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## A SYNTHESIS AND STRUCTURE OF A WATER-SOLUBLE TETRAPYRIDYLPORPHYRINATO TIN(IV) CHLORIDE

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The water-soluble octahedral tin(IV) porphyrin complex,  $\text{SnCl}_2\text{tpyp}$ , was synthesized *via* reaction of  $\text{H}_2\text{tpyp}$  with anhydrous  $\text{SnCl}_2$ . The crystal structure of this complex has been determined at room temperature. The tin(IV) atom is coordinated by four nitrogen atoms in a square-planar fashion with an average Sn-N<sub>p</sub> bond distance of 2.081(9)Å, and the coordination sphere is completed by two axial chloro ligands with an average Sn-Cl bond distance of 2.435(5)Å. Cl-Sn-Cl = 180.0 (1)°. Crystal data:  $a = 12.385(12)$ ,  $b = 26.88(2)$ ,  $c = 14.882(9)$ Å,  $\beta = 94.16(7)^\circ$ , monoclinic, space group  $C2/c$ ,  $V = 4941 \text{ \AA}^3$ ,  $Z = 4$ ,  $\text{C}_{46}\text{H}_{48}\text{Cl}_2\text{N}_8\text{O}_6\text{Sn}$ , 2687 observed data,  $R = 0.085$ .

KEYWORDS: tin, water-soluble porphyrins, X-ray structure

### INTRODUCTION

Recently, water-soluble metalloporphyrins have attracted interest in a range of fields for industrial and medical purposes. For example, water-soluble iron(III) and manganese(III) tetraarylporphyrinates have been developed as new oxidation catalysts.<sup>1</sup> Paramagnetic water-soluble porphyrins serve as useful contrast agents for NMR tomography.<sup>2</sup> Tin tetra(*N*-methyl-4-pyridyl)porphyrinate shows great promise in research involving the storage of solar energy.<sup>3</sup> Other kinds of water-soluble porphyrins are being studied in cancer therapy.<sup>4,5</sup> However, only a few crystal structure determinations of the water-soluble metalloporphyrins have been reported due to their low tendency to form crystals of well-defined composition.<sup>6,7</sup> This contrasts with the fact that many crystal structures for lipophilic metalloporphyrins have been described.<sup>8</sup> In this paper, we report the crystal structure of another water-soluble tin(IV) tetraarylporphyrin,  $[\text{SnCl}_2\text{tpyp}].6\text{CH}_3\text{OH}$ ,  $\text{tpyp} = \text{tetra}(4\text{-pyridyl})\text{porphyrin}$ , which also has lipophilic properties.

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## EXPERIMENTAL

### Reagents

Tetrapyridylporphyrin, H<sub>2</sub>tpyp, and anhydrous tin(II) chloride, SnCl<sub>2</sub>, were purchased from Aldrich. Pyridine was dried by distillation from Ca(OH)<sub>2</sub>.

### Preparation

The complex SnCl<sub>2</sub>tpyp was prepared by a similar procedure to that for SnCl<sub>2</sub>tp; 100 mg (0.527 mmol) of stannous chloride was added to 25 cm<sup>3</sup> of anhydrous pyridine containing 125 mg (0.202 mmol) of H<sub>2</sub>tpyp. The reaction solution was heated to reflux for 2 hours until conversion was complete, as monitored by the electronic absorption measurements. After cooling, 110 mg (67.5%) of small, lavender crystals of SnCl<sub>2</sub>tpyp was obtained through filtration. Anal.: calcd. for SnCl<sub>2</sub>C<sub>40</sub>H<sub>24</sub>N<sub>8</sub> [SnCl<sub>2</sub>tpyp]: C, 59.59; H, 3.00; N, 13.90; Cl, 8.79%. Found: C, 60.24; H, 3.81; N, 14.29; Cl, 8.17%. Electronic spectrum  $\lambda_{\max}$  (CHCl<sub>3</sub>): 403, 424, 523, 560, 600, 611 and 630 nm; (H<sub>2</sub>O) 396, 417, 516, 533, 590 and 625 nm. <sup>1</sup>H-NMR spectrum ( $\delta$ ): *ca* 8.28, *ca* 9.16, and 9.25 [s, J(Sn-H) 7.2 Hz] ppm. Far IR and IR spectrum ( $\bar{\nu}$ ): 310, 1347, and 1593 cm<sup>-1</sup>. Single crystals suitable for determination of the crystal and molecular structure were grown by slow diffusion of a mixture of CH<sub>3</sub>OH and hexane into a CHCl<sub>3</sub> solution of SnCl<sub>2</sub>tpyp. The resulting lavender, rectangular, blocky crystals, [SnCl<sub>2</sub>tpyp].6CH<sub>3</sub>OH, gradually decomposed in air because of the slow evaporation of the low boiling point solvent molecules of CH<sub>3</sub>OH in it. For X-ray diffraction analysis a selected crystal of size 0.4 x 0.5 x 0.8 mm was sealed in a Lindemann glass capillary with a small drop of the mother liquor. This is the reason for relatively low precision of the structure determination described below.

