

# GALLIUM(III) PORPHYRINS: SYNTHESIS AND PHYSICOCHEMICAL CHARACTERISTICS OF HALOGENO GALLIUM(III) PORPHYRINS—X-RAY CRYSTAL STRUCTURE OF CHLORO-(5,10,15,20-TETRAPHENYLPORPHYRINATO) GALLIUM(III)

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**Abstract**—Chlorogallium(III) porphyrins [Ga(Por)Cl] were obtained in good yield by treating the corresponding free bases with gallium trichloride. The action of the hydrogen halides HX (X = F or I) on chloro derivatives Ga(Por)Cl led to the corresponding halogeno complexes Ga(Por)X. These derivatives were characterized on the basis of mass spectrometry, <sup>1</sup>H NMR, and UV–visible data. The crystal structure of the title compound has been determined by X-ray diffraction methods. C<sub>44</sub>N<sub>4</sub>H<sub>28</sub>GaCl [Ga(TPP)Cl], *F*<sub>w</sub> = 717.9 g, tetragonal, *I*4/*m*, *a* = 13.508(2) Å, *c* = 9.846(2) Å, *V* = 1797(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>x</sub> = 1.326, *μ* = 11.1 cm<sup>−1</sup>, *F*(000) = 736 *e*, room temperature, *R*(*F*) = 0.044, *R*<sub>w</sub>(*F*) = 0.049 for 1237 unique reflections. Ga(TPP)Cl is isomorphic to Fe(TPP)Cl: both gallium and chloride atoms are statistically averaged by the crystallographic mirror plane. The gallium–chlorine distance is 2.196(2) Å, whereas the gallium atom lies 0.317(1) Å from the perfect porphyrin plane.

Recently, Wynne<sup>1,2</sup> and Marks<sup>3–6</sup> described the synthesis and characterization of inorganic–organic polymers in which a metallic or pseudometallic element alternates in a linear chain with an atom such as oxygen or dicoordinate fluorine. The metallic or pseudometallic element is always the central atom of a phthalocyanine system and the bridge-stacked polymeric structure is rigid. These derivatives are electrical conductors after iodine oxidation.<sup>7–13</sup> In a preliminary paper,<sup>14</sup> we pointed out a series of similar systems, the large phthalocyanine ring being replaced by a porphyrin ligand. Difference Fourier analysis of EXAFS spectra of the

hydroxo and fluorogallium(III)-2,3,7,8,12,13,17,18-octamethylporphyrins [Ga(OMP)OH<sup>†</sup> and Ga(OMP)F] afforded some evidence for the polymeric structure of the latter complex.<sup>14</sup>

In this paper we report the synthesis and complete description of the Ga(Por)F complexes, and the detailed preparation of the Ga(Por)Cl precursors. The effort below focuses also on the characterization of the Ga(Por)I complexes and on the description of the crystal structure of Ga(TPP)Cl which is, as far as we know, the first X-ray study of a gallium(III) porphyrin.

## EXPERIMENTAL

### Preparation of complexes

The chloro, fluoro, and iodo complexes were synthesized following a general procedure described below.

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† Abbreviations: Por, unspecified porphyrinate(2−); OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−); TPP, 5,10,15,20-tetraphenylporphyrinate(2−); OMP, 2,3,7,8,12,13,17,18-octamethylporphyrinate(2−).

**Chloro-(porphyrinato) gallium(III).** To a solution of porphyrin (9.35 mmol) and  $\text{GaCl}_3$  (13.7 mmol) in acetic acid (400  $\text{cm}^3$ ) sodium acetate (61 mmol) was added in acetic acid (25  $\text{cm}^3$ ). The mixture was refluxed for 12 h, then the resulting solution was cooled down to  $0^\circ\text{C}$  and the precipitate obtained was recrystallized. The reaction mixture also contains small amounts of acetato-(porphyrinato) gallium(III).

**Fluoro-(porphyrinato) gallium(III).** Chloro-(porphyrinato) gallium(III) (80 mmol) was dissolved in 200  $\text{cm}^3$  of methanol. After the addition of 10  $\text{cm}^3$  of an aqueous solution of hydrofluoric acid (40%) the mixture was stirred for 16 h. The excess hydrofluoric acid was removed by vacuum distillation (at  $240^\circ\text{C}$  and  $2.5 \times 10^{-3}$  mmHg). The residual precipitate was washed with heptane and cooled methanol, and recrystallized.

