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TIN(IV) PORPHYRIN COMPLEXES—VII.* CRYSTAL STRUCTURES OF *MESO*-TETRAPHENYLPORPHYRINATOTIN(IV) DIFLUORIDE AND DINITRATE, AND THE CORRELATION OF SPECTROSCOPIC DATA WITH CORE SIZE FOR TIN(IV) PORPHYRIN COMPLEXES

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Abstract—The structures of the complexes [Sn(tpp)F_2] (**1**) and [Sn(tpp)$(NO_3)_2$] (**2**) (tpp = dianion of 5,10,15,20-tetraphenylporphyrin) have been determined by single crystal X-ray diffraction. Bond lengths in complex **1** are Sn—F 1.946(5) Å and Sn—N 2.056(7) and 2.071(6) Å. Complex **2** has monodentate nitrato ligands, and bond lengths Sn—O 2.113(5) Å and Sn—N 2.075(5) and 2.080(5) Å. A comparison of bond length and spectroscopic data for these and other [Sn(tpp)X_2] complexes reveals that the core sizes of the complexes of O-bound ligands and [Sn(tpp)Cl_2] correlate well with the published ^{119}Sn NMR linewidths, and with Raman shifts for the band assigned as $\nu(C_aC_b)$. However, the Sn—N bond lengths of **1** are significantly shorter than those predicted by such correlations.

In earlier papers of this series, we have documented studies of the complexes of tetraphenylporphyrin with tin(IV), using visible absorption, ^{1}H and ^{119}Sn NMR, and FT-Raman spectroscopies.[1-4] Several complexes were also characterized by X-ray crystallography.[5] Our intention in this work has been to correlate spectroscopic and structural parameters, in the hope that these data will be useful in investigations of tin(IV) porphyrins in biological systems. Such complexes have been employed as heme oxygenase inhibitors,[6] immunostimulants,[7] photosensitizers[8] and components of ion-selective membranes.[9] The long-term goal is to be able to define the nature of axial ligands in the complexes when they are in cells or attached to proteins or other biomolecules, by a suitable combination of spectroscopic techniques. In terms of fundamental porphyrin coordination chemistry, it is desirable to see if features such as the 'core size' of the porphyrin cavity (as measured by Sn—N bond lengths in the solid state) can be related to solution spectral data. In Part 6, we reported an assessment of the value of direct NMR observation of the central ^{119}Sn nucleus in a large series of these complexes.[1] This study showed that the chemical shift δ_{Sn} is an unreliable predictor of axial ligand electronic influence, but that the ^{119}Sn linewidth $\nu_{1/2}$ seemed to give a fairly consistent indication of the *cis*-influences. We have determined the solid state structures of two more key compounds, namely [Sn(tpp)F_2] (**1**) and [Sn(tpp)$(NO_3)_2$] (**2**), and now present these results,

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* For Part VI see ref. 1.

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as well as an analysis of the inter-relations of these and previously reported data.

EXPERIMENTAL

Crystallography

The compounds were available from our earlier studies.[3,4] Purple crystals of **1** and **2** were grown from dichloromethane/methanol and dichloromethane/hexane, respectively. Intensity data for **1** and **2** were measured on a Rigaku AFC6R diffractometer employing graphite monochromatized Mo-$K\alpha$ radiation (0.71073 Å) for **1** and nickel-filtered Cu-$K\alpha$ radiation (1.5418 Å) for **2**; the $\omega:2\theta$ scan technique was used for both data collections. The data sets were corrected for Lorentz and polarization effects[10] and empirical absorption corrections were applied.[11] Relevant crystallographic data are given in Table 1.

The structures were solved by placing the Sn atom at a centre of inversion and calculating difference syntheses; refinement was by a full-matrix least-squares procedure based on F.[10] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the models in their calculated positions (C—H 0.97 Å). The nitrate anion in **2** was disordered such that one of the oxygen atoms, O(3), was disposed over two positions with 50% site occupancy. The refinements were continued until convergence employing sigma weights; final details are given in Table 1. Selected bond distances and angles are given in Table 2 and the numbering schemes employed are shown in Figs 1 and 2. All calculations were performed with the teXsan program[10] installed on an Iris Indigo workstation. Atomic coordinates, thermal parameters, and observed and calculated structure factors have been deposited with the Editor as supplementary material; copies are available upon request.

