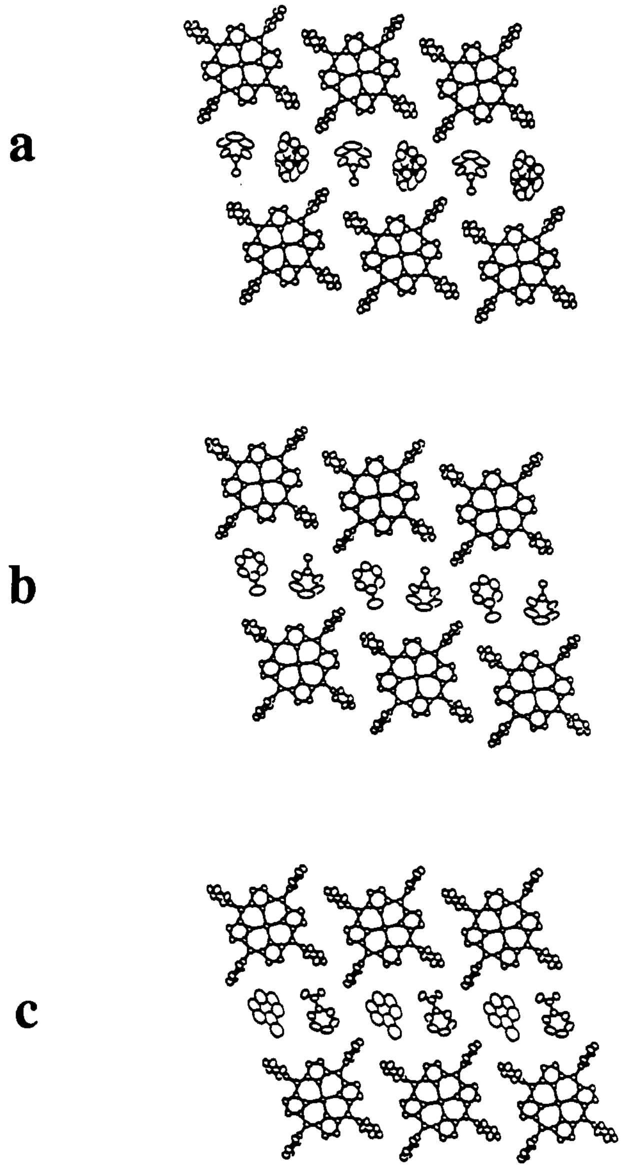

Figure 2. Sections through the structures of (a) Fe^{III}TPP(benzenethiolate) toluene solvate, (b) Fe^{III}TPP(benzenethiolate) chlorobenzene solvate, and (c) Fe^{III}TPP(benzoate) toluene solvate.

A second crystal, grown from the original mother liquor without addition of heptane, was examined at 297 K. This crystal gave an order parameter, 0.262 (4), significantly smaller than that of the first crystal, and a twinning parameter of 0.89 (9). These results indicate that while both crystals exhibit significant disorder, they are virtually untwinned and have opposite handedness. The estimated standard deviations of the twinning parameters are, however, relatively large.

In addition to the inversion disorder, both samples of this material exhibit an end-for-end disorder of the toluene solvate molecules. This disorder appears to be random (50:50) at both room temperature and 175 K.

The *R* values obtained in the room temperature refinement of the first crystal were significantly higher than those for the second. This may be because the first crystal was cooled to 175 K with some increase in peak widths and subsequently warmed to room temperature for collection of the second data set. The second crystal was never cooled.

Key structural parameters for these and subsequent refinements are tabulated in Table I. Complete structural data are provided as supplementary material. An ORTEP view of a section through the room temperature structure is shown in Figure 2a.

Fe^{III}TPP(benzenethiolate) Chlorobenzene/Benzenethiol Solvate. Like the toluene solvate, the chlorobenzene solvate exhibited a broadening of the diffraction maxima at low temperature, but in this case pronounced broadening occurs only below 125 K. The

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(5) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

(6) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, *B24*, 63–76.