### Crystallography

Diffraction data were collected at room temperature on a Siemens R3m/V diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of 4357 independent reflections were collected using the  $\omega$ -scan mode with variable scan speed, 4.51–29.30°/min, in the range  $3.0^\circ \leq \theta \leq 50.0^\circ$ . Some 2687 intensities with  $F > 6.0 \sigma(F)$  were used for structure determination. The SHELXTL PLUS program was used to solve and refine the structure. The coordinates of Sn atom were found by direct methods, and those of the remaining non-hydrogen atoms except for those of the solvent molecules were located from successive difference Fourier maps. Crystal data: C<sub>46</sub>H<sub>48</sub>Cl<sub>2</sub>N<sub>8</sub>Sn;  $M = 998.5$ ; space group *C2/c*,  $a = 12.385(12)$ ,  $b = 26.88(2)$ ,  $c = 14.882(9)$  Å,  $\beta = 94.16(7)^\circ$ ,  $V = 4941(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $d$  (calcd) = 1.342 g cm<sup>-3</sup>,  $F(000) = 2048$ ,  $\mu = 0.677$  mm<sup>-1</sup>. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located by Final values of  $R$  and  $R_w$  [ $w^{-1} = \sigma^2(F) + 0.0001F^2$ ], 0.085 and 0.114, respectively. Atomic coordinates are listed in Table 1.

**Table 1** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ).\*

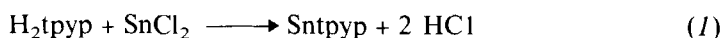
	$x/a$	$y/b$	$z/c$	$U(\text{eq})$
Sn	2500	2500	0	43(1)
Cl	802(1)	2960(1)	-128(1)	80(1)
N(1)	2898(1)	2874(1)	1203(1)	49(1)
N(2)	1792(1)	1930(1)	698(1)	47(1)
N(3)	2038(1)	1841(1)	5026(1)	71(1)
N(4)	-210(1)	-17(1)	-1306(1)	107(1)
C(1)	3393(1)	3332(1)	1294(1)	46(1)
C(2)	3565(1)	3431(1)	2242(1)	68(1)
C(3)	3163(1)	3053(1)	2707(1)	65(1)
C(4)	2722(1)	2690(1)	2064(1)	48(1)
C(5)	2226(1)	2245(1)	2245(1)	49(1)
C(6)	2160(1)	2117(1)	3230(1)	47(1)
C(7)	3022(1)	1885(1)	3695(1)	77(1)
C(8)	2933(1)	1767(1)	4608(1)	85(1)
C(9)	1289(1)	2061(1)	4596(1)	73(1)
C(10)	1276(1)	2204(1)	3675(1)	64(1)
C(11)	1791(1)	1901(1)	1631(1)	48(1)
C(12)	1327(1)	1425(1)	1846(1)	64(1)
C(13)	1040(1)	1189(1)	1043(1)	61(1)
C(14)	1364(1)	1500(1)	344(1)	50(1)
C(15)	1286(1)	1386(1)	-594(1)	46(1)
C(16)	741(1)	897(1)	-839(1)	56(1)
C(17)	1336(1)	509(1)	-1143(1)	84(1)
C(18)	855(1)	66(1)	-1359(1)	130(1)
C(19)	-737(1)	335(1)	-1025(1)	96(1)
C(20)	-325(1)	821(1)	-792(1)	71(1)
C(21)	3913(1)	806(1)	7461(1)	230(1)
C(22)	3888(1)	336(1)	4532(1)	567(1)
C(23)	3944(1)	589(1)	596(1)	460(1)
O(1)	4273(1)	1191(1)	6852(1)	677(1)
O(2)	4138(1)	641(1)	3770(1)	425(1)
O(3)	4272(1)	903(1)	1370(1)	606(1)

