total of about 200 Hz. The observed line widths were about 220 Hz.

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Crystal Structure and Molecular Stereochemistry of α,β,γ,δ-Tetraphenylporphinatodichlorotin(IV)[1]

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Abstract: Tetragonal crystals, space group $I4/m$, of α,β,γ,δ-tetraphenylporphinatodichlorotin(IV) (Cl_2SnTPP) are of extraordinarily high quality for X-ray analysis. The unit cell containing $2Cl_2SnTPP$ has a = 13.673 (1) Å and c = 9.961 (1) Å (λ 0.70926 Å) at 19°. Diffracted intensities were recorded with Mo Kα radiation on a computer-controlled diffractometer with a scanning rate of 1°/min and a background counting time of 80 sec. Of the 4450 independent reflections scanned for $(\sin\theta)/\lambda \lesssim 1.03$ Å^{-1} ($2\theta \lesssim 94°$), the 3909 retained as observable corresponded to a conventional data/parameter ratio of 54.3 for anisotropic, full-matrix, least-squares refinement of the structure. All C–H bond densities in the molecule of required C_{4h} symmetry were clearly defined in a Fourier difference synthesis; the customary quasi-refinement of the hydrogen parameters, using two distinctive weighting schemes, led to C–H distances of 0.89–1.10 Å and thermal parameters for hydrogen atoms of 1.4–5.5 Å^2. The persistent interference of the hydrogen contributions with the quantitatively unambiguous positioning of those carbon atoms which carry hydrogen atoms was then eliminated by the exclusion from the final least-squares refinements of all low-angle data (573) for which $(\sin\theta)/\lambda < 0.517$ Å^{-1}. Positions of all other carbon and heavier atoms were practically invariant to the details of refinement. The octahedral coordination group of the Cl_2SnTPP molecule has Sn–Cl = 2.420 (1) Å and Sn–N = 2.098 (2) Å. C–C and N–C bond lengths in the radially expanded porphinato core carry esd values of 0.002–0.003 Å; dimensional variations from full D_{4h} symmetry are altogether trivial. Comparison of the expanded porphinato core of a tin(IV) porphyrin with the contracted core of a nickel(II) porphyrin leads to some stereochemical generalizations of both practical and theoretical interest.

A definitive X-ray analysis of structure for truly excellent crystals of α,β,γ,δ-tetraphenylporphinatodichlorotin(IV) (written as Cl_2SnTPP; see Figures 1 and 2 for skeletal diagrams) is presented herein. Crystalline Cl_2SnTPP, as anticipated,[2] provides the first *ordered* example of the tetragonal structural type that, in a statistically disordered version, is utilized by the crystalline chloroiron(III),[3] aquozinc(II),[4] aquomagnesium(II),[5] and nitrosylcobalt(II)[6] derivatives of tetraphenylporphine. Precise intensity measurements for all independent reflections having $(\sin\theta)/\lambda \lesssim 1.03$ Å^{-1} yield a data/parameter ratio of ~54 for the comparatively simple structure, thus permitting the relative merits of various structural models and refinement procedures to be evaluated. The large, strongly complexing, tin(IV) atom is centered in a highly expanded porphinato core of required C_{4h} symmetry, with no dimensionally significant departure from the maximum possible symmetry of D_{4h}. Comprehensive analysis of the redistribution of strain in the porphinato skeleton[2] as a function of the "radius of the central hole"—the Ct···N radius shown in Figure 2 that, in the Cl_2SnTPP molecule, is identical with the complexing Sn–N bond length—is now feasible. Such analysis benefits also from stereochemical data recently obtained by other workers; see Discussion.

Experimental Section

Crystalline Cl_2SnTPP was prepared and purified following the procedures of Rothemund and Menotti.[7] Large well-formed crystals exhibiting tetragonal-bipyramidal morphology were then obtained by allowing methanol to diffuse slowly into a nearly saturated solution of Cl_2SnTPP in chloroform. Preliminary X-ray study of a single crystal by photographic techniques led to a body-centered tetragonal lattice and delimitation of the probable space groups to $I4$, $I\bar{4}$, and $I4/m$. Negative tests for piezoelectricity in the crystals, using a Geibe-Schiebe detector, and every detail of the subsequent analysis of structure supported the choice of the centrosymmetric $I4/m\text{-}C_{4h}^5$ as the space group.[8] The experimentally measured density, 1.43 g/cc at 23°, led to a two-molecule unit cell; use of the precisely measured lattice constants, a = 13.673 (1) Å and c = 9.961 (1) Å (Mo Kα_1; λ = 0.70926 Å) gave a calculated density of 1.431 g/cc at 19°. These lattice constants came

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[2] D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

[3] J. L. Hoard, G. H. Cohen, and M. D. Glick, *ibid.*, **89**, 1992 (1967).

[4] M. D. Glick, G. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1996 (1967).

[5] R. Timkovich and A. Tulinsky, *ibid.*, **91**, 4430 (1969).

[6] W. R. Scheidt and J. L. Hoard, unpublished results. The geometry of the axial Co–N–O linkage corresponds formally to the complexing of NO^- by Co(III).

[7] R. Rothemund and A. R. Menotti, *J. Amer. Chem. Soc.*, 70, 1808 (1948).

[8] "International Tables for X-ray Crystallography. Symmetry Groups," Vol. I, Kynoch Press, Birmingham, England, 1952, p 177.

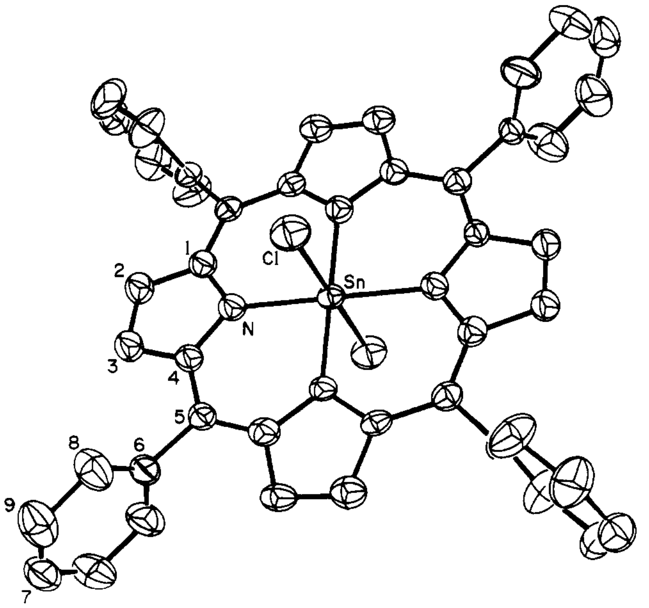

Figure 1. Computer-drawn model in perspective of the Cl_2SnTPP molecule (hydrogen atoms omitted) as it exists with required C_{4h} symmetry in the tetragonal crystal. Each atom is represented as an ellipsoid having the orientation and relative size concomitant with the thermal parameters listed in Table III. Structurally nonequivalent carbon atoms in the asymmetric subunit are numbered from 1 to 9 in agreement with Tables I–IV.

