Synthesis and Physicochemical Characteristics of Alkane (or Arene)-thio-, -sulphinato-, and -sulphonato-indium(III) Porphyrins. Crystal Structure of Methanesulphonato(5,10,15,20-tetraphenylporphyrinato)-indium(III)

By **Panayotis Cocolios, Pierre Fournari,** and **Roger Guilard,*** Laboratoire de Synthèse et d'Electrosynthèse Organométallique associé au C.N.R.S. (LA 33), Faculté des Sciences Gabriel, 21000 Dijon, France
Claude Lecomte and **Jean Protas,** Laboratoire de Minéralogie et Cristallographie, Equipe de Recherche associée au C.N.R.S., no. 162, Faculté des Sciences, Centre de 2ème Cycle, Case Officielle no. 140, 54037 Nancy Cedex, France
Jean C. Boubel, Laboratoire de Chimie Physique Organique, Equipe de Recherche associée au C.N.R.S., no. 222, Faculté des Sciences, Case Officielle no. 140, 54037 Nancy Cedex, France

Indium(III) porphyrins containing metal–sulphur bonds [InL(SR)] (L = porphyrinate, R = alkyl or aryl) are reported. The photochemical oxidation of these leads to the corresponding sulphinatoindium(III) porphyrins [$InL(SO_2R)$]. The insertion of sulphur dioxide between the indium atom and the alkyl or aryl group of [InL(R)] also gives rise to the sulphinato-compounds. The latter can easily be oxidised to the corresponding sulphonato-complexes. The crystal structure of the title compound [$In(tpp)(SO_3CH_3)]\cdot 2C_2H_4Cl_2$ has been determined by *X*-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with $a = 13.027(2)$, $b = 13.284(2)$, $c = 14.029(2)$ Å, $\alpha = 68.82(2)°$, $\beta = 85.31(2)°$, $\gamma = 88.13(2)°$, and $Z = 2$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to $R = 0.063$. This complex crystallises as a one-dimensional polymer, parallel to the *c* axis. The indium atom lies rigorously in the four-nitrogen plane and the structure may be described as the close packing of [In(tpp)]$^+$ and [SO_3CH_3]$^-$ ions. A high-resolution n.m.r. study shows that this structure is destroyed in solution at low concentrations.

THERE has been limited research on metalloporphyrinic systems in which the metal is bonded to a carbon skeleton directly or by means of an oxygen or a sulphur atom. Nevertheless, in a preliminary communication,[1] we pointed out that when starting from porphyrins, H_2L (1; L = oep or tpp),† or from chloroindium(III) porphyrins, [InL(Cl)] (2), it was possible to prepare [InL(R)] (3) and [InL(SR)] (4) (R = alkyl or aryl), the former compounds being obtained either by treating indium trichloride with a porphyrin dissolved in an arenethiol, or by using an organothiolithium compound and a chloroindium porphyrin.

In the series [ML(SR)] only the compounds with M = Fe had previously been prepared; these products are very unstable and sensitive to molecular oxygen.[2] In contrast, the [InL(SR)] complexes are rather stable and we have studied their reactivity towards molecular oxygen. Photochemical oxidation leads to the sulphinate complexes [$InL(SO_2R)$] (5), and thermal oxidation of the latter yields the corresponding sulphonate derivatives [$InL(SO_3R)$] (6). *A priori*, all these products could be made by sulphur dioxide insertion starting from alkyl- or aryl-indium(III) porphyrins [InL(R)]. However, treatment of a solution of [InL(R)] with a stream of oxygen-free SO_2 gave only the sulphinate derivatives (5).

The synthesis and characterisation of [InL(R)] compounds formed the subject of a recently published paper.[3] We now report the synthesis and properties of the complexes [InL(SR)] (4), [$InL(SO_2R)$] (5), and [$InL(SO_3R)$] (6) (R = alkyl or aryl). Physical measurements on the last two series of complexes do not allow us to define their structures with certainty. An *X*-ray study was therefore carried out for the complex [In(tpp)(SO_3CH_3)]. In a recent note [4] we showed that this product exhibits a polymeric arrangement in the crystalline state, and we reported some structural data. Here we show by an n.m.r. spectral analysis that the polymeric arrangement is destroyed in solution at low concentrations.

EXPERIMENTAL

The [InL(R)] compounds (L = porphyrinate, R = alkyl or aryl) were prepared according to the method previously reported.[3]

Preparations of the [InL(SR)] (4) *Compounds*.—(*a*) R = *Alkyl*. To a chloroindium(III) porphyrin [InL(Cl)] (2) (1.4 mmol) in dry benzene (or toluene) (500 cm^3) kept at 10—15 °C, was added dropwise a solution (5—10 cm^3) of an organothiolithium compound Li[SR] [obtained at −20 °C from 0.288 mol of lithium and 0.144 mol of thiol RSH dissolved in 100 cm^3 of peroxide-free tetrahydrofuran (thf)]. The reaction was followed by t.l.c. on basic alumina [eluant, benzene–n-hexane (1 : 1)]. When it was complete, water (100 cm^3) at 10 °C was slowly added; the reaction mixture was washed with a 5% solution of sodium hydroxide (1 l) and water until neutrality. The solution was dried on Mg[SO_4] and the solvent evaporated under reduced pressure. The residue was purified by chromatography on a basic alumina column (eluant, chloroform) and recrystallised in the absence of light.

(*b*) R = *Phenyl*. A mixture of a H_2L porphyrin (3.5 mmol), $InCl_3$ (7.3 mmol), and thiophenol (0.244 mmol, 25 cm^3) was refluxed for 5 h under a stream of nitrogen. The reaction must be followed as indicated above and when it was complete the mixture was extracted with chloroform (500 cm^3),

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† Abbreviations: oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−); tpp = 5,10,15,20-tetraphenylporphyrinate(2−).

and washed with a 5% solution of sodium hydroxide (2 l) to eliminate the excess of thiophenol. Further treatment was identical to that above.

The reaction conditions, yields, and elemental analyses for all the compounds obtained are summarised in Table 1.

Photochemical Oxidation of Compounds (4) *to give* [InL(SO_2R)] (5; R = *alkyl or aryl*).—A stream of dry oxygen was gently bubbled through an irradiated solution of a given compound (4) (0.7 mmol) in dry benzene (150 cm^3) (in order to eliminate any thermal influence, the source, an OSRAM HQI 400 W-71 lamp, was placed apart from the reactor). The progress of the reaction was monitored by t.l.c. on basic alumina (eluant, chloroform). When the transformation was complete the solvent was removed *in vacuo*, and the residual solid was recrystallised under dry and anaerobic conditions in a mixture of *p*-hydroquinone (75 mg), di-isopropyl ether (7.5 cm^3), and dry 1,2-dichloroethane (67.5 cm^3). The isolated product was dried under an argon atmosphere.

Preparation of Complexes (5) *starting from* [InL(R)] (3; R = *alkyl or aryl*).—To a solution of [InL(R)] (0.7 mmol) in methylene chloride (90 cm^3) was added *p*-hydroquinone (100 mg) in di-isopropyl ether (10 cm^3) under an argon atmosphere. The solution was cooled to −18 °C and a gentle stream of anhydrous sulphur dioxide was bubbled through it. Further treatment was identical to that described above for these complexes.

Oxidation of Complexes (5) *to give* [InL(SO_3R)] (6).—A stream of dry oxygen was bubbled through a refluxed solution of [InL(SO_2R)] (0.7 mmol) in dry toluene (100 cm^3). After reaction the solvent was removed under reduced pressure and the residual solid was recrystallised.

