

**A NEW SYNTHESIS OF ACETATO PORPHYRINATO  
INDIUM(III) FROM INDIUM(III) OXIDE AND X-RAY  
CRYSTAL STRUCTURES OF  $\text{In}(\text{tpyp})(\text{OAc})$  AND  
 $\text{In}(\text{tmpp})(\text{OAc})$**

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**Abstract**—The indium porphyrin complexes [ $\text{In}(\text{tpp})(\text{OAc})$ ,  $\text{In}(\text{tpyp})(\text{OAc})$ ,  $\text{In}(\text{tmpp})(\text{OAc})$ ] were prepared in good yields by refluxing the respective porphyrin (tpp, tpyp, tmpp) with  $\text{In}_2\text{O}_3$  in acetic acid containing sodium acetate. The structures of  $\text{In}(\text{tpyp})(\text{OAc})$  and  $\text{In}(\text{tmpp})(\text{OAc})$  were determined by a single-crystal X-ray structure analysis. The indium atom is displaced 0.731 Å from the mean porphyrin plane ( $\text{C}_{20}\text{N}_4$ ). The geometry around the indium centre of the  $\text{In}(\text{tpyp})(\text{OAc})$  molecule has  $\text{In}(1)\text{—O}(1) = 2.185(6)$ ,  $\text{In}(1)\text{—O}(2) = 2.412(6)$  and average  $\text{In}(1)\text{—N}_p = 2.177(5)$  Å. This indicates that an asymmetric-bidentate acetato group is coordinated to the indium(III) atom in  $\text{In}(\text{tpyp})(\text{OAc})$ . In the structure of  $\text{In}(\text{tmpp})(\text{OAc})$  the indium(1)–oxygen distances are  $\text{In}(1)\text{—O}(6) = 2.31(1)$  and  $\text{In}(1)\text{—O}(5) = 2.31(1)$  Å, whereas the indium(1) atom lies 0.597 and 0.758 Å from the four porphyrin nitrogens (4  $\text{N}_p$ ) and the 24-atom porphyrin plane ( $\text{C}_{20}\text{N}_4$ ), respectively. This indicates that  $\text{In}(1)(\text{tmpp})(\text{OAc})$  contains a symmetric bidentate binding of the acetate ligand. Copyright © 1996 Elsevier Science Ltd

Cocolios *et al.*<sup>1</sup> reported the preparation of the acetato (*meso*-tetraphenylporphyrinato)indium(III) complex,  $\text{In}(\text{tpp})(\text{OAc})$ , by reaction of  $\text{CH}_3\text{CO}_2\text{H}$  with aquohydroxo (*meso*-tetraphenylporphyrin-

nato)indium(III),  $\text{In}(\text{tpp})\text{OH}\cdot\text{H}_2\text{O}$ , with a yield of 75%. The synthesis of  $\text{In}(\text{tpp})\text{OH}\cdot\text{H}_2\text{O}$  was achieved starting from chloro-(*meso*-tetraphenylporphyrinato)indium(III),  $\text{In}(\text{tpp})\text{Cl}$ , by exchange reaction through a deactivated basic alumina column (eluent toluene) according to the procedure described by Abraham *et al.*<sup>2</sup> for the

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preparation of hydroxo thallium(III) porphyrins. The In(tpp)Cl was synthesized using previously published methods, with a yield of 85.5%.<sup>3</sup> Hence, the final yield for the preparation of In(tpp)(OAc) starting from tpp and InCl<sub>3</sub> was much less than 64%.

Smith *et al.*<sup>4</sup> reported the preparation and characterization of the acetato [*meso*-tetra(4-pyridyl)porphyrinato]indium(III), In(tpyp)(OAc), complex by adding a molar excess of indium nitrate to a solution of tpyp in glacial acetic acid and refluxing until the visible spectrum indicated that metallation was complete, with a yield of 32%. They reported that In(tpyp)(OAc) in deuterated DMSO (DMSO-*d*<sub>6</sub>) gave a singlet for  $\beta$ -pyrrole at 9.20 ppm, a doublet for 2,6-pyridyl [H<sub>2</sub>, H<sub>3</sub>] at 8.35 ppm and for 3,5-pyridyl [or H<sub>3</sub>, H<sub>3</sub>] at 9.15 ppm; acetate protons gave a singlet at 1.90 ppm.<sup>4</sup> However, Cocolios *et al.*<sup>1</sup> reported that the methyl protons of the acetato ligand gave a singlet at -0.25 ppm for (acetato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)indium(III), In(oep)(OAc), and -0.08 ppm for (acetato)(5,10,15,20-tetraphenylporphyrinato)indium(III), In(tpp)(OAc). Meanwhile, our previous work on Group 13 metal porphyrins such as Tl(tpyp)(OAc),<sup>5</sup> Tl(tpp)(OAc)<sup>6,7</sup> and Ga(tpp)(OAc)<sup>8</sup> at 24°C gave acetate singlets at 0.46, 0.06 and -0.67 ppm, respectively. All the data indicate that acetate protons of In(tpyp)(OAc) in DMSO-*d*<sub>6</sub> should be at about 0 ppm. Its resonance at 1.90 ppm causes some ambiguities. Finally, <sup>13</sup>C NMR data of In(tpyp)(OAc) in DMSO-*d*<sub>6</sub> (or CD<sub>3</sub>COOD) were not reported. It seems that more spectroscopic data are required to resolve the binding type of the acetato ligand coordinated to the indium atom in In(tpyp)(OAc).