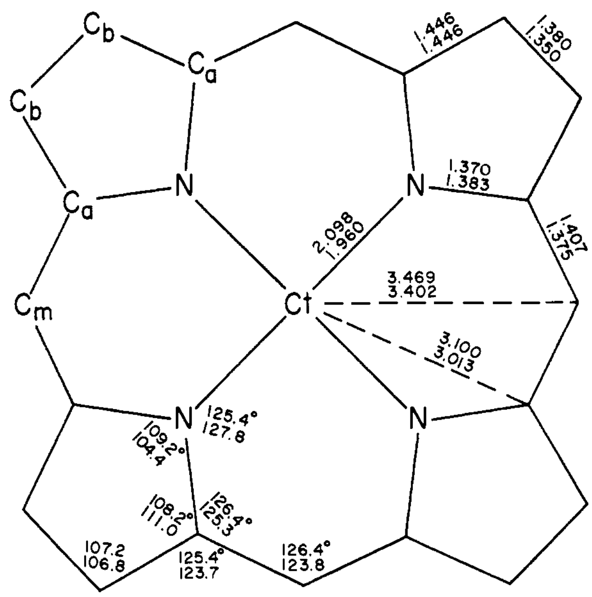

Figure 2. Diagram of the carbon–nitrogen skeleton in the porphinato core of a metalloporphyrin for the effective retention of D_{4h} symmetry. Chemically distinctive classes of carbon atoms are labeled in agreement with Table V and the text. Values of the principal radii (Å), bond lengths (Å), and bond angles (deg) in Cl_2SnTPP and NiDeut are entered on the diagram; the upper datum in each pairing is the value in the tin(IV) prophyrin.

from a least-squares treatment[9] of the diffraction geometry based on the angular settings of 24 reflections, $55° < |2\theta| < 64°$, distributed equally between positive and negative 2θ.

The crystal used for the recording of diffracted intensities was a tetragonal bipyramid, slightly truncated on {100} and {110}, with a basal edge of 0.50 mm and a length along the unique axis of 0.20 mm. All measurements utilized θ–2θ scanning with Zr-filtered Mo Kα radiation at a take-off angle of ~2° on a computer-controlled four-circle diffractometer; a scanning speed of 1°/min, a scanning range for each reflection of $(1.2 + 0.692 \tan \theta)°$, and a counting period of 40 sec at each end of a scan were employed. All of the ~4450 independent reflections having $(\sin \theta)/\lambda \lesssim 1.03$ Å^{-1} ($2\theta \lesssim 94°$) were scanned. The intensities of three standard reflections displayed no observable trend; random variations were in the range of ±2%.

Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, by application of the standard Lorentz and polarization factor (LP). Reflections retained as objectively observed satisfied the criterion $|F_o| > 0.675\sigma_F$, wherein σ_F is the standard deviation computed from $\sigma_F{}^2 = (Ct + k^2B)/4|F_o|^2(\text{LP})^2$, Ct being the total count from the scan, k the ratio of scanning time to total background counting time, and B the total background count. 3909 of the 4450 reflections scanned were thus retained for the structure analysis, giving a data/parameter ratio of 54.3 (or 43.9 with hydrogen atoms included).

With the cited dimensions of the specimen crystal and a linear absorption coefficient for Mo Kα radiation of 0.87 mm^{-1}, the maximum error in any structure factor arising from the neglect of absorption corrections was estimated to be ~4%. The determination and refinement of structure, as initially completed with neglect of corrections for absorption and extinction, proceed as follows. With tin atoms at lattice points, a Fourier synthesis employing uniformly positive values of the structure amplitudes led immediately to the placement of all other atoms, save hydrogen, in the structure. Anisotropic, full-matrix, least-squares refinement[10] of this structure (with unit weighting) to a conventional R of 0.052, followed by difference synthesis, yielded residual concentrations of electron density rationally positioned to represent C–H bond densities. Contributions from the hydrogen atoms were included in the subsequent least-squares refinements; except as noted, both the isotropic thermal parameters and the coordinates of these atoms were allowed to vary.

A total of seven, anisotropic, full-matrix, least-squares refinements, distinguished from one another as specified below, were carried to convergence. Four of the seven refinements utilized $|F_o|$ data that had been subjected to rather precise (and costly) corrections for absorption.[11] No corrections for extinction were included; apart from the extraordinarily intense (002) reflection, for which the calculated amplitude exceeded the experimental value by 6.5%, the $(|F_c| - |F_o|)$ data for the stronger, low-angle reflections were randomly distributed in respect to sign and magnitude. Two distinctive weighting schemes were employed: unit weights, $w = 1$, and empirical weights, $w = 1/\sigma^2$, calculated from $\sigma = \Sigma_0{}^3 a_n|F_o|^n$, the a_n being the coefficients from the least-squares fitting of the curve, $||F_o| - |F_c|| = \Sigma_0{}^3 a_n|F_o|^n$.

Least-squares refinements I–V, numbered in disregard of chronology, carried the following specifications. I, hydrogen atoms included; $|F_o|$ data corrected for absorption; $w = 1/\sigma^2$. II, hydrogen atoms included; $|F_o|$ data uncorrected for absorption; $w = 1/\sigma^2$. III, hydrogen atoms included; $|F_o|$ data corrected for absorption; $w = 1$. IV, hydrogen atoms included; $|F_o|$ data uncorrected for absorption; $w = 1$. V, hydrogen atoms *ignored;* $|F_o|$ data uncorrected for absorption; $w = 1$.

The combined effects of absorption and the differing weighting schemes were barely indicated by conventional R values, 0.044–0.048, given by refinements I–IV. These refinements all provided calculated values of the estimated standard deviations for the 13 structurally nonequivalent bond lengths (C–H distances not included) in the molecule of required C_{4h} symmetry that ranged from 0.001 Å for the Sn–Cl bond to 0.003 Å for the C–C bonds in the peripheral phenyl groups; immaterially larger values were indicated by refinement V. But inasmuch as significantly different values for some of the stereochemical parameters were provided by these refinements, we were led to evaluate the peak positions of

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(9) The PICK II computer program, a revision in this laboratory of W. C. Hamilton's MODE I program, was employed.