Table I. Crystallographic Parameters

structure	1	2	3	4	5
cryst	1	1	2	3	3
temp (K)	175	301	297	125	294
ligand	benzenethiolate	benzenethiolate	benzenethiolate	benzenethiolate	benzenethiolate
solvate	toluene	toluene	toluene	chlorobenzene	chlorobenzene
diffractometer	Huber	Huber	Huber	Picker	Picker
$2\theta_{max}$ (deg)	65	65	60	65	65
scan rate (deg/min)	6	6	6	12	12
a (Å)	10.622 (1)	10.720 (1)	10.715 (1)	10.691 (1)	10.750 (1)
b (Å)	11.731 (1)	11.774 (1)	11.810 (2)	11.521 (1)	11.694 (1)
c (Å)	12.492 (1)	12.554 (1)	12.571 (2)	12.375 (1)	12.502 (1)
α (deg)	57.14 (1)	57.33 (1)	57.14 (1)	58.28 (1)	57.91 (1)
β (deg)	57.25 (1)	57.14 (1)	57.23 (1)	56.84 (1)	56.98 (1)
γ (deg)	72.04 (1)	72.43 (1)	72.36 (1)	72.33 (1)	72.59 (1)
volume (Å^3)	1099	1120	1123	1085	1116
density (calc) (g/cm^3)	1.31	1.29	1.29	1.36	1.32
reflcns (unique)	7951	8092	6557	7846	8050
reflcns (obsd)	3183	2333	2511	5719	3798
cryst size (mm)	0.15 × 0.45 × 0.45	0.15 × 0.45 × 0.45	0.5 × 0.25 × 0.25	0.21 × 0.35 × 0.59	0.21 × 0.35 × 0.59
error of fit	2.2	2.5	2.0	2.2	2.0
R	0.075	0.078	0.065	0.059	0.055
R_w	0.088	0.096	0.078	0.077	0.071
OP	0.451 (4)	0.476 (6)	0.262 (4)	0.376 (3)	0.391 (3)
TP	0.04 (7)	0.03 (9)	0.89 (9)	0.48 (4)	0.47 (4)
Fe–Ct′ (Å)	0.533 (2)	0.548 (2)	0.550 (2)	0.533 (2)	0.538 (1)
Fe–S (Å)	2.312 (3)	2.307 (4)	2.326 (3)	2.292 (3)	2.306 (2)
C–S (Å)	1.76 (2)	1.76 (4)	1.74 (2)	1.75 (1)	1.74 (2)
Fe–N(1) (Å)	2.054 (4)	2.055 (5)	2.054 (4)	2.083 (2)	2.071 (2)
Fe–N(2) (Å)	2.107 (4)	2.107 (5)	2.114 (3)	2.102 (2)	2.110 (2)
Fe–N(1)′ (Å)	2.107	2.107	2.116	2.090	2.101
Fe–N(2)′ (Å)	2.068	2.073	2.064	2.063	2.059
Fe–N$_{av}$ (Å)	2.084	2.086	2.087	2.084	2.085
structure	6	7	8	9	10
cryst	4	5	5	6	7
temp (K)	20	145	298	298	294
ligand	bromobenzenethiolate	bromobenzenethiolate	bromobenzenethiolate	benzoate	benzenethiolate
solvate	toluene	toluene	toluene	toluene	
diffractometer	Huber	Picker	Picker	Picker	Huber
$2\theta_{max}$ (deg)	55	60	60	50	60
scan rate (deg/min)	6	12	12	6	3
a (Å)	10.951 (3)	11.091 (1)	11.292 (1)	12.036 (2)	11.161 (1)
b (Å)	11.562 (3)	11.560 (1)	11.563 (1)	10.955 (2)	11.647 (2)
c (Å)	12.813 (3)	12.858 (1)	12.908 (1)	12.668 (2)	16.023 (2)
α (deg)	55.86 (1)	55.79 (1)	56.32 (1)	56.13 (1)	88.15 (1)
β (deg)	55.31 (1)	55.24 (1)	55.08 (1)	54.33 (1)	81.67 (1)
γ (deg)	70.68 (1)	70.83 (1)	71.38 (1)	70.63 (1)	72.03 (1)
volume	1104	1121	1150	1126	1960
density (calc) (g/cm^3)	1.43	1.41	1.37	1.30	1.32
reflcns (unique)	5060	13060	13404	3972	11440
reflcns (obsd)	3963	6761	6604	2692	3738
cryst size (mm)	0.25 × 0.25 × 0.35	0.48 × 0.43 × 0.32	0.48 × 0.43 × 0.32		0.5 × 0.4 × 0.05
error of fit	2.2	1.6	2.3	2.3	1.9
R	0.059	0.052	0.078	0.066	0.070
R_w	0.072	0.062	0.087	0.080	0.078
OP	0.242 (2)	0.238 (2)	0.249 (2)	0.551 (4)	
TP	0.35 (3)	0.36 (2)	0.37 (2)	0.26 (6)	
Fe–Ct′ (Å)	0.391 (1)	0.419 (1)	0.455 (1)	0.524 (3)	0.470 (1)
Fe–S,O (Å)	2.301 (2)	2.290 (2)	2.285 (2)	1.859 (7)	2.315 (2)
C–S,O (Å)	1.795 (7)	1.817 (5)	1.817 (9)	1.294 (13)	1.764 (8)
Fe–N(1) (Å)	1.924 (3)	1.943 (2)	1.965 (2)	2.015 (4)	2.053 (5)
Fe–N(2) (Å)	2.007 (3)	1.995 (2)	2.014 (3)	2.052 (4)	2.076 (5)
Fe–N(1)′ (Å)	2.166	2.163	2.152	2.133	2.053 (5)
Fe–N(2)′ (Å)	2.108	2.124	2.114	2.094	2.069 (5)
Fe–N$_{av}$ (Å)	2.051	2.056	2.061	2.074	2.063

structure was determined from the same crystal at 125 and 294 K. Again the order parameter and twinning parameter were found to be virtually independent of temperature [OP = 0.376 (3) at 125 K and OP = 0.391 (3) at 294 K; TP = 0.48 (4) at 125 K and TP = 0.47 (4) at 294 K]. In this case the twinning appears to be random.