In this paper, the synthesis of the title compounds, In(tpp)(OAc) and In(tpyp)(OAc), by a new procedure with a better yield, quite different from those published previously by Cocolios *et al.*<sup>1</sup> for the complex In(tpp)(OAc) and by Smith *et al.*<sup>4</sup> for the complex In(tpyp)(OAc), are reported. X-ray crystal structure determination, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic studies of In(tpyp)(OAc) are discussed. The method is also applied to synthesize the new compound, acetato [*meso*-tetra(4-methoxyphenyl)porphyrinato]indium(III), In(tmpp)(OAc). Finally, the X-ray crystal structure of In(tmpp)(OAc) is described.

## EXPERIMENTAL

### Spectroscopy

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, on a Bruker AM-400 spectrometer in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> at 24°C. <sup>13</sup>C

NMR data are relative to the centre line of CDCl<sub>3</sub> at 77.0 ppm (or CD<sub>2</sub>Cl<sub>2</sub> at 53.6 ppm). <sup>1</sup>H NMR data are relative to CDCl<sub>3</sub> at 7.24 ppm (or CD<sub>2</sub>Cl<sub>2</sub> at 5.30 ppm). Elemental analysis was obtained using a Heraeus CHNO-Rapid elemental analyser. The positive-ion fast atom bombardment mass spectrum (FABMS) was obtained in a nitrobenzyl alcohol (NBA) matrix using a Jeol JMS-SX/SX 102A mass spectrometer.

### Syntheses

In(tpp)(OAc) (**1**). Free base (tpp; 250 mg, 0.047 mmol, from Aldrich) and In<sub>2</sub>O<sub>3</sub> (170 mg, 0.61 mmol) were refluxed for 12 h in 30 cm<sup>3</sup> of acetic acid containing sodium acetate (200 mg, 2.44 mmol). After removal of the solvent (HOAc) under reduced pressure, the dark blue residue was neutralized with a saturated aqueous solution of NaHCO<sub>3</sub> and then dissolved in CHCl<sub>3</sub>. The organic layer was extracted with distilled water (3 × 50 cm<sup>3</sup>) and then dried over Na<sub>2</sub>SO<sub>4</sub>. The product obtained was blue-purple crystals (225 mg, 71%). It was dissolved in CDCl<sub>3</sub> (99.8% from Aldrich) for NMR measurement at 24°C. <sup>13</sup>C NMR,  $\delta$  (ppm): 149.7 (C<sub>2</sub>); 142.2 [C<sub>1</sub>]; 135.1 and 134.3 [C<sub>2</sub>, C<sub>2</sub>']; 132.5 (C <sub>$\beta$</sub> ); 127.9 [C(4)]; 126.7 [C<sub>3</sub>, C<sub>3</sub>']; 121.7 (C<sub>*meso*</sub>); 18.1 (COC\*H<sub>3</sub>); 176.1 (C\*OCH<sub>3</sub>). <sup>1</sup>H NMR,  $\delta$  (ppm): 9.06 ( $\beta$ -pyrrole H); 8.41 and 8.12 [m, H<sub>2</sub>, H<sub>2</sub>'] (or *ortho*- and *ortho'*-H); 7.78 [m, H(3), H(3')], H(4) (or *meta*- and *para*-H); -0.05 (OAc).

In(tpyp)(OAc) (**2**). Free base (tpyp; 250 mg, 0.404 mmol, from Aldrich) and In<sub>2</sub>O<sub>3</sub> (168 mg, 0.606 mmol) were refluxed for 12 h in 30 cm<sup>3</sup> of acetic acid containing NaOAc (206 mg, 2.44 mmol). The following steps were the same as in the preparation of In(tpp)(OAc) (**1**). Blue crystals were obtained with a yield of 72% (230 mg). Crystals were grown by diffusion of ether vapour into a CHCl<sub>3</sub> solution. They were dissolved in CDCl<sub>3</sub> (99.8% from Aldrich) for NMR measurement at 24°C. <sup>13</sup>C NMR (shown in Fig. 1),  $\delta$  (ppm): 149.7 [C<sub>1</sub>]; 149.0 (C<sub>2</sub>); 148.4 [C<sub>3</sub>, C<sub>3</sub>']; 132.8 (C <sub>$\beta$</sub> ); 129.8 and 129.1 [C(2), C(2)']; 119.2 (C<sub>*meso*</sub>); 17.7 (COC\*H<sub>3</sub>); 176.8 (C\*OCH<sub>3</sub>). <sup>1</sup>H NMR,  $\delta$  (ppm): 9.07 ( $\beta$ -pyrrole H); 9.05 [H<sub>3</sub>, H<sub>3</sub>']; 8.35 and 8.06 [H<sub>2</sub>, H<sub>2</sub>']; -0.07 (OAc).