Characteristic i.r. bands (cm^{-1}, from CsI) and significant fragmentation patterns observed in the mass spectra of complexes (4)—(6) are given in Table 2.

Physical Measurements.—Elemental analyses were performed by the 'Service de Microanalyse du C.N.R.S.' Mass spectra were recorded in the electron-impact mode with a Finnigan 3300 spectrometer: ionising energy, 30—70 eV; * ionising current, 0.4 mA; source temperature, 250—400 °C. Hydrogen-1 n.m.r. spectra were obtained on a JEOL FX 100 spectrometer. Samples (10 mg) were dissolved in $CDCl_3$ (0.4 cm^3) with tetramethylsilane as internal reference. High-resolution ^1H n.m.r. spectra were recorded at 250 MHz using a CAMECA † spectrometer equipped with Fourier-transform attachment; according to the concentration, 20—200 scans over 16 K points were accumulated for each spectrum with a dwell time of 160 µs. During all experiments, the temperature was kept constant within 1 °C. Infrared spectra were obtained on a Beckman IR 4240 spectrometer. Samples were 1% dispersions in CsI pellets. Visible and u.v. spectra were recorded on a Beckman DK 2A spectrophotometer using 10^{-6} mol l^{-1} solutions of compound in dry and oxygen-free chloroform or benzene.

Determination of Crystal and Molecular Structure.—*Crystal data*. [In(tpp)(SO_3CH_3)]·$2C_2H_4Cl_2$, Triclinic, M = 1 020.5, a = 13.027(2), b = 13.284(2), c = 14.029(2) Å, α = 68.82(2), β = 85.31(2), γ = 88.13(2)°, U = 2 255 Å^3, Z = 2, D_c = 1.50 g cm^{-3}, space group $P\bar{1}$, nickel-filtered Cu-K_α radiation, λ = 1.542 42 Å, μ(Cu-K_α) = 72.7 cm^{-1}, $F(000)$ = 518.

Intensity measurements. Red crystals were obtained by recrystallisation of the complex from 1,2-dichloroethane. Because of their rapid decay, probably by loss of the solvent of recrystallisation, the crystals were sealed into Lindemann glass capillaries with a drop of their saturated solution. In spite of this precaution, four different crystals were needed to collect all the reflections in half of the diffraction sphere. The intensities were measured on a four-circle CAD 4 Enraf-Nonius diffractometer in the θ—1.5 θ scan mode. During counting of the diffraction peaks, three reflections were used for periodic checking (every 50 reflections) of the alignment of the crystal. When the misorientation of the scattering vector was greater than 0.15° a new orientation occurred: the values of θ, χ, and ϕ of 25 reflections were measured again and a new orientation matrix calculated. This procedure was carried out every 400 reflections. Furthermore, three reflections were used to check the decay of the crystal: when the mean relative variation $\Delta I/I_0$ of these reflections was greater than 0.1 another crystal was used.

The value of each reflection was linearly scaled according to the mean variation of the intensities of the above three reflections. Thus, each of the four groups of reflections corresponding to the four crystals was scaled and adjusted after each refinement procedure. A total of 7 985 reflections was measured in half of the diffraction sphere with $2 < 0 < 60°$, and 3 047 having $\sigma(I)/I < 0.33$ were used to solve and to refine the structure. Each reflection was corrected for Lorentz and polarisation effects. Absorption corrections were not applied.

The size of the crystals used to collect the diffraction intensities was less than 0.15 mm so that the transmission factor was smaller than 1. Furthermore, the accuracy of the structure factors was more affected by the difficulty of the diffraction experiment (crystals must be kept in their saturated solution) than by the absorption problems; for these two reasons we have neglected absorption corrections.

Solution and refinement. The intensities of the reflections hkl where $l = 2n + 1$ were very weak; this effect is similar to that observed for a sub-structure along the $\vec{c}$ axis. Hence a crystal-structure determination by direct methods was not possible. The crystal structure was solved by the Patterson method which gave the positions of the indium ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0), nitrogen, and sulphur atoms (R = 0.33). A careful study of the Fourier synthesis yielded the co-ordinates of the missing atoms. The refinement of all the atoms was made with the ORFLS [5] program without any weighting scheme. Each non-hydrogen atom was refined anisotropically. Hydrogen atoms were located from difference-Fourier maps and were included in the refinement process with an isotropic temperature factor $B_H = 1.5\ B_C$ (B_C is the isotropic temperature factor of the carbon atom to which the hydrogen is bonded); atomic scattering factors and anomalous dispersion corrections (for the indium, sulphur, and chloride atoms) were taken from ref. 6. The final conventional R index was 0.063. Final positional parameters are listed in Table 3, main bond distances and angles in Tables 4 and 5. Other bond distances and angles, hydrogen fractional co-ordinates, thermal parameters, observed and calculated structure factors, and details of the least-squares planes are listed in Supplementary Publication No. SUP 22836 (33 pp.).‡

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

† Spectrometer of the 'Groupement Régional de Mesures Physiques de l'Académie de Nancy-Metz'.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

RESULTS

The alkylthio- or arylthio-indium porphyrins [InL(SR)] (4) have been obtained by two different methods: (*a*) the arylthio-complexes were prepared by treating a solution of H_2L (1) in benzenethiol with indium trichloride [equation (i)]; (*b*) the alkylthio-derivatives were synthesised by action of an organothiolithium compound Li[SR] on the chloroindium porphyrins [InL(Cl)] (2) as in equation (ii).

$$\underset{(1)}{H_2L} + InCl_3 \xrightarrow{\text{arenethiol}} \underset{(4)\ R\,=\,\text{aryl}}{[InL(SR)]} \qquad (i)$$

The

$$\underset{(2)}{[InL(Cl)]} \xrightarrow{Li[SR]} \underset{(4)\ R\,=\,\text{alkyl}}{[InL(SR)]} \qquad (ii)$$

metalloporphyrinic systems were obtained with very satisfactory yields (*ca.* 70%). In the solid state they are relatively stable, but decay in solution and in the presence of light and their chromatographic purification must be carried out in the absence of light.

The analytical results and the mass-spectral data agree perfectly with the proposed molecular formulae. The parent peak corresponds either to $[M - SR]^+$ for the octaethylporphyrinate complexes or to the recombination ions $[M - SC_6H_5 + H]^{\cdot+}$ and $[M - SR + 2\,H]^+$ for the tetraphenylporphyrinate derivatives. All these results suggest that the SR group (R = alkyl or aryl) is probably bonded to the metal. However, this could only be confirmed after analysis of the n.m.r. spectra.

The morphology and the chemical shifts of the macrocycle protons (Table 6) of [InL(SR)] (4) are nearly identical to those observed for the [InL(Cl)] (2) complexes, but the SR protons are strongly shielded; this result implies that the sulphur atom is bonded to the indium. The presence of In–S(C) (300—340 cm^{-1}) and of (In)S–C bonds (570—700 cm^{-1}) (Table 2) in most of the complexes was confirmed by comparison of the i.r. spectra of H_2L, [InL(Cl)], and [InL(SR)]. The absorption spectra (Table 7) of compounds (4) are of the ' normal ' type and show the following α, β, and Soret bands: 580, 546, and 420 nm for L = oep and 610, 568, and 435 nm for L = tpp.

As mentioned above, complexes (4) can be photochemically oxidized to give derivatives (5). The products of irradiation, under an oxygen stream, depend on the experimental conditions (Scheme 1). Thus, near 0 °C, complex (5) is the major product with a small quantity of its oxidation derivative (6), but at 50—60 °C (6) is the only product of the reaction.

