TIN(IV) PORPHYRIN COMPLEXES—IV.* CRYSTAL STRUCTURES OF *MESO*-TETRAPHENYLPORPHYRINATOTIN(IV) COMPLEXES WITH HYDROXIDE, WATER, BENZOATE, SALICYLATE AND ACETYLSALICYLATE AS AXIAL LIGANDS

GRAHAM SMITH and DENNIS P. ARNOLD[†]

Department of Chemistry, Queensland University of Technology, Brisbane 4001, Australia

and

COLIN H. L. KENNARD

Department of Chemistry, University of Queensland, Brisbane 4072, Australia

and

THOMAS C. W. MAK

Department of Chemistry, Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract—A series of five complexes of tin(IV) with 5,10,15,20-tetraphenylporphyrin (H₂tpp) of the type [SnX₂(tpp)] has been prepared and characterized using NMR and single crystal X-ray diffraction techniques. The complexes are [Sn(OH)₂(tpp)] (1), [Sn(OH₂)₂(tpp)] (CF₃SO₃)₂ (2), [Sn(C₆H₅CO₂)₂(tpp)] (3), [Sn(2-OH-C₆H₄CO₂)₂(tpp)] (4) and [Sn(2-OCO CH₃-C₆H₄CO₂)₂(tpp)] (5). All complexes are monomeric with little structural variation within the Sn(tpp) framework. All axial substituents act as unidentate ligands with the Sn—O bond lengths varying from 2.017(4) Å (X = OH) (1) through 2.055(5) Å (3), 2.06(3) Å (mean) (5), 2.09(1) Å (4) (the substituted benzoates) to 2.16(1) Å (mean) (X = OH₂) (2).

The octahedral tin(IV) complexes of porphyrins and related ligands have attracted interest in recent years in a variety of fields. Tin(IV) proto- and mesoporphyrin show promise as therapeutic agents for neonatal jaundice, as they are potent inhibitors of haem oxygenases.² Morgan *et al.* have reported studies of photodynamic cancer treatment using the tin complexes of the porphyrin-derived purpurins and verdins.³ Water-soluble complexes such as tetrakis(N-methyl-4-pyridyl)porphyrinatotin(IV) have been used as photosensitizers for energy transfer to water and other molecules for hydrogen generation.⁴ Most recently, Meyerhoff and co-workers⁵ reported the use of dichloro-5,10,15,20-tetraphenylporphyrinatotin(IV) {[SnCl₂(tpp)]} in polymer membrane anion-selective electrodes. These electrodes displayed surprising selectivity for salicylate over benzoate, and excellent selectivity for salicylate over chloride. It was proposed that the order of anion selectivities reflects strength of binding of anions to a cationic tin porphyrin centre in the membrane.⁵

One of us has studied a wide range of Sn(tpp) complexes by NMR and visible absorption spectroscopy. The favourable chemical and NMR properties of these complexes have enabled the gen-

^{*} For part III, see ref. 1.

[†]Author to whom correspondence should be addressed.

eration of spectroscopic *cis*- and *trans*-influence series for oxygen-bound axial ligands of widely differing base strengths, and for various other ligands.^{1,6} Others have investigated the electrochemical behaviour of some tetra(aryl)porphyrin tin(IV) complexes,⁷ although some of their spectroscopic data are in conflict with an earlier communication.^{6b} It therefore appeared worthwhile to study the solid-state structures of some Sn(tpp) complexes with various axial ligands, to see if salicylate displayed any unusual coordination behaviour, and to complement the spectroscopic studies.

Tin(IV) porphyrins have not been extensively studied by crystallography. The dichloro complexes $[SnCl_2(tpp)]^8$ and $[SnCl_2(oep)]$ (H₂oep = 2,3,7,8, 12,13,17,18-octaethylporphyrin),⁹ and a partially disordered example of the dihydroxo complex $[Sn(OH)_2(tpp)]$ [as a bis(chloroform), bis(carbon tetrachloride) solvate]¹⁰ are the only published structures containing simple electronegative axial ligands. As the dihydroxo species is the normal starting material for most tin(IV) tpp bis(acido) complexes, we felt it was important to determine its structure more precisely, for comparison with other complexes. We report herein the structures of five Sn(tpp) complexes which are relevant to several of the above-mentioned studies, namely $[SnX_2(tpp)]$ (X = hydroxide, water, benzoate, salicylate and acetylsalicylate).