In(tmpp)(OAc) (**3**). Free base (tmpp; 250 mg, 0.34 mmol, from Aldrich) and In<sub>2</sub>O<sub>3</sub> (142 mg, 0.51 mmol) were refluxed for 12 h in 30 cm<sup>3</sup> of acetic acid containing NaOAc (170 mg, 2.05 mmol). The following procedures were the same as in the preparation of In(tpp)(OAc) (**1**). Purple crystals were obtained with a yield of 84% (258 mg). Crystals were grown by diffusion of ether vapour into a CHCl<sub>3</sub> solution. They were dissolved in CD<sub>2</sub>Cl<sub>2</sub>

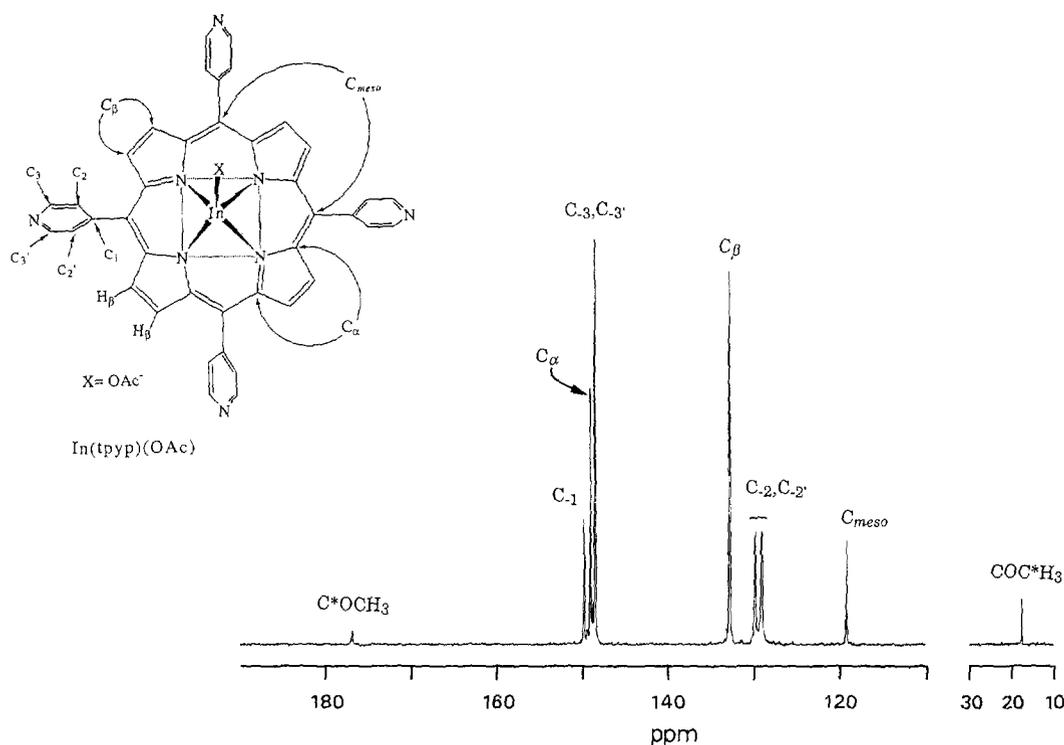


Fig. 1.  $^{13}\text{C}$  broad band NMR spectrum (75.43 MHz) of  $\text{In}(\text{tpyp})(\text{OAc})$  in  $\text{CDCl}_3$  at  $24^\circ\text{C}$ .

(99.6%, from Aldrich) for NMR measurement at  $24^\circ\text{C}$ .  $^{13}\text{C}$  NMR,  $\delta$  (ppm): 176.0 ( $\text{C}^*\text{OCH}_3$ ); 18.0 ( $\text{COC}^*\text{H}_3$ ); 160.0 [ $\text{C}_4$ ]; 150.2 ( $\text{C}_x$ ); 136.3 and 135.6 [ $\text{C}_2, \text{C}_2'$ ]; 134.6 [ $\text{C}_1$ ]; 132.5 ( $\text{C}_\beta$ ); 121.7 ( $\text{C}_{\text{meso}}$ ); 112.6 and 112.5 [ $\text{C}_3, \text{C}_3'$ ]; 55.8 ( $\text{OCH}_3$ ).  $^1\text{H}$  NMR,  $\delta$  (ppm): 9.05 ( $\beta$ -pyrrole H); 8.22 and 7.98 [ $\text{H}_2, \text{H}_2'$ ]; 7.30 and 7.22 [ $\text{H}_3, \text{H}_3'$ ]; 4.04 ( $\text{OCH}_3$ );  $-0.11$  ( $\text{OAc}$ ). MS,  $m/z$  {assignment, rel. intensity, %}: 906  $\{[^{115}\text{In}(\text{tmpp})(\text{OAc})]^+, 11.69\}$ , 847  $\{[^{115}\text{In}(\text{tmpp})]^{-}, 100\}$ .

### Crystallography

Crystal data and other information for  $\text{C}_{42}\text{H}_{27}\text{InN}_8\text{O}_2 \cdot 1.5(\text{H}_2\text{O})$  [or  $\text{In}(\text{tpyp})(\text{OAc}) \cdot 1.5\text{H}_2\text{O}$  (**2**)] and  $\text{C}_{50}\text{H}_{40}\text{InN}_4\text{O}_{6.5}$  [or  $\text{In}(\text{tmpp})(\text{OAc}) \cdot 0.5\text{H}_2\text{O}$ ] are given in Table 1. Measurements were made on a Siemens R3m/V diffractometer using monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) via the  $\theta$ - $2\theta$  ( $\omega$ - $2\theta$ ) scan technique for **2** (or **3**). Absorp-

tion corrections were applied. The structures were solved by direct methods (SHELXTL PLUS) and each structure was refined by full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were calculated using a riding model and included in the structure factor calculation. A selection of bond distances and angles for  $\text{In}(\text{tpyp})(\text{OAc})$  and  $\text{In}(\text{tmpp})(\text{OAc})$  is given in Table 2.

