served. It should be emphasized, however, that this is only a plausible hypothesis for which no direct evidence exists at present.

Because of the very favorable orientation of the molecules in the lattice, a study of the polarizations of the absorption bands has been undertaken with the hope of obtaining some direct evidence on the above spectroscopic problems.

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A Series of Phthalocyaninotin Complexes[1]

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Methods of preparing and purifying the compounds $PcSnF_2$, $PcSnBr_2$, $PcSnI_2$, and $PcSn(OH)_2$ are given together with improved procedures for the synthesis and purification of $PcSnCl_2$, Pc_2Sn, PcSn, and PcPb. Pc_2Sn is shown to have two polymorphic modifications and to form a 1:1 solvate with 1-chloronaphthalene. Both polymorphs are found to undergo thermal decomposition at elevated temperatures with the formation of PcSn and PcH_2.

Introduction

The phthalocyanino ring is a planar aromatic system which forms stable coordination compounds with many divalent, trivalent, and tetravalent metals. In the case of phthalocyanines involving trivalent and tetravalent metals appropriate substituent groups are attached to the metal atom in order to maintain electrical neutrality. With these normal phthalocyanino complexes it generally is supposed that the metal atom is located approximately in the plane of the ring and forms bonds with the four pyrrole type nitrogen atoms and that these latter atoms exhibit the approximate symmetry of a square.

An extensive series of phthalocyanines is formed by tin. Members of this series were first investigated by Linstead's group, who succeeded in establishing the existence of PcSn (as well as the analogous PcPb), $PcSnCl_2$, and Pc_2Sn.[2] Recently, Whalley, while obtaining visible spectra of a series of phthalocyanino complexes, verified the composition of Pc_2Sn and demonstrated that it is a distinct homogeneous phase.[3] At the same time Elvidge showed that the oxidation state of the tin in Pc_2Sn is four.[4]

The ratio of two phthalocyanine rings per metal atom makes Pc_2Sn unique among all of the phthalocyanines reported. It has been suggested that the structure of Pc_2Sn may involve tin atoms bonded with eight nearest neighbor nitrogen atoms.[5] The compound thus may be an example of a complex containing a post-transition metal in eight coordination. Infrared data are consistent with this proposed structure.[6]

This investigation of Pc_2Sn and other members of the phthalocyaninotin system is a continuation of our research into the chemistry and properties of the phthalocyanino complexes of the group IV metals. Both this and the earlier investigations show that the phthalocyaninotin system differs markedly from the analogous silicon and germanium systems. This is not surprising because tin is significantly larger than either silicon or germanium and because it is relatively stable in both the +2 and +4 oxidation states.

Experimental

The extractive recrystallizations were carried out in an Ace simplified extraction apparatus in which the usual extractor body was eliminated and the extraction thimble placed directly in the neck of the flask. When high boiling solvents were used, a heating tape was wrapped around the portion of the extractor containing the thimble to ensure that the extractions took place at approximately the reflux temperature of the solvent.

The carbon, hydrogen, and the halogen analyses were made by ordinary microanalytical procedures. Nitrogen was determined by a modification of the Dumas method, in which the compound was decomposed at 1000°. Lead was determined volumetrically by means of a standard method employing ethylenediaminetetraacetic acid as a titrant. Tin was determined iodometrically after an aqueous aluminum reduction.[7]

The thermogravimetric analysis data were obtained with a Stanton HT-D recording thermobalance operating with an argon atmosphere. A heating rate of 3°/min. was used.

For the collection of the differential thermal analysis data an apparatus was used in which the sample and the reference Al_2O_3 were held in two small tantalum crucibles. These had built in thermocouple wells and were placed over thermocouples in the center of a uniform temperature zone. The temperature difference was recorded as a function of the temperature of the Al_2O_3 on a recording millivolt potentiometer. A heating rate of about 10.5°/min. and an argon atmosphere were used.[8]

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(1) This work was supported by the National Science Foundation under Grant NSF-G15833. The work was presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, and is based on portions of the Ph.D. thesis of W. J. K. Pc = phthalocyanino ligand.

(2) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

(3) M. Whalley, *ibid.*, 866 (1961).

(4) J. A. Elvidge, *ibid.*, 869 (1961).

(5) W. C. Fernelius, "Chemical Architecture," R. E. Burk and O. Grummitt, Ed., Interscience Publishers, Inc., New York, N. Y., 1948, pp. 96–97.

(6) W. J. Kroenke and M. E. Kenney, in preparation.

(7) Analytical work performed by Schwarzkopf Microanalytical Laboratory.

