The X-Ray Crystal and Molecular Structure of
Chloro-α,β,γ,δ-tetraphenylporphinatopyridinegallium(III)

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Crystals of the title compound $C_{49}H_{33}N_5ClGa\cdot\frac{1}{2}C_5H_5N\cdot\frac{1}{2}C_5H_{12}$ [Ga(py)(Cl)(TPP)]·½(py)·½(n-pen) are monoclinic, P2₁/n, a = 13.162(2), b = 23.422(6), c, = 14.677(2) Å, β = 101.47(1)°, and Z = 4. The crystal structure refined to R = 0.056 for 2249 observed reflections. The coordination polyhedron of the gallium atom is an octahedron, and the distances between the central metal and axial ligands are Ga-Cl = 2.328(1) and Ga-py = 2.274(3) Å. The gallium atom is displaced slightly out of the porphyrin plane towards Cl, 0.14 Å from the 4N plane and 0.16 Å from the mean porphinato plane, with an average Ga-N distance of 2.01 Å. Although the complex is isostructural with the Mn and Co analogs, it is the first reported structure of a monomeric hexacoordinate gallium(III) porphyrin.

Introduction.

The chemical, electrochemical and spectroscopic properties of various σ-bonded [1] and ionic [2] monomeric gallium(III) porphyrins have been characterized in nonaqueous media. These types of compounds may be five or six-coordinate depending upon the specific solution conditions [2], but all X-ray investigations to date have revealed only a pentacoordination geometry for the monomeric complexes. The distance between the metal and the porphinato plane may depend upon both the nature of the axial ligand and the macrocyclic ring and this was demonstrated for the case of gallium(III) porphyrins having Cl⁻, N_3^-, or $SO_3CH_3^-$ anionic axial ligands [3-5].

The generation of polymeric gallium porphyrins is also possible and these compounds are necessarily hexacoordinate. For example, a polymeric six-coordinate fluorogallium octamethylporphyrin was synthesized and examined by EXAFS spectroscopy [6] but attempts to prepare suitable single crystals for X-ray studies by chemical doping (I_2, NOBF₄ and NOPF₆) were unsuccessful. On the other hand, a partially oxidized porphyrin stacked trimer, $(Ga(OEP))_3F_2(BF_4)_2\cdot C_7H_8$, has recently been electrocrystallyzed and structurally characterized [7]. An X-ray study of fluorogallium(III) phthalocyanine was also reported by Nohr and Wynne [8]. This compound has the gallium atom located in the macrocycle center and is the first structural example of a symmetrical hexacoordinated gallium(III) macrocyclic.

The properties of a gallium porphyrin polymer with optimum electrical conductivity should be related to properties of the six coordinate species, but to date there has been no structural characterization of a monomeric hexacoordinate gallium porphyrin with two anionic axial ligands. In fact, there have been no structural reports of any

gallium(III) porphyrin or phthalocyanine other than those which are found as part of a polymeric unit. For this reason, the crystal structure of any hexacoordinated monomeric gallium porphyrin is of interest.

An increase in electrical conductivity is observed after partial oxidation of either fluorogallium phthalocyanines [9] or fluorogallium porphyrins [10] and information concerning crystallographic data on hexacoordinated gallium(III) porphyrins might thus provide critical insight into the mechanism of electrical conductivity observed after such partial oxidation. In this paper we describe the molecular structure of hexacoordinated chloro-α,β,γ,δ-te-
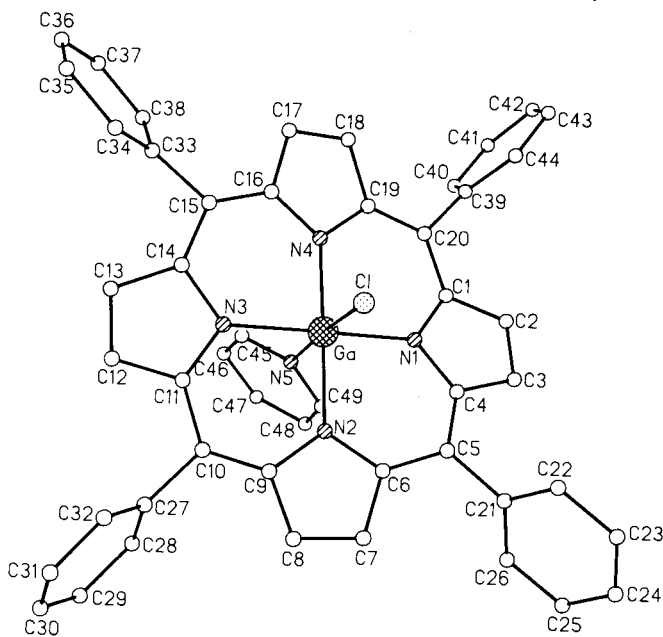

Figure 1. View of the Ga(TPP)(py)(Cl). molecule showing the atom numbering scheme.

