Synthesis and Electrode Reactions of Difluorogermanium(IV) Porphyrins. Molecular Stereochemistry and Crystal Structure of Difluoro(2,3,7,8,12,13,17,18-octaethylporphyrinato)germanium(IV) †

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The difluorogermanium(IV) porphyrins $[GeF_2(P)]$ [P = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−) (oep), 5,10,15,20-tetraphenylporphyrinate(2−) (tpp), or 5,10,15,20-tetra-*p*-tolylporphyrinate(2−) (tptp)] have been prepared by reacting hydrogen fluoride with the appropriate dichloro derivative $[GeCl_2(P)]$. The complexes were characterized by elemental analysis, ^1H n.m.r., i.r., and u.v.–visible spectroscopy. The electrochemical behaviour was investigated in non-aqueous media while spectroelectrochemistry and e.s.r. were used to characterize the oxidized and reduced complexes. Each complex could be reversibly oxidized or reduced by one electron. In each case these electron additions or abstractions were ring centred. The crystal structure $[GeF_2(oep)]$ was determined by *X*-ray diffraction methods. The complex crystallizes in the space group $I4_1/a$, with $a = b = 15.202(2)$, $c = 13.910(3)$ Å, and $R = 0.034$ and $R' = 0.035$ for 1 465 unique reflections. The germanium atom lies on a $\bar{4}$ crystallographic axis and is co-ordinated by the porphyrin ring and two fluorine atoms; the short germanium–fluorine distance [1.790(2) Å] is very close to that found in [FeF(tpp)] [1.792(2) Å].

Intensive efforts have been directed towards the synthesis of highly-conducting molecular materials which contain metallomacrocyclic complexes as the fundamental unit.[1] It has been shown that partial oxidation of nickel [1,2] or fluorogallium [3–5] phthalocyanines or the related porphyrins lead to complexes of 'molecular metals'. An *X*-ray structure determination of fluoro(phthalocyaninato)gallium(III) [6,7] and an extended *X*-ray absorption fine structure (EXAFS) study of fluoro(2,3,7,8,12,13,17,18-octamethylporphyrinato)gallium(III) [8] demonstrated that a bridge-stacked polymeric structure for these compounds existed before oxidation. It is not known however if similar bridge-stacked polymeric structures exist for difluoro complexes before or after their partial oxidation. Also, such materials should possess two bridging fluorine atoms located between two macrocycle units and this polymer should have a short metal–metal distance. This question is addressed in the present paper which reports the synthesis and characterization of three new difluorogermanium(IV) porphyrins. The ^1H n.m.r., i.r., and electronic absorption spectroscopy of each complex are reported as is the electrochemistry. In addition, the molecular stereochemistry of difluoro(2,3,7,8,12,13,17,18-octaethylporphyrinato)germanium(IV), $[GeF_2(oep)]$, is described.

Experimental

Preparation of Complexes.—The complexes $[GeF_2(P)]$, where P = oep [2,3,7,8,12,13,17,18-octaethylporphyrinate(2−)], tpp [5,10,15,20-tetraphenylporphyrinate(2−)], or tptp [5,10,15,20-tetra-*p*-tolylporphyrinate(2−)], were synthesized according to the general reaction (1). The dichlorogermanium(IV) porphyrins were prepared using previously published methods,[9,10] and the difluorogermanium(IV) porphyrins obtained following a general procedure described below.

$$[GeCl_2(P)] \xrightarrow{HF,\ CH_2Cl_2} [GeF_2(P)] \qquad (1)$$

Difluoro(2,3,7,8,12,13,17,18-octaethylporphyrinato)germanium(IV). Aqueous hydrofluoric acid (40%, 10 cm^3) was added to a solution containing $[GeCl_2(oep)]$ (0.55 mmol) in methylene chloride (100 cm^3). The mixture was stirred at room temperature for 24 h. The solution was then dried and evaporated and the residual precipitate recrystallized from chloroform–heptane (1:1) (yield 62%).

The reaction conditions, yields, and elemental analyses of the difluoro complexes are summarized in Table 1 and the u.v.–visible and ^1H n.m.r. data in Table 2.