The analytical results for complexes (5) are in accordance with the sulphinate formula assigned. Metal sulphinates of the $M(SO_2R)$ type (R = an alkyl or σ-bonded carbon group) exhibit one of the following linkages according to the nature of the metal: *S*-, *O*-, *OO'*- (inter- or intra-molecular), or *OS*-sulphinate.

In the mass spectra the molecular peak generally appears. The parent peak corresponds to $[M - SO_2R + H]^{\cdot+}$ and the main fragments to fission between the metal atom and the axial ligand, *i.e.* the $[InL]^+$ moiety resulting from this fragmentation recombines with a proton to give the

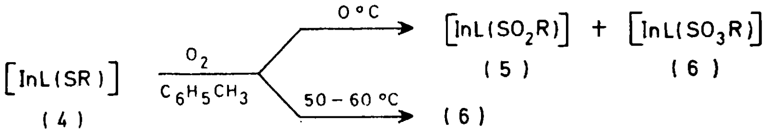
TABLE 1

Experimental data and yields

	Complex [a]	Reaction solvent	Recrystallisation solvent [b]	Yield (%)	Analysis (%) [c]				
					C	H	N	S	In
(4a)	$[In(oep)(SCH_3)]$	C_6H_6 or $C_6H_5CH_3$	A–B (1 : 1)	80	63.7 (64.0)	6.70 (6.85)	7.90 (8.05)	4.60 (4.60)	16.3 (16.55)
(4b)	$[In(oep)\{SC(CH_3)_3\}]$		B–C (1 : 2)	73	64.4 (65.2)	7.30 (7.25)	7.80 (7.60)	4.30 (4.35)	15.2 (15.6)
(4c)	$[In(oep)(SC_6H_5)]$	C_6H_5SH	B–C (1 : 3)	82	66.6 (66.65)	6.50 (6.55)	7.50 (7.40)	4.20 (4.25)	15.3 (15.15)
(4d)	$[In(tpp)(SCH_3)]$	C_6H_6 or $C_6H_5CH_3$	A–B (3 : 2)	70	69.6 (69.8)	4.20 (4.05)	7.10 (7.30)	4.00 (4.15)	14.8 (14.85)
(4e)	$[In(tpp)\{SC(CH_3)_3\}]$		B–C (1 : 1)	71	70.6 (70.6)	4.60 (4.60)	6.90 (6.85)	3.80 (3.95)	13.9 (14.05)
(4f)	$[In(tpp)(SC_6H_5)]$	C_6H_5SH	B–C (1 : 4)	70	71.6 (71.75)	4.10 (4.00)	6.70 (6.70)	3.90 (3.80)	13.2 (13.7)
(5a)	$[In(oep)(SO_2CH_3)]$	CH_2Cl_2 [d] or $C_6H_5CH_3$ [e]	A–D (9 : 1)	75	60.9 (61.15)	6.50 (6.55)	7.70 (7.70)	4.30 (4.40)	15.7 (15.8)
(5c)	$[In(oep)(SO_2C_6H_5)]$		A–B (2 : 1)	72	63.2 (63.95)	6.20 (6.25)	7.00 (7.10)	4.20 (4.05)	14.5 (14.55)
(5d)	$[In(tpp)(SO_2CH_3)]$		E–D (9 : 1)	60	66.4 (67.05)	3.90 (3.90)	6.80 (6.95)	3.50 (4.00)	14.2 (14.25)
(5f)	$[In(tpp)(SO_2C_6H_5)]$		A–B (2 : 1)	56	68.8 (69.15)	3.90 (3.85)	5.70 (6.45)	3.70 (3.70)	[f]
(6a)	$[In(oep)(SO_3CH_3)]$	$C_6H_5CH_3$	A–F (2 : 1)	70	60.0 (59.9)	6.40 (6.40)	7.50 (7.55)	4.60 (4.30)	15.5 (15.45)
(6b)	$[In(oep)\{SO_3C(CH_3)_3\}]$		A–B (1 : 2)	90	61.1 (61.2)	6.80 (6.80)	7.10 (7.15)	4.00 (4.10)	14.7 (14.65)
(6c)	$[In(oep)(SO_3C_6H_5)]$		A–B (2 : 1)	87	61.10 (62.65)	6.10 (6.15)	7.00 (6.95)	4.00 (4.00)	14.2 (14.25)
(6d)	$[In(tpp)(SO_3CH_3)]$		E	59	65.5 (65.7)	3.90 (3.80)	6.60 (6.80)	3.90 (3.90)	13.9 (13.95)
(6e)	$[In(tpp)\{SO_3C(CH_3)_3\}]$		G–H (1 : 1)	72	66.5 (66.65)	4.30 (4.30)	6.40 (6.50)	3.60 (3.70)	13.2 (13.3)
(6f)	$[In(tpp)(SO_3C_6H_5)]$		A–B (2 : 1)	50	67.6 (67.9)	3.80 (3.75)	6.10 (6.35)	3.50 (3.60)	13.0 (13.0)

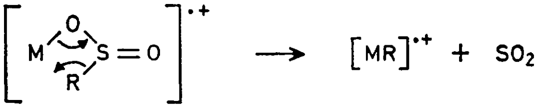
[a] The complexes $[In(oep)\{SO_2C(CH_3)_3\}]$ (5b) and $[In(tpp)\{SO_2C(CH_3)_3\}]$ (5e) are very sensitive to molecular oxygen and their elemental analyses are not satisfactory. [b] A = Methylene chloride; B = n-hexane; C = benzene; D = di-isopropyl ether; E = 1,2-dichloroethane; F = light petroleum; G = 1,2-dimethoxyethane; H = n-heptane. [c] Calculated values are given in parentheses. [d] Insertion reaction. [e] Photochemical oxidation. [f] Not obtained.

$[\mathrm{InL} + \mathrm{H}]^{\cdot +}$ ion. The characteristic fragments of the porphyrin skeleton occur at the lowest *m/e* values. All compounds (5) exhibit the $[M - \mathrm{SO_2}]^{\cdot +}$ or $[M - \mathrm{SO_2} + \mathrm{H}]^{+}$ ion; this fragmentation mode is also observed in the mass spectra of $\mathrm{M(SO_2R)}$ sulphinates. These moieties are obtained by elimination of a molecule of sulphur dioxide before fission of the $\mathrm{SO_2}$–R bond and their formation is explained by a new linkage implying a four-centre cyclic mechanism (Scheme 2). As far as we know, this characteristic has been reported only for compounds having an *O*-sulphinate linkage; complexes (5) must therefore have this structure.