(10) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic form factors were from D. T. Cromer and J. L. Mann, *Acta Crystallogr.*, 24, 321 (1968), with corrections, real and imaginary, for the anomalous scattering of the iron and chlorine atoms from D. T. Cromer, *ibid.*, 18, 17 (1965). Hydrogen scattering factors were from "International Tables for X-Ray Crystallography. Physical and Chemical Tables," Kynoch Press, Birmingham, England, 1962. Slightly modified versions of the Busing–Martin–Levy ORFLS and ORFFE programs on an IBM 360/65 computer were employed during structure refinement.

(11) A revision in this laboratory of N. W. Alcock's original program (privately communicated) was employed.

electron density for all atoms, save hydrogen,[12] in the Fourier synthesis of the 3909 $|F_o|$ amplitudes having $(\sin \theta)/\lambda \overline{<} 1.032$ Å^{-1}; the computer-programmed objective procedure described earlier,[2] including the backshift corrections of generally trifling magnitude, was utilized to this end.

It is quite unnecessary to tabulate all of the stereochemical parameters given by refinements I–V and by the Fourier synthesis in order to appreciate their significance. The lengths observed for Sn–Cl, Sn–N, and N–C bonds, as well as for the three classes of bonds between carbon atoms that carried no hydrogen atoms, were practically invariant to the six differing procedures for their evaluation; the *maximum* deviation from the mean in no case exceeded 0.002 Å. The lengths observed for the C_1–C_2 and C_3–C_4 bonds in the pyrrole rings were only slightly less consistent; the maximum deviation from the mean exceeded 0.002 Å just for the C_3–C_4 bond as evaluated by refinement V and then by only 0.004 Å as compared with an esd of 0.003 Å. Only for the C–C bonds in a phenyl group and the bond between carbon atoms C_2 and C_3 (each carrying a hydrogen atom) in the porphinato core did the variations in the derived lengths approach or attain formal significance. The results obtained for these bond lengths from the Fourier synthesis, from refinements I–V, and from the final, quantitatively definitive, least-squares refinements VI and VII (*vide infra*) are listed in Table I.

Table I. Apparent C–C Bond Lengths (Å) as Evaluated by Differing Procedures

Procedure employed[a]	Type of bond length[b] C_2–C_3	 C_6–C_8	 C_8–C_9	 C_9–C_7
Fourier	1.380	1.381	1.397	1.366
I	1.366	1.375	1.395	1.354
II	1.368	1.375	1.396	1.354
III	1.369	1.390	1.396	1.376
IV	1.372	1.394	1.398	1.385
V	1.381	1.401	1.416	1.395
VI	1.379	1.387	1.397	1.373
VII	1.380	1.386	1.397	1.374

[a] See text for the specification of procedures. [b] See Figure 1 for identification of bond types.

On the premise that the equilibrium (internuclear) C–C distance in the phenyl group does not deviate significantly from the standard 1.397 Å, the qualitative pattern of foreshortened bond lengths, C_9–C_7 < C_6–C_8 < C_8–C_9 from every refinement, is attributable to thermal motion of the phenyl group, regarded as a rigid body attached at one end to the porphinato core. The nature of this motion is readily deduced from consideration of the thermal parameters of the individual atoms in the symmetrical (C_{4h}) Cl_2SnTPP molecule; a pronounced libration of the phenyl group about its $C_6 \cdots C_7$ axis is superimposed upon a swinging of the group about the bond (C_6–C_5) connecting it to the porphinato core (Figures 1 and 2). The apparent length of the C_8–C_9 bond is unaffected by the first motion and little affected by the second. Because the bond lengths given by the usual least-squares refinement represent separations of effective centroids of electron density, the omission from the structural model used in refinement V of explicit contributions from the C–H bonds is expected to give a slightly expanded form of the carbon skeleton in the phenyl group, although the systematic effects of thermal motion should be (and are) still evident. The difference between the apparent lengths of the C_8–C_9 and C_9–C_7 bonds is maximized by refinement I (or II), wherein $w = 1/\sigma^2$; the spread in the distances is 0.041 Å, from 1.395 down to 1.354 Å. Only half as much spread, 1.396–1.376 Å, is given by refinement III, wherein $w = 1$. It is then seen (Table I) that the length derived from the Fourier synthesis for each bond in the phenyl group is approximately the mean of the paired values from refinements I and III.

Acceptance of the Fourier results as objectively most authoritative, theoretically and practically, is subject to the resolution of one troublesome point. The C_2–C_3 bond length, 1.380 Å, from the Fourier synthesis is in full agreement with the 1.381 Å from refinement V (hydrogen atoms ignored in the structural model), while being five standard deviations larger than the 1.366 Å obtained from refinement I. In these circumstances, refinements VI and VII were designed to distinguish between that which can, and that which cannot, be objectively determined from the least-squares refinement of a structural model.

Least-squares refinement VI utilized the 2620 independent F_o data in the range, $0.517 < (\sin \theta)/\lambda < 0.937$ Å^{-1}, giving a data/parameter ratio of 36.4; excluded thereby, as compared with refinements I–V, were the 573 observed F_o data from the inner half of the first Cu Kα limiting sphere and the 716 comparatively weak data from the fourth Cu Kα sphere (*cf.* the low rejection criterion specified above). Refinement VII differed from VI in retaining the 716 high-angle data and thus raising the data/parameter ratio to 46.4. The lower limit (0.517 Å^{-1}) of the ranges in $(\sin \theta)/\lambda$ within which the amplitude data were employed in these refinements was set by the observation that, for all higher $(\sin \theta)/\lambda$, the empirical weighting scheme used earlier differed insignificantly from unit weighting. Exclusion of the 573 low-angle data assured the triviality of the hydrogen contributions[13] and, more generally, of nonspherical contributions from the valence shells of the carbon and all heavier atoms. There was, consequently, the prospect that refinements VI and VII would lead to bond distances in the molecular skeleton that approximated closely to internuclear separations (apart from the inevitable foreshortening of the C_6–C_8 and C_9–C_7 distances as discussed above).

Refinement VI led to a conventional R of 0.041 and a weighted R of 0.046 as compared with the respective values of 0.044 and 0.049 from refinement I; the same schedule of formally calculated values for the estimated standard deviations in bond lengths, ranging from 0.001 Å for Sn–Cl to a maximum of 0.003 Å for peripheral C–C bonds, was given by both refinements. Although the inclusion in refinement VII of the 716 relatively weak high-angle data raised the respective R values to 0.055 and 0.062, and the formally calculated standard deviations by a trivial 15%, the values given by VI and VII for the length of any arbitrarily selected bond differed in no case by more than 0.001 Å: *cf.* the data in Table I for the four bonds between pairs of hydrogen-carrying carbon atoms.

