van der Waals contact distance found in other acac complexes[4] (*ca.* 2.6 Å), indicate that the rings may behave independently within the molecule. This nonrigid stereochemistry then allows the rotations described earlier to take place.

The determination of the scandium-oxygen bond length, 2.070 Å, in $Sc(acac)_3$ enables a value for the scandium(III) radius to be obtained. Using the relationship of Lingafelter and Braun[4] between the metal-oxygen bond length and the ionic radius of metal ions with rare gas configurations in acetylacetonate complexes, a value of 0.68 Å is obtained for the radius of the scandium(III) ion. The same authors also found for these complexes that the metal-oxygen bond length is in good agreement with the sum of the Pauling radii.[15] However, the use of the Pauling radius for the scandium(III) ion, 0.81 Å, predicts an Sc–O bond length of 2.20 Å, considerably longer than that observed. Since the crystals used to establish Pauling's radii for scandium(III) were ionic in nature, our determined value of 0.68 Å is a more acceptable one for use in coordination compounds of scandium where covalent character is expected to be present in the scandium–donor atom bond.[16]

Registry No. $Sc(C_5H_7O_2)_3$, 14284-94-7.

Acknowledgment. We wish to thank the National Science Foundation (Grant GP-28235) for financial assistance.

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[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 514.

[16] Since this work was completed, Smith and Atwood[17] have reported the crystal and molecular structure of $[(C_5H_5)_2ScCl]_2$. A similar value of 0.68 Å was obtained for the scandium(III) radius from the Sc–C bond distance.

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Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52240

Crystal Structure of Stannic Phthalocyanine, an Eight-Coordinated Tin Complex

W. E. BENNETT,* D. E. BROBERG, and N. C. BAENZIGER

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The molecular configuration of stannic phthalocyanine, $Sn(C_{32}H_{16}N_8)_2$, has been determined by three-dimensional X-ray analysis. The orthorhombic cell dimensions (at 22°) and space group are $a = 10.547 \pm 0.001$, $b = 50.743 \pm 0.004$, and $c = 8.9046 \pm 0.0009$ Å; $Z = 4$; $d_c = 1.59$, $d_m = 1.60 \pm 0.01$ g/cm^3; and $P2_12_12_1$. The final parameters were determined from 2168 independent reflections measured by counter methods. The least-squares fitting of the data refined to $R_1 = 6.8\%$. The two phthalocyanine ring systems form a sandwich-type compound with the tin atom in the center. The cores of the phthalocyanine moieties are separated from each other by 2.70 ± 0.04 Å and are rotated 42° with respect to each other. The eight isoindole nitrogen atoms form an antiprism about the tin atom with Sn–N distances (individually ±0.02 Å) ranging from 2.32 to 2.37 Å and the average Sn–N distance being 2.347 ± 0.007 Å.

Introduction

Recently, there has been a great deal of interest in compounds which show a coordination number of 8 for a metal atom.[1,2] Several crystal structures of eight-coordinated metal complexes have been reported in which the configuration around the metal atom is either an antiprism or a dodecahedron. The coordination groups of the $Mo(CN)_8{}^{4-}$ ion[3] and the tetrakis(oxalato)zirconate(IV) ion[4] are dodecahedral. The fluoride ions in $TaF_8{}^{3-}$ form a square antiprism around the tantalum atom.[5] All of these eight-coordinated complexes involve a transition metal atom.

A series of tin(IV) complexes has been prepared in which the tin atom seems to be eight-coordinated. The first of these to be prepared was the potassium tin(IV) oxalate[6] in which four oxalate anions appear to coordinate as bidentate ligands to the tin atom. More recently, tin(IV) nitrate[7] was shown by infrared evidence to contain four nitrate groups which also coordinate as bidentate ligands. Ramaiah and Martin found that a tin-phenyl cleavage of diphenylbis(8-quinolinato)tin(IV), using 8-quinolinol at 300°, yielded tetrakis(8-quinolinato)tin(IV) which appears to be eight-coordinated.[2]

Probably the best known of the postulated eight-coordinated tin compounds is stannic phthalocyanine. The phthalocyanine molecule is a rigid, macrocyclic compound which behaves as a dinegative anion. In 1936 Linstead prepared the tin(IV) phthalocyanine[8] which had a stoichiometry corresponding to two phthalocyanine groups per tin atom. It was believed that the two phthalocyanine rings formed a sandwich-type compound with a tin atom in the center. Only configurations ranging between the cubic or square-antiprismatic extremes are possible because of the rigidity of the phthalocyanine rings. The Mossbauer spectrum[9] is consistent with the symmetrical configuration of eight isoindole nitrogen atoms around the tin atom, but it does not distinguish between the cubic and antiprismatic arrangements.

The X-ray crystallographic study was carried out to determine the actual configuration of the nitrogen atoms around the tin atom and to determine whether the phthalocyanine rings retain the same structure as in other metal phthalocyanine compounds in which the metal atom is found in the