EXPERIMENTAL

General

IR spectra were recorded in KBr discs on a Perkin-Elmer 881 spectrometer, and visible spectra in CHCl₃ solutions (unless otherwise stated) on a Varian DMS100 spectrometer. NMR spectra were recorded in CDCl₃ on the Bruker CXP300 instrument at the Brisbane NMR Centre, Griffith University. Spectra were accumulated with 16K data points and zero filled to 32K, using spectral widths of 3500-5500 Hz. The individual satellites due to coupling of β -pyrrole protons with ¹¹⁷Sn and ¹¹⁹Sn were not resolved. Coupling constants are therefore averaged values determined from the top of the peak as assigned by the spectrometer computer, so are $\pm ca 0.5$ Hz at the digital resolution obtainable. Microanalyses were carried out by the Microanalytical Service, University of Queensland. Chloroform was distilled from anhydrous potassium carbonate and tetrahydrofuran (THF) from sodium under nitrogen. All other solvents were Ajax A.R. grade. Organic acids were Merck "zur Synthese" grade. Silver trifluoromethanesulphonate (triflate) was obtained from Aldrich.

Preparation of complexes

(a) $[Sn(OH)_2(tpp)]$ (1). This complex was prepared as previously reported,^{6c} and crystals were grown by diffusion of pentane vapour into a CHCl₃ solution.

(b) $[Sn(CF_3SO_3)_2(tpp)]$ or $[Sn(OH_2)_2(tpp)](CF_3)$ SO_3_2 (2). Silver triflate (160 mg, 0.63 mmol) was placed in a Schlenk flask and dried in vacuo. Nitrogen was admitted, then THF ($ca \ 15 \ cm^3$) was distilled from sodium into the flask. Solid [SnCl₂(tpp)] (250 mg, 0.31 mmol) was added, and the mixture was stirred under nitrogen for 20 min. The solution was removed from the silver chloride by decantation through a cannula with attached filter paper, and concentrated in vacuo to a volume of $ca 5 \text{ cm}^3$. Hexane (30 cm³) was slowly added with stirring, to yield a fine, dark red powder. Recrystallization from THF-pentane gave maroon microcrystals (233 mg, 73%). Crystals for X-ray analysis were grown by layering pentane over a concentrated THF solution, and leaving in a refrigerator for several weeks. Elemental analysis and the crystal structure showed these to be the diaqua complex. We have subsequently prepared 2 by reaction of triflic acid with [Sn(OH)₂(tpp)] in CH₂Cl₂ solution¹ (Found : C, 52.0; H, 3.0; N, 5.2. C₄₆H₃₂F₆N₄O₈S₂Sn requires : C, 51.8; H, 3.0; N, 5.25%); v_{max} (Nujol) 1295s and 1022s (SO₃), 1225vs and 1180m cm⁻¹ (CF₃); $\delta_{\rm H}$ ca 7.8 (m, 3', 4' and 5'), ca 8.3 (m, 2' and 6') and 9.36 [s, ${}^{4}J(\text{SnH})$ 20 Hz] (see text for discussion); λ_{max} (THF) 512, 550 and 590 nm (log ɛ 3.49, 4.32 and 3.83), (CHCl₃) 420, 511, 549 and 588 nm (log ε 5.75, 3.48, 4.37 and 3.85). (c) $[Sn(C_6H_5CO_2)_2(tpp)]$ (3). Solid benzoic acid (30 mg, 0.25 mmol) was added to a solution of $[Sn(OH)_2(tpp)](77 mg, 0.1 mmol) in CHCl_3 (5 cm^3),$ and the mixture was stirred at room temperature for 30 min. The solution was filtered through anhydrous sodium sulphate and evaporated to dryness in vacuo. The residue was recrystallized from chloroform-hexane to yield violet prisms (83 mg, 86%). Crystals for X-ray analysis were grown by diffusion of pentane vapour into a CH₂Cl₂ solution (Found: C, 71.8; H, 3.9; N, 5.75. C₅₈H₃₈N₄O₄Sn requires: C, 71.55; H, 3.9; N, 5.75%); v_{max} 1649, 1314 and 1298 cm⁻¹ (carboxylate); $\delta_{\rm H}$ 4.90 (4H, dd, 2" and 6"), 6.32 (4H, dt, 3" and 5"), 6.65 (2H, dt, 4"), ca 7.8 (12H, m, 3', 4' and 5'), ca 8.2 (8H, m, 2' and 6') and 9.18 [8H, s, ${}^{4}J(\text{SnH})$ 15 Hz, β -pyrrole]; $\lambda_{\rm max}$ 423, 517, 556 and 596 nm (log ε 5.78, 3.53, 4.33 and 3.98).