## RESULTS AND DISCUSSION

### Molecular structure of $\text{In}(\text{tpyp})(\text{OAc})$ (**2**)

The skeletal framework of the  $\text{In}(\text{tpyp})(\text{OAc})$  molecule is illustrated in Fig. 2. It reveals the six-coordination of the indium atom with the four nitrogen atoms ( $\text{N}_p$ ) of the porphyrinato group and the asymmetric-bidentate  $\text{OAc}^-$  ligand;<sup>9, 11</sup> the bond distances are:  $\text{In}(1)\text{—O}(1) = 2.185(6)$ ,  $\text{In}(1)\text{—O}(2) = 2.412(6)$ ,\*  $\text{O}(1)\text{—C}(41) = 1.222(8)$ ,  $\text{O}(2)\text{—C}(41) = 1.224(8)$ ,  $\text{C}(41)\text{—C}(42) = 1.52(1) \text{ \AA}$  and the mean  $\text{In}(1)\text{—N}_p = 2.177(5) \text{ \AA}$ . The indium atom lies  $0.731 \text{ \AA}$  above the plane ( $\text{C}_{20}\text{N}_4$ ) defined by the porphyrin ring system and is located  $0.676 \text{ \AA}$  above the  $4\text{N}_p$  plane; this results in an  $\text{O}(1)\text{—In}(1)\text{—O}(2)$  bond angle of  $55.0(2)^\circ$ . The

\* Let  $\text{M—O}(1) = r_1$ ,  $\text{M—O}(2) = r_2$  and  $\Delta r = r_2 - r_1 > 0$ . The binding modes of acetate in the mononuclear complexes,  $\text{M}(\text{Por})(\text{OAc})$ , may be classified as follows: (i) if  $\Delta r < 0.01 \text{ \AA}$ , the binding mode is symmetric-bidentate; (ii) if  $0.1 \text{ \AA} < \Delta r < 1 \text{ \AA}$ , the binding mode is asymmetric-bidentate; (iii) if  $1 \text{ \AA} < \Delta r$ , the binding mode is monodentate.

Table 1. Crystal data for In(tpyp)(OAc)·1.5(H<sub>2</sub>O) [or C<sub>42</sub>H<sub>27</sub>InN<sub>8</sub>O<sub>2</sub>·1.5(H<sub>2</sub>O) (2)] and In(tmpp)(OAc)·0.5(H<sub>2</sub>O) [or C<sub>50</sub>H<sub>40</sub>InN<sub>4</sub>O<sub>6.5</sub> (3)]

Formula	C <sub>42</sub> H <sub>27</sub> InN <sub>8</sub> O <sub>2</sub> ·1.5(H <sub>2</sub> O) (2)	C <sub>50</sub> H <sub>40</sub> InN <sub>4</sub> O <sub>6.5</sub> (3)
Formula weight	817.6	915.7
<i>a</i> (Å)	29.38(1)	16.076(2)
<i>b</i> (Å)	14.768(5)	16.668(2)
<i>c</i> (Å)	17.851(7)	17.962(2)
$\alpha$ (°)	—	88.05(1)
$\beta$ (°)	100.31(3)	88.50(1)
$\gamma$ (°)	—	70.51(1)
<i>V</i> (Å <sup>3</sup> )	7629(19)	4534.1(9)
<i>Z</i>	8	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.425	1.341
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>F</i> (000)	3328	1860
$\mu$ (cm <sup>-1</sup> )	6.71	5.75
<i>R</i> <sup><i>a</i></sup> (%)	4.74	6.70
<i>R<sub>w</sub></i> <sup><i>b</i></sup> (%)	4.66	7.85
GOF	1.00	2.74
<i>A</i> <sup><i>b</i></sup>	1	1
<i>B</i> <sup><i>b</i></sup>	6 × 10 <sup>-4</sup>	0
Crystal size (mm <sup>3</sup> )	0.54 × 0.34 × 0.32	0.40 × 0.40 × 0.20
Data collected	8006	12,316
2 $\theta$ <sub>max</sub> (°)	50	45
Temperature (K)	295	298
Data used	4232	6639
Discrimination	<i>I</i> > 3 $\sigma$ ( <i>I</i> )	<i>F</i> > 6 $\sigma$ ( <i>F</i> )

$$^a R = [\sum \|F_o\| - \|F_c\| / \sum \|F_o\|].$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}; w = A/(\sigma^2 F_o + B F_o^2).$$

dihedral angles between the mean plane of the porphyrin skeleton and the mean planes of the four pyridyl groups are 85.7° [N(5)], 69.5° [N(6)], 82.2° [N(7)] and 105.2° [N(8)].

Hoard and co-workers<sup>12</sup> has calculated that radial strain in the core of a metalloporphyrin is minimized for a 'radius of the central hole' of about 2.01 Å. The core size of In(tpyp)(OAc) is 2.07 Å, which is larger than 2.01 Å. The indium(III) atom is bonded in a highly expanded porphyrinato core in In(tpyp)(OAc) and the porphyrin skeleton is appreciably 'domed' upward toward the indium. This can be seen quantitatively in Fig. 3, which shows the displacement (in Å) of each atom of the porphyrin from the porphyrin mean plane. The average out-of-plane displacements of the indium, nitrogen (N<sub>p</sub>), C<sub>2</sub>, C<sub>meso</sub> and C<sub>β</sub> atoms are 0.73, 0.05, -0.02, -0.02 and -0.13 Å, respectively (shown in Fig. 3). This structure shows marked 'doming' with atoms approximately in descending plane indium, N<sub>p</sub>, C<sub>2</sub>, C<sub>meso</sub>, C<sub>β</sub>. The difference between the displacement of the metal centre from the mean plane of the four pyrrole nitrogens (4N<sub>p</sub>) and the

mean plane of the C<sub>20</sub>N<sub>4</sub> porphyrin skeleton has been used to describe the degree of doming. The degree of doming is 0.06 Å for In(tpyp)(OAc).