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Table I. Atomic Parameters for Stannic Phthalocyanine[a]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
Sn(1)	0.0730 (1)	0.12401 (2)	0.2010 (2)	*b*	C(42)	−0.226 (2)	0.1225 (4)	0.298 (2)	2.4 (4)
N(2)	0.029 (1)	0.1545 (3)	0.007 (2)	1.5 (4)	C(43)	−0.334 (2)	0.1403 (3)	0.347 (2)	1.5 (4)
N(3)	0.186 (1)	0.1423 (3)	−0.181 (2)	2.3 (4)	C(44)	−0.438 (2)	0.1364 (4)	0.427 (2)	3.3 (5)
N(4)	0.120 (1)	0.1041 (3)	−0.031 (2)	1.4 (4)	C(45)	−0.522 (2)	0.1579 (4)	0.451 (3)	3.4 (6)
N(5)	0.095 (1)	0.0581 (3)	0.034 (2)	1.6 (3)	C(46)	−0.480 (2)	0.1835 (4)	0.394 (2)	3.0 (5)
N(6)	−0.049 (1)	0.0859 (2)	0.177 (2)	1.0 (3)	C(47)	−0.367 (2)	0.1870 (3)	0.315 (3)	1.9 (4)
N(7)	−0.237 (1)	0.0973 (3)	0.324 (2)	1.5 (3)	C(48)	−0.297 (2)	0.1649 (3)	0.291 (3)	2.4 (4)
N(8)	−0.139 (1)	0.1363 (3)	0.220 (2)	1.4 (3)	C(49)	−0.184 (2)	0.1615 (3)	0.201 (2)	1.6 (4)
N(9)	−0.132 (1)	0.1809 (3)	0.126 (2)	1.0 (3)	C(50)	0.291 (2)	0.1707 (4)	0.139 (2)	1.9 (5)
N(10)	0.268 (2)	0.1438 (3)	0.159 (2)	2.0 (4)	C(51)	0.400 (2)	0.1746 (4)	0.043 (2)	2.4 (5)
N(11)	0.406 (2)	0.1055 (3)	0.109 (2)	2.3 (4)	C(52)	0.450 (2)	0.1978 (4)	−0.011 (2)	2.3 (5)
N(12)	0.231 (1)	0.0943 (3)	0.275 (2)	1.4 (3)	C(53)	0.558 (2)	0.1950 (4)	−0.106 (2)	3.8 (6)
N(13)	0.116 (1)	0.0674 (3)	0.454 (2)	1.5 (4)	C(54)	0.620 (2)	0.1694 (4)	−0.134 (3)	3.9 (6)
N(14)	0.034 (1)	0.1125 (3)	0.455 (2)	1.3 (3)	C(55)	0.560 (2)	0.1471 (4)	−0.074 (3)	3.8 (6)
N(15)	−0.066 (2)	0.1522 (3)	0.547 (2)	2.3 (6)	C(56)	0.453 (2)	0.1500 (3)	0.020 (2)	1.7 (4)
N(16)	0.081 (2)	0.1629 (2)	0.348 (2)	1.3 (3)	C(57)	0.367 (2)	0.1312 (4)	0.098 (2)	2.0 (5)
N(17)	0.221 (1)	0.1898 (3)	0.197 (2)	2.2 (4)	C(58)	0.336 (2)	0.0891 (4)	0.188 (3)	2.3 (4)
C(18)	−0.038 (2)	0.1776 (3)	0.030 (2)	1.6 (4)	C(59)	0.378 (2)	0.0614 (3)	0.213 (2)	1.0 (4)
C(19)	0.013 (2)	0.1976 (3)	−0.065 (2)	1.2 (4)	C(60)	0.477 (2)	0.0473 (4)	0.146 (2)	2.2 (5)
C(20)	−0.017 (2)	0.2262 (4)	−0.068 (3)	3.2 (6)	C(61)	0.483 (2)	0.0203 (4)	0.188 (3)	3.6 (5)
C(21)	0.058 (2)	0.2402 (4)	−0.167 (2)	3.1 (5)	C(62)	0.400 (2)	0.0096 (4)	0.293 (3)	3.1 (5)
C(22)	0.151 (2)	0.2296 (4)	−0.250 (2)	2.8 (5)	C(63)	0.299 (2)	0.0237 (4)	0.357 (2)	2.3 (5)
C(23)	0.183 (2)	0.2014 (4)	−0.250 (2)	2.3 (5)	C(64)	0.292 (2)	0.0505 (3)	0.306 (2)	1.4 (4)
C(24)	0.104 (2)	0.1871 (4)	−0.156 (2)	2.0 (5)	C(65)	0.205 (2)	0.0709 (4)	0.354 (2)	1.7 (4)
C(25)	0.113 (2)	0.1586 (3)	−0.106 (2)	1.5 (4)	C(66)	0.041 (2)	0.0864 (3)	0.503 (2)	1.5 (4)
C(26)	0.189 (2)	0.1164 (4)	−0.134 (2)	2.2 (5)	C(67)	−0.042 (2)	0.0842 (3)	0.630 (2)	1.8 (4)
C(27)	0.264 (2)	0.0975 (3)	−0.221 (2)	2.2 (4)	C(68)	−0.075 (2)	0.0616 (3)	0.711 (2)	2.6 (4)
C(28)	0.353 (2)	0.1013 (4)	−0.340 (3)	2.9 (5)	C(69)	−0.169 (2)	0.0655 (4)	0.822 (3)	2.5 (5)
C(29)	0.428 (2)	0.0792 (4)	−0.385 (2)	3.0 (5)	C(70)	−0.221 (2)	0.0910 (4)	0.855 (3)	3.2 (6)
C(30)	0.394 (2)	0.0538 (4)	−0.318 (3)	3.0 (5)	C(71)	−0.173 (2)	0.1136 (4)	0.783 (3)	3.4 (5)
C(31)	0.308 (2)	0.0504 (3)	−0.204 (3)	2.1 (4)	C(72)	−0.096 (2)	0.1092 (3)	0.660 (2)	2.0 (4)
C(32)	0.241 (2)	0.0727 (4)	−0.153 (2)	2.3 (5)	C(73)	−0.039 (2)	0.1265 (4)	0.550 (2)	2.4 (5)
C(33)	0.152 (2)	0.0773 (4)	−0.041 (2)	2.2 (5)	C(74)	−0.009 (2)	0.1681 (4)	0.458 (2)	1.9 (5)
C(34)	0.006 (2)	0.0622 (4)	0.129 (2)	1.7 (4)	C(75)	−0.026 (2)	0.1977 (4)	0.464 (2)	2.4 (5)
C(35)	−0.067 (2)	0.0409 (3)	0.201 (2)	1.7 (4)	C(76)	−0.117 (2)	0.2127 (4)	0.548 (2)	2.6 (5)
C(36)	−0.042 (2)	0.0136 (3)	0.195 (2)	2.0 (4)	C(77)	−0.110 (2)	0.2397 (4)	0.516 (3)	3.5 (6)
C(37)	−0.128 (2)	−0.0026 (4)	0.285 (3)	3.3 (5)	C(78)	−0.024 (2)	0.2504 (4)	0.412 (2)	2.0 (5)
C(38)	−0.223 (2)	0.0090 (4)	0.373 (3)	3.4 (6)	C(79)	0.066 (2)	0.2358 (4)	0.334 (2)	2.7 (5)
C(39)	−0.248 (2)	0.0370 (4)	0.377 (2)	2.2 (5)	C(80)	0.057 (2)	0.2081 (3)	0.360 (2)	2.0 (4)
C(40)	−0.160 (2)	0.0519 (3)	0.291 (3)	1.7 (4)	C(81)	0.131 (2)	0.1863 (3)	0.290 (3)	1.7 (4)
C(41)	−0.147 (2)	0.0809 (3)	0.269 (2)	1.1 (4)					

[a] Standard deviations in the last significant digit are given in parentheses. [b] The anisotropic U values for Sn are as follows ($\times 10^4$): $U_{11} = 149$ (9), $U_{22} = 170$ (5), $U_{33} = 260$ (6), $U_{12} = -4$ (7), $U_{13} = 11$ (8), and $U_{23} = 0$ (8) where the temperature factor is given by expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

plane of the ring. While this paper was under revision, the structure of bis(phthalocyanato)uranium(IV) was reported by Gieren and Hoppe.[10] The molecular configuration of Pc_2U is very similar to that found for Pc_2Sn.