The pattern of bond lengths given by refinement VI (or VII) for the coordination group and the porphinato core, with the sole exception of the C_2–C_3 distance, proved to be a slightly smoothed (effectively D_{4h}) version of the otherwise extraordinarily consistent patterns afforded by *all* of the other analytical procedures listed in Table I. For the C_2–C_3 bond length, however, VI and VII gave values, 1.379 and 1.380 Å, in full support of the Fourier-derived 1.380 and the 1.381 Å from refinement V. The pattern of foreshortened C–C bonds in the phenyl group from VI (or VII) was intermediate between those given by refinement III and the Fourier synthesis, while differing significantly from that provided by refinement I (Table I); indeed, the foreshortenings of the C_6–C_8 and C_9–C_7 bond lengths suggested by refinement I were larger by fully 4 and 6 esd, respectively, than those given by refinement VI or VII. Refinement III, wherein no obvious downgrading of the F_o data through the agency of a structural model was allowed ($w = 1$), led to a significantly improved description of the carbon skeleton in the phenyl group, but, on the other hand, to a quite insignificant improvement in the length derived for the more interesting C_2–C_3 bond (Table I).

Even though the strongly scattering tin atoms lent their full weight to every reflection, the least-squares refinements I–IV provided apparent C–H bond lengths and thermal parameters for the hydrogen atoms that were confined to the respective ranges, 0.89–1.10 Å and 1.4–5.5 Å^2. The undue sensitivity of these structural parameters to, in particular, the weighting scheme is underlined above; this sensitivity extends, indeed, to include every shortcoming of the very low-angle F_o data and, inevitably, every vagary of the mathematically sycophantic, grossly approximate model for the hydrogen contributions that may be used in least-squares refinement. The descriptions of the C–H bonds thus afforded have little to commend them by comparison with a simple report of the approximate peak values and associated positions of the bonding electron densities in an authoritative Fourier difference synthesis. It is rather more important to ensure that the hydrogen contributions and, more generally, the departures from spherical symmetry in the valence shells of the heavier atoms do not prejudice the determination of physically realistic parameters for all those atoms in

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(12) The concentrations of electron density associated with all C–H bonds were quite evident in the complete Fourier synthesis.

(13) Hydrogen contributions with fixed parameters from refinement I were introduced *pro forma* into VI and VII. Note also that "low-angle data" is used in a relative sense; many published structure analyses utilize data that are wholly comprised within the range, $(\sin \theta)/\lambda < 0.52$ Å^{-1}.

the basic framework which are amenable to accurate positioning by X-ray analysis.

The omission from least-squares refinement of the low-angle F_o data (as in VI and VII above) is concomitant with experimental measurements that are carried out with adequate precision over a sufficient range in $(\sin\theta)/\lambda$ to yield a satisfactorily large data/parameter ratio. These criteria, redundantly satisfied in the Cl_2SnTPP data, are usually more difficult, frequently impossible, to fulfill for molecular crystals at room temperature; they were, for example, somewhat less well satisfied in our earlier determination of structure[2] for crystalline $\alpha,\beta,\gamma,\delta$-tetra(4-pyridyl)porphinatomonopyridinezinc (written PyZnTPyP). However, experimental data that satisfy even more stringent criteria are recordable from molecular crystals at a sufficiently low temperature; indeed, the elimination thereby achieved of most, if not all, of the sensitivity of the derived bond parameters to thermal motions in the crystal is a rational substitute for the approximate correction (based upon various models) of the parameters derived from data recorded at room temperature. Thus, correction, following Schomaker and Trueblood,[14] of the pertinent coordinates from refinement VI for the effects of thermal motions lead to bond lengths in the phenyl group of C_6–C_8 = 1.401, C_8–C_9 = 1.399, and C_7–C_9 = 1.387 Å. The averaged bond length is thereby increased to 1.396 Å, but a trend, real or apparent, toward a shorter length as the bond is further displaced from the center of the molecule is still evident. This analysis also gives a corrected length for the bond (C_5–C_6) joining the phenyl group to the porphinato core of 1.498 Å, an increase of 0.004 Å beyond that obtained from refinement VI.

The coordinates listed in Table II and the thermal parameters listed in Table III of all atoms, save hydrogen, in the asymmetric unit of structure are from least-squares refinement VI. The apparent positions and thermal parameters for the hydrogen atoms given in Tables II and III, respectively, come from a final least-squares refinement that differed from refinement III only in that the positional parameters of the carbon and all heavier atoms were fixed at the values derived from the Fourier synthesis.[15,16] Unit weighting was considered to be theoretically appropriate with the Fourier-derived positions and to be empirically supported by the physically superior description of the phenyl group afforded by refinement III relative to that by refinement I. Values of the conventional R, 0.045, and the weighted R, 0.044, are comparable with the respective values from I, 0.044 and 0.049, and from III, 0.045 and 0.043. The description of the C–H bonds, Tables III and IV, is slightly less unrealistic than that provided by refinement I. The quality of the agreement between the bond lengths derived from the Fourier synthesis and those given by refinements VI and VII is displayed fully in Table IV.

Table II. Atomic Coordinates in the Unit Cell

Atom type[a]	Coordinates with standard deviations[b] 10^4x	10^4y	10^4z
Sn	0	0	0
Cl	0	0	2430 (1)
N	408 (1)	1479 (1)	0
C_1	−225 (1)	2255 (1)	0
C_2	345 (2)	3147 (2)	0
C_3	1317 (2)	2879 (2)	0
C_4	1349 (1)	1822 (1)	0
C_5	2207 (1)	1252 (1)	0
C_6	3153 (1)	1800 (1)	0
C_7	4869 (2)	2899 (2)	0
C_8	3586 (2)	2069 (2)	1203 (2)
C_9	4439 (2)	2632 (2)	1191 (3)
H_2	110 (20)	3760 (20)	0
H_3	1850 (30)	3270 (30)	0
H_7	5430 (30)	3260 (30)	0
H_8	3260 (20)	1810 (20)	2080 (30)
H_9	4760 (20)	2800 (20)	2100 (30)

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

Discussion of the Stereochemical Data

The skeletal framework of the Cl_2SnTPP molecule, as it exists with required C_{4h}–$4/m$ symmetry in the crystal, is illustrated in perspective by the computer-drawn diagram of Figure 1. A convenient notation for the three chemical types of carbon atoms in the porphinato skeleton is displayed on the diagram of Figure 2; the respective α- and β-carbon atoms of a pyrrole ring are designated C_a and C_b and methine-carbon by C_m. Because the C_{4h} symmetry of the Cl_2SnTPP molecule requires structural nonequivalence of the C_1 and C_4 atoms of C_a type and of the C_2 and C_3 atoms of C_b type, the three chemical classes of bonds, N–C_a, C_a–C_b, and C_a–C_m, divide each into two structurally distinctive subclasses. Inspection of the bond parameters listed in Table IV shows, nonetheless, that the dimensional variations from full D_{4h} symmetry are objectively altogether trivial—a conclusion that is in fact supported by the results obtained from every procedure utilized earlier for the refinement of structure. This effectively complete D_{4h} symmetry is incorporated in the averaged bond parameters of the porphinato core that are entered on Figure 2 and employed during the subsequent discussion.

