

A Cofacial, Dimeric, Metallaoxophlorin Complex: [Indium(III)(octaethyloxophlorin)]₂

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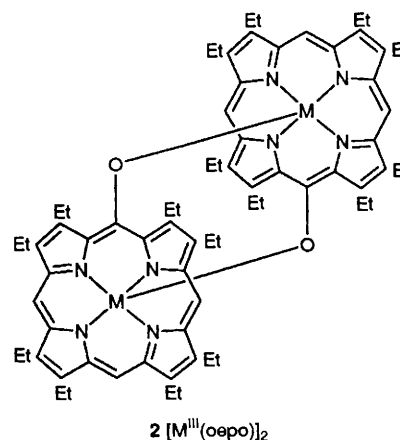
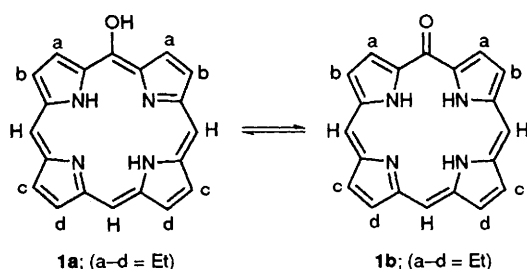
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The X-ray crystal structure of [In^{III}(octaethyloxophlorin)]₂ shows that the centrosymmetric dimeric structure places the planes of the two macrocycles 3.25 Å apart but causes only minimal distortion to the porphyrin-like cores of the molecule.

The coordination chemistry of oxophlorins, **1**,¹ has attracted attention because *meso*-hydroxylation appears to be an important first step in the oxidative degradation of iron porphyrins both in the haem oxygenase reaction and in the model system (coupled oxidation).² Studies of octaethyloxophlorin (H₂oepoH, **1**, a-d = Et) have shown that it coordinates divalent metal ions as the porphyrinic tautomer **1a**.^{3,4} These complexes are subject to oxidation to form air-stable, isolable free radicals.³ With trivalent metal ions it has been suggested that H₂oepoH will coordinate as the keto tautomer, **1b**.^{5,6} However, spectroscopic evidence indicates that the iron(III) and manganese(III) complexes have a

head-to-tail dimeric structure, **2**, with the *meso*-alkoxide groups forming bridges from one macrocycle to the metal in the adjacent macrocycle.⁷⁻⁹

However, despite persistent efforts, crystals of the iron(III) or manganese(III) dimer that would be suitable for crystallographic study have not been obtained. Because this dimeric



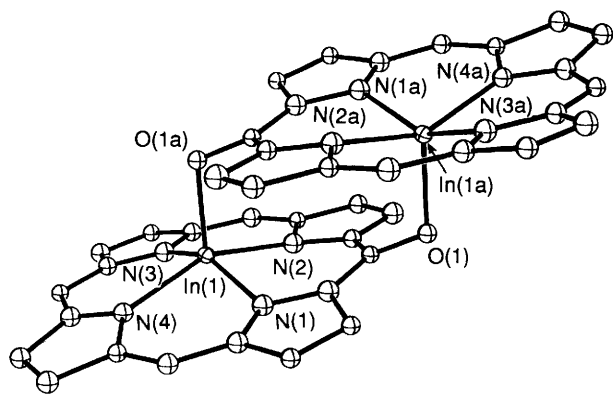


Fig. 1 Perspective view of $[\text{In}^{\text{III}}(\text{oepo})]_2$ with 50% thermal contours for all atoms. For clarity the peripheral ethyl groups have been omitted. Selected bond distances (Å), Molecule 1: In(1)–N(1) 2.152(11), In(1)–N(2) 2.131(11), In(1)–N(3) 2.133(11); In(1)–N(4) 2.166(12), In(1)–O(1a) 2.116(9), O(1)–C(2), 1.32(2). Molecule 2: In(1)–N(5) 2.151(10), In(2)–N(6) 2.159(11), In(2)–N(7) 2.123(13), In(2)–N(8) 2.141(10), In(2)–O(2a) 2.155(9). O(2)–C(38) 1.32(2).

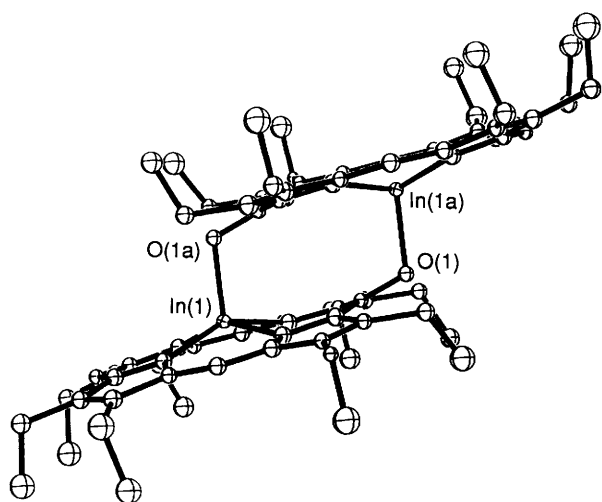


Fig. 2 View of $[\text{In}^{\text{III}}(\text{oepo})]_2$ that emphasizes the planarity of the rings and their relative orientations. Ethyl groups are shown.

structure appears to require tight, cofacial approach between macrocycles and because it has been suggested that higher oligomeric forms might actually be present in these complexes,⁹ we sought to find a trivalent metal that would give a crystalline form of $[\text{M}^{\text{III}}(\text{oepo})]_2$ suitable for X-ray diffraction. The indium(III) derivative does this.

