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Novel Seven Coordination Geometry of Sn(IV): Crystal Structures of Phthalocyaninato Bis(undecylcarboxylato)Sn(IV), Its Si(IV) Analogue, and Phthalocyaninato Bis(chloro)silicon(IV). The Electrochemistry of the Si(IV) Analogue and Related Compounds

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Three newly elucidated crystal structures of group IV phthalocyaninato complexes are reported, along with data for two further SiPc carboxylate complexes. In one of these crystal structures, bis(undecylcarboxylate)Sn(IV) phthalocyanine, the tin ion is seven coordinate, which is a unique finding for this atom in phthalocyanine ring coordination. Comparison of these structures with other group IV phthalocyaninato and related structures reveals differences, illustrating features significant in the chemistries of Si(IV) and Sn(IV) ions. These differences are thought to originate from their differing sizes and polarizabilities. The structures show that the Sn(IV) ion can only occupy an in-plane location in the phthalocyaninato ring where it elongates toward the two axial ligands. When the axial ligands do not facilitate this elongation cis coordination is preferred and the Sn(IV) ion sits above the phthalocyaninato ring plane. In contrast, the Si(IV) structures, with smaller, harder (i.e., less polarizable) Si(IV) ions, are six coordinate with the Si(IV) ion in the phthalocyaninato ring plane in a distorted octahedral symmetry. The electronic spectra and cyclic voltammetry of some of the Si compounds indicate that on the electrode the oxidized/reduced species behave as though they are in a solid film, rather than a soluble freely diffusing species.

Introduction

Group IV phthalocyanines, specifically those of Si and Sn, have a range of applications. Silicon phthalocyanine (SiPc) derivatives have been shown to possess antitumor activity under photodynamic conditions,[1−7] and nonlinear optical (NLO) properties have been investigated.[8] Tin phthalocyanines are of use in the materials field since they too have NLO properties.[9,10]

X-ray crystal structure determinations are invaluable in elucidating physical properties of a molecule that originate from its molecular structure. An example of this is seen in the structures of MoOPc, SnPc, TiOPc, and VOPc, where the planarity of the Pc (phthalocyaninato anion $= (C_{32}H_{16}N_8)^{2-}$) is thought to have effects on the third-order NLO susceptibility (χ^3) value.[9] Nonplanar Pc rings possess larger χ^3 values. To gain structural information, growth of good single crystals is essential, and herein lies the problem. Metalo-phthalocyanines have poor solubility, which is the reason for the lack of crystal structure information. A computer database search of group IV phthalocyanines finds only 28 structures in total.[11,12] Of those, 13 pertain to silicon and 7 to tin. Of the known SiPc structures, six are polymeric, possessing μ-oxo bridges between the SiPc units, and are less relevant to this work. Good crystals are more likely to be obtained if the solubility can be enhanced. This can be achieved by adding ligands able to bind at the axial metal

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positions. It is therefore important to expand the X-ray crystal structure information database in this field and advance the understanding of the differing chemistries of group IV phthalocyanines.

Attempts to prepare group IV phthalocyanines in this work enable the reporting of three new crystal structures, two containing Si and one with Sn. The differences observed in the metal coordination are assessed with interpretation based on the differences in the increased size and polarizability of the Sn to Si ions. Hence, the new and known samples used in the discussion of this paper are: SiPcCl$_2$ (**1**), SnPc(Lau)$_2$ (**2**), SiPc(Lau)$_2$ (**3**), Sn(IV)PcCl$_2$ (**4**), SiPc(OOCFc)$_2$ (**5**), SiPc(2,2,2-MEEAce.Ac)$_2$ (**6**), SiPc(AdaAceAc)$_2$ (**7**), [(O-^{t}Am)$_2$Si(Pc)] (**8**), and [{(n-C$_6$H$_{13}$)$_3$SiO}$_2$Si(Pc)] (**9**), where Lau = laurate, Fc = ferrocene, 2,2,2-MEEAce.Ac = 2-[2-(2-methoxyethoxy)ethoxy] acetate, AdaAceAc = adamantane carboxylate, and O-^{t}Am = *tert*-amyloxy.

Experimental Section

SiPcCl$_2$ (**1**) was prepared by the previously documented method (yield, 64%).[13] SnPc(Lau)$_2$ (**2**) and SiPc(Lau)$_2$ (**3**) were prepared by an analogous method to that used for the preparation of SiPc(OOCFc)$_2$ (**5**), involving the use of lauric acid instead of ferrocene carboxylic acid and either SnPcCl$_2$ or SiPcCl$_2$ as starting materials.[14,15] Also, SiPc(2,2,2-MEEAce.Ac)$_2$ (**6**) and SiPc(AdaAceAc)$_2$ (**7**) were prepared via replacement of ferrocene carboxylic acid in the reaction with SiPcCl$_2$ with 2-[2-(2-methoxyethoxy)ethoxy] acetic acid and adamantane carboxylic acid in **6** and **7**, respectively.