(d) $[Sn(2-OH-C_6H_4CO_2)_2(tpp)]$ (4). This complex

(94 mg, 94%) was prepared and purified as for 3 above, using salicylic acid (30 mg, 0.22 mmol) and $[Sn(OH)_2(tpp)]$ (77 mg, 0.1 mmol) (Found : C, 69.2; H, 3.7; N, 5.6. $C_{58}H_{38}N_4O_6Sn$ requires: C, 69.3; H, 3.8; N, 5.6%); v_{max} 1667, 1634 and 1307 (carboxylate) and 1363 cm⁻¹ (phenol C—O); δ_H 3.96 (2H; br d, 6"), 5.67 (2H, dt, 5"), 5.97 (2H, dd, 3"), 6.57 (2H, dt, 4"), *ca* 7.8 (12H, m, 3', 4' and 5'), *ca* 8.2 (8H, m, 2' and 6'), 9.21 [8H, s, ${}^4J(SnH)$ 16 Hz, β -pyrrole] and 9.3 (2H, br s, OH); λ_{max} 423, 517, 556 and 595 nm (log ε 5.76, 3.53, 4.34 and 3.98).

(e) $[\text{Sn}(2\text{-}\text{OCOCH}_3\text{-}\text{C}_6\text{H}_4\text{CO}_2)_2(\text{tpp})]$ (5). This complex (97 mg, 89%) was prepared as for 3 above, using acetylsalicylic acid (42 mg, 0.23 mmol) and $[\text{Sn}(\text{OH})_2(\text{tpp})]$ (77 mg, 0.1 mmol). Crystals were grown by diffusion of pentane vapour into a CHCl₃ solution (Found: C, 68.0; H, 3.9; N, 5.0. $\text{C}_{62}\text{H}_{42}\text{N}_4\text{O}_8\text{Sn}$ requires: C, 68.3; H, 3.9; N, 5.1%); v_{max} 1766, 1750 and 1363 (acetate), 1654 and 1313 cm⁻¹ (carboxylate); δ_{H} 1.19 (6H, s, CH₃), 4.18 (2H, dd, 6″), 6.01 (2H, dd, 3″), 6.08 (2H, dt, 5″), 6.61 (2H, dt, 4″), *ca* 7.8 (12H, m, 3', 4' and 5'), *ca* 8.3 (8H, m, 2' and 6'), and 9.15 [8H, s, ⁴J(SnH) 15 Hz, β -pyrrole]; λ_{max} 424, 518, 557 and 596 nm (log ε 5.77, 3.53, 4.32 and 3.95).

X-ray data collection, structure solution and refinement

Data for complexes 1-5 were collected on Nicolet R3m diffractometers, 3, 4 and 5 at normal temperature (293 K), 1 and 2 at low temperature (163 K). Data were corrected for absorption. Structures were solved using SHELXS 8611 and refined using SHELX 76.12 Disorder problems were resolved using partial site occupancies for atoms in structures 2 (in the $CF_3SO_3^-$ groups) and 5 (the peripheral phenyl rings and acetylsalicylate groups). This accounts for the rather high refinement residuals for these structures. Anisotropic thermal parameters were used for all non-hydrogen atoms in structures 1, 3 and 4, while for 2 and 5 isotropic factors were used. Hydrogens were incorporated only in the structures showing no disorder. These were located by difference methods and were included with refinement of both positional and thermal parameters. Neutral atom scattering factors were used,¹³ while the heavy atoms were corrected for the effects of anomalous dispersion.¹³

Atomic coordinates, thermal parameters, and observed and calculated structure factors have been