Treatment of **1** with indium(III) chloride and sodium acetate in boiling acetic acid produced a magenta solution. After neutralization with aqueous sodium hydrogencarbonate, extraction with chloroform gave a brown–green solution from which $[\text{In}^{\text{III}}(\text{oepo})]_2$ was isolated after evaporation. A crystal suitable for X-ray diffraction was obtained by slow diffusion of propan-2-ol into a solution of the complex in 1,2-dichlorobenzene.† The complex has a porphyrin-like absorption spectrum: λ_{max} (nm); 413 (Soret), 545, 579, 630.

† *Crystal data*: Dark green–brown blocks of $[\text{In}^{\text{III}}(\text{oepo})]_2 \cdot 4$ $o\text{-Cl}_2\text{C}_6\text{H}_4$ crystallize in the triclinic space group $P\bar{1}$ with $a = 14.794(2)$, $b = 14.812(3)$, $c = 21.364(4)$ Å, $\alpha = 71.314(13)$, $\beta = 87.078(13)$, $\gamma = 89.957(14)^\circ$ at 123 K with $Z = 2$ using $\text{Cu-K}\alpha(\lambda = 1.54178 \text{ Å})$ Ni-filtered radiation. Refinement of 6124 reflections with $F > 6.0 \sigma(F)$ and 515 parameters yields $R = 0.068$; $R_w = 0.074$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

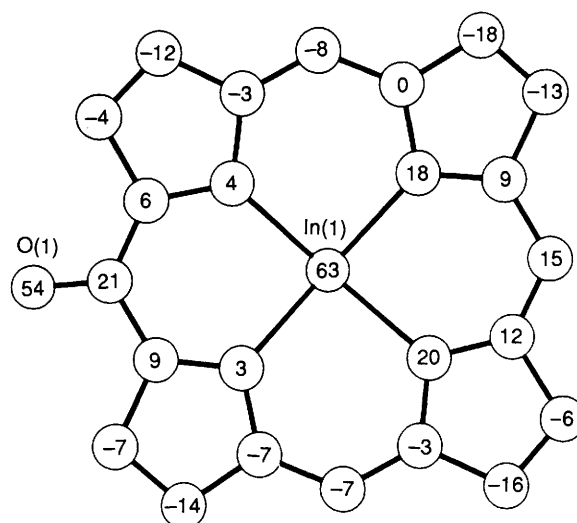


Fig. 3 Formal diagram which shows the out-of-plane displacements (in units of 0.01 Å) of the core atoms from the mean plane of the oxophlorin in the two independent molecules of $[\text{In}^{\text{III}}(\text{oepo})]_2$.

The compound crystallizes with two independent, half-molecules of $[\text{In}^{\text{III}}(\text{oepo})]_2$ and four molecules of 1,2-dichlorobenzene in the asymmetric unit. The two indium dimers are centrosymmetric and have very similar structural parameters. Views of one of the dimers are given in Figs. 1 and 2. The two dimers have different relationships to the 1,2-dichlorobenzene molecules in the solid, but there are no unusually close contacts between the individual molecules that comprise the solid.

Each indium ion is five-coordinate. The average In–N distance is 2.144 Å, and the average In–O distance is 2.115 Å. These distances are consistent with the bond distances in related indium(III) porphyrins.^{10,11}

As Fig. 2 shows, the individual macrocycles are nearly planar. Fig. 3 gives the out-of-plane distances for the atoms in the core. Large out-of-plane distances are observed only for the indium and the oxygen atoms. Otherwise the oxophlorin core is remarkably planar with only a small bowl shaped distortion. The distances between the mean planes of the two macrocycles within the two dimers are 3.263 and 3.242 Å. This places these two units within π – π contact.^{12,13} The distances between the two indium ions in the dimers are 5.471(1) and 5.484(1) Å. It is gratifying to notice that the structural features seen in the previous molecular mechanics calculations on $[\text{Fe}^{\text{III}}(\text{oepo})]_2$ ⁸ are borne out in the structural study of

[In^{III}(oepo)]₂. However, the smaller size of iron(III) and manganese(III), relative to indium(III), suggests that the structure of [Fe^{III}(oepo)]₂ and [Mn^{III}(oepo)]₂ will suffer some distortion. Either the interplanar separation within the dimer will be closer with the smaller metal ions, the M–O distances will be elongated from their ideal values, the out-of-plane displacements of the iron, manganese, or oxygen atoms will be greater, or some combination of all of these will occur in the first row transition and metal dimers.

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