The CV measurements were carried with the apparatus previously described. The solvent used was freshly distilled dichloromethane with 0.02 M tetrabutylammonium tetrafluoroborate (TBA/TFB) as support electrolyte. Potentials were internally referenced to the ferrocene/ferrocinium couple, which was set at 0.45 V relative to the standard calomel electrode (SCE).

Analysis for **2**. IR (KBr disk; ν in cm^{-1}; intensities, v = very, s = strong, m = medium, w = weak): 3061 (w), 2954 (m), 2923 (s), 2852 (s), 2645 (w), 2607 (w), 2569 (w), 1624 (w), 1609 (m), 1503 (m), 1467 (m), 1422 (m), 1389 (w), 1333 (s), 1289 (s), 1165 (m), 1119 (s), 1081 (s), 1001 (w), 895 (m), 873 (w), 829 (w), 777 (m), 751 (m), 728 (s), 693 (w), 669 (w), 633 (w), 570 (w), 507 (w), 434 (w). UV−Vis (chloroform; $\lambda_{\max}$ in nm (absorbance normalized relative to Q-band): 692 (1.00), 666 (0.18) shoulder, 626 (0.21) overtone, 360 (0.40). ^{1}H NMR [CDCl$_3$; δ in ppm (nCH multiplicity, bs = broad singlet, s = singlet, t = triplet, m = multiplet, qt = quartet, qp = quintuplet), *total* H$_{\mathrm{type}}$]: −0.15 (2CH$_2$, t, 4H$_{\mathrm{aliph}}$), 0.02 (2CH$_2$ (signal very close to TMS peak), s, 4H$_{\mathrm{aliph}}$), 0.23 (2CH$_2$, t, 4H$_{\mathrm{aliph}}$), 0.46 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), 0.72 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), 0.88 (2CH$_3$, t, 6H$_{\mathrm{aliph}}$), 0.92, (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), 1.00−1.30 (8CH$_2$, m, 16H$_{\mathrm{aliph}}$), 8.11 (8H, m, 8H$_{\mathrm{Pc}}$), 9.11 (8H, m, 8H$_{\mathrm{Pc}}$). FAB/MS (NOBA matrix); *m*/*z* (rel. abun.): 1031.8, 702.5, 631.7, 390.2, 319.3, 260.2, 222.2, 190.2, 154.2. Microanalysis; C$_{56}$H$_{62}$N$_8$O$_4$Sn$_1$ (M. Wt. 1029.85) [Calculated (found)]: C, 65.31 (65.70); H, 6.17 (6.13); N, 10.88 (10.85).

Analysis for **3**. IR (Nujol; ν in cm^{-1}): 534 (w), 573 (m), 603 (w), 648 (m), 698 (s), 737 (vs), 762 (vs), 783 (m), 807 (m), 913 (s), 937 (m), 974 (m), 1067 (m), 1527 (s), 1595 (w), 1608 (m), 1686 (vs). IR (KBr disk) ν in cm^{-1}): 425 (m), 534 (m), 574 (m), 649 (w), 699 (w), 737 (vs), 762 (s), 784 (w), 808 (w), 914 (s), 937 (w), 1067 (m), 1082 (vs), 1122 (vs), 1165 (m), 1263 (s), 1278 (m), 1292 (s), 1336 (vs), 1352 (m), 1430 (s), 1463 (m), 1472 (m), 1528 (s), 1595 (w), 1609 (m), 1688 (vs). UV−Vis (α-chloronaphalene; $\lambda_{\max}$ in nm (absorbance normalized relative to Q-band): 686 (1.00), 656 (0.12), 618 (0.18), 360 (0.32). UV−Vis (chloroform; $\lambda_{\max}$ in nm (absorbance normalized relative to Q-band): 684 (1.00), 652 (0.12), 614 (0.14), 360 (0.27). ^{1}H NMR (CDCl$_3$; δ in ppm): −0.96 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), −0.75 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), −0.64 (2CH$_2$, t, 4H$_{\mathrm{aliph}}$), 0.07 (2CH$_2$ (signal obscured by TMS and extracted by assignment of the integrals from the other peaks), 4H$_{\mathrm{aliph}}$), 0.52 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), 0.81 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), 0.90 (2CH$_3$, t, 6H$_{\mathrm{aliph}}$), 1.03 (2CH$_2$, qp, 4H$_{\mathrm{aliph}}$), 1.13−1.31 (6CH$_2$, m, 12H$_{\mathrm{aliph}}$), 8.38 (8H$_{\mathrm{A}}$, m, 8H$_{\mathrm{Pc}}$), 9.696 (8H$_{\mathrm{B}}$, m, 8H$_{\mathrm{Pc}}$). FAB/MS (NOBA matrix); *m*/*z* (rel. abun.): 938 (10), 738 (47), 556 (63), 304 (64), 149 (100). Microanalysis; C$_{56}$H$_{62}$N$_8$O$_4$Si$_1$ (M. Wt. 939.23) [Calculated (found)]: C, 71.61 (71.32); H, 6.65 (6.70); N, 11.93 (11.13). For information on the equipment used for measurements refer to our previous paper.[14]