The 125 K structure differs from the 294 K structure in two ways. While at 294 K the solvate molecule exhibits end-for-end disorder, at 125 K it is completely ordered. Presumably there is an order/disorder transition at some intermediate temperature. An ORTEP view of a section through the structure is shown in Figure 2b.

Magnetic susceptibility measurements of this material show a transition in the neighborhood of 150 K (see Figure 3). The magnetic moment measured at 125 K, 5.505 μB, corresponds to a transformation of approximately 12% of the iron(III) to a low-spin state. The temperature at which the spin transition occurs is virtually the same as that observed for pure Fe^{III}TPP(benzenethiolate)(benzenethiol),[7] which exhibits an equilibrium between

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[7] Unpublished results.

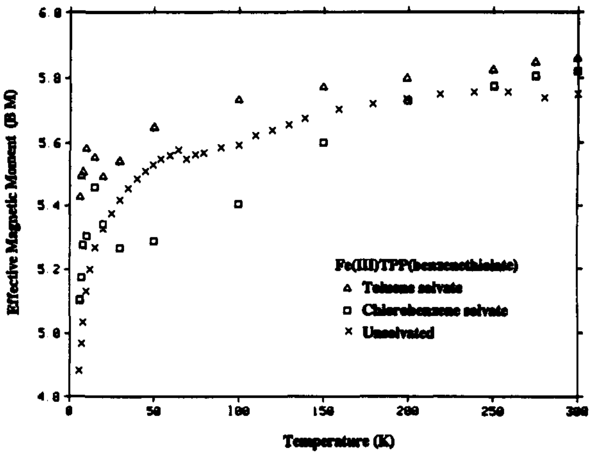

Figure 3. Effective magnetic moment versus temperature for three ferric porphyrin complexes.

five-coordinate high-spin and six-coordinate low-spin forms. Elemental analysis is consistent with approximately 10% benzenethiol in the solvate sites. The 125 K structure determination indicates that at this temperature 9 (1)% of the iron is in the porphyrin plane. The final refinement included this iron along with two centrosymmetrically related sulfur donor ligands, which also refine to a ligand occupancy of 9 (1)%. The Fe–S(6-coord) distance obtained in this refinement, 2.33 (2) Å, is the same, within the experimental error, as that observed in refinements of $Fe^{III}TPP$(benzenethiolate)(benzenethiol) at low temperature.[7]

In the foregoing studies of the toluene and chlorobenzene solvates of $Fe^{III}TPP$(benzenethiolate), the fact that both the order and twinning parameters are independent of temperature is consistent with expectation and tends to confirm the statistical significance of the measured values. However, given the lack of order reflected in the refined order parameters, the apparent untwinned nature of the toluene solvate is surprising.

$Fe^{III}TPP$(*p*-bromobenzenethiolate) Toluene Solvate. To provide more insight into the physical significance of the order and twinning parameters, multiple-temperature analysis was undertaken of $Fe^{III}TPP$(*p*-bromobenzenethiolate) as the toluene solvate with the expectation that the large scattering factor of the bromine atom and its large anomalous cross section would produce order and twinning parameters with smaller uncertainties. To further enhance the accuracy, full spheres of data were collected to $2\theta = 60°$ with a large crystal at two temperatures. An additional hemisphere of data was collected at 20 K with a smaller crystal from the same preparation.

The order and twinning parameters obtained from the three refinements are essentially the same: OP = 0.243 ± 0.007 with estimated standard deviations of the individual observations of 0.002; TP = 0.36 ± 0.01 with individual estimated standard deviations ranging from 0.02 to 0.04. No end-for-end disorder of the toluene solvate was detected in these crystals, and there was no evidence of any phase transition down to 20 K. Three views of the molecular packing in this material are given in Figure 4. The numbering system used is shown in Figure 5, and the atomic positions obtained in the 145 K determination are tabulated in Table II.

$Fe^{III}TPP$(benzoate) Toluene Solvate. Although the axial ligand in this material differs significantly from those in the materials above, it exhibits the same packing and the same incomplete disorder. Structural parameters have been reported elsewhere.[4] The order parameter of this material is 0.551 (4) and the twinning parameter is 0.26 (6). No end-for-end disorder of the toluene solvate was detected. An ORTEP view of a section through this structure is shown in Figure 2c.

$Fe^{III}TPP$(benzenethiolate). To provide a benchmark against which the accuracy of the structural parameters of the disordered structures could be measured, the structure of an unsolvated form of $Fe^{III}TPP$(benzenethiolate) was determined. This material grows in the form of thin plates; some difficulty was encountered in growing a crystal of suitable size. Key structural parameters are tabulated in Table I, atomic positions are tabulated in Table III, and additional data are supplied as supplementary material. Figure 6 shows the numbering system employed, and Figure 7 shows the displacement of atoms from the mean plane through the porphyrin core.