RESULTS AND DISCUSSION

Description of structures

The molecular structure of **1** is shown in Fig. 1, which shows the Sn atom exists in a slightly distorted octahedral geometry. The molecule is centrosymmetric and consequently the four N atoms of the tpp dianion and the Sn atom are coplanar; the two independent Sn—N bond distances are equal within experimental error at 2.056(7) and 2.071(6) Å. The coordination geometry about the Sn atom is completed by the *trans*-F atoms; Sn—F 1.946(5) Å. A similar centrosymmetric arrangement is found in the structure of **2**, as shown in Fig. 2. The two independent Sn—N bond distances of 2.080(5) and 2.075(5) Å are experimentally equivalent and the Sn—O(1) bond distance is 2.113(5) Å. For clarity only one of the equally occupied sites for the O(3) atom is shown in Fig. 2. The Sn—O(3) and Sn—O(3′) separations of 3.24(1) and 3.28(1) Å, respectively, are not representative of significant

Table 1. Crystallographic data for **1** and **2**

	1	**2**
Formula	$C_{44}H_{28}F_2N_4Sn$	$C_{44}H_{28}N_6O_6Sn$
M	769.4	855.4
Crystal size (mm)	0.16 × 0.24 × 0.32	0.08 × 0.08 × 0.08
Space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a (Å)	10.030(3)	11.064(2)
b (Å)	8.228(4)	14.558(2)
c (Å)	20.928(3)	12.259(1)
β (deg)	98.56(2)	113.089(8)
V (Å^3)	1707.8	1816.5
Z	2	2
D_{calc} (g cm^{-3})	1.496	1.564
F(000)	776	864
μ (cm^{-1})	7.98	61.13
2θ limits (deg)	2.0–25.0	4–60
Data collected	3564	3007
Data used in refinement	2001	1756
R, R_w	0.046, 0.059	0.037, 0.040

Table 2. Selected interatomic parameters (Å, °) for **1** and **2**

	1 (X = F)	**2** (X = O(1))
Sn—X	1.946(5)	2.113(5)
Sn—N(1)	2.056(7)	2.080(5)
Sn—N(8)	2.071(6)	2.075(5)
N(1)—C(2)	1.36(1)	1.372(7)
N(1)—C(5)	1.380(9)	1.391(7)
N(8)—C(7)	1.35(1)	1.387(7)
N(8)—C(9)	1.36(1)	1.379(7)
X—Sn—N(1)	90.2(3)	88.5(2)
X—Sn—N(8)	89.8(2)	94.2(2)
N(1)—Sn—N(8)	90.5(2)	90.1(2)
N(1)—Sn—N(8′)	89.5(2)	89.9(2)
Sn—N(1)—C(2)	127.1(5)	125.8(4)
Sn—N(1)—C(5)	124.5(5)	125.4(4)
C(2)—N(1)—C(5)	108.3(7)	108.7(5)
Sn—N(8)—C(7)	125.5(6)	125.8(4)
Sn—N(8)—C(9)	125.2(5)	126.3(4)
C(7)—N(8)—C(9)	109.3(7)	107.8(5)

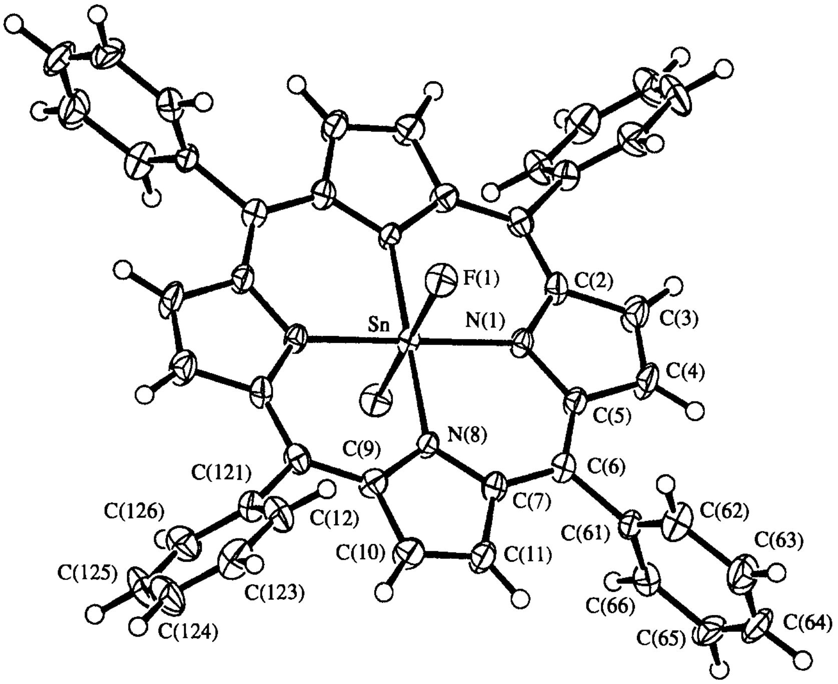

Fig. 1. Molecular structure and atom numbering scheme for **1**.

