tion between the deuterium quadrupole coupling constant and the bond force constant, the *experimental* results shown in Figure 3 indicate that the field gradient at the hydrogen nucleus is almost equal to the force constant (in atomic units)[2] even for rather complicated hydrides.

The deuterium quadrupole coupling constants of the deuterides of the light elements are plotted against their electronegativities in Figure 4. The trend of correlation is very smooth except for hydrogen, which is unique in the periodic table.

In conclusion, we would like to point out that the deuterium quadrupole coupling constant is an important quantity in connection with the electronic structure of molecules. It is directly related to, and sometimes may be used to determine, other properties of a compound. It is only fair to say that the study of deuterium quadrupole coupling deserves more attention.

Acknowledgment. This work was supported by the Atomic Energy Commission. The Varian VF-16 and HA-100 spectrometers were obtained through an Institutional Instrument grant by the National Science Foundation.

Mössbauer Spectra of Tin Complexes of Phthalocyanine and Tetraarylporphines[1]

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Received August 27, 1969

Abstract: Mössbauer spectra of a series of phthalocyaninotin(IV) complexes ($PcSnX_2$, where X = F, OH, Cl, Br, I) reveal isomer shifts that vary linearly with the electronegativity of the X ligand. The negative isomer shift for bis(phthalocyanino)tin(IV) confirms the tetravalence of tin, and its magnitude together with a lack of quadrupole splitting indicate eight equivalent Sn–N bonds. Twelve tin porphyrins have been synthesized: the dichloro, dihydroxo, and difluoro derivatives of the tin complexes of tetra(*p*-methoxyphenyl)porphine, tetra(*p*-tolyl)porphine, tetra(*p*-chlorophenyl)porphine, and tetraphenylporphine. Dichlorotetraphenylporphinotin(IV) has been synthesized directly. Isomer shifts vary regularly with the electronegativities of the chloro, hydroxo, and fluoro groups; relative charge densities at the tin nucleus appear to be determined chiefly by σ bonds. The greater quadrupole interactions observed for the phthalocyanine complexes are interpreted in terms of greater tin–nitrogen π bonding in the phthalocyanine than in the tetraarylporphine complexes. The optical spectra of the latter indicate a resonance interaction of the *para* substituents with the porphine ring and possibly with the tin atom.

Linstead's group was the first to study a series of phthalocyaninotin complexes and established the existence of phthalocyaninotin(II), PcSn; dichlorophthalocyaninotin(IV), $PcSnCl_2$; and bis(phthalocyanino)tin(IV), Pc_2Sn (Pc = phthalocyanino ligand, $C_{32}H_{16}N_8$).[4] Pc_2Sn has two phthalocyanine rings bonded to one tetravalent tin atom[5,6] and it has been suggested[7] that this may have eight Sn–N bonds. Recent X-ray analysis by Bennett has established the antiprismatic D_{4d} molecular structure.[8] Kroenke and Kenney have given preparations for the dihalophthalocyaninotin(IV) complexes and the dihydroxo analog[9] and have obtained the infrared spectra of these compounds.[10] They have assigned absorptions at 531, 563, and 299 cm^{-1} to antisymmetric F–Sn–F, O–Sn–O, and Cl–Sn–Cl stretching vibrations.

Whalley[5] reported the visible spectrum of bis(phthalocyanino)tin(IV) and also spectra of the Cu, Ni, Co, Fe, Zn, Pd, and Mg phthalocyanines, which all have an intense narrow band in the 650–675 mμ region. Stöckler, Sano, and Herber[11a] published Mössbauer parameters for PcSn and the $PcSnX_2$ series; a correction of the parameters obtained for $PcSnI_2$ was made,[11b] but no reinterpretation of the data was offered.

The tetraarylporphine ligands used in this study have been previously synthesized[12–15] and three different tin complexes of tetraphenylporphine[16–18] have been

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(1) Presented in parts at the 152nd and 154th National Meetings of the American Chemical Society, New York, N. Y., Sept 1966, and Chicago, Ill., Sept 1967.

(2) Supported by Predoctoral Fellowship 5-F1-GM-23,515-03 of the National Institute of Health Medical Services. Abstracted from the Ph.D. Thesis of Sister Mary O'Rourke, S.C.L., University of Notre Dame, 1967.