Other Refinements. Several tests were performed to determine whether the magnitude of the order parameter is influenced by

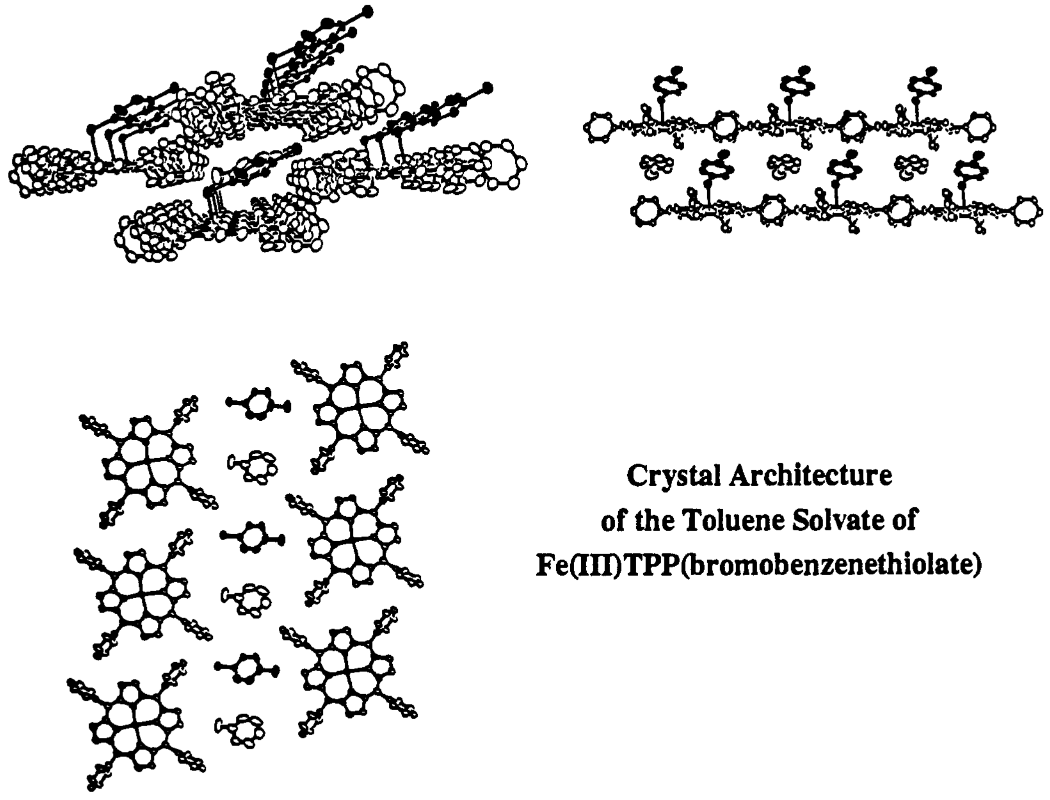

Figure 4. Molecular packing in $Fe^{III}TPP$(*p*-bromobenzenethiolate) toluene solvate.

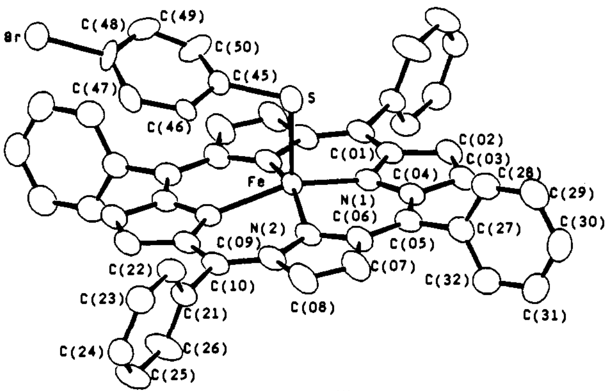

Figure 5. Numbering system for the Fe^{III}TPP(*p*-bromobenzenethiolate) toluene solvate.

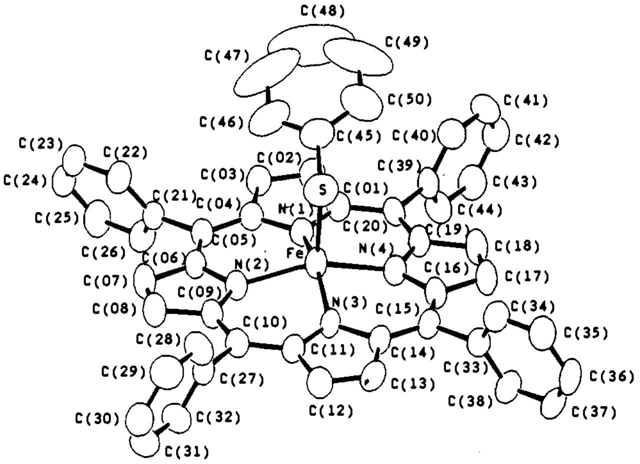

Figure 6. Numbering system for unsolvated Fe^{III}TPP(benzenethiolate).