Experimental Section

Stannic phthalocyanine (Pc_2Sn) was prepared by the reaction of dichloro(phthalocyanino)tin(IV) ($PcSnCl_2$) and disodium phthalocyanine (Na_2Pc) as described by Kenney and Kroenke.[11]

A freshly ground mixture of $PcSnCl_2$ (6.86 g, 9.8 mmol) and Na_2Pc (6.45 g, 11.6 mmol) was placed in a 200-ml round-bottom flask and dried in an oven for 3 hr at 110°. To this flask was added technical grade 1-chloronaphthalene (Eastman Organic Chemicals, 140 ml) and the resulting solution was refluxed for 90 min in a nitrogen atmosphere. This solution was allowed to cool for exactly 1 hr and filtered. The precipitate was found to be a purple gumlike solid which when peeled off gave a layer of red crystals mixed with green powder. The red crystals and green powder were washed with ether, and the slurry containing the light green precipitate was decanted, leaving the crystals behind. The red crystals were found to be rectangular platelets and were about 0.5 × 0.1 × 0.5 mm. The yield was about 0.5 g or 4.5%. *Anal.* Calcd for $C_{64}H_{32}N_{16}Sn$: C, 67.21; H, 2.82; N, 19.59. Found: C, 67.05; H, 2.92; N, 19.79.

The preparation of Pc_2Sn by Kenney and Kroenke yielded a microcrystalline product in the supernatant liquid rather than in the precipitate. It appears that the rate of cooling may be critical in obtaining crystals which are suitable for X-ray diffraction study.

The infrared spectrum of the compound in a KBr disk, taken on the Perkin-Elmer Model 21 recording spectrophotometer, was found to be consistent with that reported for the α form of Pc_2Sn.[12] X-Ray powder diagrams gave d spacings (12.5, 9.75, 8.4, 3.4, 6.7, 3.25 Å) which were very similar to those obtained by Kenney and Kroenke[12] for the α isomer.

X-Ray Data. Since oscillation photographs of five larger crystals indicated a large amount of crystal imperfection, a small crystal with the dimensions 0.32 × 0.094 × 0.28 mm was finally selected which was relatively free from imperfections. The b and c dimensions for the orthorhombic cell were obtained from an $0kl$ back-reflection Weissenberg single-crystal diagram using a least-squares extrapolation method[13] to remove systematic errors. The a cell dimension was obtained from the $h0l$ back-reflection Weissenberg diagram using a different single crystal. The cell dimensions are $a = 10.547 \pm 0.001$, $b = 50.743 \pm 0.004$, and $c = 8.9046 \pm 0.0009$ Å at 22°; [λ(Cu Kα_1) = 1.54051, λ(Cu Kα_2) 1.54433 Å].

The long b axis extends along the short dimension of the crystal. Intensity data were collected from multiple-film equiinclination Weissenberg diagrams ($0kl$-$6kl$) using Ni-filtered Cu Kα radiation.

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(13) The function, $\Sigma\{D_m - 4R[\pi/2 - \arcsin[(\lambda^2/4d^2) + \delta f(\theta)]^{1/2}]\}^2$, summed over back-reflection data was minimized with respect to the cell dimensions parameters contained in d and a systematic error parameter, δ. The function $f(\theta) = 4\sin^2\theta\cos^2\theta[(1/\theta) + (1/\sin\theta)]$, R is the camera radius, and D_m is the distance between similar reflections measured across the back-reflection region of the film.

Table II. Interatomic Distances (Å) and Angles (deg) in Stannic Phthalocyanine[a]

Sn–N	Dist	N–C	Dist	C–N	Dist	C–C	Dist
1–2	2.367 (15)	2–18	1.38 (2)	25–3	1.32 (2)	18–19	1.43 (3)
1–4	2.351 (16)	2–25	1.35 (2)	26–3	1.38 (2)	24–25	1.51 (3)
1–6	2.330 (13)	4–26	1.33 (2)	33–5	1.32 (2)	26–27	1.46 (3)
1–8	2.328 (14)	4–33	1.40 (2)	34–5	1.28 (2)	32–33	1.39 (3)
1–10	2.319 (15)	6–34	1.40 (2)	41–7	1.36 (2)	34–35	1.48 (3)
1–12	2.338 (14)	6–41	1.41 (2)	42–7	1.31 (2)	40–41	1.49 (2)
1–14	2.369 (15)	8–42	1.34 (2)	49–9	1.31 (2)	42–43	1.52 (3)
1–16	2.372 (13)	8–49	1.37 (2)	18–9	1.32 (2)	48–49	1.44 (3)
	Av 2.347	10–50	1.40 (2)	57–11	1.37 (2)	50–51	1.44 (3)
	$\bar{\sigma}$ = 0.007	10–57	1.34 (2)	58–11	1.32 (2)	56–57	1.49 (3)
		12–58	1.38 (2)	65–13	1.31 (2)	58–59	1.49 (2)
		12–65	1.40 (2)	66–13	1.32 (2)	64–65	1.44 (2)
		14–66	1.40 (2)	73–15	1.34 (2)	66–67	1.44 (3)
		14–73	1.35 (2)	74–15	1.28 (2)	72–73	1.45 (3)
		16–74	1.39 (2)	81–17	1.27 (2)	74–75	1.51 (3)
		16–81	1.40 (2)	50–17	1.33 (2)	80–81	1.49 (3)
			Av 1.375		Av 1.321		Av 1.467
			$\bar{\sigma}$ = 0.006		$\bar{\sigma}$ = 0.007		$\bar{\sigma}$ = 0.009