In(tpyp)(OAc) is soluble in chloroform but moderately soluble in DMSO. The assignment of the 8.35 and 8.06 ppm signals due to 2,2'-pyridyl protons and the 129.8 and 129.1 ppm signals due to the C<sub>2</sub>, C<sub>2'</sub> carbons indicates that the rotation of the pyridyl group along the C<sub>1</sub>—C<sub>meso</sub> bond is slow at 24°C on the NMR time-scale for In(tpyp)(OAc) in CDCl<sub>3</sub>. In(tpyp)(OAc) in CDCl<sub>3</sub> at -50°C gave a singlet for β-pyrrole protons at 9.08, 8.36 and 8.06 ppm for 2,2'-pyridyl protons, 9.09 and 9.04 ppm for 3,3'-pyridyl protons and an acetate singlet at -0.09 ppm. The <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> at both 24 and -50°C are quite similar except that the same kind of rotation is even slower at -50°C. This results in different chemical shifts for both 2,2'-pyridyl protons (8.36 vs 8.06 ppm) and 3,3'-pyridyl protons (9.09 vs 9.04 ppm) at -50°C for the complex. If In(tpyp)(OAc) is dissolved in DMSO-*d*<sub>6</sub> at 24°C, the acetate group is observed instead of the 1.90 ppm signal reported previously,<sup>4</sup> at -0.54

Table 2. Selection of bond distances (Å) and bond angles (°) for In(tpyp)(OAc) (2) and In(tmpp)(OAc) (3)

Compound 2			
In(1)—O(1)	2.185(6)	In(1)—N(1)	2.178(5)
In(1)—O(2)	2.412(6)	In(1)—N(2)	2.162(5)
O(1)—C(41)	1.222(8)	In(1)—N(3)	2.197(4)
O(2)—C(41)	1.224(8)	In(1)—N(4)	2.170(4)
C(41)—C(42)	1.52(1)		
O(1)—In(1)—N(1)	125.6(2)	O(2)—In(1)—N(1)	81.5(2)
O(1)—In(1)—N(2)	119.7(2)	O(2)—In(1)—N(2)	87.8(2)
O(1)—In(1)—N(3)	90.6(2)	O(2)—In(1)—N(3)	133.6(2)
O(1)—In(1)—N(4)	93.3(2)	O(2)—In(1)—N(4)	123.2(2)
N(1)—In(1)—N(2)	85.1(2)	N(2)—In(1)—N(3)	84.1(2)
N(1)—In(1)—N(3)	142.6(2)	N(2)—In(1)—N(4)	145.0(2)
N(1)—In(1)—N(4)	84.5(2)	N(3)—In(1)—N(4)	84.3(2)
O(1)—In(1)—O(2)	55.0(2)	In(1)—O(1)—C(41)	97.4(4)
In(1)—O(2)—C(41)	86.5(4)	O(1)—C(41)—O(2)	121.1(7)
O(1)—C(41)—C(42)	119.1(6)	O(2)—C(41)—C(42)	119.7(6)
Compound 3			
In(1)—O(5)	2.31(1)	In(1)—N(1)	2.17(1)
In(1)—O(6)	2.31(1)	In(1)—N(2)	2.17(1)
In(2)—O(11)	2.34(1)	In(1)—N(3)	2.18(1)
In(2)—O(12)	2.24(1)	In(1)—N(4)	2.19(1)
C(01)—C(02)	1.52(3)	In(2)—N(5)	2.15(1)
C(01)—O(5)	1.25(2)	In(2)—N(6)	2.17(1)
C(01)—O(6)	1.24(2)	In(2)—N(7)	2.17(1)
C(03)—C(04)	1.51(3)	In(2)—N(8)	2.20(1)
C(03)—O(11)	1.25(2)		
C(03)—O(12)	1.25(2)		
O(5)—In(1)—O(6)	54.4(4)	In(1)—O(6)—C(01)	95(1)
O(5)—C(01)—O(6)	116(2)	O(5)—C(01)—C(02)	119(2)
In(1)—O(5)—C(01)	95(1)	O(6)—C(01)—C(02)	125(2)
O(5)—In(1)—N(1)	86.3(4)	O(6)—In(1)—N(1)	128.0(5)
O(5)—In(1)—N(2)	92.5(4)	O(6)—In(1)—N(2)	124.8(4)
O(5)—In(1)—N(3)	129.5(4)	O(6)—In(1)—N(3)	87.5(4)
O(5)—In(1)—N(4)	121.9(5)	O(6)—In(1)—N(4)	89.6(4)
N(1)—In(1)—N(2)	84.3(5)	N(2)—In(1)—N(3)	83.5(5)
N(1)—In(1)—N(3)	142.5(4)	N(2)—In(1)—N(4)	142.8(4)
N(1)—In(1)—N(4)	84.2(4)	N(3)—In(1)—N(4)	84.5(4)
O(11)—In(2)—O(12)	54.4(4)	In(2)—O(12)—C(03)	98(1)
O(11)—C(03)—O(12)	115(2)	O(11)—C(03)—C(04)	121(2)
In(2)—O(11)—C(03)	93(1)	O(12)—C(03)—C(04)	124(2)

ppm. The  $^1\text{H}$  NMR signals of  $\beta$ -pyrrole, 2,2'-pyridyl and 3,3'-pyridyl protons are similar to those reported for this compound in  $\text{DMSO}-d_6$  at  $24^\circ\text{C}$  by Smith *et al.*<sup>4</sup>

Due to the ring current effect, the methyl protons of the apical acetate ligand in  $\text{CDCl}_3$  experienced upfield shifts of 1.98 ppm [from 1.91 ppm (obtained from  $\text{OAc}^-$ ) to  $-0.07$  ppm]. Its  $^1\text{H}$  resonance in  $\text{CDCl}_3$  at  $-0.07$  ppm (at  $24^\circ\text{C}$ ) is quite close to 0 ppm, as expected.