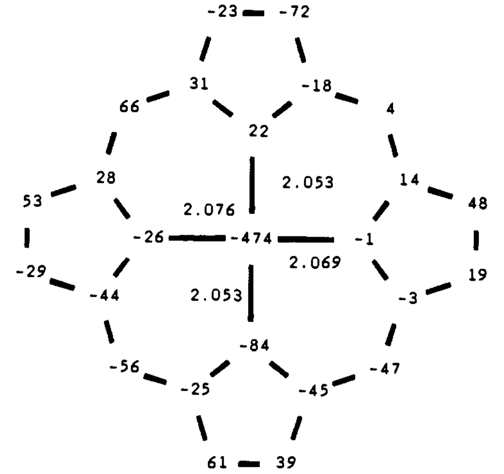

Figure 7. Displacements (in 0.001 Å) from the mean porphyrin plane for unsolvated Fe^{III}TPP(benzenethiolate).

the choice of data included in the refinement. The refinements reported in Table I were based on reflections with intensities greater than three times their estimated standard deviations. When all reflections were included, in no case did the order parameter change by more than 0.02. Similarly, a series of refinements based on F^2 rather than F produced no significant differences in the refined parameters. Finally a series of refinements was carried out in which only the order parameter was refined and in which only projection data down the three unit cell directions were included (e.g., $0kl$). There was no significant variation in the observed order parameter.

Table II. Atomic Positions for Fe^{III}TPP(*p*-bromobenzenethiolate) Toluene Solvate at 145 K[a]

atom	*X*	*Y*	*Z*
Fe	0.0297 (1)	−0.0336 (1)	−0.0001 (1)
N(1)	0.0698 (2)	0.0020 (2)	−0.1838 (2)
N(2)	−0.1424 (2)	−0.1528 (2)	0.1116 (2)
S	0.2126 (2)	−0.1979 (2)	0.0121 (2)
Br	0.3095 (1)	−0.2465 (1)	0.4821 (1)
C(01)	0.1759 (2)	0.0885 (2)	−0.3216 (2)
C(02)	0.1848 (3)	0.0650 (3)	−0.4249 (2)
C(03)	0.0862 (3)	−0.0349 (3)	−0.3506 (2)
C(04)	0.0164 (2)	−0.0750 (2)	−0.2003 (2)
C(05)	−0.0897 (3)	−0.1794 (2)	−0.0884 (2)
C(06)	−0.1618 (3)	−0.2149 (2)	0.0573 (2)
C(07)	−0.2704 (3)	−0.3235 (3)	0.1736 (3)
C(08)	−0.3184 (3)	−0.3238 (3)	0.2959 (3)
C(09)	−0.2390 (3)	−0.2177 (2)	0.2590 (2)
C(10)	−0.2573 (2)	−0.1856 (2)	0.3568 (2)
C(21)	−0.3734 (2)	−0.2615 (2)	0.5120 (2)
C(22)	−0.3525 (3)	−0.3981 (3)	0.6036 (2)
C(23)	−0.4602 (3)	−0.4646 (3)	0.7482 (3)
C(24)	−0.5888 (3)	−0.3957 (3)	0.8018 (2)
C(25)	−0.6107 (3)	−0.2607 (3)	0.7116 (3)
C(26)	−0.5030 (3)	−0.1943 (3)	0.5674 (3)
C(27)	−0.1255 (3)	−0.2580 (3)	−0.1278 (2)
C(28)	−0.0320 (3)	−0.3647 (3)	−0.1553 (3)
C(29)	−0.0648 (3)	−0.4372 (3)	−0.1931 (3)
C(30)	−0.1898 (3)	−0.4042 (3)	−0.2042 (3)
C(31)	−0.2823 (3)	−0.2993 (3)	−0.1772 (3)
C(32)	−0.2511 (3)	−0.2268 (3)	−0.1387 (3)
C(45)	0.2367 (6)	−0.2073 (5)	0.1451 (5)
C(46)	0.1326 (10)	−0.2740 (11)	0.2923 (9)
C(47)	0.1486 (11)	−0.2840 (11)	0.3968 (8)
C(48)	0.2792 (9)	−0.2271 (9)	0.3478 (9)
C(49)	0.3824 (8)	−0.1638 (8)	0.1998 (9)
C(50)	0.3443 (22)	−0.1493 (20)	0.1108 (18)
C(60)	−0.2668 (13)	0.1914 (14)	−0.3861 (13)
C(61)	−0.2522 (10)	0.2076 (8)	−0.2906 (10)
C(62)	−0.1345 (11)	0.2789 (10)	−0.3435 (11)
C(63)	−0.1191 (10)	0.2956 (9)	−0.2535 (10)
C(64)	−0.2146 (10)	0.2312 (10)	−0.0994 (11)
C(65)	−0.3230 (10)	0.1567 (9)	−0.0418 (10)
C(66)	−0.3593 (23)	0.1501 (19)	−0.1317 (21)

[a] Atoms N(1), N(2), and C(1)–C(32) have a multiplicity of 2.0; i.e., they represent pairs of atoms constrained to be related by inversion through the origin.

At the conclusion of the refinements tabulated in Table I, the parameters obtained were used as starting points for refinements in which OP was constrained to be either 0 or 1. These refinements gave significantly higher residuals (R in the range 0.09–0.12 for OP = 0 and 0.16–0.21 for OP = 1). As expected, the compound with the lowest OP gave the largest increase for the OP = 1 refinement and the smallest increase for the OP = 0 refinement. These constraints also resulted in significant changes in atomic positions. The displacement of the iron atom from the porphyrin plane increased slightly (at most 0.01 Å) for the OP = 0 refinement and decreased significantly for the OP = 1 refinement. Surprisingly, the Fe–S distance increased in both constrained refinements, on the order of 0.01 Å for the OP = 0 refinements and as much as 0.05 Å for the OP = 1 refinements.