Analysis for **6**. IR (KBr Disk; ν in cm^{-1}): 428 (m), 535 (m), 575 (w), 649 (w), 718 (s), 741 (vs), 762 (s), 792 (m), 862 (w), 914 (s), 934 (m), 1016 (w), 1063 (m), 1082 (vs), 1126 (vs), 1167 (m), 1198 (w), 1230 (m), 1294 (vs), 1310 (vs), 1338 (vs), 1432 (s), 1475 (m), 1529 (s), 1609 (m), 1687 (s), 1717 (m). IR (Nujol mull ν in cm^{-1}): 720 (vs), 736 (vs), 761 (s), 787 (w), 854 (w), 881 (w), 914 (m), 934 (m), 964 (m), 1060 (m), 1081 (s), 1122 (vs), 1144 (m), 1163 (m), 1289 (m), 1311 (m), 1336 (s), 1529 (m), 1610 (m), 1687 (m). UV−Vis (α-chloronaphalene; λ_{m}in nm (absorbance normalized relative to Q-band): 692 (2.34), 662 (0.34), 622 (0.40), 362 (0.71). UV−Vis (chloroform; $\lambda_{\max}$ in nm: 686 (1.260), 654 (0.158), 616 (0.184), 360 (0.356). ^{1}H NMR (CDCl$_3$; δ in ppm): 1.00 (2CH$_2$, s, 4H$_{\mathrm{aliph}}$), 1.77 (2CH$_2$, t, 4H$_{\mathrm{aliph}}$), 2.48 (2CH$_2$, t, 4H$_{\mathrm{aliph}}$), 2.92 (2CH$_2$, t, 4H$_{\mathrm{aliph}}$), 3.05 (2CH$_2$ + 2CH$_3$, m, 10H$_{\mathrm{aliph}}$), 8.38 (8H$_{\mathrm{A}}$, m, 8H$_{\mathrm{Pc}}$), 9.68 (8H$_{\mathrm{B}}$, m, 8H$_{\mathrm{Pc}}$). FAB/MS (NOBA matrix); *m*/*z* (rel. abun.): 917 (66), 894 (17), 717 (100), 556 (74), 308 (13), 290 (17), 224 (28), 202 (39), 187 (30), 155 (95), 136 (72). Microanalysis; C$_{46}$H$_{42}$N$_8$O$_{10}$Si$_1$ (M. Wt. 894) [Calculated (found)]: C 61.73 (62.34), H 4.73 (4.66), N 12.52 (12.30).

Analysis for **7**. IR (KBr Disk; ν in cm^{-1}): 427 (m), 498 (m), 533 (m), 575 (m), 647 (w), 677 (w), 701 (s), 734 (vs), 760 (s), 783 (w), 811 (m), 874 (vw), 912 (s), 938 (w), 1066 (m), 1082 (vs), 1123 (vs), 1163 (m), 1187 (m), 1254 (vs), 1273 (vs), 1289 (s), 1334 (vs), 1429 (s), 1452 (m), 1472 (m), 1502 (w), 1527 (m), 1612 (m), 1688 (s). UV−Vis (α-chloroform) λ_{m} in nm: 682 (1.268), 652 (0.156), 614 (0.183), 360 (0.323). ^{1}H NMR (CDCl$_3$; δ in ppm): −0.940 (6CH$_2$, s, 12H$_{\mathrm{aliph}}$), 0.391 (6CH, d, 6H$_{\mathrm{aliph}}$), 0.763 (6CH$_2$, d, 12H$_{\mathrm{aliph}}$), 8.384 (8H$_{\mathrm{A}}$, m, 8H$_{\mathrm{Pc}}$), 9.704 (8H$_{\mathrm{B}}$, m, 8H$_{\mathrm{Pc}}$). FAB/MS (NOBA matrix); *m*/*z* (rel. abun.): 901 (1.5), 812 (1), 736 (3), 719 (17), 633 (5), 557 (5), 460 (6), 391 (15), 307 (62), 290 (34). Microanalysis; C$_{54}$H$_{46}$N$_8$O$_4$Si$_1$ (M. Wt. 899.09) [Calculated (found)]: C, 72.14 (71.09); H, 5.16 (4.87); N, 12.46 (12.12).

Crystal Data for **1**. C$_{32}$H$_{16}$N$_8$Cl$_2$Si$_1$, M_r = 611.52, Bruker AXS 1K CCD diffractometer, crystal habit and dimensions: purple prism 0.22 × 0.10 × 0.06 mm, T = 123(1) K, monoclinic, space group $P2_1/n$, a = 899.7(2), b = 1458.2(4), c = 1012.9(4) pm, β = 97.74(3)°, V = 1.3169(7) nm^3, Z = 2, $\rho_{\mathrm{calc.}}$ = 1.542 Mg m^{-3}, Mo Kα radiation, (λ = 0.71069 Å), μ = 0.334 mm^{-1}, θ = 2.46−26.37°, 12793 reflections collected, 99.9% complete, 2689 unique, (R_{int} = 0.0420). No absorption correction applied. Refinement by full-matrix least-squares on F^2, 196 refined parameters, 0 restraints gave R_1 = 0.0395 based on 2329 reflections with $I > 2\sigma(I)$, wR^2 = 0.0943, S = 1.008 based on all 2689 data, max Δ/σ = 0.000, residual density +0.38 and −0.32 eÅ^3.