SCHEME 1

The high-resolution ^{1}H n.m.r. data (Table 6) do not allow us to confirm these conclusions: nevertheless we note the large deshielding of the methyl protons of $[\mathrm{In(tpp)(SO_2CH_3)}]$ with respect to $[\mathrm{In(tpp)(CH_3)}]$ $[\delta(\mathrm{CH_3}) = -1.61$ and -5.14 p.p.m, respectively]. The absence of characteristic indium–sulphur vibration bands in the range 300—340 cm^{-1} and the presence of the $\mathrm{SO_2}$-group vibrations in the range 900—1 100 cm^{-1} allow us to completely eliminate an *S*-sulphinate structure. But a choice between the arrangements *O*- or



SCHEME 2

TABLE 2

Characteristic i.r. and mass-spectral data

Complex	I.r. (cm^{-1}, CsI pellets) ν(In–S)	ν(C–S)	Mass spectra *m/e*	Relative intensity	Fragmentation pattern
(4a)	310		695	2.81	$[\mathrm{In(oep)(SCH_3)} + \mathrm{H}]^{+}$
			694	3.04	$[\mathrm{In(oep)(SCH_3)}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(4b)	340	585	737	7.98	$[\mathrm{In(oep)\{SC(CH_3)_3\}} + \mathrm{H}]^{+}$
			736	2.29	$[\mathrm{In(oep)\{SC(CH_3)_3\}}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(4c)	330		757	6.37	$[\mathrm{In(oep)(SC_6H_5)} + \mathrm{H}]^{+}$
			756	0.79	$[\mathrm{In(oep)(SC_6H_5)}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(4d)	320		775	4.39	$[\mathrm{In(tpp)(SCH_3)} + \mathrm{H}]^{+}$
			729	100.00	$[\mathrm{In(tpp)} + 2\ \mathrm{H}]^{+}$
(4e)	340	580	816	1.25	$[\mathrm{In(tpp)\{SC(CH_3)_3\}}]^{\cdot +}$
			727	100.00	$[\mathrm{In(tpp)}]^{+}$
(4f)	320, 330		837	7.00	$[\mathrm{In(tpp)(SC_6H_5)} + \mathrm{H}]^{+}$
			728	100.00	$[\mathrm{In(tpp)} + \mathrm{H}]^{\cdot +}$
	ν(S–O)				
(5a)	920, 930, 1 025, 1 100		726	0.68	$[\mathrm{In(oep)(SO_2CH_3)}]^{\cdot +}$
			662	0.19	$[\mathrm{In(oep)(CH_3)}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(5c)	900, 910, 1 040, 1 100		788	1.95	$[\mathrm{In(oep)(SO_2C_6H_5)}]^{\cdot +}$
			724	0.87	$[\mathrm{In(oep)(C_6H_5)}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(5d)	920, 970, 1 040, 1 050		728	100.00	$[\mathrm{In(tpp)} + \mathrm{H}]^{\cdot +}$
(5f)	910, 940, 1 040, 1 080		868	0.02	$[\mathrm{In(tpp)(SO_2C_6H_5)}]^{\cdot +}$
			805	4.89	$[\mathrm{In(tpp)(C_6H_5)} + \mathrm{H}]^{+}$
			804	1.22	$[\mathrm{In(tpp)(C_6H_5)}]^{\cdot +}$
			728	100.00	$[\mathrm{In(tpp)} + \mathrm{H}]^{\cdot +}$
	$\nu(\mathrm{SO_3})$				
(6a)	1 060, 1 070, 1 210, 1 290		743	100.00	$[\mathrm{In(oep)(SO_3CH_3)} + \mathrm{H}]^{+}$
			742	44.90	$[\mathrm{In(oep)(SO_3CH_3)}]^{\cdot +}$
(6b)	1 040, 1 140, 1 170, 1 200		785	19.21	$[\mathrm{In(oep)\{SO_3C(CH_3)_3\}} + \mathrm{H}]^{+}$
			784	1.97	$[\mathrm{In(oep)\{SO_2C(CH_3)_3\}}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(6c)	1 040, 1 125 1 140, 1 210, 1 270, 1 300		805	4.20	$[\mathrm{In(oep)(SO_3C_6H_5)} + \mathrm{H}]^{+}$
			804	8.60	$[\mathrm{In(oep)(SO_3C_6H_5)}]^{\cdot +}$
			647	100.00	$[\mathrm{In(oep)}]^{+}$
(6d)	1 040, 1 130, 1 150, 1 250, 1 260		823	91.11	$[\mathrm{In(tpp)(SO_3CH_3)} + \mathrm{H}]^{+}$
			822	20.00	$[\mathrm{In(tpp)(SO_3CH_3)}]^{\cdot +}$
			728	100.00	$[\mathrm{In(tpp)} + \mathrm{H}]^{\cdot +}$
(6e)	1 040, 1 120, 1 140, 1 270, 1 285		865	64.78	$[\mathrm{In(tpp)\{SO_3C(CH_3)_3\}} + \mathrm{H}]^{+}$
			864	5.22	$[\mathrm{In(tpp)\{SO_3C(CH_3)_3\}}]^{\cdot +}$
			728	100.00	$[\mathrm{In(tpp)} + \mathrm{H}]^{\cdot +}$
(6f)	1 040, 1 130, 1 160, 1 270		885	91.66	$[\mathrm{In(tpp)(SO_3C_6H_5)} + \mathrm{H}]^{+}$
			884	6.25	$[\mathrm{In(tpp)(SO_3C_6H_5)}]^{\cdot +}$
			728	100.00	$[\mathrm{In(tpp)} + \mathrm{H}]^{\cdot +}$

OO'-sulphinate is more difficult. By comparison with compounds (4), the absorption spectra of (5) show a hypsochromic shift of *ca.* 10 nm for the α and β bands and 12 nm for the Soret band.

TABLE 3

Fractional co-ordinates (× 10^4) and estimated standard deviations of $[In(tpp)(SO_3CH_3)]\cdot 2C_2H_4Cl_2$

Atom	*x/a*	*y/b*	*z/c*
In(1)	5 000(0)	5 000(0)	0(0)
In(2)	5 000(0)	5 000(0)	5 000(0)
N(1)	6 594(8)	5 108(8)	−419(9)
C(1)	7 268(11)	4 237(10)	−229(11)
C(2)	8 252(12)	4 650(11)	−697(13)
C(3)	8 172(11)	5 735(11)	−1 194(13)
C(4)	7 110(10)	6 004(10)	−1 000(12)
C(5)	6 683(11)	7 070(10)	−1 408(11)
N(2)	4 898(10)	6 698(9)	−693(11)
C(6)	5 662(11)	7 363(9)	−1 266(12)
C(7)	5 228(13)	8 420(11)	−1 782(12)
C(8)	4 179(12)	8 364(11)	−1 486(13)
C(9)	3 964(12)	7 288(11)	−837(13)
C(10)	2 999(11)	6 840(11)	−373(13)
C(11)	7 381(12)	7 930(11)	−2 097(14)
C(12)	7 798(13)	7 879(12)	−3 029(15)
C(13)	8 444(15)	8 681(15)	−3 688(15)
C(14)	8 693(13)	9 552(14)	−3 410(17)
C(15)	8 285(12)	9 629(12)	−2 500(15)
C(16)	7 637(12)	8 815(13)	−1 865(13)
C(17)	7 933(12)	2 355(11)	586(13)
C(18)	7 895(14)	1 465(13)	210(14)
C(19)	8 741(17)	767(14)	407(16)
C(20)	9 594(16)	987(15)	849(17)
C(21)	9 620(14)	1 862(16)	1 195(17)
C(22)	8 745(14)	2 539(15)	1 071(16)
2N(1)	3 512(9)	4 486(8)	4 994(10)
2C(1)	3 189(11)	3 421(10)	5 212(11)
2C(2)	2 138(11)	3 427(11)	4 951(12)
2C(3)	1 846(11)	4 486(11)	4 534(12)
2C(4)	2 699(11)	5 132(11)	4 533(12)
2C(5)	2 737(11)	6 306(11)	4 135(12)
2N(2)	4 515(10)	6 645(10)	4 444(12)
2C(6)	3 526(13)	6 951(12)	4 123(13)
2C(7)	3 553(12)	8 119(11)	3 675(13)
2C(8)	4 524(13)	8 464(12)	3 793(13)
2C(9)	5 126(11)	7 496(11)	4 255(12)
2C(10)	6 164(11)	7 497(11)	4 411(12)
2C(11)	1 786(10)	6 849(11)	3 584(13)
2C(12)	1 097(14)	7 367(13)	4 113(16)
2C(13)	219(15)	7 886(14)	3 583(18)
2C(14)	60(13)	7 864(14)	2 647(18)
2C(15)	751(15)	7 328(15)	2 164(16)
2C(16)	1 618(13)	6 824(14)	2 662(14)
2C(17)	3 352(11)	1 438(11)	5 811(12)
2C(18)	3 711(13)	776(13)	5 256(15)
2C(19)	3 274(15)	−217(14)	5 474(16)
2C(20)	2 483(15)	−567(13)	6 201(18)
2C(21)	2 087(14)	76(14)	6 752(15)
2C(22)	2 562(13)	1 076(12)	6 525(13)
S	4 915(3)	5 442(3)	7 334(3)
O(1)	4 647(8)	4 845(7)	8 441(8)
O(2)	4 589(8)	4 830(8)	6 719(8)
CH	4 089(23)	6 598(16)	6 989(18)
O(3)	4 038(11)	4 218(13)	2 870(11)
Cl(1)	4 207(13)	9 023(9)	1 142(9)
Cl(2)	6 856(15)	8 537(11)	1 188(10)
C_s(1) *	4 488(35)	7 660(22)	1 502(23)
C_s(2) *	5 733(34)	7 784(25)	1 154(32)
Cl(3)	761(13)	6 249(17)	6 937(11)
Cl(4)	1 429(12)	4 040(18)	8 818(12)
C_s(3) *	809(40)	5 109(38)	6 867(37)
C_s(4) *	1 809(28)	4 547(36)	7 334(32)