**Iodo-(porphyrinato) gallium(III).** Chloro-(porphyrinato) gallium(III) (80 mmol) was dissolved in 200  $\text{cm}^3$  of toluene and a gentle stream of hydroiodic acid was bubbled through the toluene solution (4 h). After reaction, the solvent was removed under reduced pressure and the residual precipitate was dried at  $80^\circ\text{C}$  under 15 mmHg, and recrystallized.

The reaction conditions, yields and elemental analyses for all the complexes are summarized in Table 1.

#### Physical measurements

Elemental analyses were performed by the "Service de Microanalyses du C.N.R.S.". Mass spectra were obtained in the electron-impact mode with a Finnigan 3300 spectrometer; ionizing energy 30–70 eV, ionizing current 0.4 mA, source temperature 250–400°C.  $^1\text{H}$  NMR spectra were recorded on a JEOL FX 100 or Bruker WM 400 of the CEREMA ("Centre de Résonance Magnétique" of University of Dijon). Spectra were measured for complex (5 mg) solutions in 0.6  $\text{cm}^3$  of DMSO or  $\text{CDCl}_3$  with tetramethylsilane as internal reference. IR spectra were recorded on a Perkin–Elmer 580 B apparatus. Samples were prepared as 1% dispersions in CsI pellets or Nujol mulls. Electronic absorption spectra were recorded on a Perkin–Elmer spectrophotometer using  $5 \times 10^{-3}$  mol  $\text{l}^{-1}$  methanolic solutions.

#### Crystal and molecular structure determination

A suitable crystal of  $\text{Ga}(\text{TPP})\text{Cl}$  was obtained from recrystallization of the complex in a solution of toluene. Preliminary Weissenberg photographs along the  $\bar{c}$  axis revealed a four-fold symmetry and systematic extinction of the type  $h+k+l = 2n+1$ ,

Table 1. Experimental data and yields

| Complex                                               | Recrystallization solvent <sup>a</sup> | Yield (%)       | Molecular formula                                 | Analysis (%) <sup>b</sup> |            |              |                |              |
|-------------------------------------------------------|----------------------------------------|-----------------|---------------------------------------------------|---------------------------|------------|--------------|----------------|--------------|
|                                                       |                                        |                 |                                                   | C                         | H          | N            | X <sup>c</sup> | Ga           |
| <b>1<sub>1</sub></b> $\text{Ga}(\text{OMP})\text{Cl}$ | C                                      | 86              | $\text{C}_{28}\text{H}_{28}\text{N}_4\text{ClGa}$ | 63.8 (63.97)              | 5.4 (5.37) | 10.0 (10.66) | 6.5 (6.74)     | 13.2 (13.26) |
| <b>1<sub>2</sub></b> $\text{Ga}(\text{OEP})\text{Cl}$ | B                                      | 75 <sup>d</sup> | $\text{C}_{36}\text{H}_{44}\text{N}_4\text{ClGa}$ | 67.9 (67.78)              | 7.0 (6.95) | 9.0 (8.78)   | 5.5 (5.56)     | 10.8 (10.93) |
| <b>1<sub>3</sub></b> $\text{Ga}(\text{TPP})\text{Cl}$ | B                                      | 71 <sup>d</sup> | $\text{C}_{44}\text{H}_{28}\text{N}_4\text{ClGa}$ | 73.0 (73.62)              | 3.9 (3.93) | 7.5 (7.81)   | 4.8 (4.93)     | 9.3 (9.71)   |
| <b>2<sub>1</sub></b> $\text{Ga}(\text{OMP})\text{F}$  | A                                      | 67              | $\text{C}_{28}\text{H}_{28}\text{N}_4\text{FGa}$  | 65.5 (66.04)              | 5.4 (5.54) | 10.8 (11.00) | 3.7 (3.73)     | 12.8 (13.69) |
| <b>2<sub>2</sub></b> $\text{Ga}(\text{OEP})\text{F}$  | B                                      | 75              | $\text{C}_{36}\text{H}_{44}\text{N}_4\text{FGa}$  | 69.4 (69.57)              | 7.2 (7.14) | 8.9 (9.02)   | 3.0 (3.05)     | 11.0 (11.22) |
| <b>2<sub>3</sub></b> $\text{Ga}(\text{TPP})\text{F}$  | B                                      | 80              | $\text{C}_{44}\text{H}_{28}\text{N}_4\text{FGa}$  | 75.3 (75.35)              | 3.9 (4.02) | 7.6 (7.98)   | 2.8 (2.71)     | 9.6 (9.94)   |
| <b>3<sub>1</sub></b> $\text{Ga}(\text{OMP})\text{I}$  | B                                      | 57              | $\text{C}_{28}\text{H}_{38}\text{N}_4\text{IGa}$  | 55.4 (55.47)              | 4.5 (4.65) | 9.0 (9.24)   | 20.5 (19.14)   | 11.7 (11.50) |
| <b>3<sub>2</sub></b> $\text{Ga}(\text{OEP})\text{I}$  | B                                      | 72              | $\text{C}_{36}\text{H}_{44}\text{N}_4\text{IGa}$  | 59.3 (59.36)              | 6.0 (6.09) | 7.6 (7.69)   | 17.2 (17.29)   | 8.5 (9.57)   |
| <b>3<sub>3</sub></b> $\text{Ga}(\text{TPP})\text{I}$  | B                                      | 62              | $\text{C}_{44}\text{H}_{28}\text{N}_4\text{IGa}$  | 65.3 (65.38)              | 3.4 (3.49) | 6.9 (6.93)   | 15.6 (15.58)   | 7.9 (8.62)   |

