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Spectroscopic Characterization of Iodine Doped Fluorogallium(III) Porphyrins. Determination of the Nature of the Counterion by Raman and ^{129}I Mössbauer Spectroscopies

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Abstract

The characterization of iodine counterions in doped fluorogallium(III) porphyrins is reported and the synthesis of a $^{129}I_2$ doped complex is described. The presence of I_3^- and I_5^- anions was enhanced on the basis of Raman spectroscopy data. The analysis of ^{129}I Mössbauer spectra allowed determination of the presence of I^- and the relative amounts of I^-, I_3^-, I_5^- species. Additional results obtained by ESR spectroscopy showed the localization of the positive charge on the porphyrin π-ring system. Furthermore, the X-ray diffraction measurements enhanced two different lattices corresponding to the porphyrin and iodine chains respectively.

Introduction

Considerable work has been devoted to the synthesis of highly conducting polymers using metallomacrocycles like phthalocyanines and porphyrins. Among these are the bridge stacked polymeric structures Ga(pc)F and Al(pc)F [1, 2] which after partial oxidation by nitrosonium salts ($NOPF_6$, $NOBF_4$) or molecular iodine give rise to conducting materials [3–5]. We have recently demonstrated [6] that fluorogallium porphyrins (phthalocyanine analogues) present a polymeric structure in the solid state. This was proven on the basis of EXAFS and ^{1}H NMR studies.

As recently shown by Collman *et al.* [7, 8], the preparation of doped materials via iodine chemical oxidation poses problems. Indeed it is difficult to isolate a material possessing only one type of counterion, that is to say I_3^- or I_5^-. Moreover, it is not easy to characterize such derivatives since the structure is incommensurate. In addition it is of interest to develop some methods capable of discriminating the nature of the counterion.

We report here spectroscopic results obtained from doped fluorogallium porphyrins using molecular iodine, $[Ga(p)F]I_x$ (where p = oep, omp, tpp)**. In this paper we present the characterization of these polymers by X-ray study, ESR, Raman and ^{129}I Mössbauer spectroscopies.

Experimental

Synthesis of [Ga(p)F]I$_x$ Materials

Ga(p)F complexes were synthesized using methods previously described [9]. Solvents were of spectrograde quality and distilled before use. Iodine (Riedel de Haen Laboratories) was used as purchased.

$[Ga(p)F]I_x$ polymers were prepared using the H-tube technique by diffusing together solutions of Ga(p)F in toluene and iodine in heptane. Crystals were collected by filtration and washed with heptane†.

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**oep = (2,3,7,8,12,13,17,18-octaethylporphyrinate)$^{2-}$; omp = (2,3,7,8,12,13,17,18-octamethylporphyrinate)$^{2-}$; tpp = (5,10,15,20-tetraphenylporphyrinate)$^{2-}$.

†*Anal.* (calculated values in parentheses) of [Ga(oep)FI]: C, 53.8 (53.26); H, 5.5 (5.46); N, 6.7 (6.90); I, 22.8 (23.45)%.

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Instrumentation

ESR spectra were recorded on a Varian E-4 X band spectrometer with a 100 kHz field modulation. Field was calibrated using 2.2 phenyl-1 picrylhydrazyl (DPPH, $g = 2.0036$). Samples were prepared as 7% dispersions of complex in magnesium sulfate. Resonance Raman measurements were performed on a Dilor RTI 30 spectrometer (Laboratoire PCM, Ecole Centrale des Arts et Manufactures, Chatenay Malabry, France) with an Ar^+ laser source ($\lambda = 5145$ Å). Samples (50% of compound in KBr) were spun to prevent decomposition by the laser beam.

^{129}I Mössbauer spectra were recorded with the $[Ga(oep)F]^{129}I_x$ complex. This latter polymer was prepared as above by the H-tube diffusion technique using the mixture $^{129}I_2/^{127}I_2$ (65%/35%).

The ^{129}I Mössbauer spectrum was recorded on a sinusoïdal drive using conventional methods with both the ^{129}Te:ZnTe source and the absorber at 4.2 K. The absorber of uniform thickness (2–3 mg $^{129}I/cm^2$) was encapsulated in a plexiglass holder after grinding the compound with carbon boride. The data obtained after irradiation of five sources were least-squares fitted using the appropriate Hamiltonian to calculate the transition energies and intensities: an iodine atom experiencing an axially symmetric electric field gradient gives rise to a quadrupolar subspectrum consisting of the sum of 8 resonance Lorentzian lines.

