Synthesis and Characterization of Bis(phenyltetrazolato)-germanium(IV) and -tin(IV) Porphyrins

Nadine Jagerovic, Jean-Michel Barbe, Michel Farnier, and Roger Guilard *
Laboratoire de Synthèse et d'Electrosynthèse Organométallique, associé au C.N.R.S. (U.A. 33), Faculté des Sciences 'Gabriel', 6, Boulevard Gabriel, 21100 Dijon, France

Bis(phenyltetrazolato)-germanium(IV) and -tin(IV) metalloporphyrins have been synthesized by the action of benzonitrile on diazido-germanium(IV) and -tin(IV) porphyrins. The structure of the complexes studied has been demonstrated on the basis of elemental analysis, mass spectrometry, ^{1}H n.m.r., i.r., and u.v.–visible spectroscopy.

Synthetic methods for preparing highly conductive materials have been extensively expanded during recent years. Among these a wide range of metallomacrocyclic polymers has been prepared. Of interest are the polymeric derivatives obtained by bridging metallomacrocycles with oxygen,[1,2] fluorine,[3,4] sulphur,[5,6] cyanide,[7] acetylenic dianion,[8,9] or polynitrogen derivatives.[10–15] The last group, including polymers formed by the bis-co-ordination of pyrazine[10–14] with phthalocyanines and porphyrins,[15] could present particular interest. Indeed, the partial oxidation of these polymers must lead to highly conductive materials since easy transfer of the electronic hole occurs *via* the bridging heterocycle. Similar conductive properties can be expected if a tetrazole ring is the bridging ligand.

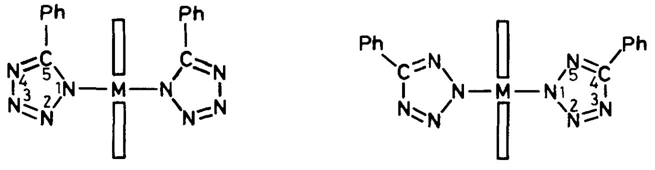
It is well known that organic azides react with nitriles *via* a dipolar 1,3-cycloaddition mechanism leading to the formation of tetrazole.[16] A similar reaction is also observed starting from organometallic azides.[17–20] Moreover, we have recently shown that azidoindium(III) porphyrins react with nitriles giving rise to a tetrazole ring directly bonded to the metal.[21] Such a reaction can be used to prepare heteropolymetallic polymers bridged with a tetrazole ring when a dicyanometalloporphyrin is treated with a diazidometalloporphyrin. As a preliminary study of these latter complexes we report here the synthesis and spectroscopic properties of bis(phenyltetrazolato)-germanium(IV) and -tin(IV) porphyrins. Characterization of these compounds was achieved on the basis of elemental analysis, mass spectrometry, ^{1}H n.m.r., i.r., and u.v.–visible spectroscopy.

Experimental

Chemicals.—The diazido-tin(IV) and -germanium(IV) porphyrins were obtained using a method previously described.[22] All solvents were distilled under argon prior to use. Syntheses of bis(phenyltetrazolato)-germanium(IV) and -tin(IV) porphyrins were carried out using Schlenk techniques.

Preparation of M(por)(N_4CPh)$_2$ (M = Sn *or* Ge; por = oep, tptp *or* tmtp).† —A solution of M(por)(N_3)$_2$ (0.46 mmol) in benzonitrile (60 cm^3) was heated to 130—140 °C with stirring for 2 h. The evolution of the reaction was checked by observing the decrease of the N_3 asymmetrical stretch (at *ca.* 2 070 cm^{-1}) in the i.r. spectrum. After evaporation of the solvent, the resulting solid was recrystallized. The reaction yields are given in Table 1.