<sup>a</sup> A = methanol, B = toluene, C = chloroform, D = heptane.

<sup>b</sup> Calculated values are given in parentheses.

<sup>c</sup> X = F, Cl or I.

<sup>d</sup> About 3.5% of the free base is transformed to the corresponding acetato derivative  $\text{Ga}(\text{Por})\text{AcO}$ .

Table 2. Experimental conditions

|                                                                |                                                     |
|----------------------------------------------------------------|-----------------------------------------------------|
| Formula                                                        | C <sub>44</sub> N <sub>4</sub> H <sub>28</sub> ClGa |
| Formula weight                                                 | 717.9                                               |
| Space group                                                    | Tetragonal <i>I4/m</i>                              |
| Extinctions                                                    | $h + k + l = 2n + 1$                                |
| Crystal dimensions (mm <sup>3</sup> )                          | 0.1 × 0.15 × 0.3                                    |
| Crystal habit                                                  | Tetragonal octahedron                               |
| Crystal color                                                  | Dark blue                                           |
| Lattice parameters                                             | See Abstract                                        |
| Diffractometer                                                 | Enraf-Nonius CAD4F                                  |
| Radiation                                                      | Cu-K <sub>α</sub>                                   |
| Scan                                                           | $\omega - 2\theta$                                  |
| $\theta_{\min} - \theta_{\max}$ (°)                            | 1–70                                                |
| Scan speed (° min <sup>-1</sup> )                              | 0.5 < $v$ < 3.0                                     |
| Scan range                                                     | 0.8 + 0.15 tan $\theta$                             |
| Take-off angle (°)                                             | 3                                                   |
| Aperture (mm)                                                  | 3 + 3 tan $\theta$                                  |
| $h, k, l$ limits                                               | $-16 < h < 16, 0 < k < 16, -10 < l < 0$             |
| Number of reflections measured                                 | 2223                                                |
| Number of unique reflections                                   | 1480                                                |
| Agreement factor $R_i(F)$ between symmetry-related reflections | 0.028                                               |
| Number of reflections used [ $I > 3\sigma(I)$ ] ( $N$ )        | 1237                                                |
| Number of parameters ( $N_p$ )                                 | 79                                                  |
| $N/N_p$                                                        | 15                                                  |
| Programs                                                       | SHELX 76 <sup>16</sup> and ORTEP                    |
| $R(F), R_w(F)$                                                 | 0.044, 0.049                                        |
| Goodness of fit                                                | 1.10                                                |
| $w$                                                            | $2.4/[\sigma^2(F) + 0.0006F^2]$                     |
| $\left(\frac{\Delta}{\sigma}\right)_{\max}$                    | $4 \times 10^{-2}$ for U <sub>33</sub> (Ga)         |