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Table 1

Data Collection and Processing Parameters

Space group	P2₁/n, monoclinic
Cell constants	a = 13.162(2) Å
	b = 23.422(6)
	c = 14.677(2)
	β = 101.47(1)°
	V = 4434 Å³
Molecular formula	[GaC₄₉H₃₃N₅Cl]·½C₅H₅N·½C₅H₁₂
Formula weight	872.7
Formula units per cell	Z = 4
Density	φ = 1.31
Absorption coefficient	μ = 7.2 cm⁻¹
Radiation (Mo Kα)	λ = 0.71073 Å
Collection range	$4° \leq 2\sigma \leq 35°$
Scan width	$\Delta\theta = (0.90 + 0.35 \tan\theta)°$
Maximum scan time	120 s
Scan speed range	0.7 to 5.0° − min⁻¹
Total data collected	3090
Independent data, I > 3σ(I)	2249
Total variables	399
$R = \Sigma\,||F_o|\cdot|F_c||\,/|\Sigma|F_o|$	0.056
$R_w = [\Sigma w(|F_o|\cdot|F_c|)^2/\Sigma w|F_o|^2]^{½}$	0.067
Weights	$w = \sigma(F)^{-2}$

traphenylporphinatopyridinegallium(III), which is the first reported structure of a monomeric hexacoordinate gallium(III) porphyrin.

Results and Discussion.

As can be seen in Figure 1, the metalloporphyrin has six-coordinate octahedral symmetry, similar to that found in Co [11] and Mn [12] porphyrin complexes. In fact the three analogs are found to be essentially isomorphous and isostructural. To obtain the Mn fractional coordinates in the same location as in the Ga compound, it is necessary to perform a (x, ½-y, ½ + z) operation. Similarly, for the Co structure the *a* and *c* axes must be interchanged and a (z, ½-y, x) operation performed. In both cases, the symmetry operation corresponds to a simple origin shift. Once transformed, the atomic coordinates of all three structures are virtually identical, with the exception of the Cℓ location, which is affected by disparate electronic forces. Despite the isostructurality, it is interesting to note that different chemical models were refined in each of the three independent cases. Very large anisotropic displacement factors in one of the phenyl rings (C33-C38) led us to treat this as disorder and propose a model with 50% occupancy at two different orientations to the macrocycle core. In both of the other structures, the same enormous thermal ellipsoids were noted in one of the phenyl rings (attached to Cm1 in Mn, and C5D in Co), but no possibility of disorder was ever mentioned. The odds of random "true"

