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SYNTHESIS AND PROPERTIES OF FLUOROTHALLIUM(III) PORPHYRINS. X-RAY CRYSTAL STRUCTURE OF FLUORO-(5,10,15,20-TETRAPHENYLPORPHYRINATO) THALLIUM(III)

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Abstract—The action of sodium fluoride on chlorothallium(III) porphyrins, Tl(Por)Cl, produces the corresponding fluoroporphyrins, Tl(Por)F. These complexes were characterized by their ^{1}H-NMR, UV–vis and IR data. The crystal structures of the title compound [Tl(TPP)F] has been determined by X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and lattice dimensions $a = 10.118(3)$, $b = 16.236(5)$, $c = 21.189(6)$ Å, $\beta = 90.86(2)°$, $V = 3480(2)$ Å^3. $C_{44}H_{28}FN_4Tl$, $F_w = 836.11$ g, $\rho = 1.60$ g cm^{-3}, $\mu = 47.3$ cm^{-1}, $F(000) = 1640$, temperature 23(1)°C, $R(F) = 0.045$, $Rw(F) = 0.050$ for 2135 observed reflections. The thallium–fluorine distance is 2.441(6) Å with the thallium atom situated 0.741(1) Å above the porphyrin ring.

Much interest has been recently directed towards the synthesis and characterization of one-dimensional inorganic–organic polymeric systems in which a metallic or pseudometallic element alternates along the chain direction with a bridging element such as oxygen or fluorine.[1–6] The metallic or pseudometallic element is usually the central atom of a phthalocyanine or a porphyrin system, resulting in a rigid bridge-stacked polymeric structure. These derivatives become electrical conductors upon iodine oxidation.[7–13] We have recently initiated a search for similar low-dimensional systems in which the central atom of the porphyrin ring is a group III_B element, in which the large phthalocyanine ring is replaced by a porphyrin ligand.[14] Difference Fourier analysis of the EXAFS spectra of the hydroxo- and fluorogallium(III)-2,3,7,8,12,13,17,18-octamethylporphyrins [Ga(OMP)OH and Ga(OMP)F] has afforded some evidence for the polymeric structure of the latter complex.[14]

In this paper, the synthesis and properties of Tl(Por)F complexes are described, the metallic ion of the porphyrin centre, gallium, having been replaced by thallium. No evidence for polymer formation is found and we present a description of the crystal structure of Tl(TPP)F which is, as far as we know, the first X-ray study of a fluorothallium(III) porphyrin.

EXPERIMENTAL

Preparation of complexes

The chloro and fluoro complexes were synthesized following the general procedure described below.

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Abbreviations. Por: unspecified porphyrinate (2^-); OEP: 2,3,7,8,12,13,17,18-octaethyl porphyrinate (2^-); TPP: 5,10,15,20-tetraphenyl porphyrinate (2^-); OMP: 2,3,7,8,12,13,17,18-octamethyl porphyrinate (2^-).

Chloro-(porphyrinato)thallium(III). $Tl(CH_3COO)_3 \cdot 3/2H_2O$ (37.7 mmol) was added to a solution of porphyrin (9.35 mmol) and tetrahydrofuran (200 cm^3) and the mixture was refluxed for 4 h. Evaporation of the reaction mixture under reduced pressure and extraction of the residue with CH_2Cl_2–H_2O, followed by drying of the organic phase and evaporation *in vacuo* gave a precipitate which was chromatographed (CH_2Cl_2, Al_2O_3). Traces of the free base were eluted first, with the chloro complex as the second fraction. After evaporation of the solvent, the precipitate was recrystallized by slow diffusion of hexane or pentane into a saturated CH_2Cl_2 solution of the porphyrinic complex.

Fluoro-(porphyrinato)thallium(III). Chloro-(porphyrinato)thallium(III) (80 mmol) was dissolved in 100 cm^3 of dichloromethane. After the addition of sodium fluoride (240 mmol) and 2 cm^3 of distilled water, the mixture was stirred for 16 h. The excess of sodium fluoride was removed by washing the organic phase with water. After drying with magnesium sulphate, the solvent was removed under reduced pressure and the residual precipitate was dried at 80°C under 15 mm Hg and recrystallized as described above for the chloro complexes.

