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**Preliminary communication**

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# FIRST SULPHINATO AND SULPHONATO REPRESENTATIVES IN THE METALLOPORPHYRINIC SERIES: ALKYL(ARYL)SULPHINATO- AND -SULPHONATO-INDIUM(III) PORPHYRINS

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## Summary

The insertion of sulphur dioxide between the indium atom and the alkyl(aryl) group bonded to the metal, leads to sulphinatoindium(III)porphyrins. The sulphinato derivatives can easily be oxidized to the corresponding sulphonato compounds. The photochemical oxidation of thioalkyl(aryl)indium(III)porphyrins also gives rise to alkyl(aryl)sulphinato- and -sulphonato-indium(III)porphyrins. The structure of methylsulphonatoindium(III)tetraphenylporphyrin has been established by X-ray diffraction.

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In a recent paper [1] we reported that the action of an organolithium compound (R(Ar)Li) or an organothiolithium compound (R(Ar)SLi) on chloroindium(III)-porphyrins PorInCl leads to alkyl(aryl)indium(III)porphyrins PorInR(Ar) and thioalkyl(aryl)indium(III)porphyrins PorInSR(Ar), respectively. The presence of an indium—carbon bond in the complexes PorInR(Ar) led us to expect that insertion of small molecules between the metal and the alkyl(aryl) groups would occur, and we have studied the insertion of sulphur dioxide; the same products can also be prepared by oxidation of the compounds PorInSR(Ar). We describe below the synthesis results and the crystal structure of methylsulphonato-indium(III)tetraphenylporphyrin.

PorInR(Ar) (0.7 mmol) was dissolved in methylene chloride (90 ml) under argon and hydroquinone (1 mmol) in isopropyl ether (10 ml) was added. The solution was cooled to –18°C and sulphur dioxide was gently bubbled through. The progress of the reaction was monitored by TLC on basic alumina (eluent: chloroform). At the end of the reaction the solvents were evaporated off under reduced pressure and the residual solid recrystallized in an inert atmosphere in a mixture of 1,2-dichloroethane (67.5 ml) and a solution of hydroquinone (0.75 mmol) in isopropyl ether (7.5 ml). The final product (yield: 60 to 75%) was dried and stored under argon.

The reaction can be summarized as in eq. 1 with Por = TPP, OEP*; R = $CH_3$, $C(CH_3)_3$; Ar = $C_6H_5$.

$$\mathrm{PorInR(Ar)} \xrightarrow{SO_2} \underset{(I)}{\mathrm{PorInSO_2R(Ar)}} \qquad (1)$$

The analytical results agree with formula I and the spectral data are: $M^{+\cdot}$ weak; parent peak: $(M - SO_2R(Ar) + H)^+$; two or three bands $\nu$(SO) (between 900 and 1100 $cm^{-1}$) and no band $\nu$(InS) (near 330 $cm^{-1}$).

Complexes I spontaneously oxidize in the presence of air but the reaction is sometimes relatively slow. Oxidation is complete and rapid when $PorInSO_2R(Ar)$ (0.7 mmol) is dissolved in refluxing anhydrous toluene as oxygen is bubbled through. The solid obtained after evaporation in vacuo of the solvent is recrystallized from a 2/1 methylene chloride-n-hexane mixture (yield 50 to 90%). The reaction can be written as eq. 2.

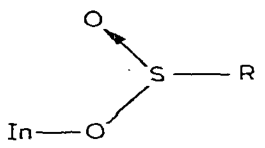
$$\underset{(I)}{\mathrm{PorInSO_2R(Ar)}} \xrightarrow[\Delta]{O_2} \underset{(II)}{\mathrm{PorInSO_3R(Ar)}} \qquad (2)$$

The analytical results agree with formula II and the spectral data are: parent peak: $M^{+\cdot}$ or $(M - SO_3R(Ar) + H)^+$; $\nu_S(SO_3)$: 1035 to 1050 $cm^{-1}$; $\nu_{as}(SO_3)$: 1160 to 1220 $cm^{-1}$; no $\nu$(InS).

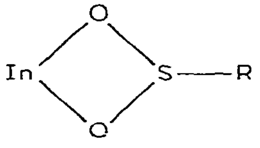
Complexes I and II have also been obtained by photochemical oxidation of thioalkyl(aryl)indium(III)porphyrins PorInSR(Ar).