#### Molecular structure of In(tmpp)(OAc) (3)

Two independent molecules exist in one asymmetric unit in crystalline  $\text{In}(\text{tmpp})(\text{OAc})$ . The skeletal framework of these two molecules with formula  $\text{In}(\text{tmpp})(\text{OAc}) \cdot 0.5\text{H}_2\text{O}$  is illustrated in Fig. 4. It reveals the similar six-coordination geometry as for  $\text{In}(\text{tpyp})(\text{OAc})$  except that the symmetric-bidentate  $\text{OAc}^-$  ligand is axially coordinated to the indium atom. The coordination polyhedra are:  $\text{In}(1)$ —

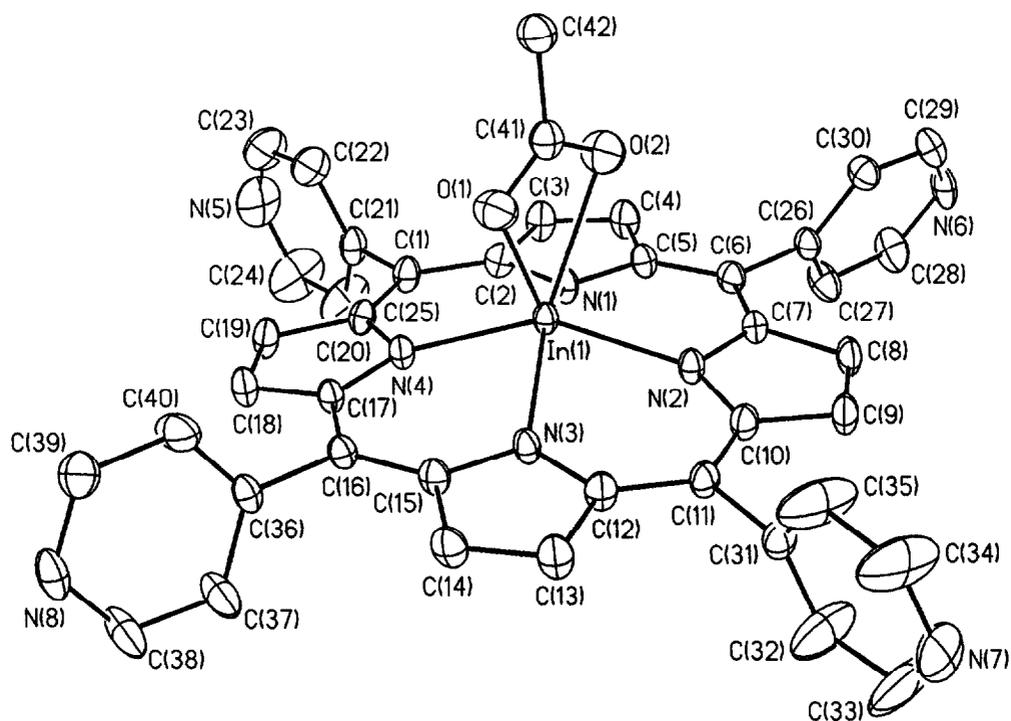


Fig. 2. Molecular configuration and scheme of labelling atoms for  $\text{In}(\text{tpyp})(\text{OAc})$  (hydrogen atoms and solvents are omitted for clarity).

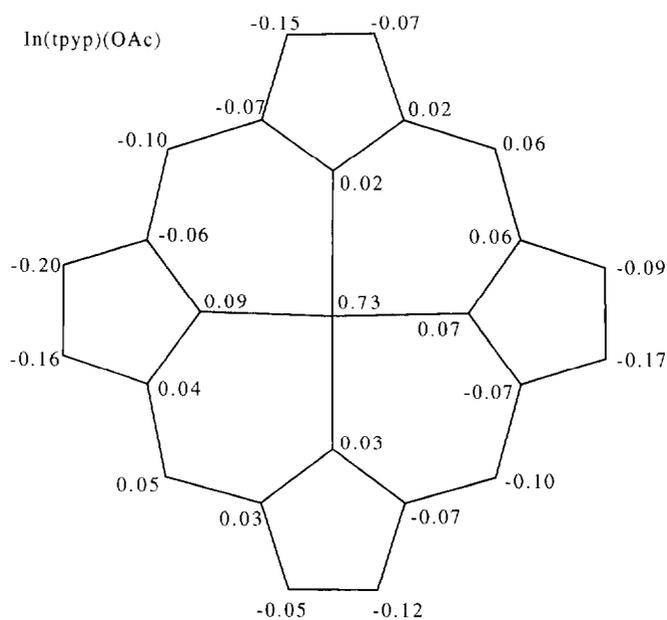


Fig. 3. Formal diagram of the porphyrin core of  $\text{In}(\text{tpyp})(\text{OAc})$  in which each atom symbol is replaced by a number showing the displacement (in units of  $\text{\AA}$ ) of that atom from the mean plane of the porphyrin.