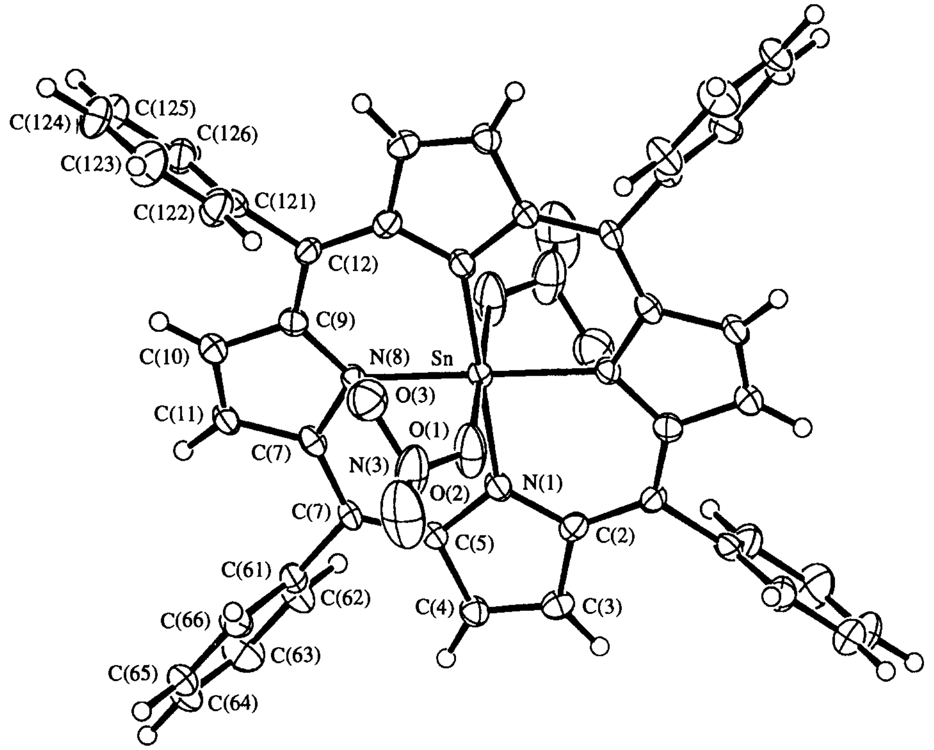

Fig. 2. Molecular structure and atom numbering scheme for **2**. For clarity, only one of the two sites for O(3) is shown.

interactions, indicating that each nitrate anion coordinates to the Sn centre in the monodentate mode. As usual for tpp complexes, the phenyl substituents are not coplanar with the porphyrin N_4 plane, as evidenced by the torsion angles C(5)/C(6)/C(61)/C(62) and C(9)/C(12)/C(121)/ C(122) for **1**, of 99(1) and 59(1)°, and for **2**, of −67.8(9) and 111.3(7)°, respectively.

Correlations of bond lengths with spectroscopic parameters

Now that the solid state structures of a representative series of [Sn(tpp)X_2] complexes are known, it is worthwhile to re-examine the published spectroscopic data. The ^{119}Sn linewidths[1] and mean Sn—N bond lengths[5,12,13] are plotted in Fig. 3. With the aberrant point for X = F omitted, the correlation is good: linewidth = 4270–2013(r_{Sn}—N) (r = −0.985). It was proposed that this linewidth represents a combination of ^{119}Sn—^{14}N coupling and quadrupolar relaxation efficiency,[1] and is a measure of the relative strength of bonding in the Sn—N_4 unit. The relationship depicted in Fig. 3 appears to confirm this pattern for all ligands except X = F. A strengthening of the in-plane bonding, as axial binding is weakened, results in a contraction of the Sn—N_4 core, and leads to stronger interaction between the ^{119}Sn and ^{14}N nuclei. In our previous work, the halides have usually deviated from the pattern exhibited by the O-bound ligands in correlations of bond strength parameters with ligand properties.[1–4] This is the case here also, but this time chloride fits in with the oxygen ligands.