Finally, a test of the refinement program on the structure of an optically active compound gave OP = 0.997 (4) and TP = 0.03 (3).

Residual Errors in the Model. An analysis of the reflections that show the largest deviations from the model reveals the presence of some systematic error. Many of these reflections are common to all five benzenethiolate/solvate refinements. Fourier analysis of these differences, however, did not reveal any obvious source of these errors.

Discussion

A primary goal of this investigation was to test the crystallographic model described above. The structural analyses carried out demonstrate the preparation dependence and temperature independence of the order and twinning parameters. In addition, they illustrate the quality of the structural information that can be obtained from the application of the crystallographic model to this class of materials. This investigation also demonstrates

Table III. Atomic Positions for Fe^{III}TPP(benzenethiolate) at Room Temperature

atom	*X*	*Y*	*Z*
Fe	0.2319 (1)	0.2238 (1)	0.2566 (1)
S	0.3386 (2)	0.2844 (2)	0.1370 (1)
N(1)	0.0954 (5)	0.1627 (4)	0.2167 (3)
N(2)	0.0869 (4)	0.3792 (4)	0.2990 (3)
N(3)	0.3317 (4)	0.2623 (4)	0.3442 (3)
N(4)	0.3392 (5)	0.0447 (4)	0.2639 (3)
C(01)	0.1167 (6)	0.0529 (5)	0.1766 (4)
C(02)	0.0133 (6)	0.0564 (6)	0.1322 (4)
C(03)	−0.0739 (6)	0.1669 (5)	0.1468 (4)
C(04)	−0.0246 (5)	0.2336 (5)	0.1986 (4)
C(05)	−0.0847 (6)	0.3530 (5)	0.2267 (4)
C(06)	−0.0325 (5)	0.4197 (5)	0.2721 (4)
C(07)	−0.0932 (6)	0.5432 (6)	0.3009 (5)
C(08)	−0.0131 (6)	0.5769 (6)	0.3404 (5)
C(09)	0.0997 (6)	0.4736 (5)	0.3417 (4)
C(10)	0.2020 (6)	0.4727 (5)	0.3814 (4)
C(11)	0.3099 (6)	0.3711 (5)	0.3852 (4)
C(12)	0.4116 (6)	0.3669 (6)	0.4313 (4)
C(13)	0.4965 (6)	0.2552 (6)	0.4174 (4)
C(14)	0.4481 (6)	0.1904 (5)	0.3643 (4)
C(15)	0.5079 (6)	0.0695 (5)	0.3381 (4)
C(16)	0.4561 (6)	0.0026 (5)	0.2932 (4)
C(17)	0.5157 (6)	−0.1218 (6)	0.2675 (5)
C(18)	0.4364 (6)	−0.1549 (6)	0.2243 (5)
C(19)	0.3260 (6)	−0.0501 (5)	0.2206 (4)
C(20)	0.2243 (6)	−0.0484 (5)	0.1797 (4)
C(21)	−0.2164 (5)	0.4112 (5)	0.2062 (4)
C(22)	−0.2385 (6)	0.5053 (6)	0.1478 (4)
C(23)	−0.3614 (7)	0.5580 (6)	0.1280 (5)
C(24)	−0.4596 (7)	0.5178 (6)	0.1652 (5)
C(25)	−0.4384 (6)	0.4257 (7)	0.2233 (5)
C(26)	−0.3171 (6)	0.3724 (6)	0.2442 (4)
C(27)	0.2004 (6)	0.5873 (6)	0.4222 (4)
C(28)	0.2723 (7)	0.6573 (6)	0.3842 (5)
C(29)	0.2680 (7)	0.7641 (7)	0.4207 (5)
C(30)	0.1942 (7)	0.8016 (6)	0.4979 (5)
C(31)	0.1245 (7)	0.7320 (7)	0.5367 (5)
C(32)	0.1264 (7)	0.6247 (6)	0.5007 (5)
C(33)	0.6388 (6)	0.0085 (5)	0.3605 (4)
C(34)	0.7439 (6)	0.0295 (6)	0.3139 (4)
C(35)	0.8664 (6)	−0.0260 (7)	0.3340 (5)
C(36)	0.8823 (7)	−0.1024 (6)	0.4012 (5)
C(37)	0.7784 (7)	−0.1250 (6)	0.4481 (5)
C(38)	0.6567 (7)	−0.0699 (7)	0.4287 (5)
C(39)	0.2299 (6)	−0.1625 (5)	0.1368 (4)
C(40)	0.2969 (7)	−0.1937 (6)	0.0572 (5)
C(41)	0.3056 (7)	−0.3023 (7)	0.0195 (5)
C(42)	0.2466 (7)	−0.3795 (6)	0.0616 (5)
C(43)	0.1791 (7)	−0.3491 (6)	0.1403 (5)
C(44)	0.1698 (6)	−0.2410 (6)	0.1777 (4)
C(45)	0.2740 (8)	0.2403 (7)	0.0538 (5)
C(46)	0.1552 (9)	0.3050 (9)	0.0367 (6)
C(47)	0.1095 (16)	0.2715 (19)	−0.0315 (11)
C(48)	0.1800 (26)	0.1750 (25)	−0.0776 (14)
C(49)	0.2975 (20)	0.1126 (17)	−0.0648 (10)
C(50)	0.3450 (10)	0.1435 (9)	0.0031 (7)

the application of these techniques to the characterization of a mixed crystal.