Results and Discussion

ESR spectra of the three studied compounds appear in Fig. 1 and the *g*-factor values are listed in Table 1. A nearly symmetrical single ESR signal is observed and *g* values are very close to that of the free electron (2.0036). These results are quite identical to those observed for doped gallium and aluminum phthalocyanines [3–5]. This proves that these signals are characteristic of porphyrin π-cation radicals and the oxidation occurs on the macrocycle. One can note in the spectrum of $[Ga(omp)F]I_x$ beside the strong middle absorption other lines exhibiting a coupling constant equal to 17 G. This results probably from a coupling between the unpaired electron and the nuclear spin of the porphyrin nitrogen atoms.

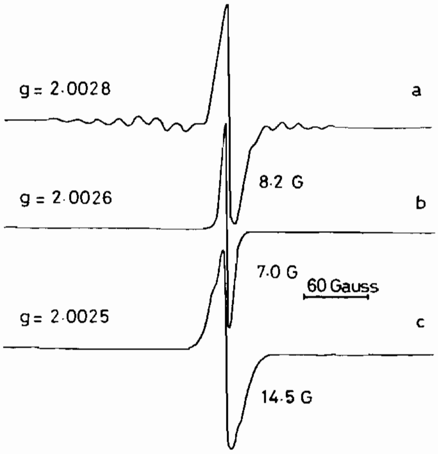

Fig. 1. ESR spectra of $[Ga(omp)F]I_x$ (a), $[Ga(oep)F]I_x$ (b) and $[Ga(tpp)F]I_x$ (c).

TABLE 1. *g*-Factor values of $[Ga(p)F]I_x$ complexes

Complexes	*g*-factor
$[Ga(omp)F]I_x$	2.0028
$[Ga(oep)F]I_x$	2.0026
$[Ga(tpp)F]I_x$	2.0025

TABLE 2. Raman data of $[Ga(p)F]I_x$ complexes

Compounds	$\nu_1(I_3^-)$	$\nu_2(I_5^-)$	$I(\nu_1)/I(\nu_2)$
$[Ga(oep)F]I_x$	111.2	165.2	0.148
$[Ga(tpp)F]I_x$	109.6	165.6	0.382
$[Ga(omp)F]I_x$	111.8	170.0	4.600

All the Raman spectra exhibit two absorptions in the ranges 109.6–111.8 and 165.2–170.0 cm^{-1} (see Table 2) characteristic of iodine doped polymers. Previous studies [10–12] have demonstrated that bands near to 110 cm^{-1} are due to the symmetrical stretching of I_3^-. The other absorption at 165.2–170.0 cm^{-1} corresponds to an I_5^- stretching mode. The ratios of these absorption intensities are different between $[Ga(oep)F]I_x$, $[Ga(tpp)F]I_x$ complexes and $[Ga(omp)F]I_x$. The anion I_3^- seems to be the dominant species in $[Ga(omp)F]I_x$ while higher concentration of I_5^- is enhanced in the spectra of both $[Ga(tpp)F]I_x$ and $[Ga(oep)F]I_x$ (see Fig. 2). However, Raman spectroscopy data cannot give the accurate amounts of I_3^- and I_5^- species in the polymers and detect the presence of I^-. In addition, no absorption at 200 cm^{-1} for I_2 appears in the spectra.

The ^{129}I Mössbauer spectrum of $[Ga(oep)F]I_x$ at 4.2 K is shown in Fig. 3. Several attempts to fit the spectrum with a superposition of quadrupolar patterns of the inequivalent iodine atoms occurring in the different polyiodide species were tried:

(a) analysis of the data to two inequivalent iodine quadrupolar sites with relative populations 2:1 (symmetrical I_3^-),

(b) analysis of the data to three inequivalent quadrupolar sites with relative populations 1:1:1 (asymmetrical I_3^-),

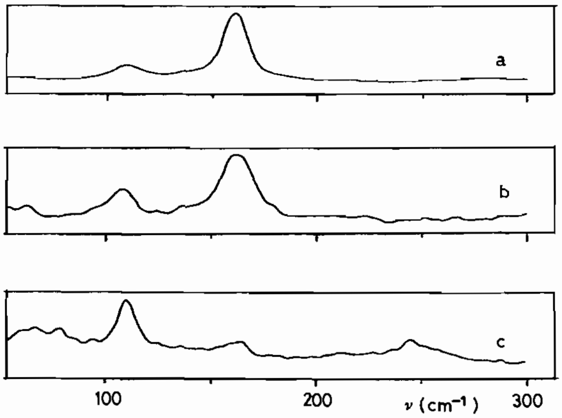

Fig. 2. Raman spectra of $[Ga(oep)F]I_x$ (a), $[Ga(tpp)F]I_x$ (b) and $[Ga(omp)F]I_x$ (c).