\*Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_i$  tensor.

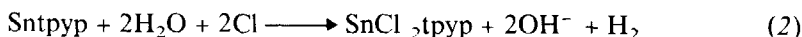
## RESULTS AND DISCUSSION

### Preparation

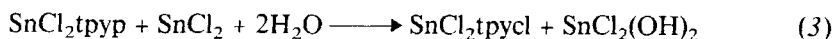
$\text{SnCl}_2 \cdot \text{tmpyp}$  was reported to be prepared through the methylation of its intermediate, tin(II) tetrapyrrolylporphyrin (Sntpyp) by Harriman *et al.*<sup>9</sup> Sntpyp was assumed to be obtained by treatment of the porphyrin with tin(II) acetate in propionic acid. However, Corwin and co-workers<sup>10</sup> found that metallation of etioporphyrin with tin(II) chloride in acetic acid resulted in tin(IV) etioporphyrin diacetate. Other studies of spectroscopic properties and X-ray crystal diffraction analyses of a number of tin tetraphenylporphyrin complexes have confirmed the tetravalence of tin.<sup>11-13</sup> In the present works we also found that reaction of tetrapyrrolylporphyrin,  $\text{H}_2\text{tpyp}$ , with  $\text{SnCl}_2$  in pyridine yielded tetravalent tin porphyrin with a small amount of hydroporphyrin (chlorin) complex as the only isolated product. The formation process is explained as follows. After initial refluxing, the divalent tin porphyrin complex, Sntpyp, was assumed to be formed through (1).



The existence of a trace amount of water in the pyridine solution made this divalent tin reaction intermediate convert to the tetravalent tin product almost immediately.<sup>12</sup>



The presence of excess  $\text{SnCl}_2$  slowly led the formation of a small amount of tin(IV) tetrapyrrolylchlorin dichloride under continuous heating and irradiation,<sup>12</sup> and this was very difficult to remove. Longer reflux times led to a lower yield of  $\text{SnCl}_2\text{tpyp}$ .



### Crystal structure

Structural analysis shows that crystals of this complex consist of discrete  $\text{SnCl}_2\text{tpyp}$  molecules with  $\text{CH}_3\text{OH}$  solvent molecules occupying spaces in the lattice. A perspective view of a single  $\text{SnCl}_2\text{tpyp}$  molecule (Fig. 1) shows that the general features of  $\text{SnCl}_2\text{tpyp}$  resemble closely those of its analogue,  $\text{SnX}_2\text{tpp}$  ( $\text{X} = \text{Cl}, \text{OH}, \text{C}_6\text{H}_4\text{CO}_2, 2\text{-OH-C}_6\text{H}_4\text{CO}_2, \text{ and } 2\text{-OCOCH}_3\text{-C}_6\text{H}_4\text{CO}_2$ )<sup>10,11</sup> As expected, the tin atom is octahedrally coordinated by the four pyrrole nitrogen atoms and two axial chlorine atoms with  $\text{Cl-Sn-Cl}$  equal to  $180.0(1)^\circ$ . In order to accommodate the tin atom within the planar porphyrin moiety, the core of the ring is enlarged to give an  $\text{M-N}_p$  bond distance which is among the longest reported for planar metalloporphyrins so far; average  $\text{Sn-N}_p = 2.081(9)\text{\AA}$ . Tin-chlorine bond distances,  $2.435(5)\text{\AA}$ ,