Crystal Data for **2**: C$_{56}$H$_{62}$N$_8$O$_4$Sn$_1$, M_r = 1029.83, Rigaku AFC7R diffractometer, crystal habit and dimensions: purple plate 0.45 × 0.42 × 0.06 mm, T = 123(1) K, triclinic, space group *P-1*, a = 1320.6(5), b = 1553.9(4), c = 1276.2(4) pm, α = 98.15(3), β = 103.26(3), γ = 100.93(3)°, V = 2.4553(13) nm^3, Z = 2, $\rho_{\mathrm{calc.}}$ = 1.393 Mg m^{-3}, Mo Kα radiation, (λ = 0.71069 Å), μ = 0.577 mm^{-1}, θ = 2.61−27.04°, 11180 reflections collected, 10709 unique, (R_{int} = 0.0238). Data were corrected for absorption by the method of ψ scans, $T_{\min}$ and $T_{\max}$ = 0.849 and 0.999, respectively. Refinement by full-matrix least-squares on F^2, 675 refined parameters, 30 restraints gave R_1 = 0.0353 based on 9259 reflections with $I > 2\sigma(I)$, wR^2 = 0.0913, S = 1.024 based on all 10709 data, max Δ/σ = 0.007, residual density +0.75 and −1.86 eÅ^3.

Crystal Data for **3**. Crystals suitable for single-crystal X-ray analysis were obtained from benzene. C$_{56}$H$_{62}$N$_8$O$_4$Si$_1$, M_r = 939.23, Enraf-Nonius CAD4 diffractometer, crystal habit and dimensions: purple prism 0.61 × 0.58 × 0.14 mm, T = 295 K, triclinic, space group *P-1*, a = 899.8(2), b = 1552.2(2), c = 1903.1(2) pm, α = 105.80(1), β = 100.62(1), γ = 93.94(1)°, V = 2.4939(6) nm^3, Z = 2, $\rho_{\mathrm{calc.}}$ = 1.251 Mg m^{-3}, Mo Kα radiation, (λ = 0.71069 Å), μ = 0.103 mm^{-1}, θ =

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Table 1. Relevant Bond Length Data, (Å), for Structures **1**−**5**

bond atoms	**1**	**2**	**3**	**4**	**5**
	$SiPcCl_2$	$SnPc(lau)_2$	$SiPc(lau)_2$	$SnPcCl_2$	$SiPc(OOCFc)_2$
M−N	1.901(2)	2.161(2)	1.909(2)	2.050(3)	1.900(2)
M−N	1.901(2)	2.170(2)	1.909(2)	2.050(3)	1.905(2)
M−N	1.902(2)	2.188(2)	1.907(2)	2.051(3)	1.907(2)
M−N	1.902(3)	2.202(2)	1.901(2)	2.051(3)	1.911(2)
M−O		2.104(2)	1.745(2)		1.749(2)
M−O		2.138(4)	1.749(2)		1.752(2)
M−O		2.479(2)			
M−Cl	2.195(1)			2.448(1)	
M−Cl	2.195(1)			2.448(1)	

1.51−24.99°, 9059 reflections collected, 8769 unique, ($R_{int} = 0.0628$). No absorption correction applied. Refinement by full-matrix least-squares on F^2, 627 refined parameters, 0 restraints gave $R_1 = 0.0494$ based on 5182 reflections with $I > 2\sigma(I)$, $wR^2 = 0.1508$, $S = 1.009$ based on all 10709 data, max $\Delta/\sigma = 0.001$, residual density +0.38 and −0.26 eÅ^3.

All structures were solved and refined using the Bruker SHELXTL suite of programs. All hydrogen atoms were placed geometrically and refined with a riding model (including free rotation about C−C bonds for methyl groups), with U_{iso} constrained to 1.2 (1.5 for methyl groups) times U_{eq} for the carrier atom. Important bond length data are presented in Table 1. Angle and fractional coordinates were submitted as Supporting Information.

Results

Crystal and Molecular Structures. As part of a program on group IV Pc complexes,[14] reported here are the preparation and crystal structures of $SiPcCl_2$ (**1**), the title Sn(IV) compound (**2**), and its Si(IV) analogue (**3**). When these structures are compared to those of other group IV and related metal phthalocyaninato structures, interesting differences become apparent, which have their origin in the sizes and polarizabilities of the Si(IV) and Sn(IV) ions.

The structure of **1** is monoclinic $P2_1/n$ ($Z = 2$), with one-half of one molecule per asymmetric unit (see Figure 1). The Si(IV) ion is in a distorted octahedral environment with no distortion of the Pc ring. In contrast $SnPcCl_2$ (**4**), although having the Sn(IV) ion in a six coordinate distorted octahedral environment, manifests a tilt on the Sn−Cl axis that is 2.5° from the normal to the Sn−N plane. This causes the Pc macrocycle to distort away from the Sn(IV) ion.[16] This distortion has the effect of ruffling the Pc ring and creating a stepped displacement of the planes of the isoindole rings.

