

# Electrocrystallization and X-ray Structure of Partially Oxidized Stacked Porphyrin Trimers of the Form [(OEP)Ga]<sub>3</sub>F<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>

R. Guillard,<sup>\*,†</sup> J.-M. Barbe,<sup>†,‡</sup> P. Richard,<sup>†,||</sup> P. Petit,<sup>§</sup> J. J. André,<sup>§</sup> C. Lecomte,<sup>||</sup> and K. M. Kadish<sup>\*,†</sup>

Contribution from the Laboratoire de Synthèse et d'Electrosynthèse Organométallique, Associé au CNRS (UA 33), Faculté des Sciences "Gabriel", 6, Bd Gabriel, 21100 Dijon, France, Department of Chemistry, University of Houston, Houston, Texas 77204-5641, Centre de Recherche sur les Macromolécules, Institut C. Sadron, 6, rue Boussingault, 67083 Strasbourg, Cedex, France, and Laboratoire de Minéralogie et Cristallographie (UA 809), Faculté des Sciences, Centre de 2ème Cycle, Boîte Postale No. 239, 54506 Vandoeuvre les Nancy, Cedex, France. Received April 4, 1988

**Abstract:** The synthesis, structural characterization, and electrical conductivity of a fluorogallium porphyrin trimer, [(OEP)Ga]<sub>3</sub>F<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>, are described. Single crystals of this compound suitable for X-ray analysis were obtained by a slow galvanostatic electrolysis of (OEP)GaF in toluene/acetonitrile. The monoclinic cell of this compound, space group *P*2<sub>1</sub>/*c* with *Z* = 2, has parameters *a* = 14.968 (3) Å, *b* = 24.80 (1) Å, *c* = 15.268 (6) Å, β = 78.82 (3)°, and *V* = 5518 Å<sup>3</sup>. The structure was refined by a full-matrix least-squares technique leading to final residuals of *R*<sub>w</sub> = 0.064 and *R* = 0.060 for the 431 variables and the 3508 unique reflections for which *I* ≥ 3σ(*I*). The structure is described as segregated linear stacks of trimers separated by one toluene of solvation along [1, 0, 0]. ESR data indicate one ligand-centered oxidation site per trimer. Direct current conductivity measurements give small values of σ between 10<sup>-7</sup> and 10<sup>-8</sup> Ω<sup>-1</sup> cm<sup>-1</sup>, but these values increase at high ac frequency (σ = 1.24–1.5 Ω<sup>-1</sup> cm<sup>-1</sup> at 10 GHz).

Polymeric phthalocyanines and hemiporphyrazines, which are bridged by fluorine,<sup>1,2</sup> oxygen,<sup>3,4</sup> or sulfur<sup>5</sup> atoms can be converted to stable conducting polymeric materials after partial oxidation by iodine<sup>6-8</sup> or nitrosonium salts.<sup>9,10</sup> In virtually all cases, the partial oxidation is done by chemical methods. However, an electrochemical generation of conducting polymers is also possible, and single crystals have been obtained by electrooxidation of (Pc)ZnCl<sup>11</sup> and (Pc)Ni(BF<sub>4</sub>)<sub>0.33</sub><sup>12</sup> (where Pc is the dianion of phthalocyanine).

Polymeric fluorogallium porphyrins can also be synthesized in the solid state,<sup>13</sup> but attempts to prepare suitable single crystals for X-ray studies and conductivity measurements by chemical doping (I<sub>2</sub>, NOBF<sub>4</sub>, NOPF<sub>6</sub>) were unsuccessful. For this reason, the partial electrochemical oxidation of a fluorogallium porphyrin was attempted in order to obtain the corresponding doped polymer.