* Carbon atom of solvent.

The results of previous studies lead us to postulate an *O*-sulphinate structure for compounds (5), but a study of their oxidation derivatives may provide further information.

TABLE 4

Main bond distances (Å) in $[In(tpp)(SO_3CH_3)]\cdot 2C_2H_4Cl_2$

First molecule		Second molecule	
(*a*) Co-ordination polyhedron			
In(1) N(21)	2.107(11)	In(2)–2N(21)	2.078(12)
In(1)–N(22)	2.113(11)	In(2)–2N(22)	2.131(12)
In(1)–O(1)	2.352(12)	In(2)–O(2)	2.357(11)
In(1)–C(10)	3.454(14)	In(2)–2C(10)	3.483(14)
In(1)–C(5)	3.468(12)	In(2)–2C(5)	3.450(14)
In(1)–S	3.581(5)	In(2)–S	3.522(5)
(*b*) Macrocycles			
N(21)–C(1)	1.39(2)	2N(21)–2C(1)	1.41(2)
N(21)–C(4)	1.34(2)	2N(21)–2C(4)	1.39(2)
C(1)–C(2)	1.42(2)	2C(1)–2C(2)	1.45(2)
C(1)–C(10)	1.41(2)	2C(1)–2C(10)	1.42(2)
C(2)–C(3)	1.36(2)	2C(2)–2C(3)	1.37(2)
C(3)–C(4)	1.45(2)	2C(3)–2C(4)	1.42(2)
C(4)–C(5)	1.43(2)	2C(4)–2C(5)	1.46(2)
C(5)–C(6)	1.39(2)	2C(5)–2C(6)	1.35(2)
C(5)–C(25)	1.48(2)	2C(5)–2C(25)	1.53(2)
N(22)–C(6)	1.35(2)	2N(22)–2C(6)	1.40(2)
N(22)–C(9)	1.41(2)	2N(22)–2C(9)	1.34(2)
C(6)–C(7)	1.45(2)	2C(6)–2C(7)	1.45(2)
C(7)–C(8)	1.39(2)	2C(7)–2C(8)	1.38(2)
C(8)–C(9)	1.41(2)	2C(8)–2C(9)	1.46(2)
C(9)–C(10)	1.41(2)	2C(9)–2C(10)	1.39(2)
C(10)–C(31)	1.56(2)	2C(10)–2C(31)	1.48(2)
(*c*) Sulphonate group			
S–O(1)	1.485(10)	S–2N(22)	3.857(17)
S–O(2)	1.474(14)	S–N(21)	3.869(14)
S–O(3)	1.424(15)	O(3)–2N(21)	3.146(22)
S–CH_3	1.786(24)	CH(3)–2N(22)	3.55(3)
S–2N(21)	3.683(14)	CH(3)–N(22)	3.55(3)
S–N(22)	3.711(17)	O(3)–C(4)	3.23(2)

We therefore endeavoured to specify the structure of complexes (6). The $[InL(SO_3R)]$ formulation is derived from the analytical results and its validity was checked by

TABLE 5

Main bond angles (°) in $[In(tpp)(SO_3CH_3)]\cdot 2C_2H_4Cl_2$*

First molecule		Second molecule	
N(1)–In(1)–N(1^{i})	180.0(0)	2N(1)–In(2)–2N(1^{i})	180.0(0)
N(1)–In(1)–N(2)	88.9(4)	2N(1)–In(2)–2N(2)	91.0(5)
N(1)–In(1)–N(2^{i})	91.1(4)	2N(1)–In(2)–2N(2^{i})	89.0(5)
N(1)–In(1)–O(1)	91.6(5)	2N(1)–In(2)–O(2)	87.4(5)
N(1)–In(1)–O(1^{i})	88.4(5)	2N(1)–In(2)–O(2^{i})	92.6(5)
N(2)–In(1)–O(1)	89.5(5)	2N(2)–In(2)–O(2)	92.2(5)
N(2)–In(1)–O(1^{i})	90.5(5)	2N(2)–In(2)–O(2^{i})	87.8(5)
C(4)–N(1)–C(1)	108.3(1.0)	2C(4)–2N(1)–2C(1)	105.1(1.1)
N(1)–C(1)–C(2)	107.4(1.1)	2N(1)–2C(1)–2C(2)	109.6(1.1)
N(1)–C(1)–C(10)	124.5(1.2)	2N(1)–2C(1)–2C(10)	123.7(1.3)
C(2)–C(1)–C(10)	128.0(1.3)	2C(2)–2C(1)–2C(10)	126.6(1.1)
C(1)–C(2)–C(3)	108.9(1.3)	2C(1)–2C(2)–2C(3)	106.8(1.3)
C(2)–C(3)–C(4)	105.7(1.2)	2C(2)–2C(3)–2C(4)	107.6(1.3)
N(1)–C(4)–C(5)	126.0(1.2)	2N(1)–2C(4)–2C(5)	123.0(1.3)
N(1)–C(4)–C(3)	109.7(1.1)	2N(1)–2C(4)–2C(3)	110.6(1.2)
C(3)–C(4)–C(5)	124.3(1.1)	2C(3)–2C(4)–2C(5)	126.3(1.3)
C(4)–C(5)–C(6)	126.4(1.1)	2C(4)–2C(5)–2C(6)	128.3(1.3)
C(6)–C(5)–C(25)	116.7(1.1)	2C(6)–2C(5)–2C(25)	117.6(1.2)
C(4)–C(5)–C(25)	116.8(1.2)	2C(4)–2C(5)–2C(25)	113.9(1.3)
C(6)–N(2)–C(9)	108.1(1.0)	2C(6)–2N(2)–2C(9)	112.2(1.2)
C(5)–C(6)–N(2)	126.1(1.1)	2C(5)–2C(6)–2N(2)	128.1(1.3)
C(5)–C(6)–C(7)	125.0(1.2)	2C(5)–2C(6)–2C(7)	126.7(1.5)
C(7)–C(6)–N(2)	108.7(1.2)	2C(7)–2C(6)–2N(2)	105.0(1.4)
C(6)–C(7)–C(8)	107.3(1.1)	2C(6)–2C(7)–2C(8)	108.8(1.4)
C(7)–C(8)–C(9)	107.2(1.2)	2C(7)–2C(8)–2C(9)	106.8(1.3)
C(8)–C(9)–C(10)	127.7(1.3)	2C(8)–2C(9)–2C(10)	124.5(1.3)
N(2)–C(9)–C(10)	123.7(1.2)	2N(2)–2C(9)–2C(10)	128.1(1.3)
N(2)–C(9)–C(8)	108.7(1.2)	2N(2)–2C(9)–2C(8)	107.1(1.3)
C(9)–C(10)–C(1)	129.9(1.3)	2C(9)–2C(10)–2C(1)	126.7(1.3)
Sulphonate group			
O(1)–S–O(2)	110.5(6)	O(1)–S–CH_3	105.3(0.9)
O(1)–S–O(3)	112.4(7)	O(2)–S–CH_3	103.4(1.0)
O(2)–S–O(3)	115.0(9)	O(3)–S–CH_3	109.5(1.1)
In(1)–O–S	136.7(6)	In(2)–O(2)–S	132.3(6)