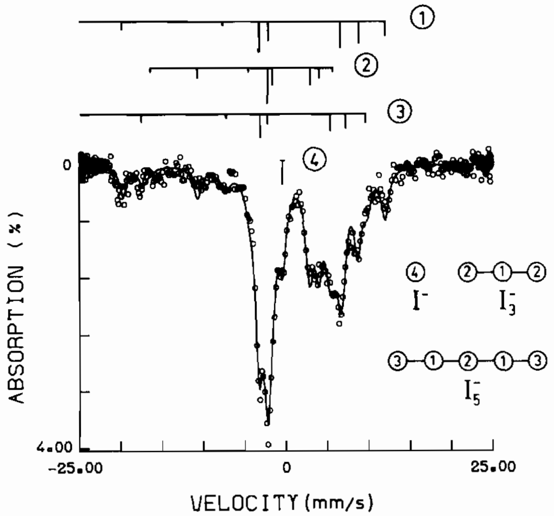

Fig. 3. ^{129}I Mössbauer spectrum of the $[Ga(oep)F]^{129}I_x$ sample at 4.2 K. The solid curve representing the best computer fit to the data is the superposition of three quadrupolar patterns (iodine sites 1, 2, 3 of the I_3^- and I_5^- ions) and of a single line (site 4, I^-). The bar diagrams indicate positions and relative intensities of the spectral components.

(c) analysis of the spectrum to three inequivalent iodine quadrupolar sites with relative populations 2:2:1 (symmetrical I_5^-),

(d) analysis of the spectrum to three inequivalent iodine quadrupolar sites with relative populations 2:2:1. This model differs however from the preceding case; a gaussian distribution of the quadrupole coupling constant of the terminal sites of the I_5^- species was assumed. This shows up by a mere broadening of the outer lines of the pattern assigned to the end iodine sites.

The hyperfine parameters characterizing the I_3^- and I_5^- species are summarized in Table 3.

Comparison of the experimental data (Fig. 3) with the calculated spectra (Fig. 4) corresponding to

TABLE 3. Typical ^{129}I hyperfine parameters in the polyiodides^{a}

Polyiodide	δ_{IS} (mm/s)	e^2qQ (MHz)	A	Reference
I_3^- (symmetrical)	1.34	−1667	1	$Ni(pc)(I_3^-)$ [13]
	0.27	−862	2	
I_3^- (asymmetrical)	1.40	−1764	1	$Cs(I_3^-)$ [14]
	0.39	−1024	1	
	0.01	−575		
I_5^- (symmetrical)	1.20	−1778	2	$Ni(dpg)_2(I_5^-)$ [15]
	0.47	−1308	2	
	0.16	−861	1	

^{a}The isomer shifts (δ_{IS}) are relative to the ZnTe source. The quadrupole coupling constants (e^2qQ) in MHz are obtained using the relation 1 mm/s = 22.45 MHz. The relative populations (A) of the inequivalent iodine sites are theoretical.

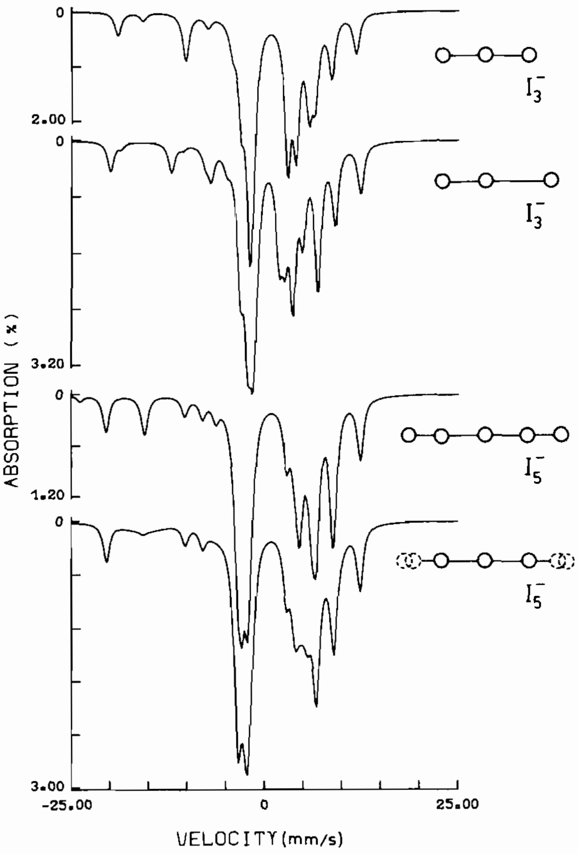

Fig. 4. Calculated ^{129}I Mössbauer spectra for symmetrical I_3^- ions, asymmetrical I_3^- ions and symmetrical I_5^- ions. The hyperfine parameters and the relative populations of the inequivalent iodine sites are given in Table 3. The lower spectrum corresponds to an I_5^- species with a gaussian distributed quadrupole coupling constant for the terminal iodine sites ($\sigma/e^2qQ = 0.15$, where σ is the standard deviation).