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Table 2

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å²)
Ga	0.1576 (1)	0.19895(6)	0.38494(9)	2.93(3)
Cl	0.0900 (3)	0.1410 (2)	0.2585 (2)	4.7(1)
N1	0.2498 (6)	0.1373 (4)	0.4502 (6)	2.4(2)
N2	0.2744 (7)	0.2252 (4)	0.3259 (6)	2.9(3)
N3	0.0711 (7)	0.2673 (4)	0.3382 (6)	4.1(3)
N4	0.0512 (7)	0.1776 (4)	0.4606 (6)	2.7(2)
N5	0.2319 (7)	0.2547 (4)	0.5069 (6)	3.4(3)
C1	0.2336 (9)	0.1034 (5)	0.5206 (8)	2.6(3)
C2	0.3204 (9)	0.0664 (5)	0.5495 (8)	3.3(3)
C3	0.3871 (9)	0.0762 (5)	0.4934 (8)	3.3(3)
C4	0.3424 (9)	0.1203 (5)	0.4319 (7)	2.9(3)
C5	0.3894 (9)	0.1413 (5)	0.3635 (8)	2.9(3)
C6	0.3578 (8)	0.1925 (5)	0.3148 (8)	3.3(3)
C7	0.4096 (9)	0.2219 (5)	0.2505 (9)	4.2(4)
C8	0.3613 (9)	0.2723 (5)	0.2287 (8)	4.0(4)
C9	0.2755 (8)	0.2743 (5)	0.2737 (8)	2.6(3)
C10	0.2026 (8)	0.3155 (5)	0.2612 (8)	3.0(3)
C11	0.1068 (9)	0.3109 (5)	0.2911 (8)	3.7(3)
C12	0.029 (1)	0.3539 (6)	0.2715 (9)	4.7(4)
C13	−0.0543 (9)	0.3361 (6)	0.307 (1)	4.9(4)
C14	−0.0305 (9)	0.2803 (5)	0.3517 (9)	4.1(3)
C15	−0.0826 (9)	0.2448 (6)	0.4054 (8)	4.4(3)
C16	−0.046 (1)	0.1983 (5)	0.4531 (8)	4.3(3)
C17	−0.1066 (9)	0.1683 (5)	0.5044 (8)	3.9(3)
C18	−0.0440 (9)	0.1291 (5)	0.5493 (8)	3.3(3)
C19	0.0557 (9)	0.1344 (5)	0.5222 (7)	2.5(3)
C20	0.1417 (9)	0.1014 (5)	0.5538 (7)	2.6(3)
C21	0.4795 (9)	0.1120 (5)	0.3359 (8)	3.2(3)*
C22	0.463 (1)	0.0618 (6)	0.2877 (9)	5.2(4)*
C23	0.548 (1)	0.0317 (6)	0.2602 (9)	5.6(4)*
C24	0.642 (1)	0.0535 (6)	0.2820 (9)	4.4(3)*
C25	0.660 (1)	0.1026 (6)	0.3289 (9)	5.1(4)*
C26	0.580 (1)	0.1331 (6)	0.3580 (9)	4.1(3)*
C27	0.226 (1)	0.3714 (5)	0.2151 (8)	3.6(3)*
C28	0.298 (1)	0.4081 (6)	0.2659 (9)	5.7(4)*
C29	0.324 (1)	0.4606 (6)	0.227 (1)	6.2(4)*
C30	0.275 (1)	0.4722 (6)	0.1383 (9)	5.1(4)*
C31	0.207 (1)	0.4369 (6)	0.0875 (9)	4.6(3)*
C32	0.180 (1)	0.3857 (6)	0.1251 (9)	4.3(3)*
C33	−0.188 (1)	0.2709 (6)	0.4078 (9)	4.6(3)*
C34	−0.273 (2)	0.271 (1)	0.306 (2)	4.7(7)*
C34'	−0.262 (2)	0.276 (1)	0.347 (2)	3.3(6)*
C35	−0.365 (2)	0.290 (1)	0.317 (2)	4.3(7)*
C35'	−0.372 (2)	0.301 (1)	0.362 (2)	5.0(7)*
C36	−0.392 (2)	0.306 (1)	0.409 (2)	3.7(6)*
C36'	−0.354 (2)	0.315 (1)	0.460 (2)	6.1(8)*
C37	−0.326 (4)	0.290 (2)	0.483 (3)	5.0(7)*
C37'	−0.293 (2)	0.313 (1)	0.515 (2)	5.3(8)*
C38	−0.218 (2)	0.281 (1)	0.479 (2)	3.9(6)*
C38'	−0.190 (2)	0.295 (1)	0.504 (2)	6.7(8)*
C39	0.132 (1)	0.0587 (5)	0.6275 (8)	3.0(3)*

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Table 2 (continued)