Physical measurements

^1H NMR spectra were recorded on a Varian FT-80. Spectra were measured for complex (5 mg) solutions in 0.6 cm^3 of $CDCl_3$ with tetramethylsilane as internal reference. IR spectra were recorded on a Perkin–Elmer 298 spectrophotometer. Samples were prepared as 1% dispersions in CsI pellets or Nujol mulls. Electronic absorption spectra were recorded on a Perkin–Elmer 330 spectrophotometer using 5×10^{-3} mol dm^{-3} dichloromethane solutions or a ORIEL diode-array visible spectrometer.

Crystal and molecular structure determination

A suitable crystal of Tl(TPP)F was obtained by slow diffusion of pentane into a dichloromethane solution of the compound. All data were collected on a Nicolet P3F diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å). The crystal data and data collection parameters are summarized in Table 1.

Preliminary Weissenberg photographs along the *b* axis revealed a two-fold symmetry, and from the reflection conditions of $h0l$, $h+l = 2n$ and $0k0$, $k = 2n$ reflections and the subsequent least-squares refinement, the space group was determined to be $P2_1/n$. Experimental conditions and details of the calculations are also included in Table 1. The structure was solved using the Patterson heavy-atom method which revealed the position of the thallium atom. The remaining atoms were located in succeeding difference Fourier syntheses with the hydrogen atoms included in the refinement, but restrained to ride on the atom to which they are bonded. Full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$, with the weight w defined as $4F_o^2/\sigma(F_o^2)^2$, converged to the agreement factors shown in Table 1. The scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_c;[16] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] Only the 2135 reflections having intensities greater than three times their standard deviations were used in the refinements. A selection of bond distances and bond angles is given in Table 2.*

RESULTS AND DISCUSSION

During the last two decades, a number of thallium(III) porphyrin complexes possessing different axial ligands have been reported.[18,19] In general, "soft" bases like Cl, I and CN tend to favour five-coordination of the thallium atom in the Tl(Por)X complexes, while a higher coordination number is achieved with hard bases like the acetate ligand.[20] Six-coordination for thallium is also known in the aquohydroxythallium(III) derivatives, Tl(Por)OH(H_2O).[19] The synthesis of metal–carbon complexes from thallium(III) porphyrins was studied first by Henrick *et al.*[21]

We have prepared the chlorothallium(III) porphyrins by the action of $Tl(CH_3COO)_3 \cdot 3/2H_2O$ on free bases in boiling tetrahydrofuran. These complexes were obtained in yields varying from 70 to 90%. Treatment of Tl(Por)Cl with sodium fluoride in dichloromethane led to Tl(Por)F derivatives, whose yields varied with the nature of the axial and equatorial ligands (57–80%).

Tl(Por)X compounds exhibit electronic absorption spectra belonging to the "normal" class[22] (Table 3). They show an intense band in the 418–436 nm region and two bands between 500 and 600 nm (α- and β-bands). One extra band [$Q(2,0)$] observed in the visible region appears blue shifted compared to the Soret band (see Fig. 1). As previously reported by Gouterman *et al.*[23,24] for tin octaethylporphyrin dihalides (with halide = F, Cl, Br, or I), the shifts in the transition energies and relative intensities of the α- and β-bands depend on

* Fractional atomic coordinates, anisotropic thermal parameters and a list of structure factors have been deposited as supplementary data with the Editor, from whom copies are available on request.