Physical Measurements.—Elemental analyses were performed by the Service de Microanalyses du C.N.R.S. ^1H N.m.r. spectra at 400 MHz were recorded on the Bruker WM 400 spectrometer of the Centre de Résonance Magnétique de l'Université de Dijon. Spectra were measured from 5-mg solutions of each complex in $CDCl_3$ with tetramethylsilane as an internal reference. E.s.r. spectra were recorded at 115 K on an IBM model ER 100 D spectrometer equipped with a microwave ER-040-X bridge and an ER 080 power supply. The *g* values were measured with respect to diphenylpicrylhydrazyl ($g = 2.0036 \pm 0.0003$). Infrared spectra were recorded on a Perkin-Elmer 580 B apparatus for 1% dispersions in CsI pellets. Electronic absorption spectra were recorded on a Perkin-Elmer 559 spectrophotometer, an IBM model 9430 spectrophotometer, or a Tracor Northern 1710 holographic optical spectrometer–multichannel analyzer.

Cyclic voltammetry measurements were obtained with the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Table 1. Elemental analyses, reaction conditions, and i.r. data

Complex	Recrystallization solvent	Yield (%)	Analysis (%)* C	H	N	F	ν(Ge–F)/ cm^{-1}
$[GeF_2(oep)]$	$CHCl_3–C_7H_{16}$ (1:1)	62	67.3 (67.2)	7.0 (6.9)	8.7 (8.7)	5.9 (5.9)	605
$[GeF_2(tptp)]$	$C_7H_{16}–C_6H_6$ (1:2)	59	74.0 (74.5)	4.7 (4.9)	7.2 (7.0)	4.8 (4.9)	621
$[GeF_2(tpp)]$	$C_7H_{16}–C_6H_6$ (1:1)	65	73.4 (73.1)	4.1 (3.9)	7.8 (7.8)	5.2 (5.2)	637

* Calculated values are given in parentheses.

Table 2. U.v.–visible and ^1H n.m.r. data

Complex	U.v.–visible[a] λ/nm ($10^{-4}ε/dm^3 mol^{-1} cm^{-1}$)					^1H N.m.r.[b]/p.p.m.
$[GeF_2(oep)]$	378 (6.1)	399 (53.05)	492 (0.20)	528 (1.65)	567 (2.57)	10.36 (s, 4 H, *meso*-H), 4.17 (q, 16 H, $-CH_2-$), 1.99 (t, 24 H, $-CH_3$)
$[GeF_2(tptp)]$	399 (4.9)	421 (52.53)	510 (0.29)	549 (1.95)	589 (0.86)	9.10 (s, 8 H, pyrrole H), 8.11 (d, 8 H, *o*-H), 7.57 (d, 8 H, *m*-H), 2.70 (s, 12 H, CH_3)
$[GeF_2(tpp)]$	397 (4.2)	418 (55.46)	509 (0.29)	547 (2.02)	586 (0.64)	9.13 (s, 8 H, pyrrole H), 8.27 (d, 8 H, *o*-H), 7.82 (m, 12 H, *m*-H, *p*-H)

[a] Solvent = PhCN. [b] Solvent = $CDCl_3$, reference $SiMe_4$; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Table 3. Crystal data for $[GeF_2(oep)]$

Formula	$C_{36}H_{44}F_2GeN_4$
M	643.36
Space group	Tetragonal $I4_1/a$
Crystal dimensions/mm	0.2 × 0.2 × 0.12
Crystal habit	Tetragonal octahedron
$a = b$/Å	15.202(2)
c/Å	13.910(3)
U/Å^3	3. 215(1)
Z	4
D_c/g cm^{-3}	1.33
F(000)	1 480
Diffractometer	Enraf-Nonius CAD4F
Radiation	Cu-K_α (λ = 1.540 81 Å) (graphite monochromatized)
Scan type	ω–2θ
$\theta_{min.}$, $\theta_{max.}$/°	1, 70
Scan speed/° min^{-1}	$0.5 < v < 3.0$
Scan range	1.0 + 0.35 tanθ
Take-off angle	3°
Aperture/mm	3 + 3 tanθ
h, *k*, *l* limits	$-19 < h < 19, 0 < k < 19,$ $0 < l < 17$
Number of reflections measured	3 599
Number of unique reflections (*N*)	1 465 [$I > 3\sigma(I)$]
Corrections	Lorentz polarization, absorption
μ(Cu-K_α)/cm^{-1}	16.33
Agreement factor between symmetry related reflections	0.024 after absorption corrections
Number of parameters (N_p)	98
N/N_p	15
R, *R'*	0.034, 0.035
Goodness of fit	1.10
w	$1/[\sigma^2(F) + 0.007 F^2]$
Δ/σ (max.)	0.10 for U_{12} of C(26)