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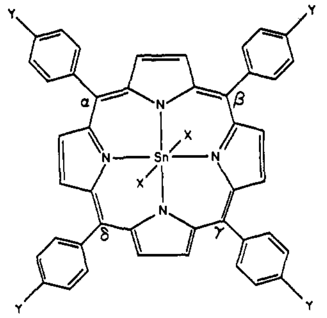

Figure 1. Dihalotetraarylporphinotin(IV).

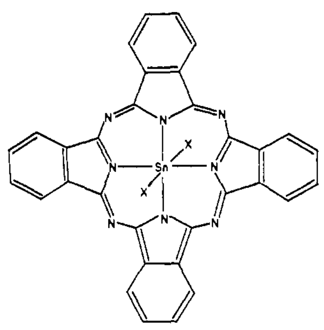

Figure 2. Dihalophthalocyaninotin(IV).

claimed. Visible and ultraviolet spectra of a group of free base porphyrins have been discussed; Thomas and Martell[18] note a shift such that bands in spectra for the tetraarylporphine derivatives occur at longer wavelength than corresponding bands in the parent tetraphenylporphine: *p*-methoxyphenyl, *p*-nitrophenyl ≫ *p*-chlorophenyl > *p*-tolyl > phenyl.

Ingram and coworkers[19] have interpreted the paramagnetic resonance spectrum of the copper(II) complex with tetra(*p*-chlorophenyl)porphine as indicating an interaction of the unpaired electron of the metal with the chlorine nucleus, presumably through the conjugated chain. This interpretation has been questioned by Kivelson and Neiman.[20] X-Ray diffraction studies reveal that in the copper complex with tetraphenylporphine the benzene rings are appreciably tilted and twisted from the porphine "plane."[21] The esr spectra of the copper(II) complexes with phthalocyanine[22] and tetraphenylporphine[23] have been interpreted as indicating negligible in-plane metal–nitrogen π bonding in these compounds and more extensive out-of-plane π bonding in the phthalocyanine complex. In the light of these findings it is of interest to look for interactions of *para* substituents with tin atoms in tin(IV) complexes with tetraarylporphines.

Experimental Section

Phthalocyaninotin Complexes. This series was prepared according to the methods of Kroenke and Kenney;[9] all complexes were vacuum dried for 1–2 hr at 110°.

Anal. (PcSn) Calcd for $SnC_{32}H_{16}N_8$: C, 60.89; H, 2.55. Found: C, 60.83; H, 2.81. (Pc_2Sn) Calcd for $SnC_{64}H_{32}N_{16}$: C, 68.53; H, 2.71. Found: C, 68.35; H, 2.93. ($PcSnF_2$) Calcd for $SnC_{32}H_{16}N_8F_2$: C, 57.43; H, 2.41; F, 5.68. Found: C, 57.19; H, 2.63; F, 5.68. ($PcSn(OH)_2$) Calcd for $SnC_{32}H_{18}N_8O_2$: C, 57.78; H, 2.73. Found: C, 57.50; H, 2.91. ($PcSnCl_2$) Calcd for $SnC_{32}H_{16}N_8Cl_2$: C, 54.74; H, 2.30. Found: C, 54.53; H, 2.05. ($PcSnBr_2$) Calcd for $SnC_{32}H_{16}Br_2$: C, 48.59; H, 2.04. Found: C, 49.47; H, 2.60. ($PcSnI_2$) Calcd for $SnC_{32}H_{16}N_8I_2$: C, 43.43; H, 1.82; N, 12.65; I, 28.68. Found: C, 43.30; H, 1.71; N, 12.03; I, 27.66.