The correlation of 'core size' of metalloporphyrins with Raman shifts of porphyrin ligand vibrations (usually measured by resonance Raman techniques) has been fairly successful for various series of complexes.[14] In our study of the solid state Fourier transform Raman spectra of the [Sn(tpp)X_2] complexes, we noted that none of the previous empirical equations fitted the structural data published at that time.[2] The availability of reliable X-ray data on the complexes of the more weakly bound anions perchlorate[13] and nitrate allows a worthwhile examination of the relationship between Raman shifts and Sn—N bond lengths. In our Raman study, we identified five bands which are fairly sensitive to the nature of the axial ligands.[2] Of these, the best correlation is with our 'band 5' [assigned as $\nu(C_aC_b)$ (A_{1g})] (Fig. 4). The equation is ν_5 = 2472–485.85(r_{Sn}—N) (r = −0.992). The insensitivity of the Raman shift in the halide complexes is again obvious in this plot. From our earlier Raman results, it might have been supposed that for some reason the halide ligands caused no change in the core size, but this is clearly not the case for X = F and X = Cl.

There are other properties of the halide complexes which show this anomalous lack of dependence on the size of the halogen. We have noted that ^4J(Sn—pyrrole H) and ^3J(Sn—O—C(O)—H) *trans* to formate in tpp complexes are almost constant for F, Cl and Br.[3,4] Kadish *et al.* reported that the first reduction potentials of the analogous tetra(p-tolyl)- and tetra(m-tolyl)porphyrin complexes are similarly virtually invariant.[15] Conversely, the electronic absorption and emission spectra are quite sensitive to the nature of the

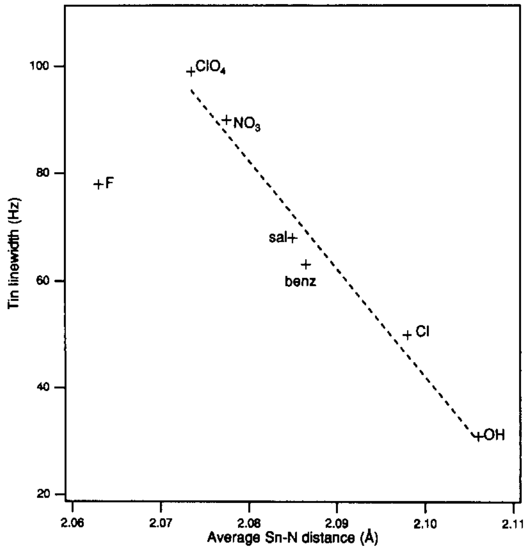

Fig. 3. Plot of the width at half-height of the ^{119}Sn resonance[1] *vs* mean Sn—N bond lengths for [Sn(tpp)X_2] complexes. Literature X-ray data for perchlorate from ref. 13, for salicylate, benzoate and hydroxide from ref. 5, and for chloride from ref. 12. The linear regression calculation excludes the point for X = F.

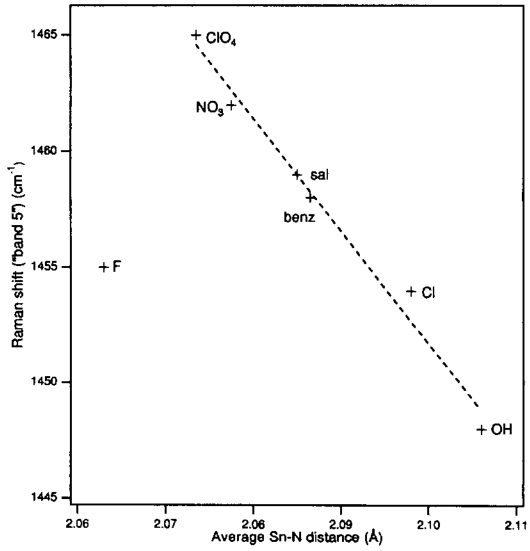

Fig. 4. Plot of the Raman shift of the $\nu(C_aC_b)$ band[2] *vs* mean Sn—N bond lengths for [Sn(tpp)X_2] complexes. X-ray data sources as for Fig. 3. The linear regression calculation excludes the point for X = F.

halide.[16] Gouterman *et al.* studied the spin-orbit coupling in Group 14 metalloporphyrins, and concluded that there is extensive mixing of the ring $e_g(\pi^*)$ orbitals with halide np_x and np_y orbitals.[16] This shift of the HOMO–LUMO gap should be detectable in the parameter $\Delta E = E^0_{ox} - E^0_{red}$ obtained from electrochemical measurements, but data are presently available only for the reduction side.[15] Unfortunately, there are few other situations in the Periodic Table of metalloporphyrins which are quite the same as that of tin(IV). The combination of a stable high oxidation state, filled *d* shells, and six-coordinate geometry is found only for silicon(IV), germanium(IV), tin(IV) and the Group 15 metalloids. Of these elements, tin and phosphorus have the most potential for producing useful comparative NMR data. It will be interesting to see what trends emerge when more data are available for the phosphorus(V) complexes.[17] Of the other heavy elements, thallium possesses $I = 1/2$ isotopes with large coupling constants. However, thallium(III) porphyrins are five-coordinate, and changes in electronic effects of the axial ligands are partly accommodated by changes in the displacement of the metal ion from the N_4 plane, and so the situation is not really comparable with that of tin(IV). Changes in NMR and electronic spectroscopic parameters are small for the thallium(III) halides [Tl(tpp)X], and the core size also varies only slightly.[18]