Table 4. Fractional atomic co-ordinates and thermal parameters, with estimated standard deviations in parentheses, for $[GeF_2(oep)]$

Atom	*X/a*	*Y/b*	*Z/c*	*B*/Å^2
Ge	0.0	0.25	0.125	2.540(6)
F	0.0	0.25	0.253 7(1)	3.12(3)
N(1)	0.008 4(1)	0.119 6(1)	0.125 6(1)	2.83(3)
C(1)	0.082 3(2)	0.069 9(1)	0.108 9(2)	2.93(4)
C(2)	0.062 1(2)	−0.022 3(1)	0.118 4(2)	3.07(4)
C(3)	−0.024 9(2)	−0.027 4(2)	0.143 8(2)	3.12(4)
C(4)	−0.058 2(2)	0.061 2(2)	0.145 9(2)	2.97(4)
C(5)	−0.145 7(2)	0.084 5(2)	0.156 4(2)	3.13(4)
C(25)	0.126 9(2)	−0.095 6(2)	0.106 8(2)	3.90(5)
C(26)	0.174 5(2)	−0.120 6(3)	0.197 8(3)	7.07(9)
C(27)	−0.077 4(2)	−0.107 5(2)	0.168 0(2)	4.02(5)
C(28)	−0.078 1(3)	−0.127 8(3)	0.273 6(3)	7.18(9)

use of a three-electrode system. The working electrode was a platinum button and the counter electrode a platinum wire. A saturated calomel electrode (s.c.e.) served as the reference electrode and was separated from the bulk of the solution by a fritted glass bridge. A BAS 100 electrochemical analyser connected to a Houston Instrument HIPLOT DMP-40 plotter was used to measure the current–voltage curves.

Controlled potential electrolysis was performed with an EG & G model 173 potentiostat or a BAS 100 electrochemical analyzer. Both the reference electrode and the platinum-wire counter electrode were separated from the bulk of the solution by a fritted glass bridge. Thin-layer spectroelectrochemical measurements were performed with an IBM EC 225 voltammetric analyzer coupled with a Tracor Northern 1710 holographic optical spectrometer–multichannel analyzer to give time-resolved spectral data. The optically transparent platinum thin-layer electrode that was utilized has been described previously.[11]

Crystal and Molecular Structure Determination.—A suitable crystal of $[GeF_2(oep)]$ was obtained by recrystallization from chloroform–heptane (1:1). Oscillation and Weissenberg photographs along the $\vec{c}$ axis revealed a four-fold symmetry. Systematic extinctions of the type *hkl* [$h + k + l = 2n + 1$ and $hk0 = h(k) = 2n + 1$] led to the space group $I4_1/a$. Crystal data and details of the calculations are given in Table 3. Data reduction used the SDP package[12] and absorption corrections were applied.[13] Atomic scattering factors were taken from ref. 13 and anomalous scattering factors from ref. 14. The crystal structure was solved by the heavy-atom method. All the hydrogen atoms were found in the Fourier difference maps and refined isotropically[13] (B = 3.15 Å^2). The final agreement factors are given in Table 3. At the end of the refinement, the electron density difference maps showed density accumulations (0.25 e Å^{-3}) in the bonding regions C–C, C–N, and Ge–F.

Table 4 lists the fractional atomic co-ordinates of the non-hydrogen atoms. Additional material available from the

Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Results and Discussion

Synthesis and Spectroscopic Measurements.—Elemental analysis (Table 1) confirmed the formulation [$GeF_2(P)$] for the complexes prepared according to equation (1). The yields were very satisfactory and varied from 59 to 65%. Infrared spectra of the isolated complexes show one band in the region 605—637 cm^{-1} (Table 1), assigned to a Ge–F stretch since the corresponding dichloro complexes exhibit a Ge–Cl stretch between 314 and 340 cm^{-1}.[9,10]