A solution of PorInSR(Ar) (0.7 mmol) in anhydrous toluene is irradiated and dry oxygen is bubbled in. At room temperature, the reaction leads to a mixture of $PorInSO_2R(Ar)$ (I) and $PorInSO_3R(Ar)$ (II); at 0°C only the compounds I are isolated and at 50°C only the complexes II are obtained. The products are isolated in the state of analytical purity as mentioned above (yield: almost 100%).

The IR data allow elimination of the sulphinato-*S* structures for complexes I or sulphonato-*S* structures for complexes II, but for products I both sulphinato-*O* (III) and sulphinato-*O,O'* (IV) structures must be considered:



(III)



(IV)

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*TPP = mesotetraphenylporphyrin, OEP = octaethylporphyrin.

The crystal structure of $TPPInSO_3CH_3$ has been determined by X-ray diffraction methods. The compound crystallizes in the triclinic system, space group $P\bar{1}$. (Crystal data: $TPPInSO_3CH_3,2C_2H_4Cl_2$: $a$ 13.027(2) Å, $b$ 13.284(2) Å; $c$ 14.029(2) Å; $\alpha$ 68°82(2); $\beta$ 85°31(2); $\gamma$ 88°13(2); $V$ 2255 Å$^3$; $d_c$ 1.46 g/cm$^3$.)

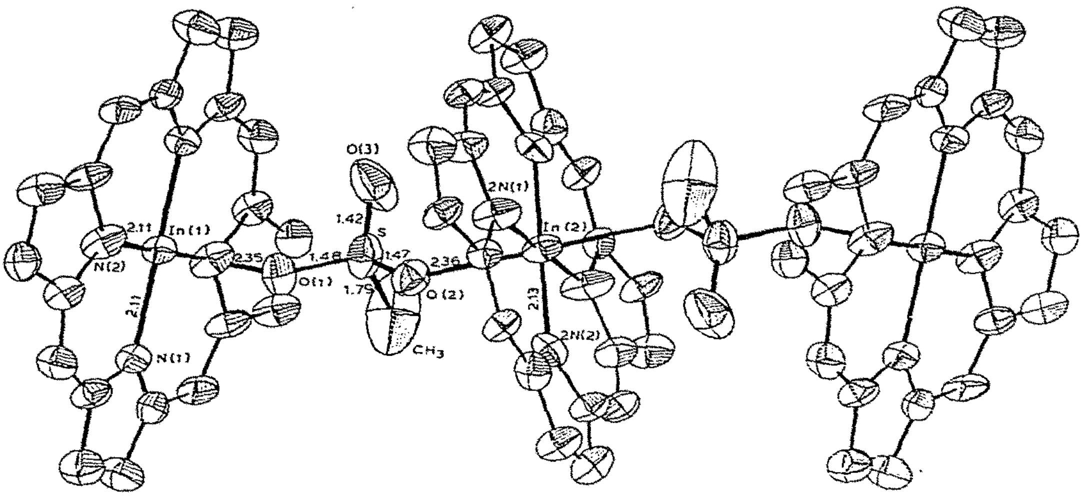

Fig. 1. Structure of $TPPInSO_3CH_3$; the solvent molecules and the phenyl groups are not included.

The structure was refined* to a conventional index of 0.0628 for 3050 reflections. The projection on the $(\vec{a}, \vec{c})$ crystallographic plane shows that the crystal structure consists of infinite polymeric chains parallel to [001]. The indium atoms lie on the inversion centers 1/2, 1/2, 0 and 1/2, 1/2, 1/2 they are octahedrally coordinated and rigorously inside the plane defined by the four nitrogen atoms. The mean ⟨In—N⟩ and ⟨In—O⟩ distances are respectively 2.108(10) and 2.355(10) Å. This latter value is the same as that observed for $(CH_3)_2InAcO$ [2], but is longer than those given for dichloroacetylacetonato-2,2′-bipyridylindium(III) [3] (2.124(3) and 2.164(3) Å), and indicates a partially ionic indium—oxygen bond.

## References

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2 F.W.B. Einstein, M.M. Gilbert and D.G. Tuck, J. Chem. Soc., Dalton, (1973) 248.
3 J.G. Contreras, F.W.B. Einstein and D.G. Tuck, Can. J. Chem., 54 (1974) 3793.

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*We are currently working on the refinement of the crystal structure of $TPPInSO_2CH_3$.