Stereochemical parameters for the 1,2,···,8-octaethylporphinatodichlorotin(IV) molecule (written Cl_2SnOEP), derived by the analysis of X-ray data limited in scope to $(\sin\theta)/\lambda \lesssim 0.423$ (giving a data/parameter ratio of ~4.2) from a monoclinic crystalline solvate,[17] are available for comparison with the data of Table IV and Figure 2. Although the symmetry required of the Cl_2SnOEP molecule in the crystal is just C_i–$\bar{1}$, the porphinato core is very nearly planar,[17a] and the averaged N–C and C–C bond lengths of the distinctive chemical classes are objectively compatible with the much more precise values obtained for the Cl_2SnTPP molecule. The radial extension of the core in Cl_2SnOEP, as measured by Ct···C_m distances (Figure 2) of 3.432 (6) and 3.426 (6) Å,[17b] is a little smaller than in Cl_2SnTPP, for which Ct···C_m = 3.469 (2) Å. This observation correlates with apparent differences in the Sn–N bond lengths within the octahedral coordination groups. It is objectively probable that the Sn–N distances of 2.081 (5) and 2.088 (5) Å in Cl_2SnOEP[17b] are actually shorter than the 2.098 (2) Å in Cl_2SnTPP. This conclusion receives indirect, but rather convincing, support from the observation that the Sn–Cl bond length of 2.451 (2) Å in Cl_2SnOEP is quite surely longer than the 2.420 (1) Å in Cl_2SnTPP; inasmuch as the packing of the six ligand atoms around the tin(IV) atom is extraordinarily tight, it follows that a shortening of the equatorial bonds virtually demands a lengthening of the axial bonds.

Of the two most remarkable structural properties of the porphinato core, its ease of deformation normal to the mean plane is less important than is its resistance to

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(14) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 24, 63 (1968).

(15) Use of the positional parameters from refinement VI or VII was, of course, a fully acceptable alternative.

(16) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journal Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6689. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(17) (a) D. L. Cullen and E. F. Meyer, Jr., *Chem. Commun.*, 616 (1971); (b) E. F. Meyer, Jr., private communication.

Table III. Thermal Parameters of the Atoms in the Crystal

Atom type[a]	Anisotropic parameters (Å²) with standard deviations[b]						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[c]
Sn	1.85 (1)	1.85 (1)	2.87 (1)	0	0	0	2.1
Cl	4.10 (5)	4.10 (5)	2.97 (3)	0	0	0	3.7
N	2.11 (5)	2.02 (5)	3.74 (8)	−0.08 (4)	0	0	2.5
C_1	2.51 (7)	1.95 (6)	3.53 (9)	0.09 (5)	0	0	2.6
C_2	3.13 (9)	2.06 (7)	4.97 (13)	−0.13 (6)	0	0	3.2
C_3	2.98 (9)	2.24 (7)	4.51 (12)	−0.40 (6)	0	0	3.1
C_4	2.28 (6)	2.17 (6)	3.39 (8)	−0.25 (5)	0	0	2.5
C_5	2.13 (6)	2.51 (7)	3.33 (8)	−0.28 (5)	0	0	2.6
C_6	2.24 (6)	2.74 (7)	3.36 (9)	−0.43 (5)	0	0	2.7
C_7	2.74 (9)	3.49 (11)	8.06 (25)	−0.91 (8)	0	0	4.1
C_8	4.30 (9)	6.29 (2)	3.93 (9)	−2.33 (9)	−0.18 (8)	−0.85 (9)	4.3
C_9	4.38 (10)	6.15 (13)	6.12 (14)	−2.28 (9)	−0.91 (10)	−1.33 (11)	4.9
H_2							1.4 (8)
H_3							2.9 (10)
H_7							2.9 (10)
H_8							3.3 (7)
H_9							4.0 (7)

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

Table IV. Selected Intramolecular Bond Parameters[a]

Bond type	Length, Å, from			Type of angle	Angle, deg[b]
	Refine. VI[b]	Refine. VII	Fourier		
Sn–Cl	2.420 (1)	2.420 (1)	2.421 (1)	$SnNC_1$	125.4 (1)
Sn–N	2.098 (2)	2.097 (2)	2.099 (2)	$SnNC_4$	125.5 (1)
$N–C_1$	1.370 (2)	1.371 (2)	1.372 (2)	C_1NC_4	109.2 (2)
$N–C_4$	1.370 (2)	1.369 (2)	1.369 (2)	NC_1C_2	108.2 (2)
$C_1–C_2$	1.447 (3)	1.447 (3)	1.448 (3)	NC_1C_5'	126.5 (2)
$C_1–C_5'$	1.407 (3)	1.406 (3)	1.404 (3)	$C_2C_1C_5'$	125.3 (2)
$C_2–C_3$	1.379 (3)	1.380 (3)	1.380 (3)	$C_1C_2C_3$	107.1 (1)
$C_3–C_4$	1.445 (3)	1.444 (3)	1.443 (3)	$C_2C_3C_4$	107.2 (2)
$C_4–C_5$	1.408 (3)	1.408 (3)	1.407 (3)	NC_4C_3	108.3 (2)
$C_5–C_6$	1.494 (2)	1.495 (2)	1.498 (2)	NC_4C_5	126.3 (2)
$C_6–C_8$	1.387 (2)	1.386 (2)	1.381 (2)	$C_3C_4C_5$	125.4 (2)
$C_7–C_9$	1.373 (3)	1.374 (3)	1.366 (3)	$C_1'C_5C_4$	126.3 (2)
$C_8–C_9$	1.397 (3)	1.397 (3)	1.397 (3)	$C_1'C_5C_6$	117.3 (2)
$H_2–C_2$			0.90 (3)	$C_4C_5C_6$	116.3 (2)
$H_3–C_3$			0.90 (4)	$C_5C_6C_8$	120.2 (1)
$H_7–C_7$			0.91 (4)	$C_8C_6C_8''$	119.6 (2)
$H_8–C_8$			1.04 (4)	$C_9C_7C_9''$	119.5 (2)
$H_9–C_9$			1.04 (4)	$C_6C_8C_9$	119.7 (2)
				$C_7C_9C_8$	120.8 (2)

[a] Numbers in parentheses are the estimated standard deviations. Primed symbols denote atoms derived from those listed in Table II by operation of the fourfold axis; doubly primed symbols denote atoms derived by operation of the mirror plane. [b] Values calculated from coordinates listed in Table II; see text for treatment of "C–H bond lengths."