(8) This equipment belongs to the National Carbon Research Laboratory and the permission of this organization to use the equipment is gratefully acknowledged.

Dichloro(phthalocyanino)tin(IV).—A reaction mixture consisting of 18 g. of anhydrous stannous chloride and 40 g. of phthalonitrile (1:3.3 mole ratio) in 500 ml. of technical 1-chloronaphthalene was refluxed for 3 hr. The product was filtered off, washed with benzene and 95% ethanol, and extracted successively with glacial acetic acid and absolute ethanol. This gave 45 g. of crystalline $PcSnCl_2$ (83% yield). A 2.0-g. sample of this was refluxed with 250 ml. of 1-chloronaphthalene, and the resultant solution was filtered. A residue consisting of 1.5 g. of $PcSnCl_2$ was left. The filtrate after standing yielded pure $PcSnCl_2$, a dark blue crystalline solid which exhibited a red reflex. This $PcSnCl_2$ weighed 0.47 g. after being washed with benzene and dried at 110°. Microscopic examination revealed green transparent needles and platelets.

Anal. Calcd. for $C_{32}H_{16}N_8SnCl_2$: C, 54.74; H, 2.30; N, 16.0; Sn, 16.9; Cl, 10.10. Found: C, 54.69; H, 2.33; N, 15.9; Sn, 17.1; Cl, 9.84.

Purification of $PcSnCl_2$ also was effected by recrystallization of it from 1-bromonaphthalene and by vacuum sublimation of it at 460°. Generally, simple extraction of the initial synthesis product with glacial acetic acid and ethanol gave a product sufficiently pure for other syntheses.

(Phthalocyanino)tin(II).—PcSn was prepared by the reduction of $PcSnCl_2$ with anhydrous $SnCl_2$ in refluxing quinoline. This was done under nitrogen since PcSn was found to be oxidized by air at elevated temperatures. A reaction mixture of 3.0 g. of $PcSnCl_2$ and 3.0 g. of $SnCl_2$ (3.7:1 mole ratio) in 120 ml. of quinoline was refluxed under nitrogen for 2 hr. The resulting mixture was filtered and the product washed with benzene and ether. After air drying, the PcSn obtained weighed 2.4 g., giving a yield of 88%. A 1.0-g. sample of this was recrystallized extractively from refluxing quinoline under a nitrogen atmosphere. At no time during the extraction was the PcSn exposed to air above 25°. The product from the extraction was washed with benzene and ether and vacuum dried for 1 hr. at 110°. A yield of 0.88 g. of PcSn, a blue-black crystalline solid which had no red reflex, was obtained. Microscopic examination showed blue transparent parallelepipeds.

Anal. Calcd. for $C_{32}H_{16}N_8Sn$: C, 60.89; H, 2.55; Sn, 18.8. Found: C, 61.07; H, 2.76; Sn, 18.9.

PcSn also was prepared by the reduction of $PcSnCl_2$ with $NaBH_4$ in ethanol; however, this reduction was difficult to control and introduced an impurity which was hard to remove. Alternate methods of purification found for PcSn were recrystallization from naphthalene or chloronaphthalene and vacuum sublimation at 400°. PcSn was shown to be inert to refluxing H_2O, C_2H_5OH, glacial acetic acid, and 3 *M* NaOH but to give $PcSnCl_2$ with refluxing HCl.

Differential thermal analysis was applied to PcSn to study its behavior upon heating. The thermogram of a 25.6-mg. sample heated to 664° showed an endothermic doublet beginning at about 570° with maxima at 600 and 606°. The residue from this run was composed of 19 mg. of blue-black shiny flakes. In another experiment, 25.0 mg. of it was heated to 588° and cooled rapidly. Only the start of the endothermic peak was observed. The residue consisted of 23.4 mg. of PcSn. In a third experiment a 27.2-mg. sample of PcSn was heated to 594° and cooled rapidly. The first peak of the doublet was completed during the cooling cycle at 592°, but the second peak was not observed. A 22.3-mg. blue-black decomposition residue was left. In all cases a blue sublimate of PcSn was observed at temperatures above about 525°. These experiments showed that PcSn is relatively stable in Ar, and that the first peak of the doublet in the thermogram represents the decomposition of the PcSn.