Table 1. Crystal data for 1-5

	1	2	3	4	5
Formula	$C_{44}H_{30}N_4O_2Sn$	$C_{46}H_{32}F_6N_4O_8S_2Sn$	$C_{58}H_{38}N_4O_4Sn$	C ₅₈ H ₃₈ N ₄ O ₆ Sn	$C_{62}H_{42}N_4O_8Sn$
M _r	765.4	1065.6	973.7	1005.7	1089.7
a (Å)	13.463(2)	20.250(5)	10.228(2)	10.597(3)	11.14(1)
b (Å)	13.463(2)	8.964(3)	11.312(2)	11.198(2)	12.59(1)
c (Å)	9.669(2)	27.926(9)	11.537(2)	11.621(3)	19.06(1)
α (°)	90	90	65.95(2)	65.29(2)	84.87(6)
β (°)	90	118.01(2)	68.61(2)	66.99(2)	88.97(7)
γ (°)	90	90	76.05(1)	74.93(2)	68.58(7)
$V(\text{\AA}^3)$	1752.6(6)	4476(2)	1128.3(4)	1145.4(5)	2478(3)
Z	2	4	1	1	2
D _c	1.446	1.581	1.432	1.457	1.460
Space group	I4/m	Cc	ΡĪ	ΡĪ	ΡĪ
F(000)	776	2144	496	512	1112
$\mu ({\rm cm}^{-1})$	7.8	7.5	6.3	6.3	5.9
R^a	0.039	0.071	0.055	0.077	0.156 ^b
R_{w}^{c}	0.040	0.074	0.058	0.081	
A^{c}	1.30	1.00	0.83	1.02	
B ^c	5.3×10^{-3}	9.0×10^{-3}	2.5×10^{-3}	4.7×10^{-3}	
Crystal size (mm)	$0.32 \times 0.15 \times 0.14$	$0.25 \times 0.08 \times 0.08$	$0.06 \times 0.16 \times 0.20$	$0.12 \times 0.16 \times 0.20$	$0.22 \times 0.30 \times 0.50$
Data collected	1495	3010	2945	2145	6493
$2\theta_{\max}$	45	45	45	40	45
Temperature (K)	163	163	293	293	293
Data used	1256	1771	2389	1711	3822
Discrimination	$I>2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$

 ${}^{"}R = [\Sigma ||F_{o}| - |F_{c}||/|F_{o}|].$

^b Unit weights.

 ${}^{c}R_{w} = [(\Sigma w(||F_{o}| - |F_{c}||^{2} / \Sigma w |F_{o}|^{2})^{1/2}]; w = A/(\sigma^{2}F_{o} + BF_{o}^{2}).$

Table 2. Bond distances (Å) and angles (°) about the coordination polyhedra for complexes 1-5

	1	2	3	4	5	
					Molecule A	Molecule B
(a) Distances						a 1 84
Sn—N(1)	2.106(3)	2.04(2)	2.088(5)	2.09(1)	2.10(3)	2.08(3)
Sn—N(1)'	2.106(3)	2.09(2)	2.088(5)	2.09(1)	2.10(3)	2.08(3)
Sn—N(8)	2.106(3)	2.07(2)	2.085(5)	2.08(1)	2.09(3)	2.12(3)
Sn—N(8)'	2.106(3)	2.04(2)	2.085(5)	2.08(1)	2.09(3)	2.12(3)
SnO	2.017(4)	2.14(1)	2.055(5)	2.08(1)	2.05(3)	2.06(3)
Sn—O′	2.017(4)	2.18(1)	2.055(5)	2.08(1)	2.05(3)	2.06(3)
(b) Angles						
N(1)— Sn — $N(8)$	90.0(2)	93(1)	90.2(2)	90.6(4)	91(1)	90(1)
N(1)	90.0(2)	91(1)	90.2(2)	90.6(4)	89(1)	90(1)
N(1)SnO	90.0(2)	91(1)	86.2(2)	91.1(4)	92(1)	85(1)
N(1)—Sn—O'	90.0(2)	87(1)	86.2(2)	91.1(4)	88(1)	95(1)
N(1)—Sn— $N(1)'$	180.0(2)	178(1)	180.0(4)	180.0(4)	180(1)	180(1)
N(8)—Sn—N(1)'	90.0(2)	88(1)	89.8(2)	89.4(4)	89(1)	90(1)
N(8)—Sn—N(8)'	180.0(2)	175(1)	180.0(4)	180.0(4)	180(1)	180(1)
N(8)—Sn—O	90.0(2)	91(1)	88.2(2)	92.7(4)	88(1)	87(1)
N(8)-Sn-O'	90.0(2)	85(1)	91.8(2)	87.3(4)	92(1)	93(1)
N(8)'SnO'	90.0(2)	87(1)	91.8(2)	92.7(4)	91(1)	87(1)
N(8)'-Sn-O	90.0(2)	86(1)	91.8(2)	87.3(4)	92(1)	93(1)
N(8)' - Sn - N(1)'	90.0(2)	88(1)	90.2(2)	90.6(4)	91(1)	90(1)
O—Sn—O′	180.0(2)	175(1)	180.0(2)	180.0(4)	180(1)	180(1)
O	90.0(2)	89(1)	93.8(2)	88.9(4)	88(1)	95(1)
N(1)'—Sn—O'	90.0(2)	94(1)	86.2(2)	91.1(4)	92(1)	85(1)