leading to the centrosymmetric space group *I4/m* and to the non-centrosymmetric *I4* or *I4̄* space groups. Experimental conditions and details of the calculations are given in Table 2. The crystal structure was solved by the heavy-atom method, assuming the space group *I4/m*. As observed for Fe(TPP)Cl,<sup>15</sup> the gallium and chlorine atoms are statistically disordered up and below the mirror plane *m*. The good convergence of the least-squares process confirmed the choice of the space group; furthermore refinements in the *I4* and *I4̄* space groups did not improve the convergence results. All the hydrogen atoms were found in difference Fourier maps and added as fixed contributors to the least-squares calculations. The scattering factors were taken from Refs 16 and 17; all non-hydrogen atoms were refined anisotropically. A summary of the least-squares results is given in Table 2. Fractional atomic coordinates, anisotropic thermal parameters and a

list of structure factors has been deposited as supplementary data with the Editor, from whom copies are available on request.\*

## RESULTS AND DISCUSSION

During the last decade gallium(III) porphyrin complexes possessing the axial ligands Cl<sup>-</sup>,<sup>18,19</sup> RO<sup>-</sup>,<sup>20,21</sup> and RCO<sub>2</sub><sup>-</sup><sup>22</sup> have been reported. Two general methods have been used to synthesize the gallium(III) porphyrins: the first one used Ga(Acac)<sub>2</sub> for metallation in phenol,<sup>20</sup> and the second NH<sub>4</sub>Ga(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O in acetic acid.<sup>19</sup> We have prepared the chloro-gallium(III) porphyrins (**1**) by the action of GaCl<sub>3</sub> on porphyrins in acetic acid. The complexes **1** were obtained with very satisfactory yields varying from 70 to 90%. Treatment of Ga(Por)Cl(**1**) with HF in methanol and HI in toluene led, respectively, to the fluoro-Ga(Por)F (**2**) and iodo-Ga(Por)I (**3**) derivatives. The yield of the reaction depends on the nature of the axial and equatorial ligands (57–80%).

In most of the mass spectra of complexes **1** and **2**, the molecular peak appears.† Its intensity is very

\* Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

† The relative intensity of the peaks M<sup>+</sup>, [M + 1]<sup>+</sup> and [M + 2]<sup>+</sup> is attributable to the abundance of the natural isotopes <sup>69</sup>Ga and <sup>71</sup>Ga (see Table 3).

high for the chloro and fluoro derivatives and corresponds in a few cases to the parent peak. However for Ga(OMP)F the fragment ion  $[M-F+1]^+$  is higher. The same ion  $[M-X]^+$  is the most abundant for the iodo complexes **3** while the intensity of the molecular peak is very low (0.32–2.50%) and does not appear for Ga(TPP)I. These data are in good agreement with the more labile character of the metal–iodine bond compared to the

metal–fluorine or metal–chlorine bonds. Moreover the typical morphology of the mass spectrum of Ga(OMP)F may be due to a particular coordination scheme when the gallium atom is bound to a planar macrocycle.

Ga(Por)X exhibit electronic absorption spectra belonging to “normal” class<sup>23</sup> (Table 4). They show an intense band in the 395–415-nm region and two bands between 500 and 600 nm ( $\alpha$ - and  $\beta$ -bands). One

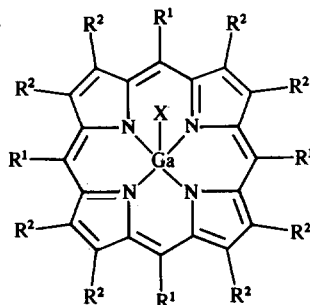
Table 3. Characteristic mass spectral and IR data