undue radial extension or contraction in the mean plane. Earlier appraisals[2,18] of the stereochemical features exhibited by the spectrum of known structures demonstrate that radial strain in the core of a metalloporphyrin is minimized for a "radius of the central hole"—the Ct· · ·N radius shown on Figure 2—of ~2.01 Å.[19] The complexing metal–nitrogen (M–N) distance is identified with the Ct· · ·N radius whenever, as in the Ni(II), Cu(II), Pd(II), Sn(IV), and the low-spin iron porphyrins, the metal atom is centered among the nitrogen atoms, whereas M–N > Ct· · ·N whenever, as in the zinc and the high-spin iron porphyrins, the metal atom lies out of plane in square-pyramidal five coordination. The pervasive constraints imposed on the complexing bonds by the porphinato core are made evident by the data displayed on Figure 2 for Cl_2SnTPP and for the nickel(II) derivative of 2,4-diacetyldeuteroporphyrin IX dimethyl ester[21] (written NiDeut); the difference of 0.14 Å between the lengths of the Sn–N and Ni–N bonds may be compared with an anticipated difference of ~0.30 Å for the corresponding bonds to nitrogen atoms of monodentate ligands.

Comparison of the averaged N–C and C–C bond lengths in the cores of the NiDeut and Cl_2SnTPP molecules, Figure 2 and Table V, suggests that the increase of 0.138 Å in the M–N (= Ct· · ·N) distance is attended by a small compression (ostensibly 0.013 Å) of the $N–C_a$ bond and by slightly larger extensions (0.030–0.032 Å) of the $C_b–C_b$ and $C_a–C_m$ bonds. The averaged values

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(18) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco Calif., 1968, pp 573–594.

(19) This conclusion receives further strong support from recent determinations of structure for two low-spin iron porphyrins, an iron(III)[20a] and an iron(II)[20b] species.

(20) (a) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972); (b) L. J. Radonovich, A. Bloom, and J. L. Hoard, *ibid.*, **94**, 2073 (1972).

(21) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *ibid.*, **87**, 2305 (1965). In this paper, the averaged value of the NCC bond angle in the pyrrole rings is correctly given as 111.0° in Figure 3 but is incorrectly listed as 110.0° in Table IV.

Table V. Averaged Bond Lengths of the Several Chemical Classes in the Porphinato Cores of Selected Metalloporphyrins[a,b]

	Length, Å, of			
Porphyrin	Ct···N	N–C_a	C_a–C_m	C_b–C_b
Cl_2SnTPP	2.098 (2)	1.307 (2)	1.407 (2)	1.380 (3)
PyZnTPyP	2.047 (2)	1.369 (2)	1.406 (2)	1.355 (3)
Set of 7[c]	2.014	1.382	1.392	1.353
Pip_2FeTPP	2.004 (2)	1.384 (2)	1.396 (3)	1.347 (4)
CuTPP[d]	1.981 (7)	1.385 (9)	1.369 (9)	1.337 (14)
NiDeut	1.960 (4)	1.383 (3)	1.375 (4)	1.350 (5)
NiOEP	1.929 (4)	1.387 (3)	1.373 (4)	1.362 (5)

[a] The unlisted C_a–C_b bond lengths range only from 1.444 to 1.448 Å. [b] The number in parentheses following a datum is the weighted standard deviation of the mean in units of 0.001 Å. [c] Includes six iron porphyrins [see ref 3, 20, and D. F. Koenig, *Acta Crystallogr.*, **18**, 663 (1965); J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965); A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *ibid.*, **94**, 3620 (1972)] and $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatopalladium(II)[23] wherein Ct···N ranges from 1.989 to 2.027 Å. [d] $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocopper(II).[23]

for the several chemical classes of bond parameters in NiDeut, each the average of either the four or the eight values that are structurally independent in the triclinic crystal of excellent quality,[21] carry formally estimated standard deviations of the mean (Table V) that are not unduly large. Such averaging is the more appropriate because the departures from planarity in the core of NiDeut are much too small to affect significantly either the bond angles or, much less, the bond distances. Detailed computations show that precise dimensional consistency of the averaged bond parameters with D_{4h} symmetry is achieved by a reduction of just 0.1° in the $C_aC_mC_a$ angle—from 123.9 to 123.8°; the concomitant increase in the Ct···C_m radius (Figure 2) is 0.001 Å.

Structure determinations for crystalline 1,2,...,8-octaethylporphinatonickel(II)[22] (written NiOEP) and $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocopper(II)[23] (CuTPP) are seen (Table V) to yield bond lengths in the porphinato core that, with the possible exception of the least accurately determined C_b–C_b distance, are in excellent agreement with those listed for NiDeut—this despite the fact that the complexing M–N bond length is significantly shorter in NiOEP and a little longer in CuTPP than it is in NiDeut. It is the very pronounced S_4 (effectively D_{2d}) ruffling of the porphinato cores in NiOEP and CuTPP which requires (or permits) significant adjustments in the M–N bond length and/or the C_aNC_a bond angle while preserving, without sensible change, the critical N–C_a and C_a–C_m bond lengths. The C_aNC_a angle increases from 104.4° in NiDeut to 105.1° in NiOEP and 107.8° in CuTPP. Both the several virtues and the evident shortcomings of a D_{2d}-ruffled porphinato core are analyzed in detail elsewhere;[24] we emphasize here just the experimentally derived conclusion that the structural differences between the expanded core of Cl_2SnTPP and the contracted core of a nickel porphyrin include significant differences in the lengths of the N–C_a, C_a–C_m, and C_b–C_b bonds.

Also included in Table V are precise bond distances obtained for the low-spin bis(piperidine)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(II) (Pip_2FeTPP) molecule.[20b] The Ct···N radius of 2.004 (2) Å corresponds nearly to minimum radial strain in the porphinato core and, moreover, the C–N and C–C bond lengths are seen (Table V) to differ immaterially from those obtained as gross averages over the values observed in a mixed lot of metalloporphyrins wherein the Ct···N radius ranges from 1.989 (2) to 2.027 (3) Å. Although only a center of inversion is required of the Pip_2FeTPP molecule in the crystal, the porphinato core and the entire octahedral coordination group approximate closely to C_{2h} symmetry.[20b] Moderate foldings of nearly uniform magnitude at the nitrogen atoms give the porphinato core a stepped quasi-C_{2h} conformation in which the deviation of any bond length or angle from the average for its chemical class is objectively quite insignificant. Otherwise put, dimensionally significant variations from a D_{4h} core are concentrated in the $FeNC_a$ angles.