Instrumentation.—Elemental analyses were performed by the Service Central de Microanalyses du C.N.R.S. Mass spectra were obtained in the electron-impact mode with a Finnigan 3300 spectrometer; ionizing current 0.4 mA, ionizing energy 70 eV (*ca.* 1.1 × 10^{-17} J), source temperature 250—350 °C. ^{1}H N.m.r. spectra were obtained at 400 MHz using a Bruker WM 400 spectrometer at the Centre de Résonance Magnétique de l'Université de Dijon. Spectra were measured on solutions of the complex (3—5 mg) in C_6D_6 or $CDCl_3$; the corresponding non-deuteriated solvent was used as internal reference. U.v.–visible spectra were recorded on a Perkin-Elmer 559 spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer 580 B spectrometer. Samples were prepared as 1% dispersions in CsI.



Isomer 1 Isomer 2

Scheme.

Results and Discussion

The results of elemental analysis and mass spectrometry agree with the proposed molecular formulae. The molecular peak could be observed for only one compound, Ge(oep)(N_4CPh)$_2$, due to the detection limit (below *m/e* 1 000) of the instrument. However, for almost all the complexes, peaks appear corresponding to the loss of one phenyltetrazole group and to those resulting from the loss of one or two nitrogen molecules. Moreover the parent peak is always the [M(por)]$^+$ ion. This corresponds well with the proposed molecular formula but the structural arrangement cannot be determined on the basis of these data. Indeed, as previously reported, cycloaddition of nitriles to azides can lead to two isomers[16–20] (Scheme). The formation of isomer 1 seems to be unlikely in this case because of possible steric interactions between the phenyl ring of the phenyltetrazole and the porphyrin macrocycle.

^{1}H N.m.r. data (listed in Table 2) may allow us unambiguously to determine the position of the phenyl ring. The chemical shifts of the phenyl protons belonging to the axial ligand appear in the range 6.51—6.97 p.p.m. and this compares with values observed for benzene derivatives. This result implies a weak interaction between the phenyl group and the metal and consequently a large metal–phenyl protons distance. Moreover, earlier ^{1}H n.m.r. studies of alkyl or aryl indium(III) and germanium(IV) porphyrins[23,24] exhibit similar characteristic data. The chemical shifts of the phenyl protons of the complexes being studied (6.51—6.97 p.p.m.) are not observed in the range

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† por = Unspecified porphyrinate(2−), oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−), tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2−), tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2−).

Table 1. Yields, recrystallization solvents, and elemental analyses for $M(por)(N_4CPh)_2$ complexes

Complex	Yield (%)	Recrystallization solvent[a]	Molecular formula	Elemental analysis (%)[b] C	H	N	M
$Sn(tptp)(N_4CPh)_2$	26	A	$C_{62}H_{46}N_{12}Sn$	67.5 (69.1)	4.4 (4.3)	11.8 (15.6)	11.0 (11.0)
$Sn(tmtp)(N_4CPh)_2$	54	A	$C_{62}H_{46}N_{12}Sn$	67.4 (69.1)	4.5 (4.3)	11.0 (15.6)	10.4 (11.0)
$Sn(oep)(N_4CPh)_2$	44	B	$C_{50}H_{54}N_{12}Sn$	61.3 (63.7)	5.8 (5.8)	15.6 (17.8)	12.5 (12.6)
$Ge(tptp)(N_4CPh)_2$	47	A	$C_{62}H_{46}GeN_{12}$	70.2 (72.2)	4.6 (4.5)	15.3 (16.3)	6.9 (7.0)
$Ge(tmtp)(N_4CPh)_2$	45	A	$C_{62}H_{46}GeN_{12}$	72.9 (72.2)	5.0 (4.5)	16.9 (16.3)	5.7 (7.0)
$Ge(oep)(N_4CPh)_2$	44	B	$C_{50}H_{54}GeN_{12}$	65.5 (67.0)	6.0 (6.0)	18.1 (18.8)	8.2 (8.1)

[a] A = toluene, B = 1,2-dichloroethane. [b] Calculated values in parentheses.