Tetraarylporphinotin Complexes. Tetra(*p*-methoxyphenyl)porphinozinc, ZnTMeOxPP; tetra(*p*-tolyl)porphinozinc, ZnTTolP; tetra(*p*-chlorophenyl)porphinozinc, ZnTClPP; tetraphenylporphinozinc, ZnTPP; and tetra(4-pyridyl)porphinozinc, ZnTPyP, were prepared according to the general method of Rothemund and Menotti[12a] and the adaptation of Ball, Dorough, and Calvin.[14] The quantities conform to those prescribed by Fleischer[15] in a similar preparation: 50 ml of pyridine (reagent grade, Aldrich Chemical Co. Inc.; purified, J. T. Baker Chemical Co.), 15 g of zinc acetate (analyzed, J. T. Baker Chemical Co.), 25 ml of pyrrole (Aldrich Chemical Co., Inc.), and 35 ml of the appropriate carboxaldehyde (benzaldehyde, certified reagent, Fisher Scientific Co.; 4-pyridinecarboxaldehyde, *p*-chlorobenzaldehyde, and *p*-anisaldehyde, Aldrich Chemical Co., Inc.; *p*-tolylaldehyde, Eastman Organic Chemicals). The glass bomb was flushed with nitrogen and kept at approximately 130 psi and maintained at 160° for 48 hr; cooling was effected during 10–12 hr. The products were separated from the black tar by filtering on a Büchner funnel and washed with a mixture of ether/acetone (10/1).

A portion of the original crystals of α,β,γ,δ-tetra(*p*-tolyl)porphinozinc(ZnTTolP) was washed with pyridine and ether and analyzed as sample A (Table I). Another portion was dissolved in chloroform and chromatographed on alumina. This solution passed quickly through the 8-cm column, developing purple and green bands, which were eluted as samples B and C, respectively (Table I). The absorption at 615 mμ noted in the spectrum for sample C strongly suggests the presence of chlorin,[14] a corresponding compound having one reduced pyrrole ring. This is an intense peak in the spectrum for sample C but does not appear in that of sample B, which was eluted as a porphyrin band. There is a slight shoulder at 616 mμ in the spectrum for sample A which was not chromatographed; the impurity was considered to be negligible.

Table I. Visible Spectra (Chloroform Solutions) of Samples from the Preparation of ZnTTolP

Sample	Chromatography band	Absorption maxima, mμ[a]			
A		423 (I)*	547 (II)	590 (III)	616 (sh)
B	Purple	421 (I)	549 (II)	591 (III)	
C	Green	421 (I)	549 (III)		615 (II)

[a] (I)* signifies the most intense band.

Anal. (ZnTTolP) Calcd for $ZnC_{48}H_{28}N_4$: C, 78.2; H, 5.20. Found for sample A: C, 77.98, 77.91; H, 5.25, 5.41. Found for sample B: C, 77.65; H, 5.22. (ZnTClPP) Calcd for $ZnC_{44}H_{24}N_4Cl_4$: C, 64.76; H, 2.96; Cl, 17.38. Found: C, 65.34; H, 3.33; Cl, 17.16.

Metal-free α,β,γ,δ-tetraphenylporphine (H_2TPP), α,β,γ,δ-tetra(*p*-methoxyphenyl)porphine ($H_2TMeOxPP$), α,β,γ,δ-tetra(*p*-tolyl)porphine (H_2TTolP), and α,β,γ,δ-tetra(*p*-chloro)porphine (H_2TClPP) were obtained by dissolving the corresponding zinc complex in ether and treating the solution with a small quantity of 6 *N* HCl. A bright green precipitate formed immediately and concentrated in the aqueous layer; thus the porphyrin was extracted in a form presumed to be the dihydrochloride. The aqueous layer was separated and shaken with chloroform and the green solid dissolved in the chloroform layer giving a deep green solution; this was then washed with water and the color changed to purple, indicating the presence of free base. This solution was dried with potassium carbonate (analyzed reagent, J. T. Baker Chemical Co.), filtered, and evaporated under vacuum. α,β,γ,δ-Tetra(4-pyridyl)porphine (H_2TPyP) was prepared by the method of Fleischer.[15]

From these ligands the α,β,γ,δ-tetraarylporphinotin(IV) complexes (SnX_2TArP, where X = Cl, OH, or F) have been prepared. The free base and/or final tin complexes were purified by washing

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with ether/acetone (10/1) or ether, shaking chloroform solutions with alumina in the case of tetra(*p*-tolyl)porphine complexes, or chromatographing chloroform solutions on alumina columns. For the tetra(*p*-methoxyphenyl)porphine complexes it was advantageous to use benzene solutions for the chromatography on alumina and a benzene/chloroform mixture as eluent. The configuration of the porphyrin complexes is indicated in Figure 1. The phthalocyanine complexes are illustrated in Figure 2. Infrared spectra indicate that for each set of complexes the halogen atoms are *trans* to each other.