Atom	x		y		z		B(Å²)
C40	0.149	(1)	0.0728	(6)	0.7200	(9)	4.7(3)*
C41	0.130	(1)	0.0330	(6)	0.7855	(9)	5.2(4)*
C42	0.096	(1)	−0.0200	(6)	0.7600	(9)	4.4(3)*
C43	0.082	(1)	−0.0356	(6)	0.6721	(9)	4.6(3)*
C44	0.102	(1)	0.0032	(6)	0.6046	(8)	4.3(3)*
C45	0.176	(1)	0.2911	(6)	0.5411	(9)	4.9(3)*
C46	0.221	(1)	0.3267	(7)	0.616	(1)	7.7(5)*
C47	0.326	(1)	0.3225	(7)	0.652	(1)	7.1(4)*
C48	0.384	(1)	0.2844	(6)	0.614	(1)	6.2(4)*
C49	0.333	(1)	0.2516	(6)	0.5404	(9)	4.5(3)*
C50	0.543	(2)	0.458	(1)	0.536	(2)	5.7(8)*
C51	0.452	(2)	0.455	(1)	0.508	(2)	6.5(8)*
C52	0.603	(3)	0.503	(2)	0.531	(3)	10(1)*
C53	0.577	(3)	−0.020	(2)	0.003	(3)	11(1)*
C54	0.527	(3)	0.043	(1)	−0.005	(2)	7.8(9)*
H2	0.3291		0.0396		0.5994		
H3	0.4517		0.0572		0.4947		
H7	0.4671		0.2076		0.2272		
H8	0.3817		0.3012		0.1904		
H12	0.0324		0.3891		0.2398		
H13	−0.1177		0.3558		0.3031		
H17	−0.1773		0.1744		0.5063		
H18	−0.0611		0.1022		0.5923		
H22	0.3943		0.0465		0.2724		
H23	0.5352		−0.0032		0.2265		
H24	0.6973		0.0336		0.2638		
H25	0.7287		0.1170		0.3429		
H26	0.5942		0.1674		0.3920		
H28	0.3309		0.3981		0.3275		
H29	0.3727		0.4863		0.2610		
H30	0.2900		0.5073		0.1111		
H31	0.1761		0.4468		0.0249		
H32	0.1305		0.3608		0.0891		
H34	−0.2530		0.2582		0.2518		
H35	−0.4163		0.2910		0.2585		
H36	−0.4509		0.3245		0.4160		
H37	−0.3412		0.3017		0.5448		
H38	−0.1653		0.2812		0.5378		
H34'	−0.2557		0.2646		0.2887		
H35'	−0.4348		0.3014		0.3100		
H36'	−0.4133		0.3370		0.4855		
H37'	−0.2913		0.3223		0.5856		
H38'	−0.1214		0.2998		0.5551		
H40	0.1750		0.1097		0.7396		
H41	0.1408		0.0434		0.8492		
H42	0.0818		−0.0462		0.8054		
H43	0.0590		−0.0732		0.6538		
H44	0.0939		−0.0087		0.5415		
H45	0.1039		0.2935		0.5160		
H46	0.1793		0.3537		0.6401		
H47	0.3575		0.3460		0.7027		
H48	0.4560		0.2805		0.6377		
H49	0.3723		0.2250		0.5126		

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

thermal motion occurring at the same site in three independently studied samples is quite remote, and thus we feel the disorder is real and should be considered part of the true model. There also seems little doubt that the authors of the Co analog missed the presence of half of the disordered solvent sites. Thus, their reported density is too low, and their R value too high. In the present Ga case, the identity of the solvent molecule at the massively disordered (½, 0, 0) site was impossible to guess, since the crystal was grown from a mixture of two structurally different solvents. No such ambiguity was found in the Mn case, since both benzene and pyridine have the same geometries and approximate molecular weights.

The most important geometrical descriptions for these compounds are the metal-nearest-neighbor distances and the location of the metal atom with respect to the porphinato plane. In the present case, M-Np (average metal-porphinatonitrogen bond distance) = 2.01(3) Å, $\Delta(N_4)$ = 0.14(1) Å towards Cl, and the displacement of the metal atom with respect to the mean plane of the 24-atom core Δ(core) = 0.16(1) Å. This is much shorter than found in the parent compound Ga(TPP)(Cl): 0.317 Å [3]. In addition, the conformation of the porphyrin core can have important effects on the nearest-neighbor distances, which are described below. The bond distances and angles in the porphyrin moiety are not significantly different from previously reported values, if one ignores the large variations noted in the disordered phenyl group. The pyridine ligand

Table 3

Selected Bond Distances (Å) and Angles (°)

Ga-Cl	2.328 (1)
Ga-N1	2.003 (3)
Ga-N2	2.006 (3)
Ga-N3	2.004 (3)
Ga-N4	2.016 (3)
Ga-N5	2.274 (3)
Cl-Ga-N1	93.45 (9)
Cl-Ga-N2	92.23 (9)
Cl-Ga-N3	95.26 (9)
Cl-Ga-N4	95.57 (9)
Cl-Ga-N5	177.02 (9)
N1-Ga-N2	89.1 (2)
N1-Ga-N3	171.1 (1)
N1-Ga-N4	88.8 (2)
N1-Ga-N5	85.0 (1)
N2-Ga-N3	92.2 (2)
N2-Ga-N4	172.0 (1)
N2-Ga-N5	85.2 (1)
N3-Ga-N4	88.7 (2)
N3-Ga-N5	86.4 (1)
N4-Ga-N5	86.9 (1)
N1-Ga-N5-C49	41.8