The comparison of the structures of **1** and **4** (see bond lengths in Table 1) shows the considerable distortion manifest in **4**, and this distortion is caused solely by the increased size of the Sn(IV) ion, compared to the Si(IV) ion. This is best understood by assuming an ionic radius[17] of 1.81 Å for the Cl^- ion, which gives approximately 0.638 Å for the radius of the Sn(IV) ion in **4**, and 0.385 Å for the radius of the Si(IV) ion in **1**. The former differs from the value of 0.71 Å (Goldsmidt and Pauling radius), whereas the latter is between 0.38 Å (Goldsmidt)[17] and 0.41 Å (Pauling) radius.[17] This illustrates the hard, nonpolarizable nature of the Si(IV) ion compared to the softer more polarizable Sn(IV) ion. Subtracting the values of 0.638 Å for Sn(IV) ion and 0.385 Å for Si(IV) ion from the M−N bond lengths in Table 1 gives 1.413 and 1.517 Å, respectively, for the N radius. This clearly indicates that the Sn(IV) ion radius in the M−N plane must be smaller than 0.638 Å and emphasizes that the Sn(IV) ion is squeezed into the Pc plane. It is worth noting that the Ti(IV) ion in $TiPcCl_2$ is displaced 0.84 Å out of the plane of the Pc ring, with the two chloride ligands adopting a cis arrangement.[18] Interestingly, the Ti(IV) radius is given as 0.60 Å by Goldsmidt and 0.68 Å by Pauling.[17] As Ti(IV) is usually thought of as a hard, nonpolarizable ion, it would not be expected to fit into the Pc plane without considerable expansion of the Pc core.

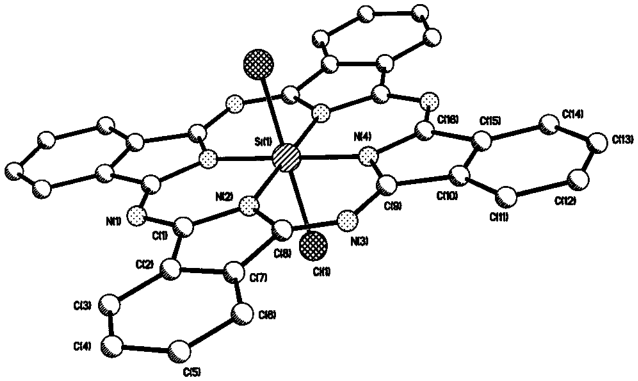

Figure 1. Crystal structure of **1**, hydrogen atoms omitted for clarity.

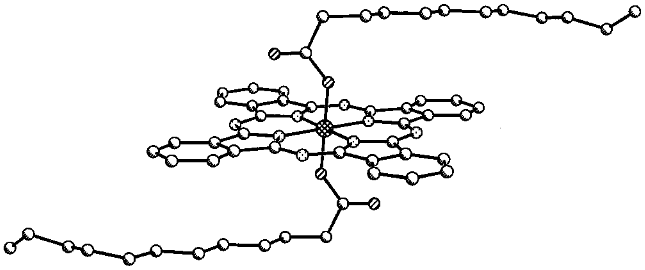

Figure 2. Crystal structure of **3**, hydrogen atoms, atom labels, and the disordered fragments of the lauric acid chain omitted for clarity.

To increase the solubility of group (IV) pc complexes for easier crystallization, axial ligands generating $MPcL_2$ complexes (L = ligand) were sought.[14] To achieve this, the lauric acid derivatives M(IV)Pc(Lau)$_2$ (M = Si, Sn) were synthesized.

Compound **3** [$SiPc(Lau)_2$] crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$), with two independent half molecules in the asymmetric unit (see Figure 2). Both of these have very similar Si(IV) ion distorted octahedral coordination environments, with no ruffling of the Pc ring. The observation is analogous to those of the structure of **1** and also the structure of $SiPc(OOCFc)_2$ (**5**) (Fc = Ferrocenyl = $(C_5H_5)Fe(C_5H_4)$).[14] The slight differences between the two independent molecules of **3** are small torsional distortions in the lauric acid chain. These are caused solely by increased thermal motion in the terminal carbon atoms of one lauric acid ligand.

The Sn(IV) analogue (**2**) [$SnPc(Lau)_2$] crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$) (see Figure 3) and adopts a completely different coordination geometry than that of **3**. As far as we are aware, this report describes the first example of a tin(IV) monophthalocyaninato derivative where the Sn(IV) ion lies above the plane of the Pc ring. There are two unsurprising examples of molecules that contain a tin atom lying out of the Pc ring plane; these are Sn(II)Pc[19] and Sn(IV)Pc$_2$ (in Sn(II)Pc the Sn(II) atom is much larger than a Sn(IV) atom, and the Sn

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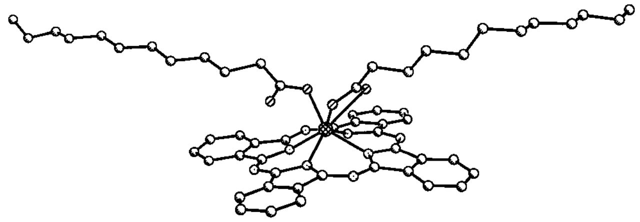

Figure 3. Crystal structure of **2**, hydrogen atoms and atom labels omitted for clarity. One molecule of the asymmetric unit is displayed.