| Complex                        | Mass spectra |                    |                       | IR (cm <sup>-1</sup> )<br>$\nu(\text{Ga-X})^a$ |
|--------------------------------|--------------|--------------------|-----------------------|------------------------------------------------|
|                                | <i>m/z</i>   | Relative intensity | Fragmentation pattern |                                                |
| <b>1<sub>1</sub></b> Ga(OMP)Cl | 524          | 83.75              | $M^{+}$               | 370                                            |
|                                | 525          | 63.38              | $[M+1]^+$             |                                                |
|                                | 526          | 100.00             | $[M+2]^+$             |                                                |
|                                | 489          | 68.09              | $[M-X]^+$             |                                                |
|                                | 490          | 74.29              | $[M-X+1]^+$           |                                                |
| <b>1<sub>2</sub></b> Ga(OEP)Cl | 636          | 35.48              | $M^{+}$               | 332                                            |
|                                | 637          | 37.32              | $[M+1]^+$             |                                                |
|                                | 638          | 100.00             | $[M+2]^+$             |                                                |
|                                | 601          | 3.22               | $[M-X]^+$             |                                                |
| <b>1<sub>3</sub></b> Ga(TPP)Cl | 716          | 90.23              | $M^{+}$               | 352                                            |
|                                | 717          | 100.00             | $[M+1]^+$             |                                                |
|                                | 718          | 78.80              | $[M+2]^+$             |                                                |
|                                | 681          | 1.87               | $[M-X]^+$             |                                                |
|                                | 682          | 1.50               | $[M-X+1]^+$           |                                                |
| <b>2<sub>1</sub></b> Ga(OMP)F  | 508          | 4.28               | $M^{+}$               | 562                                            |
|                                | 509          | 67.14              | $[M+1]^+$             |                                                |
|                                | 510          | 24.28              | $[M+2]^+$             |                                                |
|                                | 489          | 71.42              | $[M-X]^+$             |                                                |
|                                | 490          | 100.00             | $[M-X+1]^+$           |                                                |
| <b>2<sub>2</sub></b> Ga(OEP)F  | 620          | 100.00             | $M^{+}$               | 550                                            |
|                                | 621          | 91.07              | $[M+1]^+$             |                                                |
|                                | 622          | 81.25              | $[M+2]^+$             |                                                |
|                                | 601          | 11.60              | $[M-X]^+$             |                                                |
|                                | 602          | 7.14               | $[M-X+1]^+$           |                                                |
| <b>2<sub>3</sub></b> Ga(TPP)F  | 700          | 10.63              | $M^{+}$               | 588                                            |
|                                | 701          | 31.91              | $[M-1]^+$             |                                                |
|                                | 702          | 100.00             | $[M+2]^+$             |                                                |
|                                | 681          | 23.40              | $[M-X]^+$             |                                                |
|                                | 682          | 29.78              | $[M-X+1]^+$           |                                                |
| <b>3<sub>1</sub></b> Ga(OMP)I  | 616          | 0.32               | $[M+1]^+$             | 210                                            |
|                                | 489          | 100.00             | $[M-X]^+$             |                                                |
|                                | 490          | 18.95              | $[M-X+1]^+$           |                                                |
| <b>3<sub>2</sub></b> Ga(OEP)I  | 728          | 2.50               | $[M+1]^+$             | 235                                            |
|                                | 601          | 100.00             | $[M-X]^+$             |                                                |
|                                | 602          | 80.00              | $[M-X+1]^+$           |                                                |
| <b>3<sub>3</sub></b> Ga(TPP)I  | 681          | 19.48              | $[M-X]^+$             | 261                                            |
|                                | 682          | 100.00             | $[M-X+1]^+$           |                                                |

<sup>a</sup> X = Cl, F or I.