Dichlorotetraarylporphinotin(IV), $\mathrm{SnCl_2TArP}$. These compounds were prepared from the free base porphyrins by reaction with anhydrous stannous chloride (reagent grade, Matheson Coleman and Bell) in pyridine; the method was adapted from that of Corwin and Collins.[24] Approximately 0.2 g of the porphyrin was dissolved in 50 ml of pyridine and an equal weight of $\mathrm{SnCl_2}$ in concentrated pyridine solution was added. The reaction mixture was heated on a steam bath for 40–120 min, cooled to room temperature, and poured into 250 ml of ether. This purple solution was washed three times with 150-ml portions of 2 *N* HCl and twice with distilled water. A quantity of the porphyrin precipitated from the ether solution during these washings and was redissolved in chloroform; however, $\mathrm{SnTClPPCl_2}$ did not precipitate. The final solution was dried with anhydrous calcium sulfate (W. A. Hammond Drierite Co.), filtered, and evaporated under vacuum. The residue was washed with a small quantity of anhydrous ether (analytical reagent, Mallinckrodt Chemical Works) and vacuum dried at 110° for 1 hr.

A unique preparation of $\mathrm{SnCl_2TPP}$ was a direct synthesis, believed to be the first direct synthesis of a tin porphyrin: 24.8 g of dibutyltin dichloride (Alfa Inorganics, Inc.) was substituted for the zinc acetate in the general method of preparing ZnTArP and reaction conditions were kept the same. When the tar was filtered and the residue washed with ether/acetone and 2 *N* HCl, the product of lustrous purple crystals was obtained. The crystals were further washed with anhydrous ether and vacuum dried at 110° for 1 hr. The product obtained by the general method is designated sample 1, and that obtained by this direct synthesis, sample 2. Absorptions attributed to the antisymmetric Cl–Sn–Cl vibration were observed at 302–304 $\mathrm{cm^{-1}}$ in the spectra of the phenyl, *p*-tolyl, and *p*-chlorophenylporphine complexes.

Anal. ($\mathrm{SnCl_2TMeOxPP}$) Calcd for $\mathrm{SnC_{48}H_{36}N_4O_4Cl_2}$: C, 62.48; H, 3.93. Found: C, 62.76, 62.59; H, 4.04, 4.11. ($\mathrm{SnCl_2TTolP}$) Calcd for $\mathrm{SnC_{48}H_{36}N_4Cl_2}$: C, 66.98; H, 4.45. Found: C, 66.64; H, 4.39. ($\mathrm{SnCl_2TClPP}$) Calcd for $\mathrm{SnC_{44}H_{24}N_4Cl_6}$: C, 56.22; H, 2.57. Found: C, 56.41; H, 2.57. ($\mathrm{SnCl_2TPP}$) Calcd for $\mathrm{SnC_{44}H_{28}N_4Cl_2}$: C, 65.85; H, 3.52; N, 7.01; Cl, 8.84. Found for sample 1: C, 66.06; H, 3.82. Found for sample 2: C, 67.11; H, 4.00; N, 7.19; Cl, 8.54.

Dihydroxotetraarylporphinotin(IV), $\mathrm{Sn(OH)_2TArP}$. To obtain the dihydroxo complex 0.2 g of $\mathrm{SnCl_2}$ dissolved in a small amount of pyridine was added to the 50–100 ml of pyridine solution of 0.2 g of the free base porphyrin. Two pellets of KOH (analyzed reagent, J. T. Baker Chemical Co.), or approximately 0.4 g, was dissolved in a small amount of methanol; upon addition of this solution the pyridine mixture turned bright green, indicating the ionic form of the porphyrin. After approximately 3 hr of refluxing the mixture was purple again. This was cooled, diluted with chloroform, and washed repeatedly with water. Ammonium chloride (analyzed reagent, J. T. Baker Chemical Co.) was used in order to break the emulsion. A clear chloroform solution was finally separated and dried over potassium carbonate and evaporated under vacuum. The solid residue was washed with anhydrous ether and vacuum dried at 110° for 1 hr.