Dibromo(phthalocyanino)tin(IV).—$PcSnBr_2$ was prepared by oxidizing PcSn with elemental bromine. A reaction mixture of 0.66 g. of PcSn and 0.07 ml. of Br_2 (1:1.3 mole ratio) was heated at 65 to 75° for 20 min. in 120 ml. of 1-chloronaphthalene. The product was filtered off, washed with benzene, and air dried. This gave 0.75 g. of bright blue-green, powdered $PcSnBr_2$, a yield of 92%. A 0.30-g. sample of this was refluxed with 100 ml. of 1-chloronaphthalene and the solution filtered. A residue of 0.06 g. of $PcSnBr_2$ was left. The $PcSnBr_2$ which crystallized from the filtrate was washed with benzene and dried 1 hr. at 110°. It weighed 0.16 g. and consisted of a dark blue crystalline solid which had a dull red reflex. Microscopic examination showed that the recrystallized $PcSnBr_2$ was in the form of green transparent rods.

Anal. Calcd. for $C_{32}H_{16}N_8SnBr_2$: C, 48.59; H, 2.04; Sn, 15.0; Br, 20.2. Found: C, 48.87; H, 2.15; Sn, 15.2; Br, 20.5.

Diiodo(phthalocyanino)tin(IV).—$PcSnI_2$ was synthesized by a procedure analogous to that used for $PcSnBr_2$. A reaction mixture consisting of 1.0 g. of PcSn and 0.5 g. of I_2 (1:1.3 mole ratio) was refluxed for 3 min. with 200 ml. of 1-chloronaphthalene. The product after separation by filtration was washed with 1-chloronaphthalene, benzene, and absolute ethanol and air dried. This yielded 1.1 g. (76%) of $PcSnI_2$. A 0.50-g. sample of this was recrystallized from 140 ml. of 1-chloronaphthalene. Only a small blue residue was left by the initial filtration. The recrystallized $PcSnI_2$, a dark blue crystalline solid with a dull red reflex, was washed with benzene and dried 1 hr. at 110°. It weighed 0.26 g. and was made up of green transparent microscopic needles and platelets.

Anal. Calcd. for $C_{32}H_{16}N_8SnI_2$: C, 43.43; H, 1.82; Sn, 13.4; I, 28.7. Found: C, 43.76; H, 1.75; Sn, 13.4; I, 28.9.

Iodine vapor was observed during the preparation of the chloronaphthalene solutions used for recrystallizations. Its presence was apparently caused by the decomposition of a yellow impurity in the $PcSnI_2$. When the refluxing was continued until all the iodine escaped an oxo(phthalocyanino)tin impurity was introduced. The addition of a small crystal of iodine and the use of an inert atmosphere during the preparation of the solutions obviated this difficulty.

Dihydroxo(phthalocyanino)tin(IV).—$PcSn(OH)_2$ was prepared by the hydrolysis of recrystallized $PcSnI_2$ with an alcoholic aqueous ammonia solution. A 0.12-g. sample of $PcSnI_2$ was refluxed for 75 min. with 24 ml. of H_2O, 6 ml. of C_2H_5OH, and 6 ml. of NH_4OH. The product was filtered off, washed with H_2O, C_2H_5OH, and benzene, and dried at 110° for 1 hr. This produced 0.085 g. of $PcSn(OH)_2$ (95% yield), a dark blue solid with a dull red reflex. It consisted of microscopic blue transparent rods and platelets.

Anal. Calcd. for $C_{32}H_{18}N_8SnO_2$: C, 57.78; H, 2.73; Sn, 17.8. Found: C, 57.56; H, 2.92; Sn, 17.7.

$PcSn(OH)_2$ was found to be very insoluble in ordinary nonreactive solvents and upon heating to yield oxo(phthalocyanino)-tin compounds.

Difluoro(phthalocyanino)tin(IV).—$PcSnF_2$ was prepared by the reaction of $PcSn(OH)_2$ and 49% aqueous hydrofluoric acid. The $PcSn(OH)_2$ was prepared by a 66-hr. hydrolysis of $PcSnCl_2$ with refluxing alcoholic aqueous ammonia. A 0.42-g. sample of this $PcSn(OH)_2$ in a Pt dish was treated with 25 ml. of HF. The mixture immediately assumed a bright red reflex with a pronounced green tinge. This mixture was evaporated to dryness on a steam bath, and the resultant blue solid was slurried with pyridine, transferred to a glass filter, washed with pyridine and benzene, and dried. The $PcSnF_2$ thus obtained weighed 0.38 g. (90% yield). A 0.21-g. sample of this was recrystallized extractively from refluxing 1-chloronaphthalene. The recrystallized $PcSnF_2$ was washed with benzene and dried for 1 hr. at 110°. It weighed 0.074 g. and was a bright reddish purple crystalline solid. It was in the form of microscopic, well formed, blue, transparent parallelepipeds.