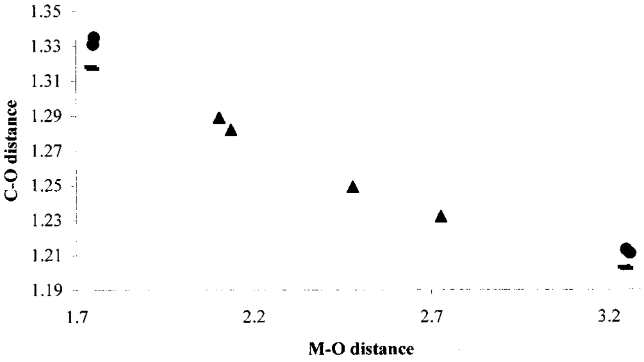

Figure 4. Plot of Metal to Oxygen Distance Against the Same Oxygen to Carbon Distance for Samples **2** (▲), **3** (−), and **5** (●) in Å.

atom sits 1.11 Å above the plane of the Pc[6,7]).[20,21] In **2** the axial lauric acid substituents have cis coordination with respect to the Pc ring. The binding mode for each lauric acid is different, one is monodentate and the other bidentate. The Sn(IV)−O bond lengths are Sn(1)−O(3) 2.104(2) Å, Sn(1)−O(2) 2.138(4) Å, and Sn(1)−O(1) 2.479(2) Å. The Sn(1)−O(1) bond length is longer than the first two by 0.341 Å, although, it is not much longer than the Sn−N bonds in Sn(Pc)$_2$ with an average length of 2.35 Å.[20,21] In addition, the C(33)−O(1) bond is 1.250(3) Å, which is significantly longer than the other comparable carboxylate bond length of C(45)=O(4) at 1.232(3) Å. A plot of metal to oxygen distance against the same oxygen to carbon distance is shown in Figure 4 . In this plot the M−O bonds are to the left and the nonbonding distances to the right, i.e., those distances in **3** and **5** with definite bonding and nonbonding ligand oxygen atoms. The four data points shown in the center of the plot are for sample **2**. The Sn(1)−O(4) distance at 2.728 Å is closer to the nonbonding distances. The Sn(1)−O(1) distance of 2.480 Å is between this and the bonding distances, indicating it has bonding character. Indeed the C(45)=O(4) bond of 1.232(3) Å is not much longer than the 1.214(3) and 1.211(3) Å distances found for the C=O bonds in structure **5**.[14] This is additional evidence that the 2.479(2) Å bond length is a bonding distance. Hence, to call the Sn(1)−O(1) distance of 2.479(2) Å a bonding interaction is reasonable. The overall coordination number of the Sn(IV) ion is, therefore, seven. The structure is thus the first known Sn(IV)Pc complex with this coordination number (see Table 1).

In the case of **3**, which is six coordinate, the bonding about the Si(IV) ion is very similar to that of **5**. The structure[14] of **5** was described with the Si(IV) ion bonding tightly to the equatorial N atoms and less tightly to the carboxylate oxygen atoms. The Si(IV) ion was shown to be small enough to locate in the Pc plane of **5** as it does in **3**. From Table 1 it is apparent that **3** is very similar to **5**. Hence elongating toward the axial ligands in this six coordinate environment electronically satisfies the Si(IV) ion in **3**.

Following the description of the coordination environment of **2**, further discussion of this seven coordinate Sn(IV)Pc is merited. There are two contributory factors explaining this finding. First, complex **4** is distorted whereas **1** is not. Hence the Sn(IV) ion is a tight fit in a Pc ring in the chloride compounds and cannot be expected to fit into the Pc plane in **2**. Second, there is the fact that the Sn−N bonds in **2** are much shorter than in Sn(Pc)$_2$. In the latter structure,[21] the Sn atom is eight coordinate and sandwiched between two Pc rings (although some lengthening of the Sn−N bonds might be influenced by steric effects). The Sn−N bond distance average is 2.35 Å, and the rings are staggered at an angle of 42°. This suggests that, relative to the bisphthalocyaninato compounds, the Sn(IV) ion in **2** cannot satisfy its electron density requirement from the oxygen atoms, even by receiving extra electron density from O(1). In addition, compared to the structure of **4** the Sn−N bond lengths in **2** are long. It is thus argued that the Sn(IV) ion in **2** is receiving more electron density from the three carboxylate oxygen atoms than the Sn(IV) ion in **4** receives from the chloride atoms. It therefore takes up an intermediate coordination between that of **4** and Sn(Pc)$_2$ (elucidated from its X-ray single-crystal structures).[20,21] Complex **2** therefore ends up with a coordination number of seven. In fact, **2** can be considered to be similar to the TiPcCl$_2$ structure discussed above, where the Ti(IV) ion is out of the Pc plane and the two chloride ions are cis.