Table 1. Experimental details (crystal data, intensity measurements, structure solution and refinement)

Formula	$C_{44}H_{28}FN_4Tl$
Formula weight	836.11
Space group	Monoclinic, $P2_1/n$
a (Å)	10.118(3)
b (Å)	16.236(5)
c (Å)	21.189(6)
β (°)	90.86(2)
V (Å^3)	3480(2)
Z	4
C (g cm^{-3})	1.60
μ (cm^{-1})	47.3
$F(000)$	1640
Temperature (°C)	23(1)
Crystal dimensions (mm)	$0.08 \times 0.20 \times 0.26$
Maximum 2θ (°)	45
Number of reflections measured	5250 total, 4568 unique
Solution	Patterson method
Refinement	Full-matrix least squares
Minimization function	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least-squares weights	$4F_o^2/\sigma(F_o^2)^2$
Anomalous dispersion	All non-hydrogen atoms
Reflections included	2135 with $I > 3\sigma(I)$
Parameters refined	446
Unweighted agreement factor	0.045
Weighted agreement factor	0.050
Factor including unobserved data	0.045
ESD of observed data of unit weight	1.41
High peak in final difference map	1.15(14)e/Å^3
Low peak in final difference map	−0.62(14)e/Å^3
Computer hardware	VAX 11/750
Computer software	SDP/VAX (Enraf–Nonius & B.A. Frenz & Associates, Inc.)

the charge and polarizability of the axial ligand and correlate with changes in the electron density in the porphyrin ring.

The IR spectra of the isolated chloro complexes show a band in the region 275–290 cm^{-1}, assigned to the Tl—Cl stretching. This characteristic band is found between 415–485 cm^{-1} for the fluoro derivatives (415 and 485 cm^{-1} for TPP and OEP, respectively).

Table 4 summarizes ^{1}H NMR data for each Tl(Por)Cl and Tl(Por)F complex. No dramatic changes in the porphyrin chemical shifts as a func-

Table 2. Selection of bond distances (Å) and angles (°)

Bond distances (Å)			
Tl(1)—F(1)	2.441(6)	Tl(1)—N(23)	2.181(12)
Tl(1)—N(21)	2.221(12)	Tl(1)—N(24)	2.225(14)
Tl(1)—N(22)	2.223(14)		

Bond angles (°)			
F(1)—Tl(1)—N(21)	108.3(4)	N(21)—Tl(1)—N(23)	140.2(5)
F(1)—Tl(1)—N(22)	110.5(4)	N(21)—Tl(1)—N(24)	83.5(5)
F(1)—Tl(1)—N(23)	111.5(4)	N(22)—Tl(1)—N(23)	83.4(5)
F(1)—Tl(1)—N(24)	107.9(4)	N(22)—Tl(1)—N(24)	141.6(5)
N(21)—Tl(1)—N(22)	82.8(5)	N(23)—Tl(1)—N(24)	84.5(5)

Table 3. UV–vis data (λ/nm)[a]

Compound	B(1,0)	B(0,0)	Q(2,0)	Q(1,0) (or α)	Q(0,0) (or β)
Tl(OEP)Cl[b]	sh	418	498	545	582
	—	(225.7)	(2.1)	(11.8)	(10.5)
Tl(OEP)F[c]	sh	421	501	549	583
	—	(296.8)	(2.3)	(19.3)	(14.5)
Tl(TPP)Cl[b]	sh	434	520	566	608
	—	(360.5)	(2.7)	(13.6)	(8.5)
Tl(TPP)F[c]	sh	436	522	569	609
	—	(445.9)	(3.1)	(22.6)	(11.3)

[a] 10^{-3} ε/dm^3 mol^{-1} cm^{-1} given in parentheses.
[b] Reference 26.
[c] This work.