Table 4. UV-visible spectroscopic data

|                |           | UV-visible [ $\lambda$ (nm)] <sup>a</sup> |                |                |                                  |                                 |
|----------------|-----------|-------------------------------------------|----------------|----------------|----------------------------------|---------------------------------|
| Compound       |           | <i>B</i> (1,0)                            | <i>B</i> (0,0) | <i>Q</i> (2,0) | <i>Q</i> (1,0)<br>(or $\alpha$ ) | <i>Q</i> (0,0)<br>(or $\beta$ ) |
| 1 <sub>1</sub> | Ga(OMP)Cl | 375 (15.9)                                | 395 (117.7)    | 489 (1.2)      | 529 (4.4)                        | 567 (5.6)                       |
| 1 <sub>2</sub> | Ga(OEP)Cl | 377 (14.6)                                | 397 (99.0)     | 489 (0.3)      | 531 (3.3)                        | 568 (4.6)                       |
| 1 <sub>3</sub> | Ga(TPP)Cl | 395 (4.5)                                 | 414 (63.3)     | 509 (0.5)      | 548 (2.3)                        | 587 (0.8)                       |
| 2 <sub>1</sub> | Ga(OMP)F  | 376 (80.1)                                | 395 (560.2)    | 488 (3.9)      | 529 (20.2)                       | 567 (27.2)                      |
| 2 <sub>2</sub> | Ga(OEP)F  | 377 (15.9)                                | 397 (139.4)    | 491 (0.7)      | 529 (4.4)                        | 567 (5.9)                       |
| 2 <sub>3</sub> | Ga(TPP)F  | 394 (10.2)                                | 414 (141.3)    | 509 (1.1)      | 548 (4.9)                        | 587 (1.7)                       |
| 3 <sub>1</sub> | Ga(OMP)I  | 375 (7.6)                                 | 395 (110.1)    | 491 (0.9)      | 530 (4.2)                        | 568 (5.4)                       |
| 3 <sub>2</sub> | Ga(OEP)I  | 377 (9.4)                                 | 397 (81.1)     | 489 (0.4)      | 529 (2.6)                        | 567 (3.4)                       |
| 3 <sub>3</sub> | Ga(TPP)I  | 395 (6.4)                                 | 414 (48.6)     |                | 548 (2.6)                        | 587 (1.1)                       |

<sup>a</sup>  $10^{-3} \epsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) given in parentheses.Table 5. <sup>1</sup>H NMR data for

| Compound                              | R <sup>1</sup>                | R <sup>2</sup>                | Protons of R <sup>1</sup>           |                      | Protons of R <sup>2</sup>  |              |
|---------------------------------------|-------------------------------|-------------------------------|-------------------------------------|----------------------|----------------------------|--------------|
|                                       |                               |                               | Multiplicity/<br>intensity          | δ                    | Multiplicity/<br>intensity | δ            |
| 1 <sub>1</sub> Ga(OMP)Cl <sup>a</sup> | H                             | CH <sub>3</sub>               | s/4                                 | 10.43                | s/24                       | 3.66         |
| 1 <sub>2</sub> Ga(OEP)Cl <sup>b</sup> | H                             | C <sub>2</sub> H <sub>5</sub> | s/4                                 | 10.34                | { t/24<br>m/16             | 1.96         |
| 1 <sub>3</sub> Ga(TPP)Cl <sup>b</sup> | C <sub>6</sub> H <sub>5</sub> | H                             | { o-H m/8<br>m,p-H m/12             | 8.20<br>7.75         | s/8                        | 9.07         |
| 2 <sub>1</sub> Ga(OMP)F <sup>a</sup>  | H                             | CH <sub>3</sub>               | s/4                                 | 10.43                | s/24                       | 3.66         |
| 2 <sub>2</sub> Ga(OEP)F <sup>b</sup>  | H                             | C <sub>2</sub> H <sub>5</sub> | s/4                                 | 10.35                | { t/24<br>m/16             | 1.96<br>4.16 |
| 2 <sub>3</sub> Ga(TPP)F <sup>b</sup>  | C <sub>6</sub> H <sub>5</sub> | H                             | { o-H m/4<br>o'-H m/4<br>m,p-H m/12 | 8.29<br>8.14<br>7.78 | s/8                        | 9.08         |
| 3 <sub>1</sub> Ga(OMP)I <sup>a</sup>  | H                             | CH <sub>3</sub>               | s/4                                 | 10.44                | s/24                       | 3.66         |
| 3 <sub>2</sub> Ga(OEP)I <sup>b</sup>  | H                             | C <sub>2</sub> H <sub>5</sub> | s/4                                 | 10.36                | { t/24<br>m/16             | 1.95<br>4.17 |
| 3 <sub>3</sub> Ga(TPP)I <sup>b</sup>  | C <sub>6</sub> H <sub>5</sub> | H                             | { o-H m/8<br>m,p-H m/12             | 8.21<br>7.75         | s/8                        | 9.07         |

Solvent: <sup>a</sup> DMSO, <sup>b</sup> CDCl<sub>3</sub>.