The formation of a conducting macrocycle polymer is related to the electrochemical properties of the monomeric macrocycle, and in this regard the electrochemistry of σ-bonded<sup>14</sup> and ionic<sup>15</sup> monomeric gallium(III) porphyrins has been investigated. Monomeric gallium(III) porphyrins of the type (OEP)GaX (where OEP is the dianion of octaethylporphyrin and X<sup>-</sup> is an anion) are oxidized via two consecutive one-electron-transfer processes, which occur at *E*<sub>1/2</sub> = 1.00 and 1.45 V vs SCE in dichloromethane, containing 0.1 M tetrabutylammonium perchlorate.<sup>15</sup> These oxidations have been characterized by UV-visible and ESR spectroscopy and involve a successive abstraction of two electrons from the porphyrin π-ring system. The oxidations are reversible in both dichloromethane and benzonitrile. On the basis of these results, a partial electrochemical oxidation of (OEP)GaF was carried out and a single-crystal X-ray analysis of the electrocrystallized compound demonstrated the formation of a trimeric porphyrin rather than a polymer.

## Experimental Section

**Electrochemical Synthesis of [(OEP)Ga]<sub>3</sub>F<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>.** (OEP)GaF was synthesized using literature methods.<sup>16</sup> Crystals of [(OEP)Ga]<sub>3</sub>F<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub> were obtained by galvanostatic electrolysis of (OEP)GaF in a 10:1 toluene/acetonitrile mixture containing 0.1 M (n-

**Table I.** Summary of Crystallographic Data for [(OEP)Ga]<sub>3</sub>F<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>

mol formula	C <sub>115</sub> H <sub>140</sub> N <sub>12</sub> Ga <sub>3</sub> B <sub>2</sub> F <sub>10</sub>
formula wt, g	2024.44
cryst syst	monoclinic
space gp	<i>P</i> 2 <sub>1</sub> / <i>c</i>
cell dimens	
<i>a</i> , Å	14.968 (3)
<i>b</i> , Å	24.80 (1)
<i>c</i> , Å	15.268 (6)
β, deg	78.82 (3)
<i>V</i> , Å <sup>3</sup>	5518
<i>Z</i>	2
temp of collcn, °C	20
<i>d</i> <sub>calc</sub> , g·cm <sup>-3</sup>	1.270
cryst dimens, mm	0.20 × 0.25 × 0.18
<i>F</i> (000)	2214
radiatn, Å	λ(Mo Kα) = 0.71073
data collcn method	ω scan
scan speed, deg·min <sup>-1</sup>	0.78–1.65
scan width, deg	Δω = 1.0 + 0.347 tan θ
reflectns measd	± <i>h</i> , ± <i>k</i> , ± <i>l</i>
θ range, deg	2.0–23.0
abs coeff (μ), cm <sup>-1</sup>	7.9
no. of reflectns measd	8650
cutoff for obsd data	<i>I</i> ≥ 3σ( <i>I</i> )
obsd data (No)	3508
no. of param (Np)	431
No <sub>o</sub> /Np	8.14
<i>R</i> = Σ(  <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>  ) / Σ  <i>F</i> <sub>o</sub>	0.060
<i>R</i> <sub>w</sub> = Σ(  <i>F</i> <sub>o</sub> - <i>F</i> <sub>c</sub>  )w <sup>1/2</sup> / (Σ  <i>F</i> <sub>o</sub>  w <sup>1/2</sup> )	0.064
weighting factor, w	0.0604 / (σ <sup>2</sup> ( <i>F</i> <sub>o</sub> ) + 0.001055( <i>F</i> <sub>o</sub> ) <sup>2</sup> )
GOF	1.70
programs used	SDP and SHELX-76

Bu<sub>4</sub>N)BF<sub>4</sub>. The design of the electrochemical cell is shown in Figure 1. The current was held at 10 μA (current density ≈ 6 × 10<sup>-6</sup> A cm<sup>-2</sup>) for

- (1) Nohr, R. S.; Wynne, K. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1210.
- (2) Wynne, K. J. *Inorg. Chem.* **1985**, *24*, 1339.
- (3) Dirk, C. W.; Inabe, T.; Schoch, K. F., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539 and references therein.
- (4) Hiller, W.; Strähle, J.; Datz, A.; Hanack, M.; Hatfield, W. E.; ter Haar, L. W.; Gütllich, P. *J. Am. Chem. Soc.* **1984**, *106*, 329.

<sup>†</sup> University of Burgundy.

<sup>‡</sup> University of Houston.

<sup>§</sup> Institut C. Sadron.