deposited with the Editor as supplementary material; copies are available on request. Table 1 lists crystal data for the five compounds. Bond distances and angles for the coordination polyhedra are given in Table 2. Intraligand bond distances and angles and hydrogen atom coordinates are available from the authors.

RESULTS AND DISCUSSION

The complexes 1 and 3–5 were prepared and purified by standard methods.^{1,6} The diaqua complex 2 was isolated as a result of attempts to extend the previously studied *cis*-influence series^{6a} to complexes of weakly basic anions. The complex was prepared either by abstraction of chloride from [SnCl₂(tpp)] with silver triflate in THF or by protonation of [Sn(OH)₂(tpp)] with anhydrous triflic acid in dichloromethane. It is very insoluble in CDCl₃, in contrast to all other known members of the family of [SnX₂(tpp)] complexes, with the exception of X = ClO₄. Moreover, solutions of 2 in CDCl₃ which initially show one major β -pyrrole signal [δ 9.36, ⁴J(SnH) 20 Hz] and a minor, broader one at slightly higher field, slowly deposit solid, with diminution of the former signal. This behaviour is similar to that reported for $[Sn(ClO_4)_2(tpp)]$,^{6a} and is explicable in terms of equilibria involving the covalent bis(triflate), and mono- and bis(solvento) ionic forms. Kadish *et al.*⁷ recently reported similar findings for $[Sn(ClO_4)_2L]$ complexes $[H_2L =$ tetrakis(*m*- and *p*-tolyl)porphyrin]. The earlier conclusion of a possible intermolecular aggregation^{6a} is probably erroneous. In any case, the species which crystallized from THF/pentane was shown by elemental and crystal structure analyses to be the diaqua complex **2**.

The structures of the five tpp complexes have been determined with varying degrees of precision. Complex 1 (Fig. 1) has crystallographically imposed 4/m symmetry and exhibits none of the disorder evident in the other complexes. Because of the fourfold rotational symmetry, the hydroxyl protons are delocalized over four quarter sites and are therefore not located in the determination. The complex is isomorphous with the dichloro analogue.⁸ Its ease of crystallization free from solvent molecules contrasts with the previously reported and considerably disordered structure for [Sn(OH)₂(tpp)].¹⁰ Importantly, for comparison with complexes of less basic



Fig. 1. Molecular configuration and atom naming scheme for 1. The molecule has four-fold rotational symmetry down the O(1)—Sn—O(1)' bond, while primed atoms are generated by mirror symmetry. Unless otherwise indicated, atoms are carbons.

axial ligands, the Sn—N and Sn—O bond distances [2.106(3) and 2.017(4) Å, respectively] have been determined to a higher precision than before [averages 2.09(5) and 2.02(4) Å].¹⁰

In crystals of compounds 2–5, approximate or exact inversion symmetry is found for the $[SnX_2$ (tpp)] species. With 2 (Fig. 2), only pseudo-inversion symmetry is present, while 3, 4 and 5 have crystallographic inversion centres. In the case of 5, the



Fig. 2. Molecular configuration and atom naming scheme for 2. Primed atoms are generated by pseudo-inversion symmetry.