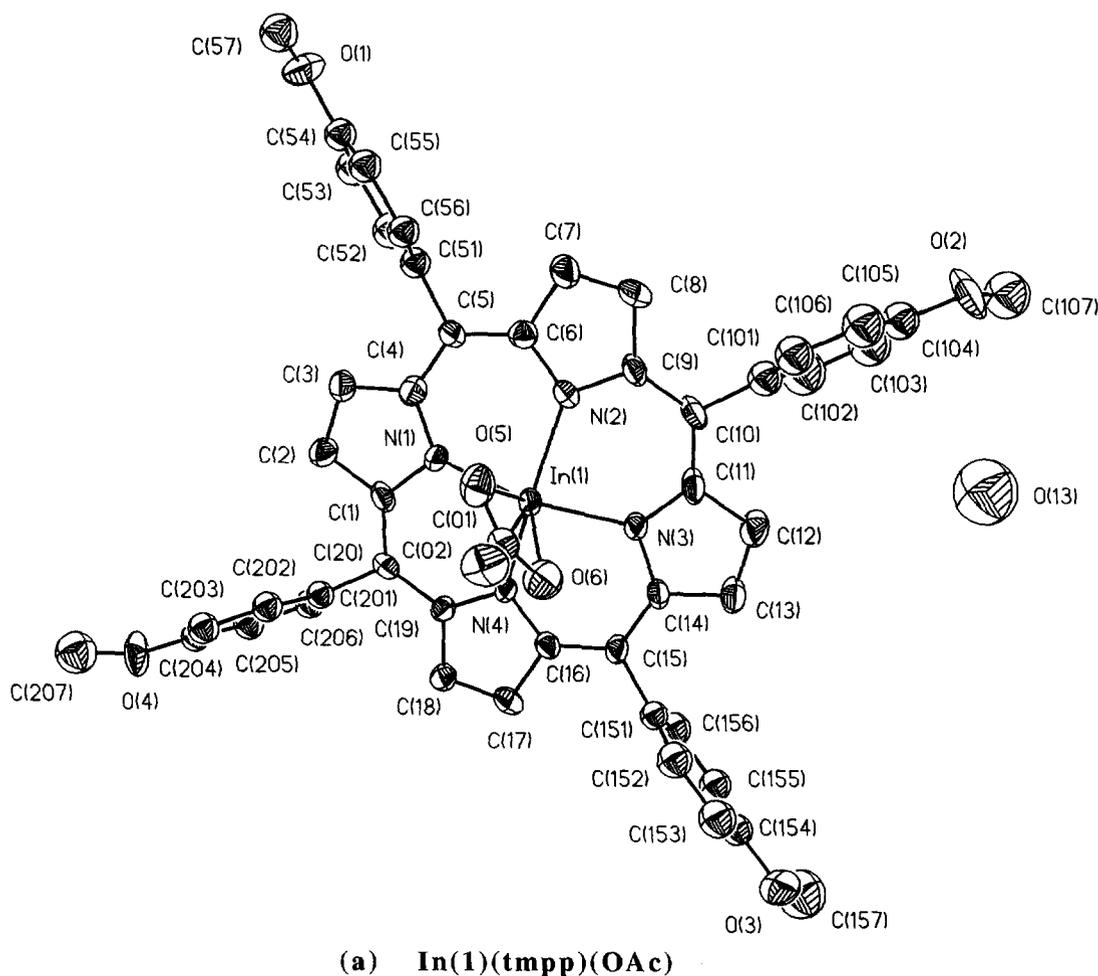


Fig. 4(a). Molecular configuration and scheme of labelling atoms (hydrogen atoms are omitted for clarity) of two independent  $\text{In}(\text{tmpp})(\text{OAc})$  molecules in one asymmetric unit for  $\text{In}(\text{I})(\text{tmpp})(\text{OAc})$ .

$\text{O}(5) = 2.31(1)$ ,  $\text{In}(1) - \text{O}(6) = 2.31(1)$ ,  $\text{C}(01) - \text{O}(5) = 1.25(2)$ ,  $\text{C}(01) - \text{O}(6) = 1.24(2)$ ,  $\text{C}(01) - \text{C}(02) = 1.52(3)$  Å and the mean  $\text{In}(1) - \text{N}_p = 2.18(1)$  Å for the molecule  $\text{In}(1)(\text{tmpp})(\text{OAc})$  (shown in Fig. 4a);  $\text{In}(2) - \text{O}(11) = 2.34(1)$ ,  $\text{In}(2) - \text{O}(12) = 2.24(1)$ ,  $\text{C}(03) - \text{O}(11) = 1.25(2)$ ,  $\text{C}(03) - \text{O}(12) = 1.25(2)$ ,  $\text{C}(03) - \text{C}(04) = 1.51(3)$  and the mean  $\text{In}(2) - \text{N}_p = 2.17(1)$  Å for the molecule  $\text{In}(2)(\text{tmpp})(\text{OAc})$  (shown in Fig. 4b). The  $\text{In}(1)$  atom lies 0.697 and 0.758 Å from the plane of the four porphyrin nitrogens ( $4\text{N}_p$ ) and the  $\text{C}_{20}\text{N}_4$  porphyrin plane, respectively; this results in an  $\text{O}(5) - \text{In}(1) - \text{O}(6)$  bond angle of  $54.4(4)^\circ$ . The porphyrin has a domed shape and its degree of doming is  $\sim 0.06$  Å. The dihedral angles between the mean plane of  $\text{C}_{20}\text{N}_4$  and the planes of the four phenyl groups are  $70.9^\circ$  [ $\text{C}(51)$ ],  $79.8^\circ$  [ $\text{C}(101)$ ],