<sup>||</sup> University of Nancy I.

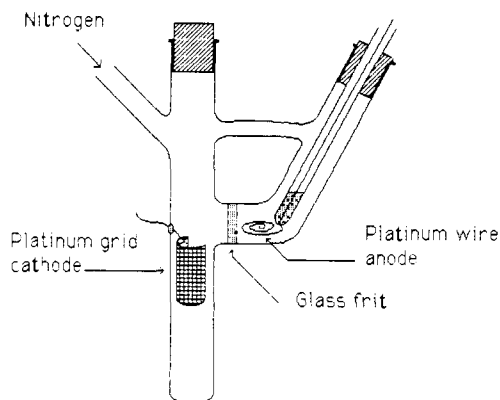


Figure 1. Design of the electrochemical cell.

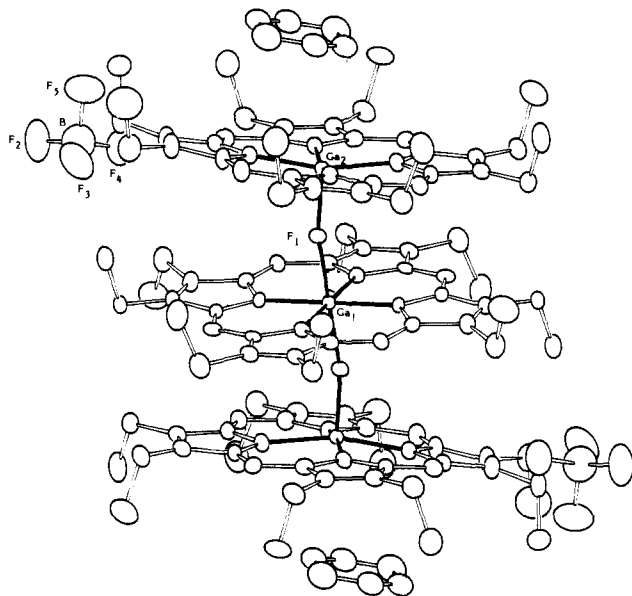


Figure 2. ORTEP drawing of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$ . (Only the phenyl ring of the disordered toluene molecule is shown.)

150 h, and the cell was thermostated at 20 °C. The galvanostatic electrolysis was carried out on a Princeton Applied Research, EG & G, Model 173 potentiostat.

**IR Spectroscopy.** The IR spectrum was recorded on a Perkin-Elmer 580 B spectrometer. The sample was prepared as 1% dispersion of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$  in CsI.

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(16) Coutsolelos, A.; Guillard, R.; Bayeul, D.; Lecomte, C. *Polyhedron* **1986**, *5*, 1157.

(17) Elemental anal. Found (calcd for  $\text{C}_{115}\text{H}_{140}\text{N}_{12}\text{Ga}_3\text{B}_2\text{F}_{10}$ ): C, 64.5 (65.42); H, 6.6 (6.68); N, 7.6 (7.96); Ga, 9.9 (9.91); B, 1.0 (1.02); F, 7.7 (9.00).