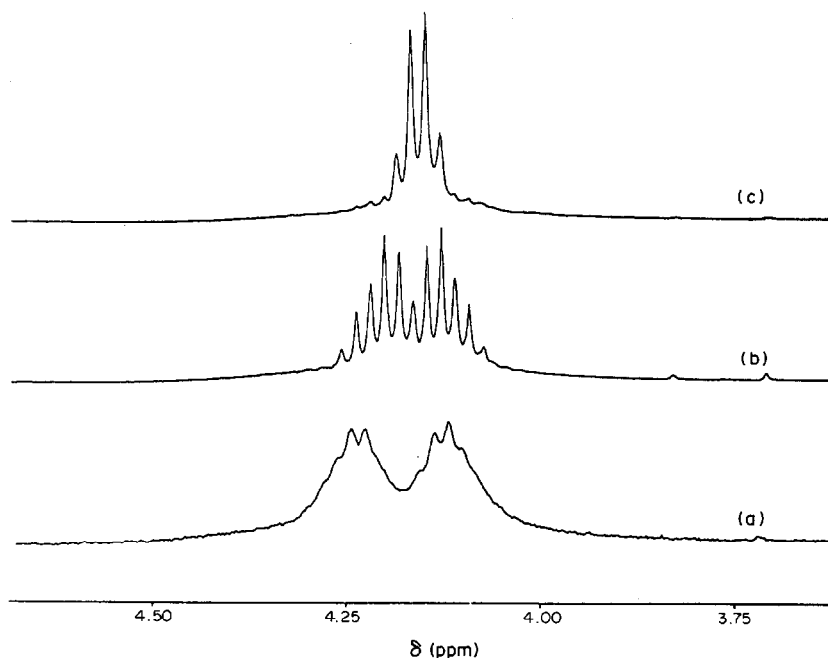


Fig. 1. Resonance signal of A and B methylenic protons of: (a) Ga(OEP)I, (b) Ga(OEP)Cl, and (c) Ga(OEP)F.

extra band [ $Q(2, 0)$ ] is observed in the visible region and another one appears blue shifted compared to the Soret band. As previously reported by Gouterman *et al.*<sup>24,25</sup> in tin octaethylporphyrin dihalides (with halide = F, Cl, Br or I), the shifts in the transition energies and relative intensities of the  $\alpha$ - and  $\beta$ -bands depend on 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 whole isolated chloro complexes show one band in the region  $330\text{--}370\text{ cm}^{-1}$ , assigned to the Ga—Cl stretching (Table 3). This characteristic band is found between  $550$  and  $590\text{ cm}^{-1}$  for the fluoro derivatives, and between  $210$  and  $261\text{ cm}^{-1}$  for the iodo compounds.

$^1\text{H}$  NMR characteristics of the Ga(Por)X complexes at ambient temperatures are listed in Table 5. The spectra of Ga(OMP)X give poor structural information since the resonance lines corresponding to the *meso* and methylic protons are two singlets which appear in the same region whatever the nature of X. The bridge-stacked polymeric structure of Ga(OMP)F being demonstrated on the basis of EXAFS spectroscopy,<sup>14</sup> the same arrangement could be postulated for Ga(OMP)Cl and Ga(OMP)I in the solid state. We have also studied NMR characteristics of the gallio-octaethylporphyrin systems. At the same concentration we observe an  $\text{ABR}_3$  multiplet for the ethyl groups of Ga(OEP)Cl and Ga(OEP)I which can be explained only by the presence of a non-octahedral monomeric structure.<sup>26,27</sup> In contrast

the resonance signal of the methylenic protons of Ga(OEP)F is a quadruplet and these protons have very similar chemical shifts (see Fig. 1). These observations may be consistent with a polymeric structure for Ga(OEP)F similar to that of Ga(OMP)F, the two other complexes 'being pentacoordinate.