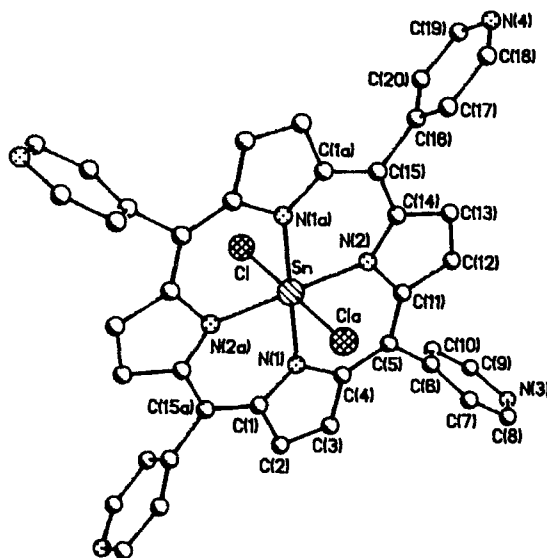


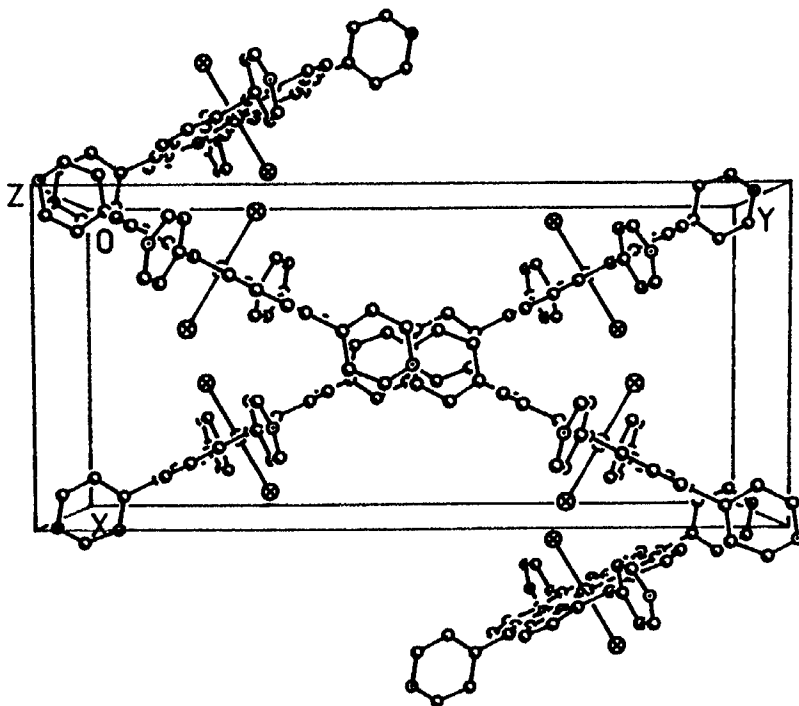
Figure 1 Perspective view of the  $\text{SnCl}_2\text{tpyp}$  molecule (hydrogen atoms omitted).

**Table 2** Selected bond distances (Å) for  $[\text{SnCl}_2\text{tpp}]\cdot 6\text{CH}_3\text{OH}$ .

Sn-N(1)	2.081 (9)	Sn-Cl	2.435 (5)
Sn-N(2)	2.080 (10)	Sn-Cl <sub>a</sub>	2.435 (5)
Sn-N(1a)	2.081 (9)		
Sn-N(2a)	2.080 (10)		

are comparable with those observed in  $\text{SnCl}_2\text{tpp}$ <sup>12</sup> and  $\text{SnCl}_2\text{oep}$ .<sup>14</sup> The nearly perpendicularly oriented pyridyl groups, relative to the mean plane of the 24-atom porphyrin core (the dihedral angles being 88.3° and 94.7°, respectively), and the C-C bond between the pyridyl and porphyrin rings, 1.511(18)Å, indicate negligible conjugation between the two systems. Other significant bond distances and angles are recorded in Tables 2 and 3, respectively. Full lists of atomic coordinates, thermal parameters, and observed and calculated structure factors are available on request from the authors.