Table II. Bond Distances in Angstroms

bond	distance	bond	distance
Ga1-F1	1.952 (4)	C20-C19	1.41 (2)
Ga1-N5	2.017 (6)	C19-C18	1.43 (1)
Ga1-N6	2.003 (6)	C18-C17	1.32 (1)
Ga2-F1	1.870 (4)	C18-C39	1.54 (2)
Ga2-N1	2.006 (8)	C17-C16	1.45 (2)
Ga2-N2	1.997 (7)	C17-C37	1.52 (2)
Ga2-N3	2.023 (7)	C16-C15	1.40 (1)
Ga2-N4	2.019 (8)	C15-C14	1.36 (1)
N1-C1	1.39 (1)	C14-C13	1.45 (1)
N1-C4	1.39 (1)	C13-C12	1.36 (1)
N2-C19	1.38 (1)	C13-C35	1.53 (2)
N2-C16	1.40 (1)	C12-C11	1.43 (1)
N3-C14	1.41 (1)	C12-C33	1.52 (2)
N3-C11	1.40 (1)	C11-C10	1.37 (1)
N4-C9	1.41 (1)	C10-C9	1.39 (1)
N4-C6	1.38 (1)	C9-C8	1.44 (1)
N5-C101	1.40 (1)	C8-C7	1.34 (1)
N5-C104	1.38 (2)	C8-C31	1.53 (2)
N6-C106	1.37 (2)	C7-C6	1.43 (1)
C101-C102	1.47 (1)	C7-C29	1.52 (2)
C101-C120	1.38 (1)	C6-C5	1.41 (1)
C102-C103	1.32 (1)	C5-C4	1.41 (2)
C102-C125	1.54 (2)	C4-C3	1.41 (2)
C103-C104	1.45 (1)	C3-C2	1.33 (2)
C103-C127	1.51 (2)	C3-C27	1.53 (3)
C104-C105	1.37 (1)	C2-C25	1.57 (1)
C105-C106	1.40 (1)	C39-C40	1.53 (2)
C106-C107	1.47 (1)	C37-C38	1.59 (2)
C107-C108	1.33 (1)	C35-C36	1.57 (2)
C107-C129	1.54 (2)	C33-C34	1.57 (2)
C108-C131	1.50 (3)	C31-C32	1.55 (2)
C119-C120	1.37 (1)	C29-C30	1.52 (2)
C125-C126	1.52 (2)	C27-C28	1.53 (3)
C127-C128	1.57 (3)	C25-C26	1.40 (3)
C129-C130	1.57 (2)	B-F2	1.28 (3)
C131-C132	1.54 (3)	B-F3	1.34 (3)
C1-C20	1.41 (1)	B-F4	1.25 (3)
C1-C2	1.45 (1)	B-F5	1.52 (2)

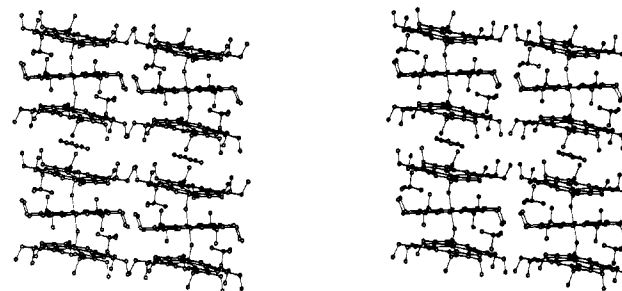


Figure 3. Stereoview of the trimers in the  $a, c$  plane.

**X-ray Crystal Structure of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$ .** Crystals of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$  were obtained as described above, and X-ray data were collected on an Enraf Nonius CAD 4 diffractometer. The crystallographic data are summarized in Table I. The intensities were corrected for Lorentz, polarization, and decay effects but not for absorption. Of 8650 unique reflections collected with  $\theta < 23^\circ$ , 3508 with  $I \geq 3\sigma(I)$  were used in the structure determination and final refinement.

The structure was solved by interpretation of the Patterson map and was refined via standard least-squares and Fourier techniques using SDP<sup>18</sup> and SHELX-76<sup>19</sup> programs. During refinement, a large region of electron density near  $(\frac{1}{2}, 0, 0)$  was interpreted as a disordered toluene of solvation. This was modeled by taking into account two molecular positions with different occupancy. The multiplicity of the carbon atoms of the first toluene molecule converged to  $m_1 = 0.663$  (CO1, CO2, CO3, CO1\*, CO2\*, CO3\*).<sup>20</sup> The multiplicity of the second molecule (CO4, CO5, CO6, CO4\*, CO5\*, CO6\*) was constrained to  $m_2 = 1 - m_1$ . Furthermore, electronic residual densities for all positions around phenyl rings

(18) SDP: Structure Determination Package; Enraf Nonius: Delft, The Netherlands, 1985.

(19) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

(20) Asterisks indicate atoms that are symmetrically related.

showed a disorder for the methyl position, and this latter group was not included in the least-squares calculations. All atoms, except those of the toluene solvate, were refined using full-matrix least-squares methods with anisotropic thermal parameters.