Physical Significance of Observed Order and Twinning Parameters. In all, nine data sets from six crystals of four isostructural porphyrin sponges are reported herein. The order parameters from these refinements range from 0.24 to 0.55, with individual estimated standard deviations ranging from 0.002 to 0.006. Twinning parameters range from 0.04 to 0.48,[8] with individual estimated standard deviations ranging from 0.02 to 0.09. There is no obvious correlation between the order parameter and the twinning parameter. Both parameters are essentially temperature independent.

While the inclusion of these parameters in the refinement significantly improves the fit of the crystallographic model to the X-ray observations, an interpretation of the refined parameters in terms of a physical description of the disorder is not unambiguous. All the solvate structures exhibit substantial disorder; order parameters of 0.25 and 0.5 correspond to ratios of inverted forms (1 − OP/1 + OP) of 3:5 and 1:3.

An order parameter less than one could be explained by the presence of an undetected supercell, i.e., some alternating arrangement along one or more directions, with either long- or short-range order. However, heavily overexposed rotation photographs around all three axes for a large crystal of the *p*-bromobenzenethiolate complex failed to reveal any scattering, sharp or diffuse, between the Bragg reflections.

In a previous report[9] from this laboratory, another five-coordinate porphyrin complex was found to exhibit one-dimensional order in the orientation of the axial ligand, with only short-range order in the other two directions. This produced disks of diffuse density between the Bragg reflections. A model of the crystal growth was developed that successfully accounted for the X-ray observations. Had the correlation length of the order been substantially shorter than the ca. 100 Å observed or had the order been short range in all three directions, the diffuse density would have been difficult to detect.

With only short-range order in one or more directions, one is left with the problem of accounting for the enantiomeric purity. For most of the samples studied, the twinning parameter deviated significantly from the value expected for a 50:50 twin. It is difficult to account for a twinning parameter different from 0.5 if the order parameter is small and if one presumes that it arises from short-range order.

Since the structure is determined as molecules are incorporated into the growing surface, one must consider the energetics at the crystal/solution interface. If, during crystal growth, there is a slight preference for one orientation compared to the other at the crystal/solution interface, the order parameter would be small (and presumably solvent dependent) but this preference would be maintained throughout the growth. This could lead to crystals of high enantiomeric purity. In such a system, deviation of the order parameter from zero is determined by an equilibrium at the crystal surface and does not necessarily reflect the existence of any short-range order in the crystal.

On the basis of the observed structure, it seems likely that there is in fact substantial order in one or two dimensions. An alternating arrangement of anionic ligands and solvate molecules in the channels of these sponges should have a lower energy than a random arrangement. This order could easily be propagated in a second direction by preference of each iron ion to be associated with one anionic ligand and one solvate in its axial coordination sites. In the third direction, adjacent channels are separated by sheets of phenyl groups that may effectively isolate them (see Figure 5). It is possible that the energetics of growth in this direction determine the observed order and twinning parameters.

Although the six solvate crystals examined in this investigation do not constitute a systematic study of the effect of crystallization conditions on the observed order parameter, the results are suggestive. The two crystals grown by heptane diffusion (crystals 1 and 6 in Table I) give the largest order parameters (about 0.5), while the three grown by cooling toluene solutions from elevated temperatures (crystals 2, 4, and 5) gave significantly smaller order parameters (about 0.25). The crystal grown from chlorobenzene gave an intermediate order parameter. The two crystals of the *p*-bromobenzenethiolate complex from the same batch gave very similar order and twinning parameters. It certainly appears that the order in these materials is governed by the crystallization conditions.

Structural Comparisons. Introduction of the order and twinning parameters into the refinement model was undertaken to improve the accuracy of the structural information that could be extracted from the X-ray observations. The series of determinations reported herein provides the basis for a detailed assessment of the accuracy available and also provides some unexpected information related to the electronic structure of these ferric porphyrin complexes.

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(8) A twinning parameter of 0.89 is equivalent to one of 0.11 with the opposite choice of enantiomer.

(9) Miller, K. M.; Strouse, C. E. *Inorg. Chem.* **1984**, *23*, 2395–2400.