The entirely general conclusion to be drawn from the data of Figure 2 and Table V is that, irrespective of the value taken by the Ct···N radius, the porphinato core is far from being a strain-free system. Thus, for example, the NC_aC_b angle in the trigonal bond system centered at the bridgehead carbon atom C_a is always restricted to values substantially below the ideal 120°. For not unduly large Ct···N radii, the NC_aC_b angle is allowed to be significantly greater than $540/5 = 108°$ (the averaged value for a pyrrole ring angle), the C_aNC_a angle being simultaneously restricted to values below 106° and the $C_aC_bC_b$ angle to ~107°. In the most expanded core, that of Cl_2SnTPP, the C_aNC_a angle is necessarily opened to the relatively large value of 109.2°, but the geometrical consequence of the simultaneous stretching of the C_b–C_b bond (by 0.02–0.03 Å) is to keep the $C_aC_bC_b$ angle nearly unaltered at 107.2°. Thus the reduction required of the critical NC_aC_b angle is minimized.

A shrinkage of the Ct···C_m radius in the core of Cl_2SnTPP (Figure 2) by just 0.0285 Å is the most efficient geometrical mechanism for reducing the stretched C_a–C_m bond length of 1.407 Å to the 1.395 Å that corresponds to a Ct···N radius of ~2.01 Å. It is also a physically realistic mechanism; the concomitant alterations in the $C_aC_mC_b$ and NC_aC_m bond angles, an increase of 2.1° and a decrease of 1.05°, respectively, represent a modest increase in angular strain that appears to be energetically less cogent than the decreased strain in the C_a–C_m bond distance. Indeed, this slightly less expanded form of the core is very likely to have preference in the externally unconstrained molecule.

Inasmuch as the magnitude of the stabilizing energy contributed by delocalized π bonding is a maximum for a planar conformation of the porphinato core, it is natural to ascribe the observed predominance of nonplanar conformations in crystalline metalloporphyrins to packing constraints imposed upon the molecules. Even in the absence of such constraints, however, moderately nonplanar cores must be anticipated for all

(22) E. F. Meyer, Jr., *Acta Crystallogr.*, in press.

(23) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, **86**, 2342 (1964).

(24) See J. L. Hoard, *Ann. N. Y. Acad. Sci.*, in press, for a treatment of the dimensional constraints on the porphinato core that are concomitant with the bonding geometry in those point groups (D_{4h}, C_{4v}, and D_{2d}) which require structural equivalence to be maintained for the bond parameters within each chemical class and, simultaneously, permit near or exact planarity of the trigonal bond systems centered at the bridgehead (C_a) carbon atoms to be preserved.

five-coordinate metalloporphyrins and, depending on the structural characteristics of the axial ligands, for some six-coordinate species as well.[20,24] A more interesting question is whether strain in either the highly contracted core of a nickel porphyrin or the highly expanded core of a dichlorotin(IV) porphyrin might be sufficiently relieved in the nonplanar conformation most appropriate to each species as to more than compensate for the constraints simultaneously imposed on the π bonding. Although no unqualified answer to either part of this question is feasible, the geometrical analysis which is outlined below and developed in detail elsewhere[24] suggests that the expanded core is not at all likely to exhibit spontaneous deformation from planarity. A C_{4v} cupping of the expanded core and, not surprisingly, a D_{2d} ruffling of the contracted core provide the conformations that are most pertinent to discussion of the two limiting cases. The low geometrical efficiency of a physically admissible C_{4v} cupping for the reduction of strain in the chelate rings of the Cl_2SnTPP molecule can be demonstrated with the aid of the following model.

We take each pyrrole ring and the pair of C_a-C_m bonds attached to it (Figure 2) as a rigid planar entity within which only the C_a-C_m bond length is allowed to vary during the cupping operation. Each such entity is hinged at a nitrogen atom and is folded (or rotated) out of the plane of the nitrogen atoms through the angle τ; the four simultaneous foldings observe C_{4v} symmetry. If the Sn–N distance also be fixed, the conformation retains just one degree of freedom,[24] conveniently taken as τ; values of the C_a-C_m distance, the $Ct\cdots C_m$ and $Ct\cdots C_a$ radii, and the $C_aC_mC_a$ and $CtNC_a$ angles in the chelate ring all are determined by the specification of τ. Using the observed values from the D_{4h} conformation of Cl_2SnTPP for all fixed parameters in the C_{4v} model, the increment $\Delta(C_a-C_m)$ in the C_a-C_m bond length as a function of τ is given by[24]

$$\Delta(C_a-C_m) = [-0.710 \sin^2(\tau/2)]/[1.262 - 0.624 \sin^2(\tau/2)]$$

but for $\tau \lesssim 20°$ $(\pi/9)$, the approximate relation, $\Delta(C_a-C_m) = -0.1403\,\tau^2$, is accurate within 2×10^{-4} Å. The parabolic form of this relation exemplifies the fact that, starting from planarity ($\tau = 0$), the initial rate of change of any bond parameter in the core with the deformation parameter is zero.[24]

Calculated shortenings, $-\Delta(C_a-C_m)$, of the C_a-C_m bond length are 0.004 and 0.017 Å for $\tau = 10$ and $20°$, respectively. Reduction of the stretched C_a-C_m distance of 1.407 Å in Cl_2SnTPP to 1.395 Å (*vide supra*) by way of this C_{4v} deformation requires τ to be $\sim 16°$. For $\tau = 10°$, a physically rational value of subsequent interest, the C_{4v} model gives $C_aC_mC_a$ and $SnNC_a$ angles that are reduced by 0.48 and 0.62°, respectively, from the values in the D_{4h} conformation. A more substantial reduction in the C_a-C_m bond length can, of course, still be achieved—just as in the D_{4h} conformation—by relatively minor adjustment of the $C_aC_mC_a$ and NC_aC_m angles. (But a further opening of the highly expanded C_aNC_a angle as a geometrical variant for the efficient reduction of the C_a-C_m distance is, as noted above, strongly inhibited by concomitant structural constraints.) We conclude that a C_{4v} cupping of the expanded core is a quite inefficient mechanism, either on a quasi-absolute basis or relative to a D_{2d} ruffling of a contracted core,[24,25] for the reduction of strain in the critical bond parameters.

The somewhat inimical constraints that are imposed on the delocalized π bonding by a significant C_{4v} cupping of the core may be summarized qualitatively as follows. The polar deformation demands nonequivalence of the inner and outer surfaces of the core. Although the geometry of the deformation allows the trigonal bond systems centered at the carbon atoms C_a and C_m to retain exact planarity, it does not allow any pair of these systems to retain coplanarity or, indeed, to remain parallel to one another. Thus for $\tau = 10°$ in the C_{4v} model specified above, the angle of tilt between the normals to the trigonal bond systems centered at contiguous (joined) C_a and C_m carbon atoms is 8.7°; these bond systems are simultaneously tilted by 10 and 6.8°, respectively, from coplanarity with the equatorial plane of the coordination group. The required loss of planarity by the trigonal bond system emanating from each nitrogen atom must also be energetically somewhat disadvantageous.