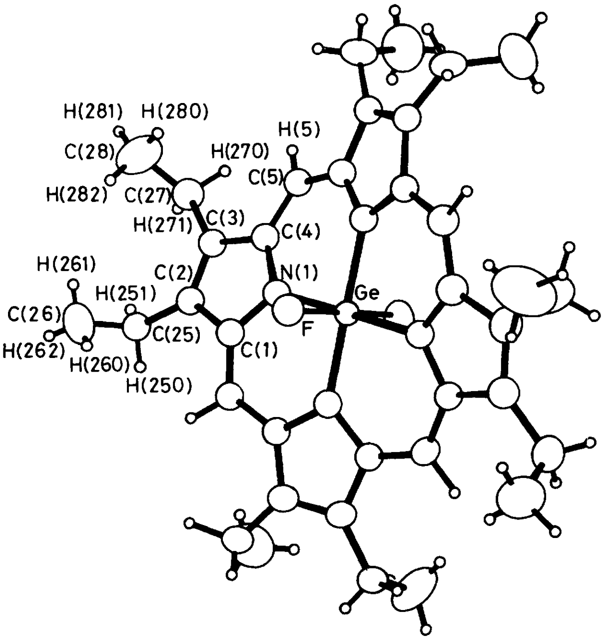

Figure 1. ORTEP view of [$GeF_2(oep)$]

The difluoro complexes exhibit 'normal class' electronic absorption spectra.[15] They show an intense Soret band in the 399—421 nm region [*B*(0,0)] and two visible bands between 528 and 589 nm [the *Q*(1,0) and *Q*(0,0) bands].[15] There is also another band at 378—399 nm which is blue shifted compared to the Soret band (see Table 2).

^1H N.m.r. characteristics of the [$GeF_2(P)$] complexes at ambient temperature are also listed in Table 2. The resonance for the [$GeF_2(oep)$] ethyl groups is an A_2B_3 type so that the magnetic environments of both faces of the macrocycle are equivalent. Signals for the *ortho* and *meta* protons of the tetra-arylporphyrin complex [$GeF_2(tptp)$] are those for an AA'BB' type coupling. These data agree with a symmetrical co-ordination of the germanium(IV) atom and with the metal ion being strictly in the macrocyclic plane. However, the n.m.r. data cannot discriminate between a polymeric and non-polymeric structure since the germanium atom can be six-co-ordinated in both cases. For this reason, the structure of [$GeF_2(oep)$] was determined by *X*-ray diffraction.

Molecular Structure.—Figure 1 shows an ORTEP view of [$GeF_2(oep)$] while Figure 2 gives structural characteristics of the molecule (numbering scheme, bond distances, angles, least-squares planes).

The germanium atom lies on a $\bar{4}$ crystallographic axis. It is six-co-ordinated by the porphyrin ring and two fluorine atoms. The germanium–nitrogen distance [1.986(2) Å] is equal to that found in [$Ge(N_3)_2(tptp)$] [1.983(2) Å][16,17] and slightly longer than that found in [$Ge(OCH_3)_2(P)$] (P = porphyrinate)