Table 2. ^1H N.m.r. data (400 MHz) for $M(por)(N_4CPh)_2$ complexes[a]

Complex[b]	R^1	R^2	Protons of R^1	Protons of R^2	Protons of N_4CPh
$Sn(tptp)(N_4CPh)_2$	$p-C_6H_4CH_3$	H	d, 8, 7.90 d, 8, 7.35 s, 12, 2.36	s, 8, 9.23	m, 4, 6.95 m, 6, 6.54
$Sn(tmtp)(N_4CPh)_2$	$m-C_6H_4CH_3$	H	m, 8, 7.85 m, 8, 7.32 s, 12, 2.25	s, 8, 9.20	m, 4, 6.97 m, 6, 6.52
$Sn(oep)(N_4CPh)_2$	H	C_2H_5	s, 4, 10.63	t, 24, 1.78 q, 16, 3.89	d, 4, 6.95 t, 2, 6.78 t, 4, 6.61
$Ge(tptp)(N_4CPh)_2$	$p-C_6H_4CH_3$	H	d, 8, 7.85 d, 8, 7.15 s, 12, 2.33	s, 8, 9.21	m, 4, 6.91 m, 6, 6.53
$Ge(tmtp)(N_4CPh)_2$	$m-C_6H_4CH_3$	H	m, 8, 7.83 m, 8, 7.28 s, 12, 2.21	s, 8, 9.18	m, 4, 6.92 m, 6, 6.51
$Ge(oep)(N_4CPh)_2$	H	C_2H_5	s, 4, 10.36	t, 24, 1.96 q, 16, 4.18	t, 2, 6.80 t, 4, 6.71 d, 4, 6.36

[a] Data given as multiplicity, intensity, δ/p.p.m.; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] Solvent = C_6D_6, except $CDCl_3$ for $Ge(oep)(N_4CPh)_2$.

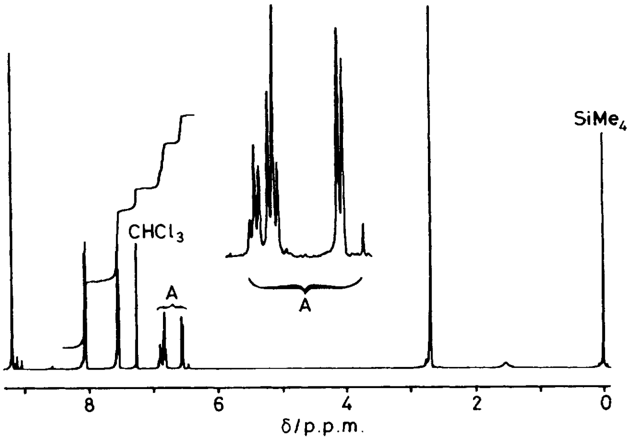

Figure 1. ^1H N.m.r. spectrum (400 MHz) of $Ge(tptp)(N_4CPh)_2$ in $CDCl_3$

in which the phenyl groups of In(por)(CH=CHPh) appear.[25] This indicates that the structure probably corresponds to isomer 2. The complete characterization of the (phenyltetrazolato)-germanium and -tin derivatives can be enhanced by comparison of ^1H n.m.r. data with those of the corresponding indium complexes $In(por)(N_4CPh)$ whose isomer 2 structural arrangement has been established by an *X*-ray study.[21] The chemical shifts of the phenyl protons of these two series appear in strictly the same region [6.51—6.97 (Sn,Ge), 6.41—6.87 p.p.m. (In)].

The presence of two phenyltetrazole ligands co-ordinated *trans* to the metal is demonstrated by the morphology of the methylenic proton signals of the octaethylporphyrin derivatives and the phenyl protons of the tetra-*p*-tolylporphyrin complexes which appear as a quartet and two doublets respectively. This is illustrated by the spectrum of $Ge(tptp)(N_4CPh)_2$, shown in Figure 1.