plane almost bisects the N(1)-Ga-N(2) angle, an orientation with respect to rotation around the complexing Ga-N(5) bond which is thus quite favorable for minimizing steric interactions between the *ortho* hydrogen atoms of the pyridine and the porphinato core. The dihedral angle between the pyridine plane and the mean porphyrin plane is 89°, and the Ga-N(py) distance is 2.27 Å. This is much shorter than in the Mn complex (2.44 Å) and much longer than in the Co complex (1.98 Å).

The manganese(III) ion of Mn(TPP)(py)(Cl) is displaced by 0.15 Å from the mean porphyrin plane and is 0.12 Å out of the plane of the four nitrogens in the direction of the chloride ligand. The Mn-N(py) bond (2.44 Å) appears long while the increase in the Mn-Cl bond is only $\cong$ 0.1 Å. This lengthening of the two axial bonds has been attributed to the unpaired electron in the d_{z^2} orbital of the high-spin manganese(III) ion [13]. In contrast, the metal atom of the cobalt complex is located in the mean plane of the pyrrole nitrogen atoms and its coordination scheme is pseudo octahedral. The Co-N(py) distance of 1.98 Å is very close to that found in the symmetrical six-coordinate Co(III) porphyrin, Co(TPP)(Im)$_2$(OAc)·H$_2$O·CHCl$_3$ [14]. The porphyrin core of Co(TPP)(py)(Cl) is quite ruffled, as observed for the gallium(III) complex.

In conclusion, the coordination of a pyridine molecule to the central metal of monochloro non-transition or transition metal porphyrins induces a $\cong$ 0.1 Å lengthening of the M-Cl bond as one progresses from a five to six-coordinate metal(III) complex. The elongation of the M-N(py) bond is critically dependent on the population of the metal d orbitals for the transition metal complex M(TPP)(py)(Cl) but no crystal structures of similar non-transition metal complexes are available for comparison with the M-N(py) bond of Ga(TPP)(py)(Cl).

EXPERIMENTAL

Crystals of the title metalloporphyrin were prepared by recrystallization of the chlorogallium porphyrin complex in pyridine with slow diffusion of pentane into the solution. Large single crystals were obtained and washed with pentane. A magenta-colored fragment of a prismatic plate of dimensions 0.75 × 0.50 × 0.25 mm was mounted on a glass fiber in a random orientation on an Enraf-Nonius CAD-4 automatic diffractometer. The radiation used was Mo Kα monochromatized by a dense graphite crystal assumed for all purposes to be 50% imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be 2/m and from the systematic absences found the space group was shown unambiguously to be P2$_1$/n. Intensities were measured using the θ-2θ scan technique, with a variable scan rate depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability and electronic reliability, and these did not vary significantly over the period of four days. (However, over a period of a few weeks the crystals were visually noted to decompose.) In reducing the data, Lorentz and polarization factors were applied. Due to the small absorption coefficient, no correction for absorption was made.

The structure was solved by the Patterson method to locate the position of the gallium atom. The remaining atoms were found in subsequent difference Fourier syntheses. Heavily disordered solvent molecules of crystallization were found, and one of the four phenyl rings was found to be disordered (~ 50:50) over two positions. One of the solvent molecules, which lies about an inversion center, was found to have a 50% occupancy and could be clearly identified as a pyridine molecule. The location of the N atom could not be determined, so all three of the refined atomic positions were assigned as carbons. The other heavily disordered solvent molecule could not be clearly identified since only two refineable atoms could be located amid a large diffuse area of residual electron density. This molecule is assumed to be pentane, although pyridine cannot be ruled out. It also seems to be present in 50% occupancy, near an inversion center.

The usual sequence of isotropic and anisotropic refinement was followed, after which all tetraphenylporphyrin hydrogens were entered in ideal calculated positions. Only the tetraphenylporphyrin core atoms were refined anisotropically. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of least squares refinement, and the final difference density map showed no peaks greater than 0.30 e/Å^3. All calculations were made using Molecular Structure Corporation's TEXRAY 230 modifications of the SDP-PLUS series of programs. The final positional and thermal parameters are given in Table 2, with selected bond distances and angles listed in Table 3.

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