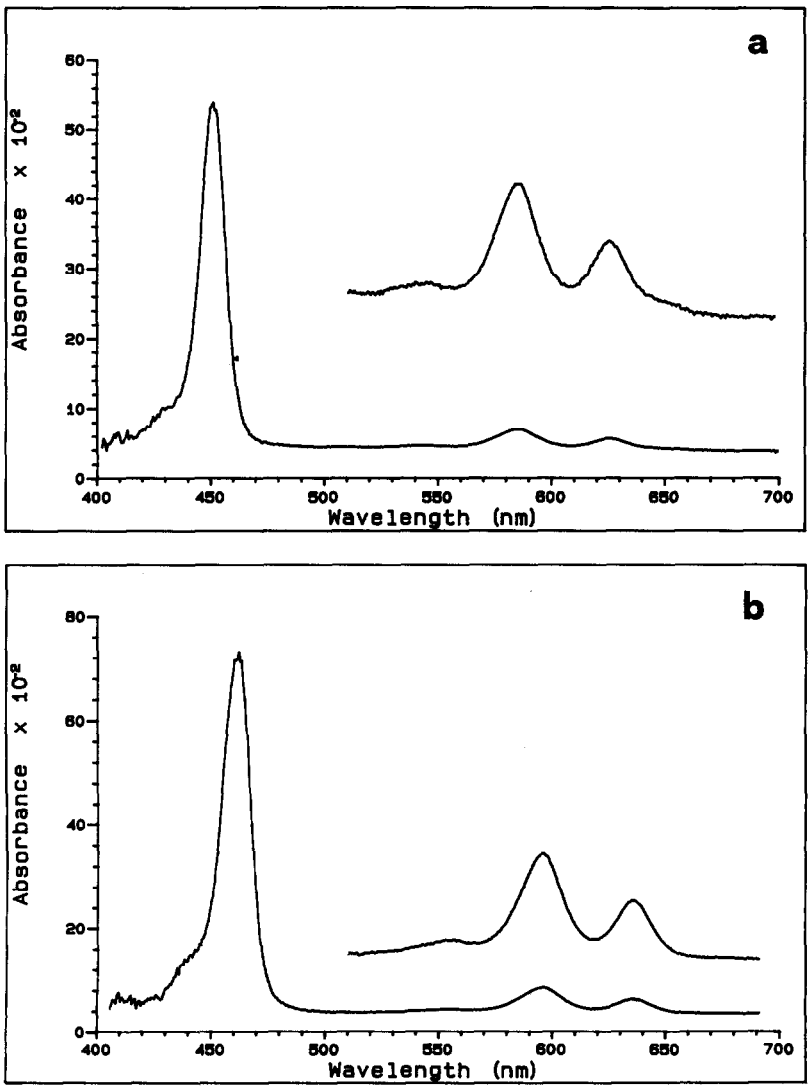

Fig. 1. UV–vis spectra of (a) Tl(TPP)F and (b) Tl(TPP)Cl complexes.

Table 4. ^{1}H NMR[a] data

Compound	R^1	R^2	Protons of R^1	Protons of R^2
Tl(OEP)Cl[b]	H	Et	d/4 10.33(39)[c]	t,24 1.79 m,16 3.87
Tl(OEP)F[d]	H	Et	d/4 10.25(44)[c]	t,24 1.86 m/16 4.06
Tl(TPP)Cl[b]	Ph	H	*o*-H, m/8 7.98	d/8 9.03(63) *m,p*-H m/12 7.42
Tl(TPP)F[c]	Ph	H	*o*-H, m/8 7.83	d/8 9.01(64) *m,p*-H m/12 7.73

[a] Spectra recorded on $CDCl_3$. Data given as multiplicity, intensity, δ/ppm.
[b] Reference 26.
[c] Values in parentheses are ^1H–$^{203,205}Tl$ coupling constants in Hz.
[d] This work.

tion of the axial ligand are observed. More positively charged central metal ions reduce the electron density on the porphyrin macrocycle and thus deshield the porphyrin protons.[25] The porphyrin electron density is also dependent on the electron-withdrawing properties of the axial ligand,[26] and the *meso* proton chemical shift of Tl(OEP)X varies with the axial ligand X, as Cl < F (Fig. 2 with some ^{1}H NMR spectra). The central metal of Tl(Por)R is a heavy metal and this fact appears to be more important in influencing deshielding than the electron-donor or acceptor properties of the axial ligand. For comparison, the porphyrin proton resonances of Ga(Por)R do not depend upon the electron-donor ability of the axial ligand.[27]