The pyrrole or methine protons of the macrocycle are deshielded with respect to those of starting azido complexes according to the higher electron-withdrawing effect of the phenyltetrazole ring. All the ^1H n.m.r. data are summarized in Table 2.

Figure 2 shows the i.r. spectrum of $Ge(tmtp)(N_4CPh)_2$ in a CsI dispersion and characteristic vibration wavenumbers are listed in Table 3. Asymmetric and symmetric deformation modes appear in the expected regions, *i.e.* 733—788 and 1 039—

Table 3. U.v.-visible and i.r. data for $M(por)(N_4CPh)_2$ complexes

	I.r. (cm^{-1})							U.v.-visible λ/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})				
Complex	Tetrazolato				Phenyl ring			*B*(1,0)	*B*(0,0)	*Q*(2,0)	*Q*(1,0)	*Q*(0,0)
$Sn(tptp)(N_4CPh)_2$	1 444			1 165	1 130	733	693	407 (2.7)	429 (48.6)	522 (0.3)	564 (1.7)	604 (1.5)
$Sn(tmtp)(N_4CPh)_2$	1 445	1 357		1 166		734	695	406 (3.4)	426 (57.5)	521 (0.3)	560 (1.9)	600 (1.2)
$Sn(oep)(N_4CPh)_2$				1 174	1 039	781	695	389 (4.3)	409 (38.7)	491 (0.2)	539 (2.4)	577 (2.3)
$Ge(tptp)(N_4CPh)_2$	1 464			1 147		729	692	411 (3.7)	428 (45.9)	521 (0.2)	560 (1.6)	602 (0.9)
$Ge(tmtp)(N_4CPh)_2$	1 461		1 230	1 130		730	692	406 (3.1)	427 (51.7)	522 (0.2)	560 (1.7)	602 (0.8)
$Ge(oep)(N_4CPh)_2$				1 128	1 039	788	693	387 (5.0)	409 (48.9)	500 (0.2)	538 (1.7)	577 (1.8)

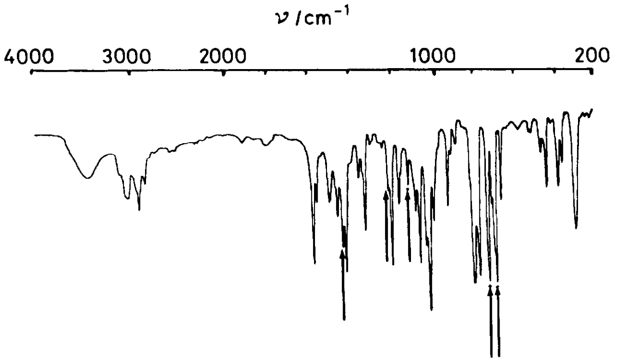

Figure 2. I.r. spectrum of $Ge(tmtp)(N_4CPh)_2$ (arrows indicate positions of tetrazole- and phenyl-ring vibrations, see Table 3)

1 464 cm^{-1} respectively. These values are close to those observed for the palladium complex $[Pd(PPh_3)_2(N_4CPh)_2]$[19] and other reported organometallic tetrazole derivatives.[17,18] At lower wavenumbers other vibrations can be observed around 693 cm^{-1}, which are probably due to the phenyl ring.

Electronic absorption spectral data are given in Table 3. The spectra belong to the 'normal' class[26] and present the same morphology as that of the starting diazido complexes. Three *Q* bands are observed between 491 and 604 nm and the Soret band appears near 428 nm for the tetratolylporphyrins and at 409 nm for the octaethylporphyrins. All the absorptions are only blue or red shifted by 1 or 2 nm with respect to the diazido porphyrins.

No significant spectroscopic differences are observed within the tin and germanium series. This supports our previous studies regarding the starting diazido complexes.[22]

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