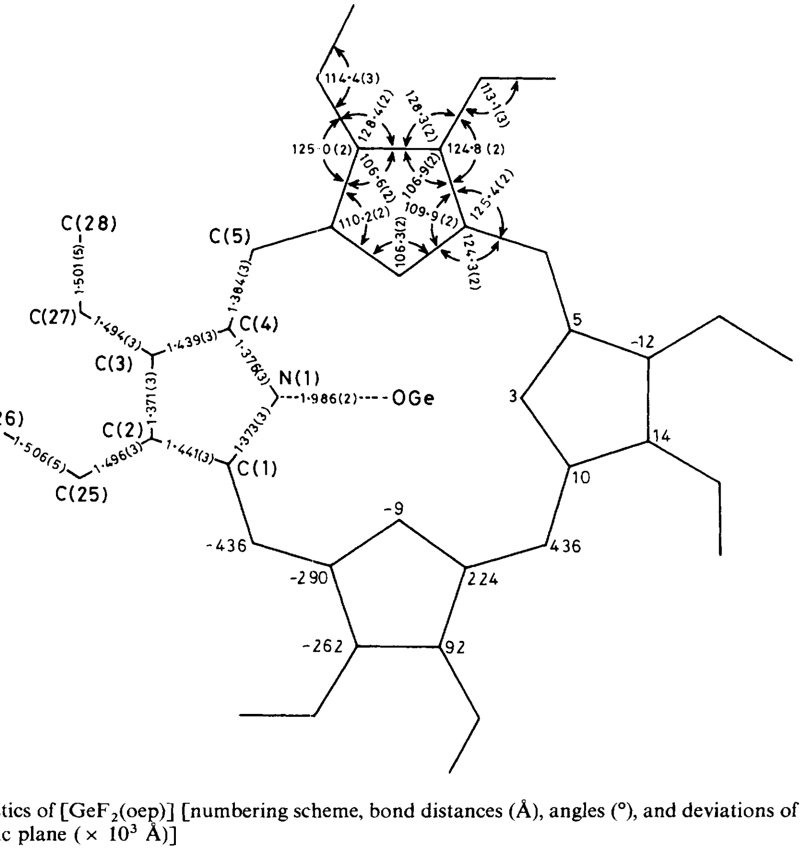

Figure 2. Structural characteristics of [$GeF_2(oep)$] [numbering scheme, bond distances (Å), angles (°), and deviations of the atoms from the pyrrole plane and from the macrocyclic plane (× 10^3 Å)]

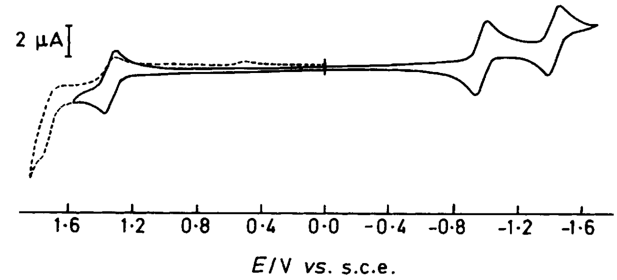

Figure 3. Cyclic voltammogram of a 1.0 × 10^{-3} mol dm^{-3} solution of $[GeF_2(tpp)]$ in CH_2Cl_2; 0.1 mol dm^{-3} $NBu^n_4ClO_4$ at 0.1 V s^{-1}

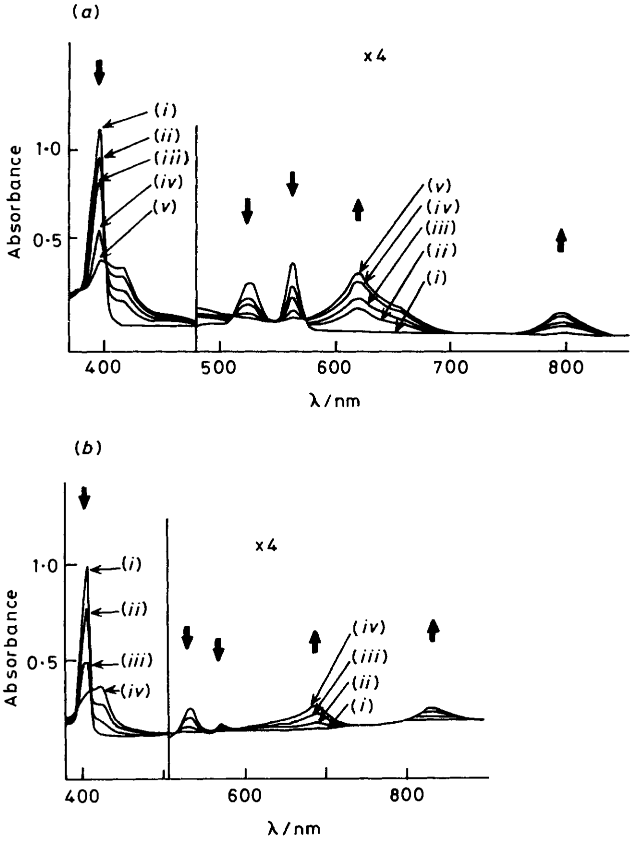

Figure 4. (*a*) Voltage-resolved spectra in PhCN, 0.1 mol dm^{-3} $NBu^n_4ClO_4$, for the first reduction of 2 × 10^{-4} mol dm^{-3} $[GeF_2(oep)]$. Applied potentials: (*i*) −1.40, (*ii*) −1.55, (*iii*) −1.57, (*iv*) −1.61, and (*v*) −1.66 V *vs.* s.c.e. (*b*) Time-resolved spectra for the first reduction of 2 × 10^{-4} mol dm^{-3} $[GeF_2(tpp)]$ at −1.20 V *vs.* s.c.e. in PhCN, 0.1 mol dm^{-3} $NBu^n_4ClO_4$: (*i*) 0, (*ii*) 15, (*iii*) 60, (*iv*) 240 s