TABLE 4. ^{129}I hyperfine parameters of the inequivalent iodine sites occurring in the [Ga(oep)F]I$_x$ sample[a]

	I(1)	I(2)	I(3)	I(4)
δ_{IS} (mm/s)[b]	1.24 (4)	0.11 (3)	0.63 (6)	−0.42 (7)
e^2qQ (MHz)	−1720 (10)	−887 (10)	−1470 (15)	0

[a]The assignment of the different sites is illustrated in Fig. 3. [b]Relative to ZnTe.

models (a) to (d) shows that neither I_3^- nor I_5^- ions occur as a single species in our sample. Instead a satisfactory fit to the data was obtained assuming that three types of anions contribute to the complex Mössbauer spectrum, namely I^-, I_3^- and I_5^-, the polyiodide ions being linear molecules. The resulting spectrum is then a superposition of three axially symmetrical quadrupole split subspectra ($I_3^- + I_5^-$) and of a single line (I^-) whose hyperfine parameters are collected in Table 4. The relative population of the inequivalent iodine sites 1, 2, 3 and 4 (Fig. 3) being $(c_3/3 + 2c_5/5):(2c_3/3 + c_5/5):(2c_5/5):(c_1)$ where $c_3 = 39 \pm 3\%$, $c_5 = 55 \pm 4\%$ and $c_1 = 6 \pm 1\%$ are the relative amount of the three respective anions I_3^-, I_5^- and I^-.

The analysis of the isomer shift and quadrupole coupling constant yields information on the charge of the iodine atoms in the polyiodide ions I_3^- and I_5^-. Indeed, simple semi-empirical formulas express the isomer shift (δ_{IS}) and the quadrupole coupling constant (e^2qQ) in terms of the number of holes h_s, h_p and h_{pz} in the $5s^2$, $5p^6$ and $5p_z^2$ shells of an I^- ion [13, 15].

$$\delta_{IS}\ (\mathrm{mm/s}) = -9.2h_s + 1.5h_p - 0.54h_{pz}\ (\mathrm{vs.\ ZnTe}) \quad (1)$$

$$e^2qQ = U_p(e^2qQ)_{at}; \quad U_p = 3/2(h_{pz} - 1/3h_p) \qquad (2)$$

where $(e^2qQ)_{at}$ is the atomic quadrupole coupling constant (−1607.8 MHz for ^{129}I).

Since the I_3^- and I_5^- ions are linear it is safe to assume that the bonding is predominantly of σ-type thus, $h_s = 0$ and $h_p = h_{pz} = U_p$. The charge distribution results based upon the analysis of the hyperfine parameters are summarized in Table 5. The charges $q(e^2qQ)$ calculated from eqn. (2) are the most reliable since the errors on the e^2qQ values are small; on the other hand even small s–p hybridation will greatly affect $q(\delta_{IS})$. With the $q(e^2qQ)$ values of Table 5 total charges of −0.83 and −0.49 are calculated for the I_3^- and I_5^- ions respectively. It should be noticed that very similar results have been obtained in iodine doped polyacetylene [16, 17] and the amylose–iodine complex [18]. Iodine acts, as expected, as an acceptor in doped gallium porphyrins.

TABLE 5. Charges q on the inequivalent iodine sites in I_3^- and I_5^- derived from the isomer shifts, $q(\delta_{IS})$, and the quadrupole coupling constants, $q(e^2qQ)$

Site[a]	$q(\delta_{IS})$	$q(e^2qQ)$
1	+0.18	+0.07
2	−0.57	−0.45
3	−0.22	−0.09

[a]The assignment of the different sites refers to Fig. 3.

For the X-ray diffraction measurements, the oscillation photograph around the c axis shows normal and diffuse reciprocal layers which correspond to two different lattices ($c_A = 9.82$ Å, $c_B = 3.69$ Å). The c_B/c_A ratio ($c_B/c_A = 0.38$) demonstrates that these two lattices are not commensurate. As previously reported by Comes *et al.* [19] and later by Ibers *et al.* [12], the c_A parameter agrees with the $I_3^-(I_5^-)$ lattice. The c_B parameter is close to that found by Ibers *et al.* [12] in Ni(pc)I and corresponds to the porphyrin stacking axis. However, we failed to solve the average crystal structure.

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