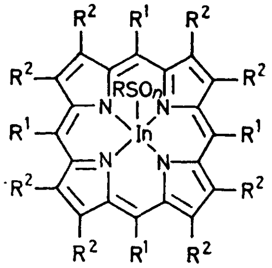
* Symmetry equivalent position i: $1 - x$, $1 - y$, $\bar{z}$.

mass spectrometry. In each case, the molecular peak appears at the expected value and corresponds to the parent peak for L = oep; for L = tpp the parent peak is the recombination ion $[M - SO_3R + H]^{\cdot +}$.

The morphology and chemical shifts of the macrocyclic protons are practically the same for complexes (5) and their oxidation products (6): only the protons of the R groups of $[InL(SO_3R)]$ complexes are more deshielded than those of the corresponding sulphinates $[InL(SO_2R)]$ [$\delta(CH_3)$ = +0.06 and −0.61 p.p.m. respectively (L = tpp)]. This result can be attributed to the effect of the third oxygen atom bonded to the sulphur. The ^1H n.m.r. spectra therefore give meaningful structural information. Indeed, complexes (6) show a structure of the sulphonate type, which is usual for compounds arising from oxidation of *O*- or *OO'*-sulphinate structures.

TABLE 6

N.m.r. data *



n = 0,2 or 3

Compound	R^1	R^2	R	Protons of R^1		Protons of R^2		Protons of R	
				multiplicity, intensity	δ	multiplicity, intensity	δ	multiplicity, intensity	δ
(4a)	H	C_2H_5	CH_3	s, 4	10.30	t, 24 q, 16	1.95 4.15	s, 3	−1.95
(4b)	H	C_2H_5	$C(CH_3)_3$	s, 4	10.30	t, 24 q, 16	1.93 4.15	s, 9	−1.43
(4c)	H	C_2H_5	C_6H_5	s, 4	10.31	t, 24 q, 16	1.97 4.15	*o*-H d, 2 *m*-H t, 2 *p*-H t, 1	4.02 6.15 6.54
(4d)	C_6H_5	H	CH_3	*m*-, *p*-H M, 12 *o*-H M, 8	7.75 8.27	s, 8	9.00	s, 3	−1.61
(4e)	C_6H_5	H	$C(CH_3)_3$	*m*-, *p*-H M, 12 *o*-H M, 8	7.70 8.15	s, 8	8.98	s, 9	−1.16
(4f)	C_6H_5	H	C_6H_5	*m*-, *p*-H M, 12 *o*-H M, 8	7.85 8.25	s, 8	9.02	*o*-H d, 2 *m*-H t, 2 *p*-H t, 1	4.30 6.24 6.56
(5a)	H	C_2H_5	CH_3	s, 4	10.38	t, 24 q, 16	1.98 4.19	s, 3	−0.91
(5b) $[In(oep)\{SO_2C(CH_3)_3\}]$	H	C_2H_5	$C(CH_3)_3$	s, 4	10.34	t, 24 q, 16	1.96 4.17	s, 9	−1.23
(5c)	H	C_2H_5	C_6H_5	s, 4	10.14	t, 24 q, 16	1.91 4.06	*o*-H d, 2 *m*-, *p*-H qnt, 3	4.76 6.73
(5d)	C_6H_5	H	CH_3	*m*-, *p*-H M, 12 *o*-H M, 8	7.73 8.23	s, 8	9.06	s, 3	−0.61
(5e) $[In(tpp)\{SO_2C(CH_3)_3\}]$	C_6H_5	H	$C(CH_3)_3$	*m*-, *p*-H M, 12 *o*-H M, 8	7.79 8.28	s, 8	9.06	s, 9	−1.05
(5f)	C_6H_5	H	C_6H_5	*m*-, *p*-H M, 12 *o*-H M, 8	7.68 8.14	s, 8	9.00	*o*-H d, 2 *m*-, *p*-H qnt, 3	5.02 6.77
(6a)	H	C_2H_5	CH_3	s, 4	10.38	t, 24 q, 16	1.95 4.18	s, 3	−0.36
(6b)	H	C_2H_5	$C(CH_3)_3$	s, 4	10.37	t, 24 q, 16	1.94 4.18	s, 9	−0.86
(6c)	H	C_2H_5	C_6H_5	s, 4	10.24	t, 24 q, 16	1.98 4.09	*o*-H d, 2 *m*-, *p*-H qnt, 3	5.04 6.75
(6d)	C_6H_5	H	CH_3	*m*-, *p*-H M, 12 *o*-H M, 8	7.78 8.28	s, 8	9.16	s, 3	0.06
(6e)	C_6H_5	H	$C(CH_3)_3$	*m*-, *p*-H M, 12 *o*-H M, 8	7.79 8.28	s, 8	9.08	s, 9	−0.63
(6f)	C_6H_5	H	C_6H_5	*m*-, *p*-H M, 12 *o*-H M, 8	7.75 8.15	s, 8	9.06	*o*-H d, 2 *m*-, *p*-H qnt, 3	5.30 6.76

* s = Singlet; d = doublet; t = triplet; q = quadruplet; qnt = quintuplet; M = massive.

The position and intensity of the i.r. bands confirm the sulphonate structure. However, it is very difficult to distinguish between the symmetrical and the asymmetrical SO_3 bands and a choice between an *O*- and an *OO'*-linkage is more difficult than in the case of the corresponding sulphinate compounds. The absorption spectra of compounds (6) and (5) are of the same type and do not give any structural information. Only an *X*-ray study can lead to an unambiguous assignment.

The sulphinate complexes (5) can also be obtained at low temperature by the action of sulphur dioxide on (3), according to equation (iii). Methylene chloride is the solvent and

$$\underset{(3)}{[\mathrm{InL(R)}]} + \mathrm{SO_2} \xrightarrow[-18^{\circ}\mathrm{C}]{\mathrm{CH_2Cl_2}} \underset{(5)}{[\mathrm{InL(SO_2R)}]} \qquad \text{(iii)}$$

the reaction yield is practically quantitative. In order to avoid oxidation of the complexes obtained, it is necessary to work under an inert atmosphere and to use some *p*-hydroquinone in the recrystallisation solvent. The products (5) can be converted into the sulphonates (6) by the action of oxygen [equation (iv)]. The transformations were practically quantitative; for octaethylporphyrin complexes the

$$\underset{(5)}{[\mathrm{InL(SO_2R)}]} \xrightarrow[\text{toluene}]{\mathrm{O_2}} \underset{(6)}{[\mathrm{InL(SO_3R)}]} \qquad \text{(iv)}$$

reaction was often much slower (2 h) than for tetraphenylporphyrin derivatives (0.5 h).