Lacking the quantitative basis for an unambiguous conclusion, it still seems improbable that the relief of strain in the expanded core of a tin(IV) porphyrin—or, indeed, of a tin(IV) phthalocyanine (*vide infra*)—can be so compelling as to stabilize the externally unconstrained molecule in a C_{4v} conformation. It is still less probable that the energy barrier to reflection of such a C_{4v} conformation through the equatorial plane of the coordination group could be large enough to withstand thermal motion at room temperature. The obverse conclusion, that modest external constraints on the molecule can give rise to significant deformation of the core from planarity, must then obtain, but with the proviso that such an expanded core is markedly less susceptible to substantial deformation than is the contracted core of a nickel porphyrin. In evident agreement with this proviso is the trivial departure from planarity reported for the expanded core of the Cl_2SnOEP molecule in the monoclinic crystal.[17] Recent structure determinations for crystalline $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatosilver(II)[26–29] (AgTPP) and phthalocyaninatodichlorotin(IV)[30] (Cl_2SnPhc) are also pertinent in this connection.

With an anticipated Ag–N bond length of $\sim 2.08 \pm 0.01$ Å, AgTPP does not crystallize isomorphously with CuTPP in the tetragonal structural type which requires the porphinato core to be markedly ruffled in agreement with S_4 (quasi-D_{2d}) symmetry.[23] Pure AgTPP crystallizes in a triclinic structural type[26] in which the required molecular symmetry is $C_i-\bar{1}$, the

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(25) In the analogous model of a D_{2d} ruffled core, each rigid planar entity (pyrrole ring with attached C_a-C_m bonds) is rotated around the complexing M–N bond through the angle ϕ. Using values for the fixed parameters (including the Ni–N distance) from NiDeut, the approximate relation, $\Delta(C_a-C_m) = 0.9651\phi^2 + 0.370\phi^4$, is accurate to better than 2×10^{-4} Å for $\phi \lesssim 20°$. Thus for $\phi = \tau$, the magnitude of $\Delta(C_a-C_m)$ is about sevenfold larger in the contracted core. Other geometrically advantageous features of the D_{2d} contracted core that receive only passing mention in this paper are treated in detail elsewhere.[24]

(26) A. Tulinsky, private communication.

(27) S. J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, **89**, 3331 (1967).

(28) G. Donnay and C. B. Storm, *Mol. Cryst.*, **2**, 287 (1967).

(29) (a) M. L. Schneider and G. Donnay, American Crystallographic Association, Summer Meeting, Aug 15–20, 1971, Abstract K14; (b) M. L. Schneider, *J. Chem. Soc., Dalton Trans.*, 1093 (1972).

(30) D. Rogers and R. S. Osborn, *Chem. Commun.*, 840 (1970).

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Ag–N bond lengths are 2.08 and 2.10 Å, and the expanded porphinato core displays significant, but still modest, deviations from planarity that are attributable to packing constraints. The structural type differs only in detail from that of the triclinic modification of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine[27] (H_2TPP), and, indeed, AgTPP and H_2TPP form a complete series of solid solutions.[28] Of particular interest, however, are tetragonal crystals having the composition, $(AgTPP)_x(H_2TPP)_{1-x}$ for $0.08 < x < 0.54$, that are obtained simultaneously in small yield during preparation of the triclinic solid solutions.[28,29] This tetragonal solid solution crystallizes as a somewhat disordered variant[29] of the Cl_2SnTPP structural type wherein the AgTPP and H_2TPP molecules are required to observe C_{4h} symmetry.[31] That pure AgTPP does not crystallize as the ordered tetragonal variant of the Cl_2SnTPP structural type is presumably because the packing density in the triclinic modification is the larger by nearly 8%. In the tetragonal solid solution, however, the energetic preference of the AgTPP molecule for a planar core is buttressed by especially favorable entropic relations;[31] consequently the tetragonal phase should be favored by an increase in the preparative temperature.

The precise stereochemical description of the Cl_2SnPhc molecule, as it occurs with required C_i-$\bar{1}$ symmetry in monoclinic crystals,[30] is quite in agreement with the investigators' expectation[30] of a "tight fit" for insertion of a tin(IV) atom in the phthalocyaninato ring. Inasmuch as the value of the Ct···N radius for minimizing radial strain in the phthalocyaninato skeleton of a metallophtahlocyanine seems to be ~0.10 Å smaller than the analogous datum for metalloporphyrins,[24] the values of the Sn–N bond lengths, 2.050 (3) and 2.051 (3) Å, and of all other critical bond parameters in Cl_2SnPhc[30] correspond to a more expanded framework, relatively and absolutely, than that in Cl_2SnTPP. The C_i conformation of the Cl_2SnPhc molecule, as observed in the crystal, involves two structurally independent foldings at the nitrogen atoms. Two equivalent, oppositely situated, nearly planar, isoindole entities are folded out of plane, one up and the other down, by ~10.6°, and the two other such entities are similarly folded out of plane by ~5.1°. The substantial difference between the two folding angles prevents this conformation from achieving the close approximation to effective C_{2h} symmetry which characterizes the otherwise analogous conformation of the porphinato core in $(Pip)_2FeTPP$.

That such a C_{2h} or C_i conformation is adaptable to the simple redistribution of internal strain in a molecule which is subjected to external constraints of the corresponding symmetry type is made apparent by the $(Pip)_2FeTPP$ structure.[20b] Neither conformation, however, has any evident capacity for the *reduction* of overall strain in the highly expanded D_{4h} conformations of externally unconstrained Cl_2SnTPP and Cl_2SnPhc molecules. Examination of the averaged bond parameters of the several chemical types in Cl_2SnPhc shows that just one of these parameters need be altered significantly in order to make the averaged phthalocyaninato skeleton dimensionally compatible with D_{4h} geometry. Unfolding of the averaged skeleton is accomplished by an increase of ~0.55° in the averaged $SnNC_a$ angle with concomitant alterations in other bond parameters in the chelate rings that are nearly trivial for any angle (<0.1°) and quite negligible for any bond length. That only the $SnNC_a$ angles need be significantly altered by a C_{2h} deformation from planarity stems from the circumstance that the effect of the contiguous foldings of opposite sense (up and down) on the other bond parameters can offset or neutralize the effect of the contiguous foldings having the same sense.[24] We conclude, consequently, that spontaneous deformation from D_{4h} symmetry of an externally unconstrained Cl_2SnPhc molecule is improbable.

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(31) The H_2TPP molecules statistically satisfy C_{4h} symmetry.[29]