C–C	Dist	C–C	Dist	C–C	Dist	C–C	Dist
19–24	1.36 (3)	19–20	1.49 (3)	20–21	1.39 (3)	21–22	1.33 (3)
27–32	1.42 (3)	23–24	1.39 (3)	22–23	1.47 (3)	29–30	1.46 (3)
35–40	1.39 (3)	27–28	1.43 (3)	28–29	1.43 (3)	37–38	1.40 (3)
43–48	1.40 (3)	31–32	1.41 (3)	30–31	1.38 (3)	45–46	1.46 (3)
51–56	1.38 (3)	35–36	1.41 (2)	36–37	1.46 (3)	53–54	1.48 (3)
59–64	1.35 (3)	39–40	1.42 (3)	38–39	1.45 (3)	61–62	1.40 (3)
67–72	1.42 (3)	43–44	1.32 (3)	44–45	1.42 (3)	69–70	1.43 (3)
75–80	1.38 (3)	47–48	1.42 (2)	46–47	1.32 (3)	77–78	1.41 (3)
	Av 1.387	51–52	1.38 (3)	52–53	1.42 (3)		Av 1.42
	$\bar{\sigma}$ = 0.008	55–56	1.41 (3)	54–55	1.40 (3)		$\bar{\sigma}$ = 0.02
		59–60	1.40 (3)	60–61	1.42 (3)		
		63–64	1.44 (3)	62–63	1.40 (3)		
		67–68	1.40 (3)	68–69	1.41 (3)		
		71–72	1.39 (3)	70–71	1.40 (3)		
		75–76	1.43 (3)	76–77	1.40 (3)		
		79–80	1.43 (2)	78–79	1.39 (3)		
			Av 1.409		Av 1.410		
			$\bar{\sigma}$ = 0.009		$\bar{\sigma}$ = 0.009		

C–C	Dist	N–N	Dist	N–C	Dist	N–C	Dist
18–81	2.95 (3)	2–10	2.91 (2)	3–51	3.42 (3)	3–50	3.38 (5)
25–50	2.94 (3)	4–12	3.01 (2)	3–56	3.36 (3)	3–57	3.18 (3)
26–57	2.89 (3)	6–14	2.95 (2)	5–59	3.39 (2)	5–58	3.30 (2)
33–58	2.88 (3)	8–16	2.92 (2)	5–64	3.22 (3)	5–65	3.15 (2)
34–65	2.93 (3)	2–16	3.12 (2)	7–67	3.47 (2)	7–66	3.38 (2)
41–66	2.89 (3)	4–10	3.06 (2)	7–72	3.40 (2)	7–73	3.25 (2)
42–73	2.99 (3)	6–12	3.10 (2)	9–75	3.20 (3)	9–74	3.29 (2)
49–74	2.96 (3)	8–14	3.02 (2)	9–80	3.19 (2)	9–81	3.14 (2)
				11–27	3.32 (3)	11–26	3.20 (3)
				11–32	3.35 (3)	11–33	3.31 (3)
				13–35	3.26 (2)	13–34	3.13 (3)
				13–40	3.34 (2)	13–41	3.30 (2)
				15–43	3.39 (3)	15–42	3.16 (3)
				15–48	3.40 (3)	15–49	3.35 (3)
				17–19	3.23 (2)	17–18	3.17 (2)
				17–24	3.38 (3)	17–25	3.34 (3)

N–C–N	Angle	C–N–C	Angle	C–N–C	Angle	N–C–C	Angle	C–C–C	Angle
9–18–2	126	25–3–26	117	18–2–25	108	2–18–19	109	18–19–24	110
2–25–3	131	33–5–34	123	26–4–33	106	2–25–24	109	19–24–25	104
3–26–4	130	41–7–42	118	34–6–41	110	4–26–27	111	26–27–32	105
4–33–5	125	49–9–18	123	42–8–49	108	4–33–32	112	27–32–33	106
5–34–6	130	57–11–58	118	50–10–57	106	6–34–35	106	34–35–40	109
6–41–7	130	65–13–66	124	58–12–65	106	6–41–40	110	35–40–41	105
7–42–8	131	73–15–74	122	66–14–73	110	8–42–43	110	42–43–48	103
8–49–9	128	81–17–50	125	74–16–81	111	8–49–48	109	43–48–49	109
17–50–10	124		Av 121.3		Av 108.1	10–50–51	111	50–51–56	107
10–57–11	131		$\bar{\sigma}$ = 1.0		$\bar{\sigma}$ = 0.7	10–57–56	111	51–56–57	105
11–58–12	129					12–58–59	110	58–59–64	106
12–65–13	126					12–65–64	110	59–64–65	108
13–66–14	124					14–66–67	107	66–67–72	109
14–73–15	128					14–73–72	110	67–72–73	105
15–74–16	130					16–74–75	107	74–75–80	106
16–81–17	130					16–81–80	106	75–80–81	109
	Av 128.7						Av 109.2		Av 106.6
	$\bar{\sigma}$ = 0.5						$\bar{\sigma}$ = 0.4		$\bar{\sigma}$ = 0.5

Table II (*Continued*)

N-C-C	Angle	C-C-C	Angle	C-C-C	Angle	C-C-C	Angle	C-C-C	Angle
9-18-19	125	18-19-20	129	20-19-24	122	19-20-21	113	20-21-22	124
3-25-24	119	23-24-25	130	19-24-23	125	22-23-24	112	21-22-23	124
3-26-27	118	26-27-28	131	32-27-28	123	27-28-29	118	28-29-30	116
5-33-32	123	31-32-33	135	27-32-31	120	30-31-32	118	29-30-31	125
5-34-35	123	34-35-36	128	40-35-36	123	35-36-37	115	36-37-38	121
7-41-40	119	39-40-41	131	35-40-39	124	38-39-40	113	37-38-39	124
7-42-43	118	42-43-44	133	48-43-44	124	43-44-45	119	44-45-46	116
9-49-48	123	47-48-49	131	43-48-47	120	46-47-48	117	45-46-47	124
17-50-51	125	50-51-52	129	52-51-56	124	51-52-53	116	52-53-54	123
11-57-56	117	55-56-57	134	51-56-55	120	54-55-56	120	53-54-55	116
11-58-59	121	58-59-60	130	64-59-50	124	59-60-61	114	60-61-62	122
13-65-64	124	63-64-65	128	59-64-63	123	62-63-64	113	61-62-63	123
13-66-67	125	66-67-68	129	72-67-68	122	67-68-69	115	68-69-70	122
15-73-72	122	71-72-73	133	67-72-71	122	70-71-72	115	69-70-71	121
15-74-75	123	74-75-76	129	80-75-76	125	75-76-77	113	76-77-78	123
17-81-80	124	79-80-81	129	75-80-79	122	78-79-80	114	77-78-79	124
	Av 121.8		Av 130.5		Av 122.7		Av 115.3		Av 121.8
	$\bar{\sigma} =$ 0.6		$\bar{\sigma} =$ 0.5		$\bar{\sigma} =$ 0.4		$\bar{\sigma} =$ 0.6		$\bar{\sigma} =$ 0.7

[a] Standard deviations are given in parentheses for the distances and those for the individual angles are 2°; atom numbers are given under the atoms in the column headings.