In preparations of $\alpha,\beta,\gamma,\delta$-tetra(*p*-chlorophenyl)porphinotin(IV) complexes it was found that extended reflux resulted in low chlorine analyses. As the color of the reaction mixture had not changed to purple and optical spectra of samples indicated that the complex had not formed completely after 3 hr of reflux, the mixture was transferred to a steam bath for an additional 6 hr and allowed to stand overnight before processing. All the spectra of the $\mathrm{Sn(OH)_2TArP}$ preparations showed a characteristic stretching frequency at 3619-20 $\mathrm{cm^{-1}}$ in chloroform solutions.

Anal. ($\mathrm{Sn(OH)_2TMeOxPP}$) Calcd for $\mathrm{SnC_{48}H_{38}N_4O_6}$: C, 65.08; H, 4.33. Found: C, 64.86; H, 5.03. ($\mathrm{Sn(OH)_2TTolP}$) Calcd for $\mathrm{SnC_{48}H_{38}N_4O_2}$: C, 70.15; H, 4.66. Found: C, 69.91; H, 4.83. ($\mathrm{Sn(OH)_2TClPP}$) Calcd for $\mathrm{SnC_{44}H_{26}N_4O_2Cl_4}$: C, 58.50; H, 2.90. Found: C, 58.43; H, 3.11. ($\mathrm{Sn(OH)_2TPP}$) Calcd for $\mathrm{SnC_{44}H_{30}N_4O_2}$: C, 69.02; H, 3.95. Found: C, 68.19; H, 4.62. ($\mathrm{Sn(OH)_2TPyP}$) Calcd for $\mathrm{SnC_{40}H_{26}N_8O_2}$: C, 62.40; H, 3.40. *F*ound: C, 63.40; H, 4.53.

Difluorotetraarylporphinotin(IV), $\mathrm{SnF_2TArP}$. Approximately 0.1–0.2 g of the $\mathrm{Sn(OH)_2TArP}$ complex was placed in a 25-ml platinum crucible, which was then filled with 49% hydrofluoric acid (analyzed reagent, J. T. Baker Chemical Co.) and evaporated on a steam bath. The residue was vacuum dried at 110° for 1 hr. Chloroform solutions of the difluoro derivatives are red; the solid phenyl, tolyl, and chlorophenyl derivatives are red violet, and the anisyl and pyridyl derivatives are purple.

Anal. ($\mathrm{SnF_2TMeOxPP}$) Calcd for $\mathrm{SnC_{48}H_{36}N_4O_4F_2}$: C, 64.79; H, 4.08; F, 4.27. Found: C, 65.09; H, 4.46; F, 4.05. ($\mathrm{SnF_2TTolP}$) Calcd for $\mathrm{SnC_{48}H_{36}N_4F_2}$: C, 69.81; H, 4.40; F, 4.60. Found: C, 69.24; H, 4.58; F, 4.44. ($\mathrm{SnF_2TClPP}$) Calcd for $\mathrm{SnC_{44}H_{24}N_4Cl_4F_2}$: C, 58.24; H, 2.66; F, 4.19. Found: C, 58.23; H, 2.86; F, 4.08. ($\mathrm{SnF_2TPP}$) Calcd for $\mathrm{SnC_{44}H_{28}N_4F_2}$: C, 68.66; H, 3.67; F, 4.94. Found: C, 67.78; H, 3.92; F, 4.85. ($\mathrm{SnF_2TPyP}$) Calcd for $\mathrm{SnC_{40}H_{24}N_8F_2}$: C, 62.00; H, 3.12; F, 4.91. Found: C, 62.24; H, 3.58; F, 3.82.

The infrared absorption maxima assigned to the F–Sn–F antisymmetric stretching vibration occur at 540, 546, 547, and 547 $\mathrm{cm^{-1}}$ for the *p*-methoxyphenyl, *p*-tolyl, *p*-chlorophenyl, and phenylporphine complexes, respectively. These compare with a value of 530 $\mathrm{cm^{-1}}$ for $\mathrm{PcSnF_2}$.