Anal. Calcd. for $C_{32}H_{16}N_8SnF_2$: C, 57.43; H, 2.41; Sn, 17.7; F, 5.68. Found: C, 57.28; H, 2.49; Sn, 17.4; F, 5.98.

X-Ray Powder Patterns.—The *d*-spacings in Ångstroms of the three strongest lines from powder photographs along with visually estimated intensities for the simple phthalocyanines described above are: $PcSn(OH)_2$: 12.6, 10; 6.79, 8; 5.28, 9; $PcSnF_2$: 8.22, 10; 7.06, 3; 3.30, 6; $PcSnCl_2$: 10.4, 10; 8.25, 7; 3.12, 8; $PcSnBr_2$: 10.6, 10; 8.25, 4; 3.14, 5; $PcSnI_2$: 10.7, 10; 8.02, 2; 3.28, 5; PcSn: 11.5, 10; 6.95, 4; 3.93, 5; PcPb: 12.6, 10; 4.59, 3; 3.64, 5. The chloride, bromide, and iodide have quite similar patterns and probably have closely related crystal structures.

β-Bis(phthalocyanino)tin(IV).—β-Pc$_2$Sn was prepared by the reaction of PcSnCl$_2$ and PcNa$_2$[2] in refluxing 1-chloronaphthalene. A well-ground mixture consisting of 6.86 g. of PcSnCl$_2$ and 6.45 g. of PcNa$_2$ (1:1.2 mole ratio) was dried for 3 hr. at 110°. The hot mixture was placed in a dry flask, 137 ml. of 1-chloronaphthalene was added, and the reaction system was purged with N$_2$. The mixture was refluxed for 90 min. under N$_2$, allowed to cool for 1 hr., and filtered. The 9.00-g. residue left by this filtration contained PcSn, PcH$_2$, and NaCl. Red reflecting crystals of Pc$_2$Sn·C$_{10}$H$_7$Cl were observed in the dark blue-green filtrate after a time. The Pc$_2$Sn·C$_{10}$H$_7$Cl, after being separated, washed with benzene, and air dried, weighed 1.98 g. (approximately a 15% yield).

A 0.76-g. sample of this solvate was refluxed 45 min. with 40 g. of naphthalene while a stream of air was being bubbled through the refluxing solution (to convert the PcSn to an insoluble oxo complex). After filtration, the solution was allowed to stand at approximately 80°. It gave 0.42 g. of red reflecting crystalline Pc$_2$Sn. A 0.19-g. sample of this was recrystallized extractively from benzene with a yield of 0.096 g. of β-Pc$_2$Sn. Finally, 0.050 g. of this was heated to 285° under vacuum. A small amount of PcH$_2$ was sublimed out. Microscopic examination of the purple, red reflecting crystals remaining revealed green transparent columnar parallelepipeds.

Anal. Calcd. for C$_{64}$H$_{32}$N$_{16}$Sn: C, 67.21; H, 2.82; Sn, 10.4. Found: C, 67.31; H, 2.94; Sn, 10.6.

Dried reagents, baked equipment, and a N$_2$ atmosphere were all found to be important in getting good yields of Pc$_2$Sn. The separation of the PcH$_2$–PcSn–Pc$_2$Sn mixture was made relatively easy because Pc$_2$Sn forms supersaturated solutions with 1-chloronaphthalene. Neither naphthalene nor 1,2,4-trimethylbenzene form supersaturated solutions with it.

When β-Pc$_2$Sn was vacuum sublimed at temperatures between 410 and 460° with collecting finger temperatures of 150–390° crystalline deposits of β-Pc$_2$Sn were obtained. However, when Pc$_2$Sn was heated in evacuated sealed tubes at 410 or 460° for 1 to 5 days with collecting temperatures of 300 to 375° sublimates of PcH$_2$–PcSn mixtures were obtained. The residues were made up of crystals of β-Pc$_2$Sn with surface decomposition.

A differential thermal analysis of an 18.5-mg. sample of β-Pc$_2$Sn carried to 650° gave a thermogram which showed an endothermic doublet beginning at about 560–580° with maxima at 600 and 601° followed by a very sharp endothermic peak with a maximum at 609°. The 609° peak was accompanied by the evolution of brown vapors. Above 525° a noticeable dark blue deposit of PcH$_2$ and PcSn formed on the chamber walls. A 9.7-mg. shiny black solid decomposition residue was left in the crucible. In another run with a 16.4-mg. sample, the temperature was carried to 600° and then dropped rapidly. The first endothermic doublet was observed. The 13.7-mg. residue was identified as an approximately 1:1 PcSn–PcH$_2$ mixture. In a third run an 18.5-mg. sample was heated to 560° and held at this temperature for 45 min., at which time an endothermic event took place. The sample was quickly cooled and upon examination was found to weigh 15.1 mg. and to consist of an approximately 1:1 PcSn–PcH$_2$ mixture.