**ESR Experiments.** The ESR experiments were made on a Bruker ESP 300 X-band spectrometer provided with a TE 104 cavity, an NMR gaussmeter, and a frequency meter. The spectra were recorded at low enough power to prevent saturation effects (5 mW) and with a sufficiently low modulation amplitude (100 kHz) to prevent line distortion.

**Conductivity Measurements.** Direct current conductivity measurements were made on  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2\cdot\text{C}_7\text{H}_8$  along both axes of the (0, 1, 0) plane. Contacts were made with silver paint and 10- $\mu\text{m}$  diameter gold thread. Microwave conductivity measurements were performed with a laboratory-built apparatus based on the principle of the perturbation of resonant cavities.<sup>21,22</sup>

## Results

Analytical results on the electrocrystallized compound agree with the molecular formula  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2\cdot\text{C}_7\text{H}_8$ .<sup>17</sup> A B-F stretch for the two associated  $\text{BF}_4^-$  counterions is detected at 1059  $\text{cm}^{-1}$  in the infrared spectrum.

**X-ray Crystal Structure.** Single crystals suitable for a crystallographic study were grown on the anode of the electrochemical cell shown in Figure 1. Refinement, which appears in the Experimental Section, yielded the structure shown on Figure 2. Bond distances and bond angles are given in Tables II and III. Thermal parameters, least-square planes, positional parameters, structure factors, and numbering scheme are reported in the supplementary material.

As shown in Figure 3, the structure of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2\cdot\text{C}_7\text{H}_8$  can be described as segregated stacks of trimers along [1, 0, 0] separated by one toluene solvate. The  $\text{BF}_4^-$  counterions are located close to the porphyrin rings in the interstack separation. The central gallium atom Ga1 and the disordered toluene molecule are located on the (0, 0, 0) and  $(\frac{1}{2}, 0, 0)$  inversion centers, respectively.

The two symmetrically related terminal macrocycles of the trimer are tilted by 12.2° with respect to the central macrocycle with an inter-ring rotation  $\theta = 27^\circ$ . This result seems to be due to steric interactions between the macrocycle rings. As a consequence, the observed Ga-F-Ga angle is not 180° but bent to 162.7°. The spacing of macrocycles in the molecule (Ga1 to N1, N2, N3, and N4 center distance) averages 4.0 Å, but the tilt of the rings results in somewhat shorter inter-ring separations. The shorter one is 3.61 (1) Å between the two pyrrolic carbon atoms, C119...C9.

The central gallium atom Ga1 is octahedrally coordinated by four nitrogen atoms (N5, N6, N5\*, and N6\*)<sup>20</sup> and two fluorine atoms (F1 and F1\*) and is strictly located in the mean nitrogen plane (inversion center). The terminal gallium atoms Ga2 and Ga2\* are pentacoordinated by N1, N2, N3, N4, and F1 and are shifted out of the mean nitrogen plane by 0.251 (1) Å toward the central macrocycle. Two different Ga-F bond lengths are observed as expected for such coordination geometries. The larger value is 1.952 (4) Å for the central Ga atom and the shorter is 1.870 (4) Å for the two terminal Ga atoms. The larger value indicates a strong ionic character of the bond and is in agreement with the distance calculated using ionic radii (1.95 Å). These values compare to those previously reported in the literature. For example, the hexacoordinated gallium atom exhibits a 1.936 (1) Å Ga-F bond length in  $[(\text{Pc})\text{GaF}]_n$ <sup>1,2</sup> while  $[(\text{OMP})\text{GaF}]_n$ <sup>13</sup> (where OMP is the dianion of octamethylporphyrin) has a Ga-F distance of 1.93 (3) Å as measured by EXAFS. The shorter Ga2-F1 bond length in  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2\cdot\text{C}_7\text{H}_8$  is closer to the single terminal Ga-F bond lengths in  $\text{LiMnGaF}_6$  (1.883–1.905 Å)<sup>23</sup> and  $\text{GaF}_3$  (1.89 Å).<sup>24</sup>

A disordered toluene solvate (see the Experimental Section for a detailed description of refinement) is located between each trimer (see Figure 3) near the inversion center  $(\frac{1}{2}, 0, 0)$ . The distance