In summary, we now have structural data for a series of tin(IV) tpp complexes spanning a representative array of O-bound ligands. Parameters which correlated well with the core size are Raman shifts and ^{119}Sn NMR linewidths. It is noteworthy that solid state (Raman) and solution (NMR) data are both related to the bond lengths in the crystals. Whilst the data for [Sn(tpp)Cl$_2$] appear to fit in with the linewidth and Raman ‘band 5’ trends, in several of the other parameters we have examined, this is not the case. The Sn—N distances in **1** are clearly shorter than those predicted by the relationships which apply to the complexes of oxyanions.

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REFERENCES

1. D. P. Arnold and J. P. Bartley, *Inorg. Chem.* 1994, **33**, 1486.
2. D. P. Arnold, *Inorg. Chim. Acta* 1992, **193**, 27.
3. D. P. Arnold, E. A. Morrison and J. V. Hanna, *Polyhedron* 1990, **9**, 1331.
4. D. P. Arnold, *Polyhedron* 1986, **5**, 1957.
5. G. Smith, D. P. Arnold, C. H. L. Kennard and T. C. W. Mak, *Polyhedron* 1991, **10**, 509.
6. (a) J. B. Cannon, *J. Pharm. Sci.* 1993, **82**, 435; (b) G. S. Drummond, R. A. Galbraith, M. K. Sardana and A. Kappas, *Arch. Biochem. Biophys.* 1989, **255**, 64; (c) P. A. Dennery, H. J. Vreman, P. A. Rodgers and D. K. Stevenson, *Pediatr. Res.* 1993, **33**, 87; (d) H. J. Vreman, B. C. Edstrand and D. K. Stevenson, *Pediatr. Res.* 1993, **33**, 195; (e) J. Scott, J. M. E. Quirke, H. J. Vreman, D. K. Stevenson and K. R. Downum, *J. Photochem. Photobiol. B.* 1990, **72**, 149.
7. A. Novogrodsky, M. Suthanthiran and K. H. Stenzel, *J. Immunol.* 1989, **143**, 3981.
8. (a) D. Kessel, A. Morgan and G. M. Garbo, *Photochem. Photobiol.* 1990, **54**, 193; (b) A. R. Morgan, G. M. Garbo, R. W. Keck, L. D. Eriksen and S. H. Selman, *Photochem. Photobiol.* 1990, **51**, 589.
9. (a) N. A. Chaniotakis, S. B. Park and M. E. Meyerhoff, *Anal. Chem.* 1989, **61**, 566; (b) C. E. Kibbey, S. B. Park, G. De Adwyler and M. E. Meyerhoff, *J. Electroanal. Chem.* 1992, **335**, 135.
10. teXsan, Structure Analysis Package. Molecular Structure Corporation, Texas (1992).
11. N. Walker and D. Stuart, *Acta Cryst.* 1983, **A39**, 158.
12. D. M. Collins, W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.* 1972, **94**, 6689.
13. W. B. Lee, S. C. Suen, F. E. Hong, J. H. Chen, T. T. Jong and L. P. Hwang, *J. Chin. Chem. Soc.* 1992, **39**, 143.
14. J. D. Stong, T. G. Spiro, R. J. Kubaska and S. I. Shupack, *J. Raman Spectrosc.* 1980, **9**, 312.
15. K. M. Kadish, Q. Y. Xu, G. B. Maiya, J.-M. Barbe and R. Guilard, *J. Chem. Soc., Dalton Trans.* 1989, 1531.
16. M. G. Gouterman, F. P. Schwarz, P. D. Smith and D. Dolphin, *J. Chem. Phys.* 1973, **59**, 676.
17. T. Barbour, W. J. Belcher, P. J. Brothers, C. E. F. Rickard and D. C. Ware, *Inorg. Chem.* 1992, **31**, 746.
18. M. O. Senge, K. Ruhlandt-Senge, K. J. Regli and K. M. Smith, *J. Chem. Soc., Dalton Trans.* 1993, 3519.