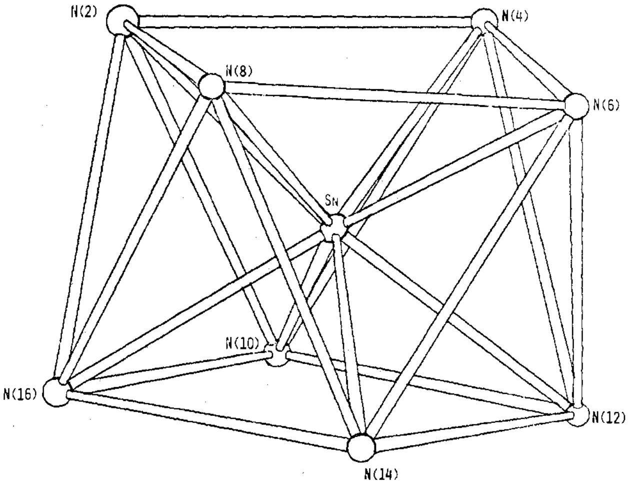

Figure 1. Configuration of the nitrogen atoms surrounding the tin atom in Pc_2Sn.

The intensities were visually estimated using a relative intensity scale. Intensity data were also obtained using a Supper Weissenberg camera which was modified for direct counting techniques. A stationary counter and moving crystal (2° ω scan) were employed. A proportional counter was used as the detector for Ni-filtered Cu Kα radiation. The same crystal which was used for the film data was used for the $0kl$-$6kl$ counter data, and it was remounted along the c axis to obtain $hk0$, $hk\bar{1}$, and $hk\bar{2}$ data. One reflection was used as a reference to monitor the X-ray source during the course of the intensity measurements. The background was found to be independent of ω, and therefore the background was measured for every 5° 2θ. The background for each reflection was then obtained by interpolation from the list of background values. A separate set of background measurements was used for each layer of data. Reflections were considered as being observed if the net intensity was greater than two standard deviations in the background count. The intensities were corrected for the Lorentz-polarization factors and for absorption. The absorption correction varied from 0.64 (max) to 0.26 (min) with 95% of all corrections ranging between 0.60 and 0.40.

Characteristic absences of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd indicate that the space group is $P2_12_12_1$. The density, assuming four formula weights of Pc_2Sn per cell, is 1.59 g/cm^3; the measured (pycnometer) density is 1.60 ± 1 g/cm^3.

Atomic scattering factors were taken from ref 14. The Thomas-Fermi values were used for Sn, while the neutral-atom values for C and N were those based on self-consistent wave functions. For the final refinement, both the real and imaginary dispersion corrections to the atomic scattering factor of Sn were made.[14] The total number of electrons per unit cell (F_{000}) is 2184; hydrogen atoms were not included in the calculation.

Determination of the Structure. The structure was solved by using the film data to calculate a three-dimensional Patterson map which clearly showed the position of the tin atom. Structure factors based on the position of the tin atom alone gave a discrepancy factor, $R_1 = [\Sigma \| F_o | - | F_c \|] / \Sigma | F_o |$, of 0.37. A three-dimensional electron density map calculated at this point revealed the positions of 25 atoms around the tin atom. Thirty-five additional atoms were located from the next electron density map, and the final electron density map showed a total of 79 atoms. The positions of the two remaining carbon atoms, which were on the same phenyl ring, were found by assuming typical phenyl ring distances. Several cycles of a block-diagonal least-squares refinement, in which the positional coordinates, isotropic temperature factors, and individual scale factors were varied, gave an R_1 value of 0.19.

The structure determination up to this point ignored the breakdown of Friedel's law due to anomalous dispersion, and the observed intensity values which were used were the average of reflections which would be equivalent except for the dispersion correction. Careful examination of the films showed that reflections hkl and $\overline{hkl}$ which are normally equivalent for an orthorhombic lattice, differed in intensity by 20–300%. The counter measurements were made in order to obtain more reliable values for the intensities, and these measurements showed that the breakdown of Friedel's law was real. The nonequivalence of the hkl and $\overline{hkl}$ reflections arises from the anomalous scattering by the tin atom. Including both the real and imaginary part of the dispersion correction in the atom scattering factor for Sn in the structure factor calculation adequately accounted for the experimentally observed differences in intensity. To reduce computing time, the reflections were calculated in pairs, since the difference between the structure factor for one reflection and its pseudoequivalent involves just the imaginary dispersion correction for Sn.

The refinement of the structure proceeded using only the intensity data obtained by counter measurements. A block-diagonal least-squares program was used to reduce the computation time per cycle. Seven cycles reduced R_1 to 0.070 with all reflections given the same weight. The weighting scheme for the final refinement is $w^{1/2} = 1/\sigma(F)$, where $\sigma(F)$ is the standard deviation estimated from counter measurements as $\sigma(F)/F_o = (T + B)^{1/2}/2(T - B)$, where T is the total count and B is the background count. The final discrepancy factor is $R_1 = 0.068$ for the parameters listed in Table I. Hydrogen atoms were not included in the refinement of the structure. The number of independent reflections was 2168 (*i.e.*, 1441 pairs of reflections involving a breakdown of Friedel's law and 727 reflections in which anomalous dispersion does not create a nonequivalent reflection or for which the nonequivalent reflection was not measured). Observed and calculated structure factors are available.[15]

Results and Discussion

The structure of stannic phthalocyanine can be represented by two phthalocyanine ring systems between which the tin atom is sandwiched. The ring systems are rotated 42° with

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(14) "International Tables for X-Ray Crystallography," Vol III, Kynoch Press, Birmingham, England, pp 202, 210, 215.