Table III. Bond Angles in Degrees<sup>a</sup>

bond	angle	bond	angle
F1-Ga1-N5	92.8 (2)	C16-C17-C37	125 (1)
F1-Ga1-N6	91.8 (2)	N2-C16-C17	111.4 (9)
N5-Ga1-N6	89.3 (3)	N2-C16-C15	123.8 (9)
F1-Ga2-N1	98.4 (2)	C17-C16-C15	124.8 (9)
F1-Ga2-N2	94.9 (2)	C16-C15-C14	125.6 (9)
F1-Ga2-N3	97.5 (3)	N3-C14-C15	125.8 (8)
F1-Ga2-N4	98.0 (2)	N3-C14-C13	107.7 (9)
N1-Ga2-N2	89.0 (3)	C15-C14-C13	126.6 (9)
N1-Ga2-N3	164.2 (3)	C14-C13-C12	108.5 (9)
N1-Ga2-N4	88.8 (3)	C14-C13-C35	122 (1)
N2-Ga2-N3	89.2 (3)	C12-C13-C35	129 (1)
N2-Ga2-N4	167.1 (3)	C13-C12-C11	107.7 (8)
N3-Ga2-N4	89.6 (3)	C13-C12-C33	127 (1)
C1-N1-C4	104.7 (8)	C11-C12-C33	125.1 (9)
C19-N2-C16	102.6 (7)	N3-C11-C12	109.5 (8)
C14-N3-C11	106.7 (7)	N3-C11-C10	126 (1)
C9-N4-C6	105.0 (8)	C12-C11-C10	124.3 (9)
C101-N5-C104	105.9 (7)	C11-C10-C9	123.6 (9)
N5-C101-C102	107.6 (7)	N4-C9-C10	126.9 (9)
N5-C101-C120	125.0 (8)	N4-C9-C8	108.2 (8)
C102-C101-C120	127.5 (9)	C10-C9-C8	124.8 (8)
C101-C102-C103	108.7 (8)	C9-C8-C7	108.8 (8)
C101-C102-C125	120.7 (8)	C9-C8-C31	123 (1)
C103-C102-C125	130.5 (9)	C7-C8-C31	127.9 (9)
C102-C103-C104	107.5 (8)	C8-C7-C6	106.4 (8)
C102-C103-C127	128.3 (9)	C8-C7-C29	128.1 (9)
C104-C103-C127	124.2 (9)	C6-C7-C29	125.5 (9)
N5-C104-C103	110.3 (8)	N4-C6-C7	111.6 (8)
N5-C104-C105	125.7 (8)	N4-C6-C5	123.3 (9)
C103-C104-C105	124.0 (8)	C7-C6-C5	125.0 (9)
C104-C105-C106	124.3 (8)	C6-C5-C4	124.5 (9)
N6-C106-C105	125.6 (7)	N1-C4-C5	126 (1)
N6-C106-C107	109.5 (7)	N1-C4-C3	111 (2)
C105-C106-C107	125.0 (8)	C5-C4-C3	124 (2)
C106-C107-C108	107.2 (8)	C4-C3-C2	108 (1)
C106-C107-C129	123.8 (9)	C4-C3-C27	126 (1)
C108-C107-C129	129 (1)	C2-C3-C27	127 (1)
C107-C108-C131	128 (1)	C1-C2-C3	107 (1)
C101-C120-C119	125.4 (9)	C1-C2-C25	122.5 (9)
C102-C125-C126	114 (2)	C3-C2-C25	130 (2)
C103-C127-C128	111 (1)	C18-C39-C40	108 (2)
C107-C129-C130	108 (1)	C17-C37-C38	107 (2)
C108-C131-C132	113 (2)	C13-C35-C36	111 (2)
N1-C1-C20	125 (1)	C12-C33-C34	111.4 (9)
N1-C1-C2	109.5 (8)	C8-C31-C32	113 (2)
C20-C1-C2	125.0 (9)	C7-C29-C30	113.4 (9)
C1-C20-C19	124 (1)	C3-C27-C28	113 (1)
N2-C19-C20	124.0 (9)	C2-C25-C26	110 (2)
N2-C19-C18	111.9 (8)	F2-B-F3	117 (2)
C20-C19-C18	124.1 (9)	F2-B-F4	121 (3)
C19-C18-C17	108.1 (9)	F2-B-F5	99 (2)
C19-C18-C39	123.8 (9)	F3-B-F4	117 (2)
C17-C18-C39	128 (2)	F3-B-F5	99 (2)
C18-C17-C16	106.0 (9)	F4-B-F5	96 (2)
C18-C17-C37	129 (2)	CO2-CO1-CO3	126.4 (9)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