[2.013(2) Å].[18] The short metal–fluorine distance [1.790(2) Å] compares with that found in GeH_3F by microwave spectroscopy (1.73 Å)[19] and agrees well with a covalent character for the Ge–F bond. Furthermore, this distance is the same as that found in [FeF(tpp)] [1.792(2) Å].[20] The macrocycle has a 'ruffled' structure which is usually observed for porphyrins with S_4 symmetry. The dihedral angles between the porphyrin and pyrrole planes, and between the adjacent and opposite pyrrole rings are 19.8, 14.1, and 28.2° respectively.

Electrode Reactions.—The complexes $[GeF_2(P)]$ have straightforward electrochemical behaviour. One or two reversible waves are observed both for oxidation and reduction (the exact number depends on the porphyrin). The cyclic voltammogram of $[GeF_2(tpp)]$ is shown in Figure 3 and half-wave potentials for oxidation and reduction of each $[GeF_2(P)]$ complex in PhCN and CH_2Cl_2 are given in Table 5.

Table 5. Half-wave potentials (*E*/V *vs.* s.c.e.) for oxidation and reduction of $[GeF_2(P)]$ in PhCN and CH_2Cl_2; 0.1 mol dm^{-3} $NBu^n_4ClO_4$

		Oxidation		Reduction	
Compound	Solvent	2nd	1st	1st	2nd
$[GeF_2(tpp)]$	CH_2Cl_2	1.72	1.35	−0.99	−1.43
	PhCN	*a*	1.39	−0.93	−1.45
$[GeF_2(tptp)]$	CH_2Cl_2	1.66	1.27	−0.99	−1.44
	PhCN	1.67	1.31	−0.97	−1.49
$[GeF_2(oep)]$	CH_2Cl_2	1.78[b]	1.16	−1.25	−1.75
	PhCN	*a*	1.15	−1.25	−1.77

[a] Second oxidation wave not observed due to limited solvent range. [b] E_{pa} measured at 0.1 V s^{-1}.

The absolute potential difference between the two reduction potentials of the three $[GeF_2(P)]$ complexes are the same, 0.52 V, in PhCN. This is greater than that (0.42 ± 0.05 V) generally observed for ring-centred reductions of different metalloporphyrin complexes.[21] The potential difference between the first oxidation and the first reduction is 2.40 V for $[GeF_2(oep)]$, 2.32 V for $[GeF_2(tpp)]$, and 2.28 V for $[GeF_2(tptp)]$.

Voltage-resolved thin-layer spectra were recorded during the first one-electron reduction of $[GeF_2(oep)]$ and $[GeF_2(tpp)]$ and are shown in Figure 4. One electron is added to the starting species to give a product with properties characteristic of a radical anion. In general, the oxidation and reduction waves were reversible on the thin-layer spectroelectrochemical timescale. $[GeF_2(oep)]$ exhibits a Soret band at 399 nm in PhCN and two *Q*-bands at 528 and 567 nm. Upon addition of one electron to this complex, the peak is shifted towards higher wavelengths (422 nm) and two broad absorptions appear at 623 and 801 nm. Four isosbestic points are observed at 402, 511, 546, and 573 nm. This is shown in Figure 4(*a*).

Time-resolved electronic absorption spectra of $[GeF_2(tpp)]$ electroreduced at −1.2 V are depicted in Figure 4(*b*). The intense Soret band at 418 nm decreases and shifts to 439 nm. Two bands in the visible region disappear upon reduction. Simultaneously, two broad peaks appear at 703 and 847 nm. These spectral changes are reversible and the original spectrum can be regenerated upon application of a controlled potential more positive than −1.2 V. Thus, the two reductions can be described as being ring centred and are described by equations (2) and (3).