It is worth noting that, despite of the formation of extensive solvent channels in crystals of  $\text{SnCl}_2\text{tpp}$ , the structure shows marked differences, particularly in the packing of the porphyrin rings, to those previously described for tetraarylporphyrin sponges<sup>13</sup> and other tin porphyrin analogues.<sup>12,13</sup> In the cell of this complex, there are two differently oriented porphyrin planes which are approximately parallel to (110) and (1 $\bar{1}$ 0), respectively (Fig. 2). To some degree, this is similar to another water-soluble porphyrin,  $\text{Fe}(\text{tmpyp})$ .<sup>7</sup> The porphyrin planes

**Figure 2** Packing of  $[\text{SnCl}_2\text{tpp}]\cdot 6\text{CH}_3\text{OH}$  in the unit cell.

**Table 3** Selected bond angles (degrees) for [SnCl<sub>2</sub>tpyp].6CH<sub>3</sub>OH.

Cl-Sn-Cl <sub>a</sub>	180.0 (1)	N(1)-Sn-N(2)	90.5 (4)
Cl-Sn-N(1)	88.4 (3)	N(1)-Sn-N(1a)	180.0 (1)
Cl-Sn-N(2)	91.1 (3)	N(1)-Sn-N(2a)	89.5 (4)
Cl-Sn-N(1a)	91.6 (3)	N(2)-Sn-N(1a)	89.5 (4)
Cl-Sn-N(2a)	88.9 (3)	N(2)-Sn-N(2a)	180.0 (1)
Cl <sub>a</sub> -Sn-N(1)	91.6 (3)	N(1a)-Sn-N(2a)	90.5 (4)
Cl <sub>a</sub> -Sn-N(2)	88.9 (3)		
Cl <sub>a</sub> -Sn-N(1a)	88.4 (3)		
Cl <sub>a</sub> -Sn-N(2a)	91.1 (3)		

of the majority of reported tetraarylporphyrins pack in a parallel way, showing only one orientation in the unit cell.<sup>15</sup>

### References

1. B. Meunier, *Chem. Rev.*, **92**, 1411 (1992).
2. M. Hoehn-Berlage, O. Norris, K. Bockhorst, R.-I. Ernestus, O. Kloiber, P. Bonneholz, O. Leibfritz and K.-A. Hossmann, *Magn. Res. Med.*, **27**, 201 (1992).
3. J. Handman, A. Harriman and G. Porter, *Nature*, **307**, 537 (1984).
4. A.R. Morgan, G.M. Garbo, R.W. Keek and S.H. Schman, *Cancer Res.*, **48**, 194 (1988).
5. T.J. Dougherty, *Photochem. Photobiol.*, **45**, 879 (1987).
6. M.A. Ivanca, A.G. Lappin and W.R. Scheidt, *Inorg. Chem.*, **30**, 711 (1991).
7. F.C.F. Korber, J.R. Lindsay Smith, S. Prince, P. Rizkallah, C.D. Reynolds and D.R. Shawcross, *J. Chem. Soc., Dalton Trans.*, 3291 (1991).
8. W.R. Scheidt and Y.J. Lee, *Struct. Bonding (Berlin)*, **64**, 1 (1987).
9. A. Harriman and M.C. Richoux, *J. Phys. Chem.*, **87**, 4957 (1983).
10. A.H. Corwin and O.D. Collins, III, *J. Org. Chem.*, **27**, 3060 (1962).
11. D.G. Whitten, J. C. Yan and F.A. Carroll, *J. Am. Chem. Soc.*, **93**, 2291 (1971).
12. D.M. Collins, W.R. Scheidt and J.L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972).
13. G. Smith, D.P. Arnold, C.H.L. Kennard and T.C.W. Mak, *Polyhedron*, **10**, 509 (1991).
14. D.L. Cullen and E.L. Meyer, *Acta Cryst.*, **29B**, 2507 (1973).
15. M.P. Byrn, C.J. Curtis, S.I. Khan, P.A. Sawin, R. Tsurumi and C.E. Strouse, *J. Amer. Chem. Soc.*, **112**, 1865 (1990).