Table III. Equations of Planes in Stannic Phthalocyanine[a]

Atom no. (deviations from plane, Å $\times 10^{-2}$)	*X*	*Y*	*Z*	*D*
Nitrogen Planes[b]				
2 (+1), 4 (−1), 6 (+1), 8 (−1)	−0.6795	−0.1532	−0.7176	−1.460
10 (+4), 12 (−4), 14 (+4), 16 (−4)	−0.6674	−0.1654	−0.7281	−4.157
Phthalocyanine Planes[c]				
2 (−25), 4 (−22), 6 (−33), 8 (−40) 18 (−14), 25 (−9), 26 (−9), 33 (−16), 34 (−19), 41 (−24), 42 (−22), 49 (−16) 3 (+4), 5 (−12), 7 (−13), 9 (−17) 19 (0), 24 (07), 27 (13), 32 (02), 35 (−1), 40 (−7), 43 (4), 48 (−2) 20 (0), 23 (6), 28 (29), 31 (9), 36 (7), 39 (7), 44 (24), 47 (12) 21 (4), 22 (5), 29 (26), 30 (24), 37 (18), 38 (14), 45 (48), 46 (37)	−0.6416	−0.1542	−0.7514	−1.200
10 (40), 12 (32), 14 (36), 16 (29) 50 (15), 57 (23), 58 (20), 65 (18), 66 (21), 73 (12), 74 (16), 81 (13) 11 (10), 13 (18), 15 (11), 17 (8) 51 (−1), 56 (−3), 59 (−1), 64 (7), 67 (−2), 72 (−6), 75 (−2), 80 (0) 52 (−20), 55 (−12), 60 (−14), 63 (−8), 68 (−13), 71 (−35), 76 (−6), 79 (−13) 53 (−31), 54 (−34), 61 (−23), 62 (−25), 69 (−24), 70 (−31), 77 (−13), 78 (−14)	−0.6572	−0.1679	−0.7348	−4.526
Quarter Phthalocyanine Ring Planes				
2 (−12), 18 (0), 25 (−4), 9 (2), 3 (7), 19 (5), 24 (8), 20 (3), 23 (−2), 21 (−2), 22 (−5)	−0.6768	−0.1822	−0.7132	−1.561
4 (−7), 26 (−6), 33 (−4), 3 (−4), 5 (9), 27 (5), 32 (0), 28 (7), 31 (−2), 29 (−5), 30 (0)	−0.7153	−0.1541	−0.6816	−1.460
6 (−8), 34 (−3), 41 (−6), 5 (7), 7 (9), 35 (3), 40 (−2), 36 (0), 39 (2), 37 (1), 38 (−2)	−0.6236	−0.0689	−0.7787	−1.126
8 (−9), 42 (−6), 49 (4), 7 (7), 9 (10), 43 (−1), 48 (−5), 44 (1), 47 (−7), 45 (7), 46 (−1)	−0.5169	−0.2019	−0.8319	−2.176
10 (14), 50 (1), 57 (5), 17 (−9), 11 (−13), 51 (2), 56 (−1), 52 (−2), 55 (4), 53 (2), 54 (−2)	−0.5762	−0.1054	−0.8104	−3.689
12 (7), 58 (5), 65 (0), 11 (−7), 13 (−6), 59 (−2), 64 (4), 60 (−1), 63 (0), 61 (2), 62 (−2)	−0.6065	−0.2577	−0.7569	−4.614
14 (11), 66 (3), 73 (1), 13 (−10), 15 (−1), 67 (−2), 72 (−1), 68 (0), 71 (−12), 69 (7), 70 (4)	−0.7450	−0.1895	−0.6396	−4.049
16 (11), 74 (2), 81 (2), 15 (−7), 17 (−5), 75 (−4), 80 (−1), 76 (0), 79 (−4), 77 (3), 78 (3)	−0.6806	−0.0940	−0.7266	−3.722
Pyrrole Rings				
2 (−2), 18 (2), 19 (−2), 24 (1), 25 (1)	−0.6859	−0.2508	−0.6831	−2.195
4 (1), 26 (−2), 27 (2), 32 (−2), 33 (0)	−0.7474	−0.1401	−0.6494	−1.518
6 (0), 34 (−1), 35 (1), 40 (−2), 41 (1)	−0.6280	−0.0260	−0.7778	−1.103
8 (−4), 42 (1), 43 (2), 48 (−5), 49 (5)	−0.5084	−0.2281	−0.8304	−2.420
10 (4), 50 (−5), 51 (3), 56 (−1), 57 (−2)	−0.5422	−0.0761	−0.8368	−3.312
12 (1), 58 (1), 59 (−3), 64 (4), 65 (−3)	−0.5922	−0.2773	−0.7565	−4.633
14 (3), 66 (−2), 67 (0), 72 (2), 73 (−3)	−0.7712	−0.2043	−0.6030	−3.914
16 (3), 74 (−1), 75 (0), 80 (2), 81 (−3)	−0.7000	−0.0494	−0.7124	−3.247
Phenyl Planes				
19 (−2), 20 (0), 21 (1), 22 (−1), 23 (−1), 24 (2)	−0.6599	−0.1496	−0.7363	−1.148
27 (0), 28 (3), 29 (−4), 30 (3), 31 (0), 32 (−2)	−0.7035	−0.1810	−0.6872	−1.501
35 (2), 36 (−1), 37 (1), 38 (−2), 39 (3), 40 (−3)	−0.6292	−0.0719	−0.7740	−1.108
43 (1), 44 (−3), 45 (2), 46 (−1), 47 (−1), 48 (1)	−0.4885	−0.1841	−0.8529	−2.232
51 (2), 52 (−2), 53 (2), 54 (−3), 55 (3), 56 (−2)	−0.5773	−0.1006	−0.8103	−3.649
59 (−2), 60 (0), 61 (3), 62 (−2), 63 (−1), 64 (3)	−0.5945	−0.2596	−0.7611	−4.599
67 (0), 68 (−4), 69 (2), 70 (4), 71 (−7), 72 (5)	−0.7410	−0.1502	−0.6544	−3.985
75 (−1), 76 (0), 77 (0), 78 (1), 79 (−3), 80 (3)	−0.6686	−0.1120	−0.7351	−3.969

[a] Equations of the planes are in the form $Xi + Yj + Zk = D$, where *X*, *Y*, *Z* are direction cosines of the plane normal and *D* is the perpendicular distance, in Å, of the plane from the origin. [b] Angle between plane normals 1.1°. [c] Angle between plane normals 1.5°.

respect to one another to form a square antiprism of nitrogen atoms around the central tin atom. (See Figure 1.) The two squares of nitrogen atoms are parallel to each other (1.1° between normals) and are 2.70 Å apart. For comparison, in the UPc_2 structure the rings are rotated by 37° and the planes are separated by 2.81 Å. In μ-oxo-phthalocyanatopyridine(phthalocyanatopyridine)dimanganese(III) dipyridinate[16] the two phthalocyanine moieties are bridged by an oxygen atom and are rotated by 41° and the ring separation is 3.42 Å.