As reported[28,29] in the literature, ^{1}H–^{203,205}Tl

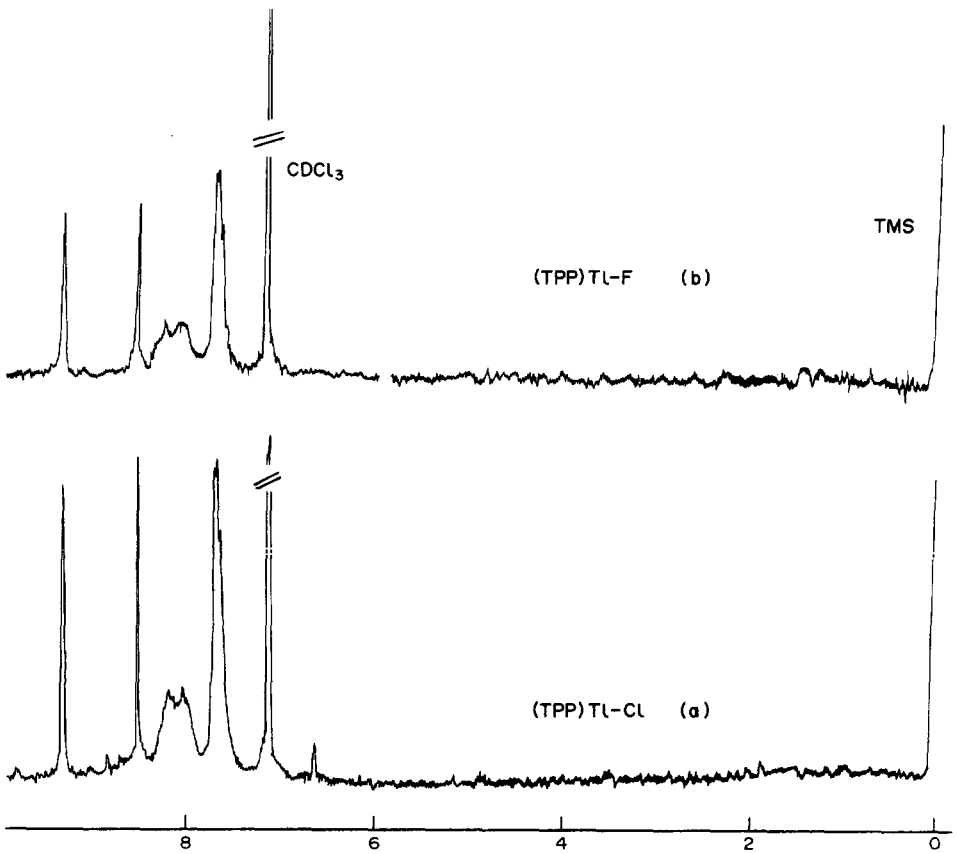

Fig. 2. ^{1}H NMR spectra of (a) Tl(TPP)Cl and (b) Tl(TPP)F complexes.

couplings are observed, but only between thallium(III) and *meso* or pyrrole protons of the porphyrin macrocycle, and the axial ligand proton. The magnitude of the coupling varies with the proton–thallium distance. The signals of octaethylporphyrin complexes show a multiplet for the methylene protons as the AB part of the ABX_3 system. This is similar to the case for complexes in the gallium or indium series and agrees with pentacoordination of the thallium(III) metal as well as an out-of-plane metal atom. The specific chemical shifts for each of Tl(OEP)X and Tl(TPP)X are given in Table 4. As seen in this table, only small and insignificant variations of the chemical shifts occur. The resonances of the methine protons or *meso* protons depend on the electron-donating ability of the axial ligands, which is a conclusion reached by comparison with other five-coordinated thallium porphyrins, where X = —CN, —SCN and $—N_3$.[30]