Mössbauer Spectra. Instrumentation and experimental conditions under which Mössbauer spectra were obtained have been previously described.[25] Isomer shifts relative to the $\mathrm{Pd\text{-}Sn^{119m}}$ (12 wt% tin) source were obtained for anhydrous $\mathrm{SnCl_2}$ (δ 2.53 ± 0.04 mm/sec), β-tin (δ 1.05 ± 0.03 mm/sec), and $\mathrm{SnO_2}$ (δ −1.52 ± 0.03 mm/sec). Absorbers in this study were finely divided solids mounted in a sample holder so that a tin density of 1–11 mg/$\mathrm{cm^2}$ resulted. Generally 50,000–150,000 counts were accumulated for each data point allowing a statistical deviation of 0.47–0.26%. Two programs designed for the Univac 1107 fit experimental points for a single or double absorption according to a least-squares adjustment developed by Wentworth,[26] and treat Lorentz equations which approximate the Mössbauer curve. Both programs provide for plotter output of experimental points and final theoretical curves, including the component curves in the case of quadrupole splitting.

Infrared Spectra. These were obtained with Perkin-Elmer instruments, Models 421, 457, and 21 (CsBr prism), in chloroform solution for the porphyrin·$\mathrm{Sn(OH)_2}$ complexes, and in KBr disks for the other compounds.

Optical Spectra. The Cary-14 spectrophotometer was used to record optical spectra. In general the Soret peak, which occurs in

Table II. Mössbauer Data (mm/sec) at 80°K with Tin–Palladium Source

	% absorbance	Isomer shift	Quadrupole splitting	Line width L_1	L_2
PcSn	5.4	1.26	1.40	0.89	0.84
$\mathrm{Pc_2Sn}$	6.4	−1.41		0.98	
$\mathrm{PcSnI_2}$	3.7	−1.07	0.99	0.92	0.75
$\mathrm{PcSnBr_2}$	5.2	−1.18	1.09	0.89	0.83
$\mathrm{PcSnCl_2}$	7.5	−1.24	0.99	0.89	0.89
$\mathrm{PcSn(OH)_2}$	11.5	−1.43		1.75	
$\mathrm{PcSnF_2}$	10.0	−1.49	0.70	0.94	0.96
$\mathrm{SnCl_2TMeOxPP}$	1.9	−1.28		1.33	
$\mathrm{SnCl_2TTolP}$	4.5	−1.29		1.25	
$\mathrm{SnCl_2TClPP}$	3.6	−1.29		1.23	
$\mathrm{SnCl_2TPP}$	5.4	−1.29		1.21	
$\mathrm{Sn(OH)_2TMeOx}$	4.5	−1.33		1.03	
$\mathrm{Sn(OH)_2TTolP}$	4.2	−1.37	0.76	0.82	0.80
$\mathrm{Sn(OH)_2TClPP}$	2.8	−1.37		1.37	
$\mathrm{Sn(OH)_2TPP}$	3.0	−1.37		1.10	
$\mathrm{SnF_2TMeOxPP}$	3.8	−1.51		0.92	
$\mathrm{SnF_2TTolP}$	2.1	−1.58		1.03	
$\mathrm{SnF_2TClPP}$	3.2	−1.50		1.03	
$\mathrm{SnF_2TPP}$	3.6	−1.51		0.87	

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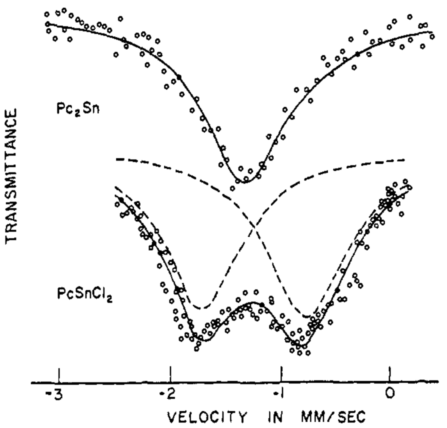

Figure 3. Mössbauer spectra obtained with a tin–palladium source.

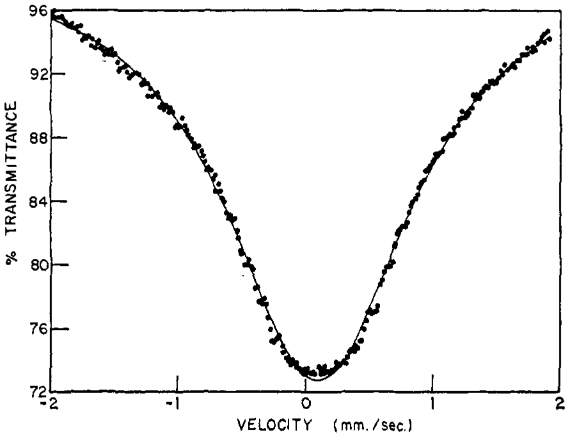

Figure 4. Mössbauer spectrum of $PcSn(OH)_2$ with a barium stannate source.

the 420-mμ region of the porphyrin spectra, was measured in solutions only 5% as concentrated as those used in the 650–450 mμ range.