It appears that a rotation of exactly 45° in the stannic phthalocyanine structure would be hindered by the overlap of the α pyrrole carbon atoms of the two rings. The rings, being separated by 2.70 Å, are much closer than the van der Waals distance of 3.4 Å for an aromatic carbon atom.[17] The average distance for an α pyrrole carbon atom of ring A to one of ring B is 2.93 ± 1 Å. It appears that these carbon atoms interact weakly causing the slight distortion from the equilateral antiprism. An extensive list of interatomic distances is given in Table II.

The two phthalocyanine ring systems are neither perfectly planar nor parallel to one another, but rather parts of each ring system bend away from the other. (See Figure 2.) The pyrrole rings bend outward (*i.e.*, away from the other phthalocyanine moiety) at angles of 1-12° relative to the plane defined by the square of four nitrogen atoms bound to the Sn. The phenyl rings make angles of 2-14° with respect to the same plane. The resultant saucer-shaped ring is very similar to that found in the UPc_2 structure. The equations of the planes are given in Table III and a comparison with UPc_2 is given in Table IV.

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(15) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-930.

(16) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Science*, 151, 569 (1966).

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 262.

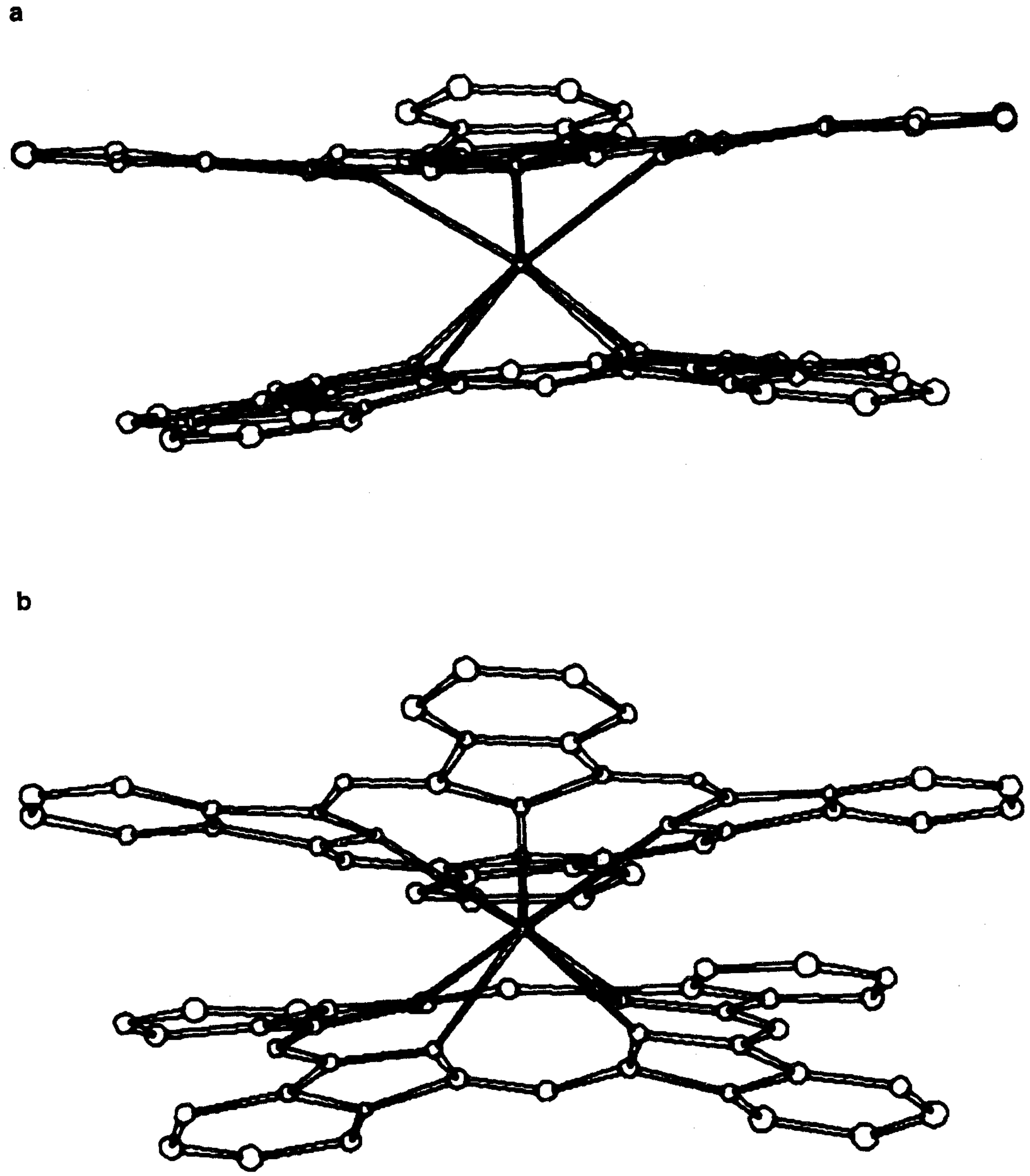

Figure 2. (a) Elevation view of the Pc_2Sn molecule. (b) Pc_2Sn molecule rotated 10° from the elevation view to give perspective view.

The average of the eight chemically equivalent bond distances for the two rings is shown in Figure 3 and Table II. The averaging gives very consistent bond distances and angles in the benzene and pyrrole portions of the molecule and they are not significantly different from those reported for UPc_2. (See Table IV.)

The isoindole nitrogen atoms within one ring form a square with a side 2.75 ± 6 Å in length. The comparable value observed for UPc_2 is 2.80 Å; for PcH_2,[18] 2.69 Å; for NiPc,[18] 2.65 Å; for PtPc,[19] 2.80 Å; and for PyMnPcOPcMnPy, 2.79 Å.[16] The average Sn-N bond distance is 2.347 ± 7 Å. The Sn-N bond distance reported in the literature for the chloro(trimethyl)pyridinetin(IV)[20] is 2.261 Å, but the tin atom in this case is surrounded by five atoms in a trigonal-bipyramidal configuration so that a quantitative comparison of the bond distances would not be significant.