As no structure of a fluorothallium porphyrin has been reported before, and in order to provide a comparison with the case of gallium and indium fluoroporphyrins, the crystal structure of Tl(TPP)F has been determined (Fig. 3). The ORTEP drawing of the molecule reveals the five-coordination geometry of the thallium atom to the four nitrogen atoms (N_p) of the porphyrinato group and the fluorine atom; the coordination polyhedron is very close to a square pyramid with a Tl—F bond distance of 2.441(6) Å, and a mean Tl—N_p bond of 2.21(1) Å; the thallium atom lies 0.741(1) Å above the plane defined by the porphyrinato nitrogen atoms, resulting in a mean F—Tl—N_p bond angle of 109.6(6)°. The above values are very similar to the ones encountered in Tl(TPP)Cl and $Tl(TPP)CH_3$, where, for example, the bond distances to the axial ligands are 2.420(4) and 2.147(12) Å, respectively. From these data, the reason for the adoption of five-coordinate geometry by thallium becomes apparent: in order to minimize radial strain, the approach of a second axial ligand would require either a major distortion from planarity of the N_4 donor set, or a significant shortening of the Tl—N bonds from the average of 2.21 Å to a value of 2.01 Å. In Table 5, are collected the M—L and the average M—N_p distances for a number of metalloporphyrins of group III_B with various axial ligands. It is apparent that these distances correlate well with the increase in ionic radii from Ga^{3+} to Tl^{3+}, with the absolute values depending on the axial ligand also. Nevertheless, even though the size of the cation plays a major role in the resulting geometry of the metalloporphyrin complex, the case of the $[In(TPP)OSO_2CH_3]_n$ polymeric system clearly demonstrates that this rule is not always

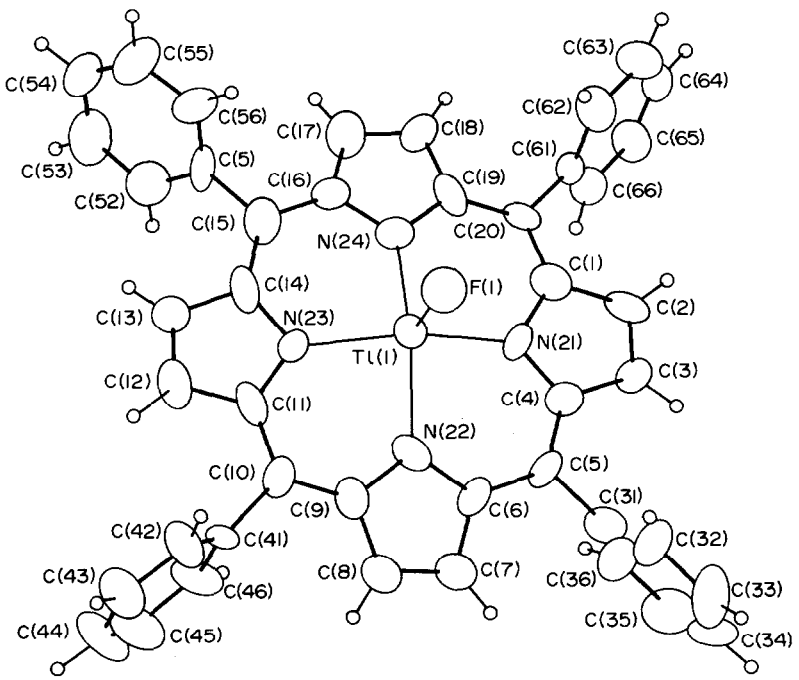

Fig. 3. ORTEP view of the Tl(TPP)F complex.

Table 5. Comparative X-ray data for metalloporphyrins of group III_B

Compound	M—L (Å)	M—4N_n (Å)	Reference
$Ga(OEP)OSO_2CH_3$	1.908(6)	2.013(5)	38
$Ga(OEP)N_3$	1.955(2)	2.034(3)	39
Ga(OMP)F	1.97(3)	2.04	14
Ga(TPP)Cl	2.196(2)	2.021	37
Ga(TPP)Cl,py	2.33 and 2.27	2.01	30
In(TPP)Cl	2.369(2)	2.156(6)	35
$In(TPP)CH_3$	2.132(15)	2.205(10)	21
In(TPP)[$(N_4C)R$]	2.183(5)	2.128(4)	36
$In(TPP)CO_2CH_3$	2.15 and 2.60	2.16	33
$[In(TPP)OSO_2CH_3]_n$	2.352(12), 2.357(11)	2.13, 2.08	40
$Tl(TPP)CH_3$	2.147(6)	2.229	21
Tl(TPP)Cl	2.420(4)	2.21(1)	21
Tl(TPP)F	2.441	2.213	This work

obeyed. We are continuing our systematic exploration of the metalloporphyrin complexes of group III_B.

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