two independent molecules (A and B) are located about inversion centres at (0,0,0) and $(0,\frac{1}{2},\frac{1}{2})$, respectively. With these examples (2-5), various degrees of disorder were found in the peripheral substituents. However, bond distances and angles within the coordination polyhedra are considered precise enough to allow a meaningful comparison for the series. The tin(IV) ion is amongst the largest which can be accommodated within a planar tpp moiety. The Sn-N bond distances in complexes 1-5, and in [SnCl₂(tpp)], vary only slightly, as expected for such a situation. While the core size is constrained, variation is certainly evident in the axial Sn-O distances. These increase in the order hydroxide <benzoate \approx acetylsalicylate < salicylate < water, and so broadly follow the trend expected for mutually trans ligands of decreasing basicity. To complement our spectroscopic studies of the cis- and trans-influences in [Sn(tpp)] complexes, it would be interesting to determine the structures of some unsymmetrical derivatives [SnXY(tpp)]. Such studies would most likely be frustrated by redistribution equilibria, which prevent crystallization of pure complexes.¹

The benzoate and salicylate structures are very similar (Figs 3 and 4). This is apparent not only from cell data (Table 1), but also from structural features, e.g. the conformations of the phenyl rings and the disposition of the axial ligands. The comparative C(5)-C(6)-C(61)-C(62) and C(9)-C(12)-C(121)-C(122) torsion angles for the phenyl rings are +79, -74° (3) and -82, $+75^{\circ}$



Fig. 3. Molecular configuration and atom naming scheme for 3. Primed atoms are generated by inversion symmetry. For the tpp moiety, naming follows the convention used in 2.

(4), which compare with 90° in 1, which has mirror symmetry. The maximum deviation from 90° is found in 2 (-61°). In all carboxylate examples, the interaction with the metal is purely unidentate, the second carboxylate oxygen being 3.356(5) Å (3), 3.44(1) Å (4) and 3.28, 3.36(3) Å (5) from the tin atom. This further confirms the IR spectroscopic method of assigning bonding type in metalloporphyrin carboxylates,¹⁴ since the present series shows frequency differences for the two carboxylate bands of ca 330 cm⁻¹. Ionic/bidentate carboxylates exhibit frequency differences of ≤ 150 cm⁻¹. Furthermore, the ortho-hydroxy group in 3 does not interact in any way with either the tin or any atoms from adjacent molecules. However, it is clearly instrumental in maintaining the planar conformation of the whole axial ligand via intramolecular hydrogen-bonding, leading to an O-O distance of 2.50(2) Å to the non-coordinated carboxylate oxygen. In this respect it is similar to the parent salicylic acid¹⁵ (O-O, 2.62 Å). The comparative torsion angles [C(22)-C(21)-C(27)-O(29)] for 3, 4 and salicylic acid are +166, +174 and 180°, respectively. For the acetylsalicylate derivative 5 (Fig. 5), the complex molecule not showing disorder in the axial substituent (Molecule B), is also found to be conformationally similar to the parent acid.¹⁶ The carboxylate group is approximately co-planar with the phenyl ring $[C(22)-C(21)-C(27)-O(29), +172^{\circ}]$ while the acetyl group is synclinally related to the ring $[C(21)-C(22)-O(22)-C(30), +73^{\circ}]$. These compare with +178 and -85° , respectively, for acetylsalicylic acid. The packing of all complexes in their respective unit cells involves few intermolecular associations. This may be seen in Fig. 6 for 1. The aquated porphyrin cation in 2 shows O-O contacts with the disordered triflate anions $O_w(2)$ -O(3)A (2.64 Å) and $O_w(2)$ —O(5)A (2.86 Å) (Fig. 7).



Fig. 4. Molecular configuration and atom naming scheme for 4.



Fig. 5. Molecular configuration and atom naming scheme for 5 (Molecule B).



Fig. 6. Packing of 1 in the cell viewed down the four-fold axis.



Fig. 7. Packing of 2 in the unit cell viewed down the b axis.

Finally, do these structures indicate any specific structural reasons for the salicylate selectivity of the [Sn(tpp)] based membrane electrode?⁵ With the obvious caveat regarding comparisons of solution and solid-state structures, there appear to be no such special factors in operation. Likewise, the NMR data for 3, 4 and 5 are unexceptional, although in this series only *cis*-influences can be studied. Even in the complexes [Sn(HCO₂)(X)(tpp)], where *trans*-influences are observable, the ligands benzoate and salicylate are well-behaved within a series of oxygen-bound ligands.¹ The ion-selectivity displayed by the electrodes appears to have its origin in factors other than simply relative binding strengths of anions.

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