The antiprism formed around the tin atom has the dimensions s, the average length of the side of the square, and l, the average length of the sides of the isosceles triangles of the distorted antiprism. Hoard and Silverton[1] suggested that for monodentate ligands, if the ligand repulsion and coulombic repulsion energy terms are minimized, a "most favorable" l/s would be 1.057. For stannic phthalocyanine with $s =$ 2.756 ± 6 Å and $l = 3.025$ Å, $l/s = 1.098$. This ratio is consistent with Hoard and Silverton's prediction that a multidentate ligand will reduce the coulombic energy and thus increase the l/s ratio. The s distance remains small to minimize ring strains in the phthalocyanine moiety; s is smaller than it would be if the ligand atoms were not bonded to one another. The distance l is large because of the repulsion between the very large phthalocyanine groups.

The closest intermolecular approach in the crystal is 3.70 Å between two of the phenyl carbon atoms. The orientation of the C-H bond direction indicates that there is no hydrogen bonding.

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(18) These results were obtained by refining the data obtained from J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

(19) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 36 (1940).

(20) R. Hulme, *J. Chem. Soc.*, 1527 (1965).

Table IV. Comparison between $SnPc_2$ and UPc_2 [a]

		Sn	U
Metal Coordination–Square Antiprism Dimensions			
Metal-N, Å		2.347 ± 7	2.43
Metal-square nitrogen planes, Å		1.35 ± 2	1.40_5
N-N in square, Å		2.756 ± 6	2.80
N-N between squares, Å		2.95 ± 2 3.08 ± 2	
Rotation of the rings, deg		42	37
Phthalocyanine Rings			
Pyrrole ring	N-C, Å	1.375 ± 6	1.38
	C-C, Å	1.467 ± 9	1.46
Pyrrole-pyrrole link	C-N, Å	1.321 ± 7	1.32
Phenyl-pyrrole	C-C, Å	1.387 ± 8	1.40
Phenyl	C-C, Å	1.409 ± 9	1.40
	C-C, Å	1.410 ± 9	1.39
	C-C, Å	1.42 ± 2	1.41
Pyrrole ring	C-N-C, deg	108.1 ± 7	107.9
	N-C-C, deg	109.2 ± 4	109.4
	C-C-C, deg	106.6 ± 5	106.6
Pyrrole-pyrrole′	N-C-N′, deg	128.7 ± 5	127.6
	C-C-N′, deg	121.8 ± 6	123.0
	C-N′-C, deg	121.3 ± 10	123.9
Pyrrole-phenyl	C-C-C, deg	130.5 ± 5	131.8
	C-C-C, deg	122.7 ± 4	121.6
Phenyl	C-C-C, deg	115.3 ± 6	116.8
	C-C-C, deg	121.8 ± 7	121.5

[a] Deviations given are standard deviations in the mean.

Registry No. $Sn(C_{32}H_{16}N_8)_2$, 12581-75-8.

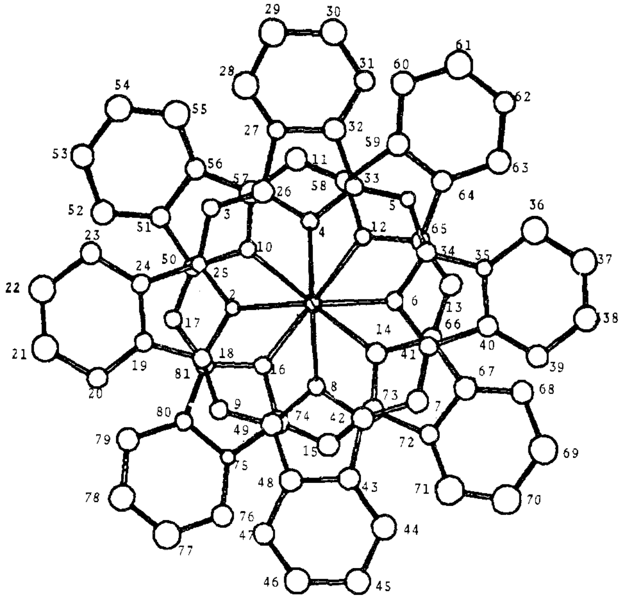

Figure 3. Plan view of the Pc_2Sn molecule.

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Contribution from the Department of Chemistry,
Ithaca College, Ithaca, New York 14850

Lewis Acid-Base Interactions of Zinc α,β,γ,δ-Tetraphenylporphine with Several Neutral Donors

GLENN C. VOGEL* and LYNN A. SEARBY[1]

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The thermodynamic parameters for the formation of a 1:1 adduct between zinc α, β, γ, δ-tetraphenylporphine and several neutral Lewis bases are reported. For the bases studied, the enthalpies of adduct formation increase in the order S < O < P < N. The effect of change in extinction coefficient of the adduct on the determination of the equilibrium constant is discussed in terms of the Rose–Drago equation.

Introduction

Much work has been done in recent years on the structure and reactivity of porphyrins and metalloporphyrins.[2,3] One area of interest has been the Lewis acid-base interaction between metalloporphyrins and neutral ligands whose donor atom is nitrogen. The literature contains essentially no thermodynamic data describing the interaction of metalloporphyrins with Lewis bases other than nitrogen donors and, in many cases involving the nitrogen donors, these studies are limited to the determination of stability constants.[3]

In addition to iron–porphyrin systems, considerable work has been done on the Lewis acid-base interaction between nitrogen donors (pyridines) and zinc α, β, γ, δ-tetraphenylporphine (ZnTPP).[4-6] Miller and Dorough[4] have determined the equilibrium constant and enthalpy and entropy for the formation of the adduct between ZnTPP and pyridine in the solvent benzene. Their data indicate that ZnTPP forms a 1:1 adduct with pyridine. In order to obtain information concerning the Lewis acidity of ZnTPP, we have extended the study of the Lewis acid-base interaction of ZnTPP in benzene to oxygen, sulfur, and phosphorus donors.

Experimental Section

Materials and Apparatus. Tetraphenylporphine and zinc tetraphenylporphine were synthesized by literature methods.[7,8] The

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(1) Supported by NSF-URP Grant GY-8880 during the summer of 1971.

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