Discussion of Results

The Mössbauer parameters obtained for the tin complexes of phthalocyanine and tetraarylporphines are listed in Table II and spectra of three complexes are shown in Figures 3 and 4.

PcSn. If the unshared electron pair in the valence shell of divalent tin has a large s character, the positive isomer shift of tin(II) complexes is expected to decrease with increasing coordination of tin, as the electrons of the dative bonds partially shield the unshared pair from the nucleus. Isomer shifts for a number of tin(II) complexes have been correlated with this expectation.[27] A comparison of the isomer shift for PcSn, 1.26 mm/sec, with that for bis(oxinato)tin(II), 1.38 mm/sec, indicates a greater overall electron release by the phthalocyanine nitrogen atoms than by the oxygen and nitrogen atoms of oxine. The quadrupole splitting for PcSn, 1.40 mm/sec, compares with values of 2.01 for $Sn(ox)_2$ (in which the tin atom is very likely at the apex of a tetragonal pyramid), and 1.34 mm/sec for bis(salicylaldato)-phenylenediiminetin(II) (for which the tetradentate ring is expected to be planar).

Pc_2Sn. The narrow line width, 0.98 mm/sec, of the Mössbauer absorption for Pc_2Sn indicates no unresolved doublet, Figure 3. The magnitude of the isomer shift, −1.41 mm/sec, and the lack of quadrupole splitting, together with the square antiprism configuration of the eight nitrogen atoms about the tin atom, indicate eight equivalent N–Sn bonds.

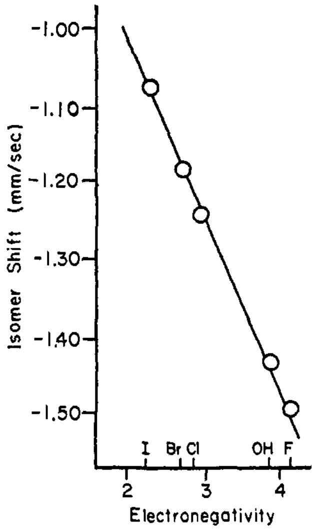

Figure 5. Variation of isomer shift with electronegativity of the X ligand in $PcSnX_2$ complexes.

$PcSnX_2$. The isomer shifts for the $PcSnX_2$ compounds are expected to become more negative with increasing electron attraction of the ligand X. Figure 5 illustrates the linear relation between the observed isomer shifts and the electronegativity of X. Values of electronegativities are according to Allred and Rochow[28] and Jaffé and coworkers.[29] These results suggest appreciable and equivalent s character for each Sn–X bond.

As indicated in Table II, the spectra of all the $PcSnX_2$ complexes except the hydroxide show quadrupole splittings. The spectrum of $PcSn(OH)_2$ was obtained by accumulating 230,000 counts per channel using a barium stannate source (Figure 4). The deviation from Lorentzian curvature and the large half-width, 1.75 mm/sec, are evidence of an unresolved splitting. The splittings for the phthalocyanine complexes compare with values of 0.5–0.6 mm/sec for dihalobis(8-hydroxyquinolinato-N-oxide) in which the halogen atoms appears to be *cis*, and 0.65 mm/sec for dichlorobis-(salicylaldato)ethylenediiminetin(IV) in which the chlorine atoms are probably *trans*.[30]

SnX_2TArP. The isomer shifts for the four sets of tetraarylporphine complexes, Table II, become more negative from chlorides to hydroxides to fluorides in the same manner as the values for the phthalocyanine complexes. As electrons in π (shielding) and σ (with partial s character) bond orbitals have opposite effects on the electron density at the tin nucleus, the extent of N=S π bonding cannot be ascertained from the magnitudes of the isomer shifts. The very small differences between the isomer shifts for complexes of phthalocyanine and tetraarylporphines with the same SnX_2 group are an indication of similar overall electron releases by the two sets of rings.