At room temperature the resonances of the *ortho* phenyl protons are broad for Ga(TPP)Cl and Ga(TPP)I, and split in a doublet for Ga(TPP)F. This reflects the well-known phenomenon of the restricted rotation of phenyl rings.<sup>18,19,28–31</sup> If the effect of axial ligands on the rate of phenyl ring rotation is not very well established, it is clear that the

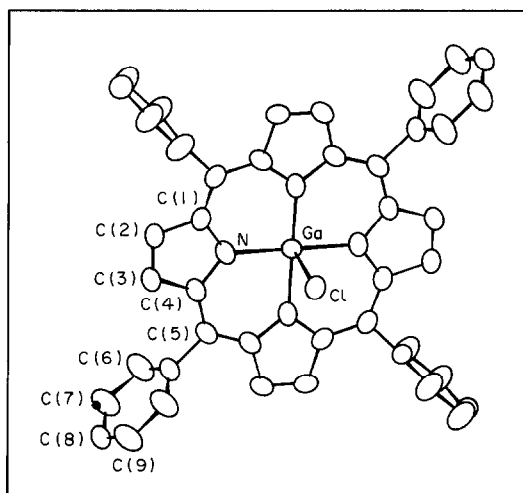


Fig. 2. ORTEP view of Ga(TPP)Cl.

Table 6. Bond distances (Å) and angles (°)

|                            |           |                           |          |
|----------------------------|-----------|---------------------------|----------|
| Ga—N(1)                    | 2.021(2)  | Ga—Cl                     | 2.196(2) |
| N(1)—C(1)                  | 1.385(4)  | N(1)—C(4)                 | 1.381(4) |
| C(1)—C(2)                  | 1.434(4)  | C(3)—C(4)                 | 1.432(5) |
| C(4)—C(5)                  | 1.390(4)  | C(1)—C(5)                 | 1.390(5) |
| C(2)—C(3)                  | 1.340(5)  | C(5)—C(6)                 | 1.498(4) |
| C(6)—C(7)                  | 1.364(3)  | C(7)—C(8)                 | 1.398(5) |
| C(8)—C(9)                  | 1.358(4)  | Cl(1)—N(1)                | 3.210(2) |
| N(1)—Ga—Cl(1)              | 99.06(3)  | N(1)—Ga—N(1) <sup>i</sup> | 88.58(9) |
| N(1)—Ga—N(1) <sup>ii</sup> | 161.89(5) | C(1)—N(1)—C(4)            | 105.5(3) |
| C(1)—C(2)—C(3)             | 107.3(3)  | C(2)—C(1)—N(1)            | 109.8(3) |
| C(2)—C(3)—C(4)             | 107.7(3)  | C(3)—C(4)—C(5)            | 124.3(3) |
| N(1)—C(4)—C(5)             | 125.9(3)  | N(1)—C(1)—C(5)            | 125.9(3) |
| C(5)—C(6)—C(7)             | 120.5(2)  | C(3)—C(4)—N(1)            | 109.8(3) |
| C(7)—C(8)—C(9)             | 119.9(2)  | C(6)—C(7)—C(8)            | 120.5(2) |

chemical-shift difference is higher when the axial ligand is the more electronegative halide ( $X = F$ ). It thus appears that the coordination polyhedron of the metal does not possess planar symmetry with respect to the porphyrinic plane and the metal should be out of this plane. The above assumptions are confirmed by the X-ray crystal structure of Ga(TPP)Cl.

Figure 2 is an ORTEP view of the molecule and Table 6 gives the bond lengths and angles. The crystal structure is isomorphic to that of Fe(TPP)Cl<sup>15</sup> and Ti(TPP)Br<sub>2</sub>.<sup>32</sup> The statistically averaged molecule of  $I4/m$  symmetry is centered at the origin and at every other lattice point of the unit cell. Hence the coordination polyhedron of the metallic atom is a square pyramid [Ga—N = 2.021(1) Å, Ga—Cl = 2.196(2) Å]. Eaton *et al.*<sup>19</sup> postulated an in-plane position of the gallium atom and a highly distorted macrocycle for the chloro substituted tetraphenylporphyrinate gallium(III). In contrast for Ga(TPP)Cl the metal atom lies 0.317(1) Å from the crystallographically required perfect porphyrin plane. The bond distances and angles in the porphyrinic group are statistically equal to those usually found.

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