(3.49 Å) between geometrical centers of the four nitrogen atoms and the toluene molecule is larger than the sum of the corresponding van der Waals radii. Nevertheless, the shorter interaction distance between a nitrogen atom and a carbon atom of the toluene ring is 3.29 (4) Å (N2...CO6\*).

The two  $\text{BF}_4^-$  counterions are related by the (0, 0, 0) inversion center and are located near the terminal macrocycles (see Figure 3). The shorter interaction distance between the  $\text{BF}_4^-$  anion and an ethyl group of the macrocycle is 3.17 Å (F4...C27). It is noteworthy that the B-F5 bond length of 1.52 (3) Å is consistent with a strong ionic character and is significantly larger than the B-F2, -F3, and -F4 bonds, which exhibit an average bond length of 1.29 (5) Å. Furthermore, the bond angles between the boron atom and F2, F3, or F4 average 118 (2)° while the bond angles between F5, B, and either F2, F3, or F4 average only 98 (2)° (see Table III). As a consequence, the boron atom lies only 0.177 (3) Å from the plane defined by F2, F3, and F4. These results suggest

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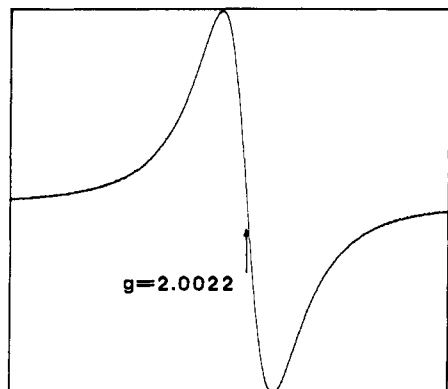


Figure 4. Solid-state ESR spectrum of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$ .

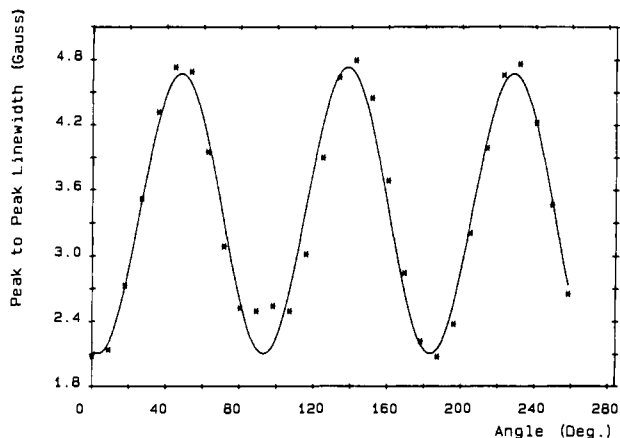


Figure 5. Peak to peak linewidth (G) versus orientation of the crystal in the magnetic field (deg).

that this ion does not exhibit a pure tetrahedral geometry and is better described by a  $(\text{BF}_3)\text{F}^-$  formulation.

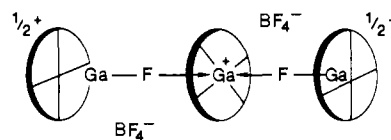
**Electron Spin Resonance.** The electrocrystallized compound is paramagnetic and the ESR spectrum in the solid state is characteristic of electrons localized on the porphyrin ring ( $g = 2.0022$ ) (see Figure 4). The peak to peak linewidth of a single crystal is strongly anisotropic and depends on the orientation of the crystal in the applied magnetic field. This anisotropy exhibits two minima at the magic angles, characteristic of a low-dimensional spin diffusion in a localized spin system<sup>25</sup> (Figure 5).