Electronic Spectra. The UV−visible absorbance spectra for **3**, **5**−**7** in chloroform all have their Q-bands between 682 and 688 nm. Compounds **3** and **6** also dissolve well in 1-choronaphthalene, where their Q-bands are at 686 and 692 nm, respectively. The Q-band range therefore is between 682 and 692 nm (including solvent shifts), corresponding to a range of 1.82−1.79 eV. This corresponds to the difference between the HOMO and the LUMO and, therefore, to the difference between the first oxidation and first reduction potential of these compounds.[22,23] Compound **5** also had its Q-band at 690 nm in 1-chloronaphthalene (corresponding to 1.80 eV). All the electronic spectra of these biscarboxylate complexes are very similar, which is indicative of the fact that only the Si−O−C interaction is significant in influencing the positions of the phthalocyanine's HOMO and LUMO.

Cyclic Voltametry (CV). Three redox processes are observed in each case for compounds **3**, **6**, and **7** (Table 2), and are due to the macrocyclic ring.[24] Similar redox processes were also found for compound **5**, which, in addition, manifested the oxidation potential of the ferrocenecarboxylato groups.[24] By comparison to compounds **3**, **6**, and **7**, the first oxidation potential for compound **5** was raised due to the presence of the ferrocenecarboxylato groups.

It has been established that in the main group phthalocyanines, the first oxidation potential is separated from the first reduction potential by about 1.5 V. This value is said to correspond to the magnitude of the energy difference between the HOMO and LUMO (except for molecules in which the metal ions are not in the macrocyclic plane, examples are Pb^{2+} and Cd^{2+}).[24] It has been shown, however, that the individual potentials for the first ring reduction and first ring oxidation do vary and are

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Table 2. Oxidation and Reduction Potentials of Some Relevant Phthalocyanine Complexes

compound	oxidation potentials (V) 2nd	oxidation potentials (V) 1st	oxidation potentials (V) other oxidatn^a	reduction potentials (V) 1st	reduction potentials (V) 2nd	solvent	ref
3^{bc}		1.05		−0.60(2)	−1.05(2)	CH_2Cl_2	this work
5^{bc}		1.23(2)	0.69(2)	−0.55(2)	−1.02(2)	CH_2Cl_2	14
6^{b}		1.07(2)		−0.61(2)	−1.03(2)	CH_2Cl_2	this work
7^{bcd}		1.05(2)		−0.66(2)	−1.13(2)	CH_2Cl_2	this work
8^{b}				−0.540(5)	−1.14	DMF	24
9^{b}		1.00		−0.90	−1.48	CH_2Cl_2	25
$ClGa^{III}Pc$		0.86		−0.74	−1.14	DMF	24
$ClIn^{III}Pc$		0.83		−0.72	−0.95	DMF	24
$Cd^{II}Pc$	0.88	0.54		−1.17		DMF	24
$Hg^{II}Pc$		0.25		−1.30		DMF	24
$Mg^{II}Pc$	1.26	0.65		−0.92	−1.26	DMF	24

^{a} Oxidation potential of the ferrocenylcarboxylato groups in **5**. ^{b} Structure given in text of this paper. ^{c} Relative to SCE. ^{d} Partially studied.

functions of the polarizing potential of the central metal ion (taken as charge/radius{ze/r}). It has been demonstrated that the more polarizing the central metal ion, the more difficult it is to oxidize and the easier it is to reduce the macrocyclic ring.[24] Linear plots of r/ze versus the first oxidation and first reduction potentials have been obtained for many M(Pc) species.[24] On the reduction plot [(O-^{t}Am)$_2$Si(Pc)] (where O-^{t}Am = *tert*-amyloxy) (**8**), the reduction potential of −0.540 V fitted well, though no oxidation potential was given for the compound.

Compounds **3**, **6**, and **7** have first reduction potentials ranging between −0.60(2) and −0.69(2) V, which are in keeping with the above, and their first oxidation potentials, which range from 0.98(2) to 1.07(2) V, are very close to the straight line established for the oxidation potentials.[24] The separation between the first reduction and first oxidation potentials range from 1.65(4) V for **3** to 1.71(4) V for **7**. These values are less than those observed for **5**, which has a value of 1.79(4) V, and [{(n-$C_6H_{13})_3SiO\}_2Si(Pc)$] (**9**), which has a value of 1.90 V.[25] It was shown that the latter two values match the splitting of the a_{1u} and e_g levels (in the electronic spectra) of 1.80[24] and 1.86 eV;[24] the values for compounds **3**, **6**, and **7** are also all in this range (1.79−1.82 eV). Surprisingly, the values from the electronic spectra for these compounds do not match the electrochemistry measurements very well. If it is assumed that in compound **5** the first ring oxidation potential was raised by the presence of the ferrocenyl carboxylate groups (which oxidize first),[24] then compound **5** would fit well with compounds **3**, **6**, and **7**. The critical Si−O and Si−N bonds (around the silicon atoms) are all very similar in the structures of **3** and **5**, so we would expect similar electrochemistry (and indeed similar electronic spectra). We previously pointed out[14] that compound **9** does not fit the polarization plot, whereas compound **5** (and also **3**, **6**, and **7**) does. It was suggested that compound **9** had a geometry around the Si atom that was very similar to that of [$\{(CH_3)_3SiO\}_2(CH_3)$-OSi(Pc)-OSi(Pc)OSi(Pc)OSi(CH_3){OSi(CH3)$_3$}$_2$],[14] whereas the Si−O bond length in compound **8** is more likely to be similar to compounds **3** and **5**, as in these compounds the O atom bonds to a C atom. Compounds **3**, **5**, and **8** (and also **6** and **7**) would all then be expected to have oxidation and reduction potentials that are close to each other, and we would expect compound **9** to have different values.[24] The shorter Si−O bonds in compound **9** would imply that the polarizing power of the Si atom in this compound is smaller in the Pc ring, and hence, it is more difficult to reduce it.