$$[GeF_2(P)] + e^- \rightleftharpoons [GeF_2(P)]^- \qquad (2)$$

$$[GeF_2(P)]^- + e^- \rightleftharpoons [GeF_2(P)]^{2-} \qquad (3)$$

The electronic absorption spectra of singly oxidized $[GeF_2(oep)]$ are shown in Figure 5. The compound exhibits a shift in the Soret peak towards lower wavelengths as well as a decrease in the peak intensity upon oxidation. In addition, the two *Q*-band peaks disappear but no broad absorptions typical of a radical cation[22] are detected above 700 nm. Similarly to oxidized [GaCl(oep)] and [GaCl(tpp)],[23] the assignment of the first electron abstraction site in $[GeF_2(P)]$ (π ring or axial ligand) is not totally clear from thin-layer spectroelectrochemical data. Additional e.s.r. data, however, suggest a ring-centred oxidation.

E.S.R. of Oxidized and Reduced $[GeF_2(P)]$.—The difluoro complexes exhibit a singlet e.s.r. spectrum after the addition of one electron. The complete electrolysis of $[GeF_2(tpp)]$ at −1.2

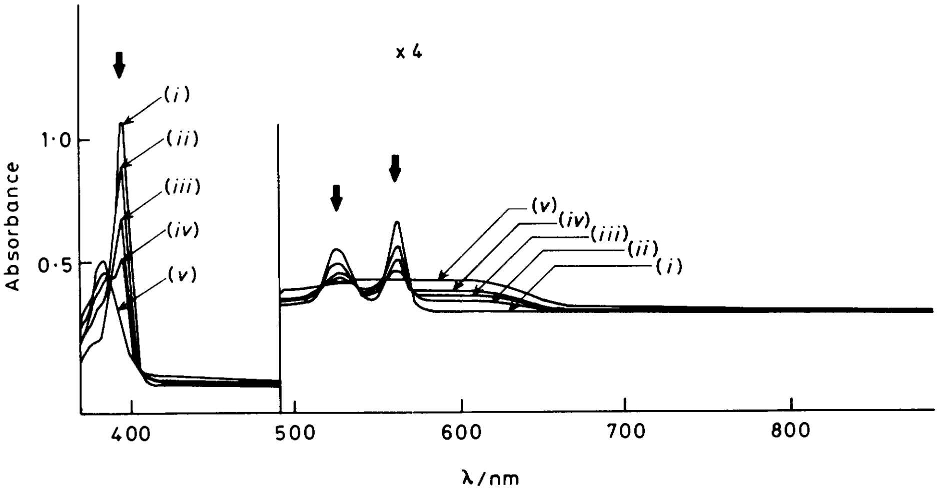

Figure 5. Voltage-resolved spectra for the first oxidation of 2 × 10^{-4} mol dm^{-3} [GeF_2(oep)] in PhCN, 0.1 mol dm^{-3} $NBu^n_4ClO_4$. Applied potentials: (*i*) +0.91, (*ii*) +1.07, (*iii*) +1.09, (*iv*) +1.11, and (*v*) +1.27 V *vs.* s.c.e.

V in CH_2Cl_2 containing 0.1 mol dm^{-3} $NBu^n_4ClO_4$ leads to a solution whose e.s.r. spectrum has a g value of 2.001 ± 0.005 and a total width of 8.06 G (G = 10^{-4} T), typical of a metalloporphyrin radical anion. This observation agrees with the spectroelectrochemistry results which suggest a ring-centred reduction. Similarly, reduced [GeF_2(tptp)] gives a singlet e.s.r. signal with g = 2.001 ± 0.005 and ΔH_{pp} = 7.7 G.

The one-electron oxidation of [GeF_2(tpp)] at 1.58 V leads to a species with an e.s.r. spectrum similar to that of [GeF_2(tpp)]$^{\bullet -}$. The g value is 2.004 ± 0.005 and the peak separation of 8.06 G is typical of a metalloporphyrin radical cation [GeF_2(tpp)]$^{\bullet +}$. It should be noted that no hyperfine structure is observed in the e.s.r. spectra of [GeF_2(tpp)]$^{\bullet -}$ and [GeF_2(tpp)]$^{\bullet +}$.

In summary, this work unambiguously demonstrates the monomeric structure of difluorogermanium(IV) porphyrins. However, even if the neutral form is not polymeric, partial oxidation of the difluorometallomacrocyclic complexes can lead to 'molecular metals'. The charge carrier of such materials would be the macrocycle unit. Their preparation is now underway.

Acknowledgements

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