TABLE 7

U.v.–visible spectroscopic data *

Compound	Band between 300 and 400 nm	Soret band		β	α
(4a)	353 (43)	420 (327)	508 (3)	546 (20)	583 (15)
(4b)	355 (42)	420 (307)	508 (2)	547 (19)	584 (14)
(4c)	365 (35)	421 (166)	508 (2)	546 (16)	573 (13)
(4d)	341 (26)	434 (425)	528 (3)	568 (17)	612 (10)
(4e)	343 (33)	435 (257)	528 (4)	568 (20)	612 (13)
(4f)		437 (352)		567 (18)	610 (12)
(5a)	345 (25.5)	407 (516)	503 (2.7)	541 (19.3)	578 (21.7)
(5c)	350 (24.5)	407 (516)	503 (2.7)	541 (19.2)	578 (21.4)
(5d)	325 (16.1)	424 (634)	523 (3.6)	559 (21.5)	598 (8.4)
(5f)	325 (15.9)	426 (677)	523 (3.5)	562 (22.5)	600 (8.4)
(6a)	342 (23.3)	407 (500)	503 (2.7)	538 (18.8)	577 (21.3)
(6b)	342 (21.6)	407 (526)	503 (2.2)	538 (17.5)	577 (20.4)
(6c)	342 (21.6)	407 (472)	503 (3.5)	538 (18.3)	577 (21.7)
(6d)	323 (14.4)	424 (632)	518 (3.2)	556 (22.9)	595 (7.6)
(6e)	323 (14.2)	423 (676)	518 (3.2)	558 (21.6)	596 (7.1)
(6f)	325 (14.9)	426 (668)	518 (3.5)	557 (23)	597 (7.8)

* Values given are of λ/nm with 10^{-3} ε/dm^3 mol^{-1} cm^{-1} in parentheses.

Figure 1 is a stereoscopic view of the complex (6d) in the unit cell. In the solid state, [In(tpp)(SO$_3$CH$_3$)] is an *OO'*-sulphonato-intermolecular complex. It crystallises as a one-dimensional polymer, in the direction parallel to the $\vec{c}$ axis. The fundamental unit of the polymer (Figure 2) comprises two In(tpp) entities bridged by a sulphonato-group. Both non-crystallographically equivalent macrocycles have an inversion centre and are not parallel: the angle between the mean planes of these macrocycles is 28.6(1.2)°. The distance between the porphyrinate cores, measured by the length In(1)–In(2), is *c*/2 [7.015(2) Å]. The sulphur atom is at the same distance from both metal ions [In(1)–S 3.522(5), In(2)–S 3.581(5) Å]. The present crystal structure is the first example of a polymer in metalloporphyrin chemistry.

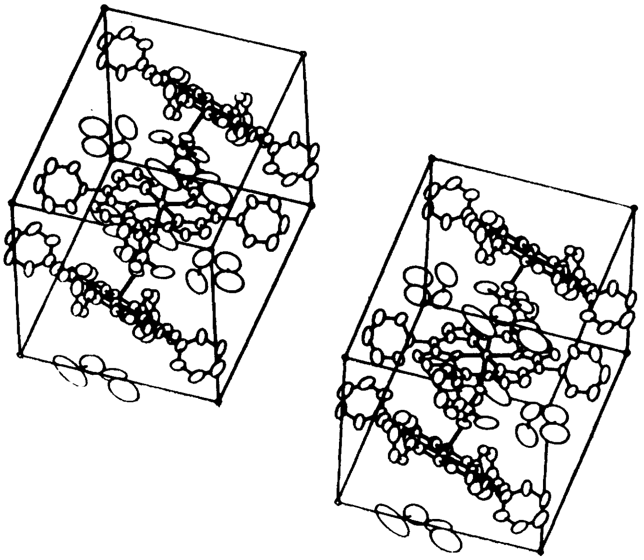


FIGURE 1 Stereoscopic view of the unit cell of the complex [In(tpp)(SO$_3$CH$_3$)]·2C$_2$H$_4$Cl$_2$

Both octahedrally co-ordinated indium atoms lie on the inversion centres ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0) and are rigorously in the perfect plane of the nitrogen atoms. Indeed, the thermal coefficients of the metal atoms are small [2.6(3) and 2.8(3) Å^2] so that these atoms cannot be statistically distributed above and below the porphyrinate plane as observed in [Mn^{II}(tpp)];[7] thus, to accommodate a large ion such as In^{III}, the porphyrinate core must expand and the radius of the central hole [2.11(1) Å] is the same as that observed in Sn(tpp)Cl$_2$.[8] Indium–nitrogen bond lengths are much smaller than those found in [In(tpp)(CH$_3$)][9] [2.205(10) Å] where the indium atom is 0.79(1) Å above the porphyrinate plane.

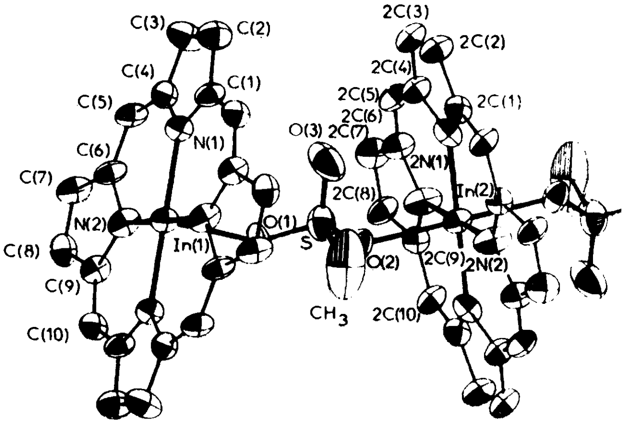


FIGURE 2 Fundamental unit of the polymer and numbering scheme used

Oxygen atoms O(1),O(2) are on the pseudo-quaternary axis of each macrocycle [87.5(4)° < N–In–O < 92.5(4)°]. The sulphonate group is equidistant from both macrocycles and the oxygen–indium distances are statistically equal [2.352(12) and 2.357(11) Å].

The symmetrical position of both macrocycles, with respect to the SO_3CH_3 group, is not dictated by the space group since the sulphur atom is in a general position in the unit cell. This means that the crystal structure must be described by a close packing of $[In(tpp)]^+$ and $[SO_3CH_3]^-$ ions. This assumption is easily verified because the two macrocycles are not parallel and intersect along a straight line parallel to the O(3)–CH_3 ridge of the sulphonate tetrahedron.

The sulphur atom is almost tetrahedrally co-ordinated. The S–O(3) distance [1.42(1) Å] is shorter than the S–O(2) [1.47(1) Å] and S–O(3) [1.48(1)Å] distances corresponding to the metal–oxygen bonds. Because of the ionic interaction between O(1)–In(1) and O(2)–In(2), the S–O(2) bond has double-bond character. Furthermore, the oxygen–sulphur–oxygen bond angles are greater than those of a regular tetrahedron while the methyl–sulphur–oxygen angles are smaller (Table 5).

The porphyrinate core is highly distorted: the nitrogen atoms are not in the mean plane of the macrocycles, their distance from these being ±0.10(2) Å, so that the β-carbon atoms are out of the four-nitrogen plane [0.39(2) for C(7), 0.38(2) for 2C(3), 0.36(2) for C(8), and 0.30(2) Å for 2C(2)]. Finally, the angles between the four-nitrogen plane and the pyrrole groups lie in the range 4.7—10°.