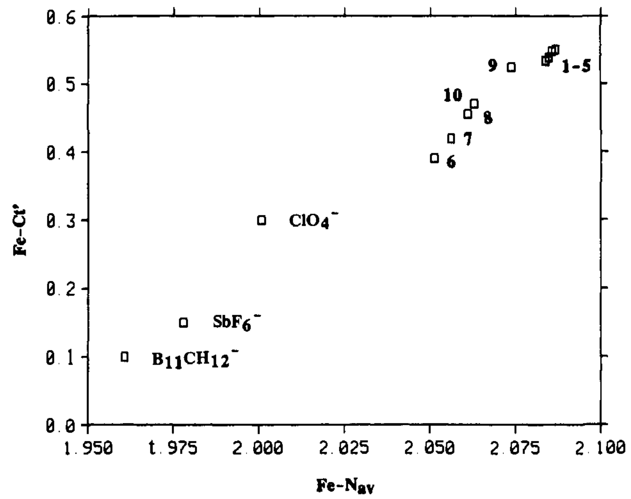

Figure 8. Displacement of the iron atom from the center of the porphyrin core versus average Fe–N distance.

The success of the refinement procedure developed herein is reflected in a comparison of the five refinements of the species containing a benzenethiolate ligand and a toluene or chlorobenzene molecule of solvation (structures 1–5 in Table I). While these materials exhibit differing order and twinning parameters and while data were collected over a range of temperatures, there is good consistency in the structural parameters obtained. Specifically, the Fe–N_{av} distances for the five refinements fall in the range 2.085 ± 0.002 Å, the Fe–Ct′ (Ct′ represents the center of the 24 atom porphyrin core) distances fall in the range 0.54 ± 0.01 Å, and the Fe–S distances fall in the range 2.32 ± 0.02 Å. This last range is on the order of 10 times the estimated standard deviations of the individual observations and may reflect some residual error associated with the disorder.

Although the Fe–N_{av} distances in the five refinements are virtually identical, the large range of individual Fe–N distances in each case probably reflects a systematic error caused by constraint of the porphyrin ligand to inversion symmetry. The range of Fe–N distances observed for the unsolvated species (structure 10, Table I) is much smaller.

Previous reviews[10] of the structures of metalloporphyrin complexes have noted the variation in the Fe–Ct′ distance and the Fe–N_{av} distance with the strength of the axial ligand. These variations are associated with differing admixtures of $S = {}^3/_2$ and $S = {}^5/_2$ character in the ground-state wavefunction. Weak axial ligands produce smaller out-of-plane displacements, smaller Fe–N distances, and greater $S = {}^3/_2$ character in the ground state.

In Figure 8, the Fe–Ct′ distance is plotted versus the Fe–N_{av} distance for the 10 refinements carried out in this investigation and for three $Fe^{III}TPP$ complexes[11-13] with weak axial ligands. This figure shows a clear distinction between the five refinements of benzenethiolate-based solvates and the three refinements of the bromobenzenethiolate solvate, consistent with the expectation that bromo substitution of the axial ligand should result in reduced basicity. It also reveals systematic temperature dependences in these structural parameters consistent with increased $S = {}^3/_2$ character at lower temperature. The admixed nature of the FeTPP(*p*-bromobenzenethiolate) spin state suggested by these measurements will be examined by magnetic and spectroscopic probes as a part of an ongoing investigation of the electronic structures of ferric porphyrins.

The large difference between the parameters for the unsolvated and solvated benzenethiolate complexes is surprising, but similar differences have been reported previously for five-coordinatee $Mn^{III}TPP$ complexes. Williamson and Hill[14] attributed these differences to an electronic interaction between the porphyrin and the solvate.

The bromobenzenethiolate complex, for which the most accurate data are available over the widest range of temperature, appears to exhibit a small but significant decrease in the Fe–S distance with increasing temperature. This decrease is consistent with increases in the C–S distance, the Fe–Ct′ distance, and the Fe–N_{av} distance with increasing temperature. The room temperature Fe–S distance of 2.285 (2) Å is smaller than any of the others observed. This appears to be inconsistent with a lower basicity for the brominated ligand. However, the relatively large and apparently random variation in the Fe–S distances in refinements of the benzenethiolate complexes makes distinctions based on this parameter difficult.

Conclusions

As a practical tool for the characterization of porphyrin sponges, the introduction of an order parameter into the crystallographic refinement has proved quite useful. Without this parameter the structural analyses of many of these materials would be entirely unsatisfactory. This technique has now been successfully applied to a number of "problem" structures in addition to those described herein. It can be used without modification for any system that exhibits inversion disorder.

The order parameters and twinning parameters observed for a number of specimens suggest that the residual order in these materials may be controlled by energetics at the crystal/solution interface during crystal growth. This hypothesis could be tested by growth of additional specimens under carefully controlled conditions.

Acknowledgment. This work was supported by the National Science Foundation (CHE 87-06780), by the National Institutes of Health (GM 35329), and by a UCLA BRSG grant. We thank Dr. Dilip Sansharma for obtaining the mass spectra and Prof. Christopher Reed for access to the susceptometer. We also thank Prof. Joan Valentine and Dr. Judith Burstyn for use of their data for the FeTPP(benzoate) complex.

Supplementary Material Available: Tables of atomic positions and thermal parameters for nine data sets and ORTEP plots and numbering systems for selected compounds (109 pages); listing of observed and calculated structure factors for nine data sets (172 pages). Ordering information is given on any current masthead page.

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