

Preliminary communication

NOVEL SERIES OF METALLOPORPHYRINS. INDIUM(III) PORPHYRINS WITH METAL—CARBON AND METAL—SULPHUR BONDS

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Summary

The first indium(III) porphyrins containing metal—carbon or metal—sulphur bonds are reported.

Metal—carbon bonds in metalloporphyrins are known only when the metal is rhodium [1, 2] or cobalt [3, 4]. In the latter case, it was recently shown [5] that it is possible to insert molecular oxygen between the metal and the carbon atom. However, biomimetic systems of the $\text{PorFeSR}(\text{Ar})$ type, which are moderately stable, have recently been isolated [6].

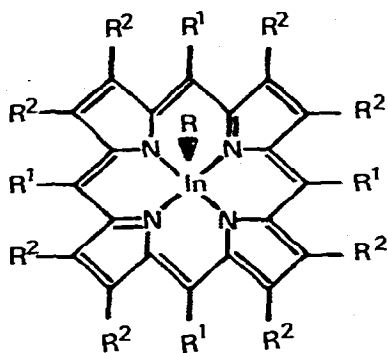
It seemed likely that metal—carbon and metal—sulphur bonds could be produced with other metalloporphyrin systems, in particular with indium(III) porphyrins. Indeed, it has been reported recently [7] that the transport of ^{111}In and ^{59}Fe into reticulocytes is very similar. Moreover, model complexes for the active site of myoglobin and oxymyoglobin have been synthesized, for example, by the action of oxygen on iron(II) "picket fence porphyrins" [8], and the mechanism of oxygen activation is an important current problem [9]. We report here the preparation of the first indium(III) porphyrins with metal—carbon or metal—sulphur bonds.

Indium—carbon bond porphyrins

A certain number of porphyrins with the general formula PorInCl are known, with Por = mesotetraphenyl (TPP) or octaethyl (OEP) porphyrins [10–12]. We have prepared the new metalloporphyrins, I and II, by treating PorInCl with alkyl- (or aryl-)lithium in dry benzene.

The yields of the reaction products and the recrystallization solvents are given in Table 1.

The structure of the compounds can be easily established from the ^1H NMR spectra: the alkyl or aryl protons are strongly shielded; the NMR data are given in Table 2.



(Ia-Ie) $R^1 = C_6H_5$; $R^2 = H$; $R(Ar) = CH_3, C_2H_5, n-C_4H_9, t-C_4H_9, C_6H_5$

(IIa-IIe) $R^1 = H$; $R^2 = C_2H_5$; $R(Ar) = CH_3, C_2H_5, n-C_4H_9, t-C_4H_9, C_6H_5$

TABLE 1
YIELDS OF REACTION AND RECRYSTALLIZATION SOLVENTS OF PorInR COMPOUNDS

Compound	R(Ar)	Molecular formula	Recrystallization solvent	Yield (%)
Ia	CH ₃	C ₄₅ H ₃₁ N ₄ In	CHCl ₃ /CH ₃ OH	70
Ib	C ₂ H ₅	C ₄₆ H ₃₃ N ₄ In	CHCl ₃ /CH ₃ OH	45
Ic	n-C ₄ H ₉	C ₄₈ H ₃₇ N ₄ In	C ₆ H ₆ /CH ₃ OH	67
Id	t-C ₄ H ₉	C ₄₈ H ₃₇ N ₄ In	C ₆ H ₆ /n-hexane	35
Ie	C ₆ H ₅	C ₅₀ H ₃₃ N ₄ In	CH ₂ Cl ₂ /n-hexane	75
IIa	CH ₃	C ₃₇ H ₄₉ N ₄ In	CH ₂ Cl ₂ /petroleum ether	65
IIb	C ₂ H ₅	C ₃₈ H ₄₉ N ₄ In	CH ₂ Cl ₂ /petroleum ether	40
IIc	n-C ₄ H ₉	C ₄₀ H ₅₃ N ₄ In	CH ₂ Cl ₂	64
IId	t-C ₄ H ₉	C ₄₀ H ₅₃ N ₄ In	C ₆ H ₆ /petroleum ether	45
IIe	C ₆ H ₅	C ₄₂ H ₄₉ N ₄ In	C ₆ H ₆	75

TABLE 2
NMR DATA^a OF PorInR COMPOUNDS

Por	CH ₃		C ₂ H ₅		n-C ₄ H ₉		t-C ₄ H ₉		C ₆ H ₅	
	m/i	δ (ppm)	m/i	δ (ppm)	m/i	δ (ppm)	m/i	δ (ppm)	m/i	δ (ppm)
TPP	s/3	-5.08	t/3	-2.48	t/3	-0.48	s/9	-2.68	oHd/2	
			q/2	-4.23	s ₆ /2	-1.56			mHt/2	
					q ₅ /2	-2.20			pHt/1	
					t/2	-4.24				
OEP	s/3	-5.52	t/3	-2.84	t/3	-0.60	s/9	-3.04	oHd/2	
			q/2	-4.68	s ₆ /2	-1.76			mHt/2	
					q ₅ /2	-2.56			pHt/1	
					t/2	-4.64				

^as = singlet; d = doublet; t = triplet; q = quadruplet; q₅ = quintuplet; s₆ = sextuplet.

Indium-sulphur bond porphyrins

We have obtained the indium(III) porphyrins PorInSC₆H₅ (III and IV) (Table 1) by treating PorH₂ with InCl₃ in C₆H₅SH. These compounds are stable, in contrast with their iron analogs.

TABLE 3

YIELDS, MOLECULAR FORMULAE, RECRYSTALLIZATION SOLVENTS AND NMR DATA OF
 PorInSC₆H₅ COMPOUNDS

Compound	Por	Molecular formula	Recrystallization solvent	Yield (%)	NMR data of Ar	
					m/i	δ (ppm)
III	TPP	C ₃₀ H ₃₃ N ₄ SiIn	toluene	50	oH d/2	4.30
					mH t/2	6.24
					pH t/1	6.56
IV	OEP	C ₄₁ H ₄₉ N ₄ SiIn	C ₆ H ₆ /n-hexane	56	oH m/18	4.05
					mH t/2	6.15
					pH t/1	6.54

We are currently investigating insertions of SO₂, CO, CO₂ into the indium-alkyl (or -aryl) bonds and the reaction of molecular oxygen with the compounds of Table 1 and Table 3.

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