The solvent molecules are in the cavities of the crystal structure and their thermal parameters are very large. The distances between the $C_2H_4Cl_2$ molecules and the polymer are greater than 3.4(2) Å. There is no interaction between the metalloporphyrin and the solvent so that these molecules can easily leave the crystal lattice and thus destroy the crystal periodicity.

DISCUSSION

We have demonstrated the existence in the solid state of the first ionic one-dimensional polymer in metalloporphyrin chemistry. Other polymeric arrangements are known. Thus in $[Sb(oep)(OH_2)][ClO_4]$ [10] the polymeric association occurs *via* hydrogen bonds between the hydroxyl and perchlorate groups, and in 5,10,15,20-tetrakis(*o*-pivalamidophenyl)porphyrinatoiron(II) [11] a bond between an oxygen atom of a pivalamide group and the iron(II) of another molecule stabilises the polymeric arrangement (Fe–O 2.20 Å). The polymeric association of $[In(tpp)(SO_3CH_3)]$ is very different, comprising an ionic association between the $[In(tpp)]^+$ and $[SO_3CH_3]^-$ ions. Such a structure has been postulated by Buchler *et al.*[12] for tin(IV) porphyrins bridged by dicarboxylic acids.

While the polymer described in this paper is unusual in metalloporphyrinic series, such associated structures are frequently observed for the insertion derivatives of sulphur dioxide in d^{10} metal–carbon bonds (*e.g.* trimethyltin methanesulphinate [13] and trimethyltin butanesulphinate [14]). In these compounds, the polymeric chain is also formed by an ionic association of the $[SO_2R]^-$ and $[SnR'_3]^+$ ions. Furthermore, an *OO'*-sulphinate dimeric structure has been postulated by Hsieh [15] for $[\{In(CH_3)_2(SO_2CH_3)\}_2]$.

In conclusion, the polymer described probably results from the nature of the inserted group and also from the electronic state of the metal (d^{10}). In transition-metal complexes with an unfilled *d* shell, such as bis[2-(2-pyridylmethylamino)ethanesulphinato]cobalt(III),[16] an *S*-sulphinate structure is frequently observed, the lone pair of the sulphur atom completing the *d* shell.

These results observed in the solid state raise the question of whether in solution the complex is polymeric or monomeric. Recently Busby and Dolphin [17] have shown that the methylenic protons of metallo-octaethylporphyrin systems are anisochronous if the co-ordination polyhedron of the metal does not possess planar symmetry with respect to the porphyrinate plane, *i.e.* if the metal is out of this plane. Thus, we have studied the n.m.r. characteristics of different concentrations of $[In(oep)(SO_3CH_3)]$ in $CDCl_3$.

At low and medium concentrations (Figure 3) we observe an ABR_3 multiplet for the ethyl groups which can be explained only by the presence of a non-octahedral monomeric structure in solution: in this case the dissolution of the complex destroys the polymeric chains; the structure of the complex is similar to that of $[In(tpp)(CH_3)]$ [9] for which we have shown that the metal is 0.79 Å out of the porphyrinate plane. In a saturated solution (0.1 mmol), the ^1H n.m.r. spectrum of the methylene groups is a large quadruplet which reduces to a singlet by decoupling the methyl groups. Then, the methylenic protons have very similar chemical shifts ($\delta_A - \delta_B \leqslant 0.02$ p.p.m. obtained by simulation of the spectra). The spectrum is approximately an A_2B_3 type so that the magnetic environments of both faces of the macrocycle are equivalent. It follows that aggregates are formed similar to those described in the solid state. This assumption is supported by the fact

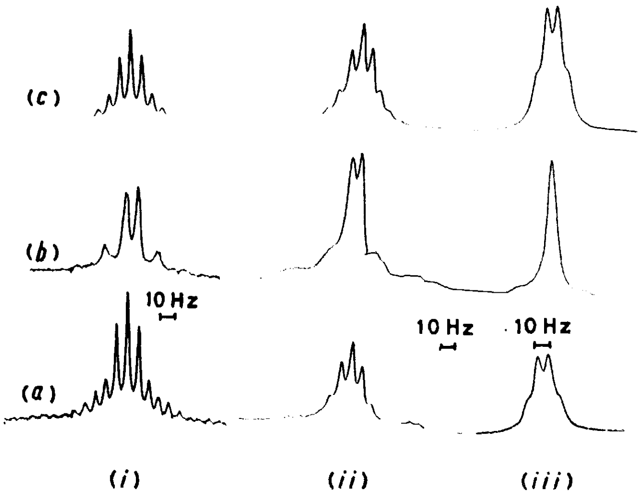


FIGURE 3 250 MHz n.m.r. spectra of A and B methylenic protons of $[In(oep)(SO_3CH_3)]$ in $CDCl_3$: (*a*) experimental, (*b*) decoupled, and (*c*) simulated [$\delta(CH_2)$ = 4.18 p.p.m., $|^2J|$ = 14.5 Hz, $|^3J|$ = 7.6 Hz]. Concentrations: (*i*) 0.0056 mol l^{-1} (δ_A = 4.166, δ_B = 4.234 p.p.m.); (*ii*) 0.070 mol l^{-1} (δ_A = 4.176, δ_B = 4.240 p.p.m.); and (*iii*) 0.13 mol l^{-1} (mean δ = 4.100 p.p.m., $\delta_A - \delta_B \leqslant 0.02$ Hz) that the signal width of the polymeric form is 12.5 Hz but that of the monomeric form is only 1.6 Hz. These observations may certainly be explained by a more rigid structure of the SO_3CH_3 group induced by the polymeric form.

In sulphinate complexes, the RSO_2 group usually forms *OO'*-sulphinate intermolecular complexes when bonded to a *d* closed-shell transition metal such as Sn^{4+}. The complex $[In(tpp)(SO_2CH_3)]$, which is the precursor of $[In(tpp)(SO_3CH_3)]$, probably has an *OO'*-sulphinate intermolecular structure for the following reasons. (*a*) The complex $[In(tpp)(SO_3CH_3)]$ presents this type of co-ordination. (*b*) The In^{3+} ion is ' hard ' and $[SO_2R]^-$ may be a soft electron donor *via* the sulphur atom or a hard donor *via* the oxygen atoms; the hard acid–hard base and soft acid–soft base associations are particularly stable. Thus $[In(tpp)(SO_2CH_3)]$ may be considered as an *O*- or *OO'*-sulphinato-complex. (*c*) Based on an *S*-sulphinato-structure, the very easy oxidation of $[In(tpp)(SO_2CH_3)]$ would have been unexpected and difficult to understand because the sulphur atom already possesses a co-ordination number of four.

Conclusion.—In the solid state, $[In(tpp)(SO_3CH_3)]$ is a polymer and the octahedrally co-ordinated indium atom lies rigorously in the perfect plane of the four nitrogen atoms; the indium–nitrogen bonds are short (2.11 Å) and the indium–oxygen bonds have a large ionic character. It is generally assumed that metal ions, of which the ionic radii are greater than that of Sn^{IV} (0.69 Å),[18] cannot lie in the porphyrinate plane. If we had postulated the geometry of $[In(tpp)(SO_3CH_3)]$ by looking only at the ionic radius of In^{III} (0.79 Å) [18] we would have said that the metal ion was out of the porphyrinate plane and suggested a *cis* configuration of an *O*- or *OO'*-sulphonate intramolecular complex. However, the ^1H n.m.r. study has shown that the central ion could be either in or out of the plane, depending on the complex concentration. From this study, it is seen that the size of a cation is not always an important factor in the geometry of a complex.

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