$72.5^\circ$  [ $\text{C}(151)$ ],  $72.9^\circ$  [ $\text{C}(201)$ ] for  $\text{In}(1)$ . The dihedral angles among the phenyl groups [ $\text{C}(51)$ ,  $\text{C}(52)$ ,  $\text{C}(53)$ ,  $\text{C}(54)$ ,  $\text{C}(55)$ ,  $\text{C}(56)$ ;  $\text{C}(101)$ ,  $\text{C}(102)$ ,  $\text{C}(103)$ ,  $\text{C}(104)$ ,  $\text{C}(105)$ ,  $\text{C}(106)$ ;  $\text{C}(151)$ ,  $\text{C}(152)$ ,  $\text{C}(153)$ ,  $\text{C}(154)$ ,  $\text{C}(155)$ ,  $\text{C}(156)$ ;  $\text{C}(201)$ ,  $\text{C}(202)$ ,  $\text{C}(203)$ ,  $\text{C}(204)$ ,  $\text{C}(205)$ ,  $\text{C}(206)$ ] and the OMe groups [ $\text{C}(57)$ ,  $\text{O}(1)$ ,  $\text{C}(54)$ ;  $\text{C}(107)$ ,  $\text{O}(2)$ ,  $\text{C}(104)$ ;  $\text{C}(157)$ ,  $\text{O}(3)$ ,  $\text{C}(154)$ ;  $\text{C}(207)$ ,  $\text{O}(4)$ ,  $\text{C}(204)$ ] are  $8^\circ$ ,  $5^\circ$ ,  $2.8^\circ$  and  $12.8^\circ$ , respectively.

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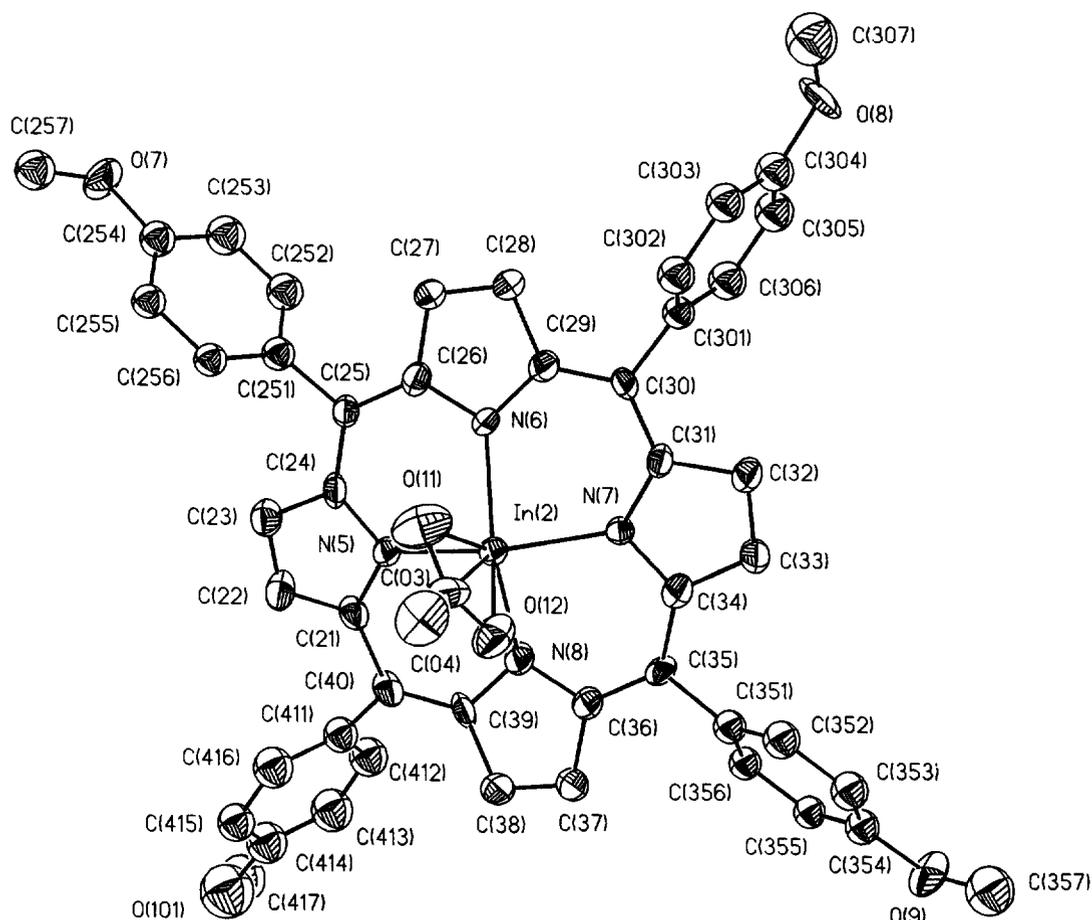
(b) **In(2)(tmpp)(OAc)**

Fig. 4(b). O(13) is the solvent ( $\text{H}_2\text{O}$ ). The distance between O(101) and C(417) is fixed at 1.550 Å. One anisole group of In(2)(tmpp)(OAc) is disordered between [C(411), C(412), C(413), C(414), C(415), C(416), C(417)] and [C(421), C(422), C(423), C(424), C(425), C(426), C(427)].

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