The reason for the discrepancy between the electrochemical results and the position of the Q-band now needs to be addressed. During the CV experiments in CH_2Cl_2, the oxidized and reduced species will stay at the electrode surface (and may even pack as they do in thin films). The Q-band of compound **5** in the solid state is at 710 nm,[14] which corresponds to 1.75 eV. The latter value is closer to the electrochemistry results for **3**, **6**, and **7** of 1.65(4)−1.741(4) V. It therefore appears that the electrochemical oxidation and reduction potentials reflect the solid-state structure of the thin films and hence should be compared to Q-bands of solid-state materials rather than the solution Q-bands.

^{1}H NMR. The experimental data for samples **2**, **3**, **6**, and **7** are presented in the Experimental Section. The ^{1}H resonances manifest a pronounced high field shift due to their proximity to the Pc ring, in keeping with compound **5** and as suggested elsewhere.[26,27] Compounds **2** and **3** both have as the ligand the lauric acid residue. When the lauric acid is analyzed in solution alone, the proton resonances are very close together; however, due to the phthalocyanine ring, the proton resonances are separated depending upon their proximity to the large aromatic ring in the complexes. Compounds **2** and **3** show a very similar effect, the Sn giving slightly larger downfield shifts (with the largest being approximately −3 ppm). Compounds **6** and **8** have shifts assigned with the furthest upfield shifts due to the ligand hydrogen atoms closest to the Si atom. The ring protons are not sensitive to the ligand for like central atoms. These only significantly change when the Si is replaced with the Sn, where the Pc hydrogen peaks shift upfield.

Mass Spectra. The mass spectra data confirm that the complexes were present, when supported by our additional analyses. The spectrometer that the experiments were carried out on had a tendency to drift so that the high mass data calibration is not exact. However, an indication of some aspects of the compounds behavior can be found. Compounds **2**, **3**, and **7** show that the mass ion can be seen in the spectrum as the largest m/z peak. Compound **6** has as the main mass ion, a peak at 917 m/z which corresponds to the addition of sodium. The mass ion peak at 895 m/z is also seen for the [**6**]$^+$ ion. Compound **3** also shows evidence for the uptake of one sodium ion, whereas **2** and **7** show only the protonated positive ion peaks. For the Si containing samples no peak is seen for [SiPc]$^+$, but a peak at 557 m/z is seen and assigned to [SiPc + O]$^+$, as observed in other phthalocyanine complexes.[28,29] Sample **2** does

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however show the $[SnPc]^+$ at 631 *m*/*z* and the 830 *m*/*z* peak assigned to $[SnPc(lau)]^+$.

Conclusions

The preparation of soluble Si and one Sn phthalocyanine carboxylate complexes is presented. Three newly elucidated crystal structures of group IV phthalocyaninato complexes are reported along with data for two further SiPc carboxylate complexes. In the crystal structure of bis(undecylcarboxylate)-Sn(IV) phthalocyanine, the tin ion is seven coordinate, which is a unique finding for this atom in phthalocyanine ring coordination. Comparison of the structures with other group IV phthalocyaninato ($SiPcL_2$ {where L = ligand} in six coordination) and related structures reveals that the differences in coordination are explained due to the size and polarizability of the Sn and Si ion. The structures show the Sn(IV) ion can only occupy an in-plane location in the phthalocyaninato ring, where it elongates toward the two axial ligands. When the axial ligands do not facilitate this elongation, cis coordination is preferred and the Sn(IV) ion sits above the phthalocyaninato ring plane. In contrast the Si(IV) structures with smaller, harder (i.e., less polarizable) Si(IV) ions are six coordinate, with the Si(IV) ion in the phthalocyaninato ring plane in a distorted octahedral symmetry.

For compounds **3**, **6**, and **7**, the electronic solution spectra yield values for the difference between the HOMO and LUMO between 1.65 and 1.71 V. This has led to the suggestion that during oxidation and reduction of these compounds on an electrode, the molecules order as in a thin film.

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Supporting Information Available: Three X-ray crystallographic information files (CIF) are available, one for each of samples **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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