**Conductivity Measurements.** The direct current conductivity experiments indicate a small anisotropy in the  $(0, 1, 0)$  plane ( $\sigma_1 = 10^{-8} \Omega^{-1} \text{cm}^{-1}$ ;  $\sigma_2 = 10^{-7} \Omega^{-1} \text{cm}^{-1}$ ). A strong increase of conductivity is observed at high frequency ( $\sigma_1 = 1.24 \Omega^{-1} \text{cm}^{-1}$ ;  $\sigma_2 = 1.5 \Omega^{-1} \text{cm}^{-1}$  at 10 GHz), suggesting the presence of some impurities. This is also suggested by a nonlinearity in the resistivity as a function of the electric field, thus indicating a small concentration of intrinsic charge carriers.

### Discussion and Conclusion

The trimer unit bears two centrosymmetrical positive charges as demonstrated by the presence of two symmetrically related  $\text{BF}_4^-$  counterions. One charge on  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$  is due

### Scheme I



to the electro doping, and the ESR spectrum in Figure 4 clearly indicates a  $\pi$  cation radical with a  $g = 2.0022$ . The other charge on the trimer is due to the replacement of a  $\text{F}^-$  ion of  $(\text{OEP})\text{GaF}$  by  $\text{BF}_4^-$  during electrocrystallization of the trimer. Hence, the proposed charge distribution of the trimer is shown in Scheme I, where each Ga atom is in a +III oxidation state.

On the basis of the ESR and structural results, it appears that a partial oxidation of the initial monomeric  $(\text{OEP})\text{GaF}$  compound has been successful. One electron has been extracted from three porphyrin macrocycles, and the same ratio is observed for doped metallomacrocylic phthalocyanine polymers such as  $[(\text{Pc})\text{Ni}(\text{I}_3)_{0.33}]_n$ .<sup>26</sup>

The steric hindrance of the ethyl groups in the terminal OEP macrocycles leads to the loss of a fluorine atom and thus prohibits the formation of a polymeric structure as is observed with other porphyrin compounds having "flatter" macrocycles such as  $[(\text{OMP})\text{GaF}]_n$ <sup>13</sup> and  $[(\text{Pc})\text{GaF}]_n$ .<sup>1,2</sup> In addition, the dc conductivity of  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$  is very low, and on the basis of the X-ray data, it appears that the  $\pi$ -orbital overlap between the two porphyrin rings of the same trimer as well as between the toluene molecule and the terminal macrocycles of two trimers is weak. This is due to the large inter-ring separation and the staggered ring conformation of the trimer (ca.  $27^\circ$ ), which leads to a decreased conduction bandwidth. However, it is worthy to note that  $[(\text{Pc})\text{GaF}(\text{I}_{0.93})]_n$  has a large inter-ring spacing ( $3.871 \text{ \AA}$ ), but the conductivity of this polymer is still relatively large because the staggering angle is equal to  $0^\circ$ .<sup>27</sup>

Finally, we believe that it is possible to modulate the orbital overlap by changing parameters such as the inserted molecule between the two trimers (in this case toluene) or the counterion ( $\text{BF}_4^-$ ). It may also be necessary to change the type of coordination scheme and/or the macrocycle since OEP complexes with hexacoordinated metals will not easily form conducting polymers because of steric hindrance. For example, a good stacking of  $(\text{OEP})\text{Ni}$  triclinic phase<sup>28</sup> has been observed. This compound is tetracoordinated and exhibits an interplanar distance of  $3.44 \text{ \AA}$ .

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**Registry No.**  $[(\text{OEP})\text{Ga}]_3\text{F}_2(\text{BF}_4)_2 \cdot \text{C}_7\text{H}_8$ , 120771-50-8;  $(\text{OEP})\text{GaF}$ , 104453-21-6;  $(n\text{-Bu}_4\text{N})\text{BF}_4$ , 429-42-5.

**Supplementary Material Available:** Figures indicating numbering schemes and tables of anisotropic thermal parameters, least-squares planes, and fractional coordinates and equivalent temperature factors (11 pages); listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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