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Table III. Visible Spectra of Tetraarylporphinotin(IV) Complexes in Chloroform

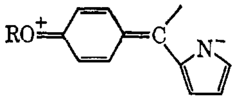
	Absorption maxima, mμ (log ε)			
$SnCl_2TMeOxPP$	435 (5.81)	526 (3.65)	566 (4.35)	609 (4.40)
$SnCl_2TTolP$	430 (5.81)	524 (3.56)	563 (4.29)	604 (4.21)
$SnCl_2TClPP$	429 (5.84)	520 (3.64)	561 (4.38)	601 (4.17)
$SnCl_2TPP$	427 (5.84)	522 (3.55)	561 (4.32)	601 (4.12)
$Sn(OH)_2TMeOxPP$	434 (5.70)	527 (3.67)	566 (4.38)	609 (4.26)
$Sn(OH)_2TTolP$	430 (5.37)	523 (3.57)	563 (4.33)	604 (4.24)
$Sn(OH)_2TClPP$	429 (5.87)	522 (3.56)	562 (4.36)	601 (4.15)
$Sn(OH)_2TPP$	428 (5.46)	521 (3.56)	562 (4.26)	601 (4.09)
$SnF_2TMeOxPP$	429 (5.75)	521 (3.59)	558 (4.26)	600 (4.17)
SnF_2TTolP	424 (5.86)	517 (3.58)	556 (4.42)	596 (4.17)
SnF_2TClPP	422 (5.90)	516 (3.57)	554 (4.43)	593 (4.03)
SnF_2TPP	420 (5.84)	514 (3.56)	553 (4.36)	592 (3.98)

In contrast to the phthalocyanine complexes, only one of the tetraarylporphine complexes, $SnTTolP(OH)_2$, yielded a resolvable quadrupole splitting. The Mössbauer spectra of the difluoro complexes show singlet absorptions with an average line width of 0.99 mm/sec. The spectra of the dichloro and the other two hydroxo complexes give indications of splittings, but these could not be resolved. The average line width of the chlorides and hydroxides (unsplit), 1.2 mm/sec, compare with values of 1.82 and 1.75 mm/sec for the absorption envelopes for $PcSnCl_2$ and $PcSn(OH)_2$, respectively.

As the difference in quadrupole interactions for the two sets of compounds cannot be explained in terms of σ bonding, a difference in Sn=N π bonding is suggested. This interpretation is supported by the relatively small interactions observed for the difluorides. Tin–halogen double bond character, involving metal d_{xz} and d_{yz} orbitals, is expected to be a maximum for the tin–fluorine bond, and this π bonding is at the expense of ring–metal π interactions. The smaller quadrupole interactions observed for the tetraarylporphine complexes than for those of phthalocyanine appear to be associated with weaker ring–metal π interactions, probably related to the departure from planarity of the tetraarylporphine ring system.

The above interpretation is compatible with the visible absorption maxima listed in Table III. Extended conjugation of the chains (greater π-electron delocalization) in these complexes is expected to shift the absorption maxima to longer wavelengths. The absorption maxima for the $SnTArPF_2$ complexes are at shorter wavelengths than those for the corresponding chlorides, consistent with the suggestion from Mössbauer data that there is less Sn=N double bond character in the fluorides.

Omitted from Table III are weak absorptions in the 625-mμ region for two of the dichlorides, which may be explained by the slight contamination with chlorins, and a weak absorption by $SnTMeOxPPF_2$ at 649 mμ, due to a trace of free base. With the exception of the 520-mμ peak for $SnTClPPCl_2$, all the wavelengths of the absorption maxima listed in Table III are in the order: *p*-methoxyphenyl > *p*-tolyl > *p*-chlorophenyl ≥ phenyl. This suggests resonance interaction between the *para* substituents and the porphine ring for the complexes in solution; it may be that the twist of the benzene rings from the "plane" of the porphine ring is less than that observed for solid tetraphenylporphinocopper(II).



Acknowledgments. The junior author is grateful to Dr. E. B. Fleischer for samples of tetraphenylporphine and tetrapyridylporphinozinc, to Professor Rolfe Herber for helpful discussions, and to the Kansas City Regional Council of Higher Education for financial assistance in completing this research.