α-Bis(phthalocyanino)tin(IV).—α-Pc$_2$Sn was made by the recrystallization of purified β-Pc$_2$Sn from naphthalene. The purified β-Pc$_2$Sn was prepared with the aid of the air–naphthalene process given above and a benzene extractive crystallization.

A mixture of 200 mg. of this Pc$_2$Sn and 12.0 g. naphthalene was refluxed 40 min. and filtered. This left a residue of approximately 30 mg. of β-Pc$_2$Sn. The filtrate was cooled rapidly to 85° and refiltered. After washing with benzene and anhydrous ether, 97.3 mg. of α-Pc$_2$Sn was recovered as a purple crystalline solid. Microscopic examination revealed green transparent platelets.

Anal. Calcd. for C$_{64}$H$_{32}$N$_{16}$Sn: C, 67.21; H, 2.82; N, 19.59; Sn, 10.4. Found: C, 67.41, H, 2.87; N, 19.5; Sn, 10.1.

The thermogram from the differential thermal analysis of a 19.7-mg. sample of α-Pc$_2$Sn was very similar to that for β-Pc$_2$Sn. The small endothermic doublet began at about 580° and had maxima at 605 and 607°. The large endothermic peak was at 616°. A black decomposition residue was left at the end of the run. A repeat of the experiment in which the sample was heated only until the doublet was observed resulted in the recovery of a residue of an equimolar PcH$_2$–Pc$_2$Sn mixture. The small temperature differences observed for the α and β forms were reproducible.

Interconversions of α- and β-Pc$_2$Sn.—Recrystallization of Pc$_2$Sn·C$_{10}$H$_7$Cl, α-Pc$_2$Sn, or β-Pc$_2$Sn from naphthalene or from 1,2,4-trimethylbenzene yielded α-Pc$_2$Sn. Digestion of the α form with either benzene or naphthalene yielded a mixture of α and β forms while similar treatment of the β form gave only the β form. Naphthalene digestion of the solvate resulted in the β form. Extractive recrystallizations of the solvate and the α and β forms with benzene or 1,2,4-trimethylbenzene gave the β form.

Although the infrared spectra of α- and β-Pc$_2$Sn are quite similar, the X-ray powder photographs are very different. The d-spacings in Ångstroms of the three strongest lines along with the visually estimated intensities for the two polymorphs are: α: 12.4, 10; 9.69, 9; 8.37, 8 and β: 12.5, 10; 8.02, 5; 3.45, 3.

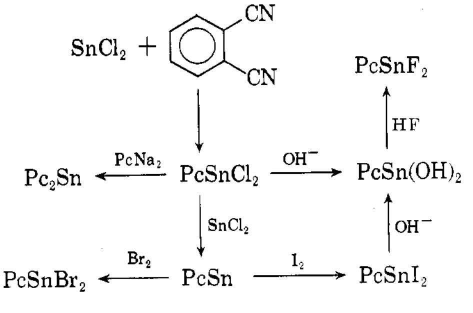
Pc$_2$Sn·1-chloronaphthalene.—A sample of the solvate obtained from the Pc$_2$Sn synthesis in 1-chloronaphthalene was washed carefully with benzene (vigorous washing sometimes resulted in complete desolvation of the crystals) and air dried at room temperature. Small transparent green rods with a red reflex were obtained. Differential thermal analysis of this solvate gave a curve which showed an irreversible endothermic peak beginning at approximately 130° and a further endothermic doublet beginning at approximately 560° with maxima at 596 and 607°. The residue left was a black decomposition product. The product of a run terminated at 300° was identified as β-Pc$_2$Sn. The rate of weight loss curve from a thermogravimetric analysis experiment on the solvate showed that the solvate lost a small amount of weight up to 130° and that a major weight loss occurred between approximately 130 and 195°. The weight loss between 133 and 195° for the sample which weighed 40.6 mg. at 133° was 5.1 mg., and the calculated weight loss for a 1:1 solvate was 5.1 mg.

(Phthalocyanino)lead(II).—PcPb was prepared by the reaction of PbO and phthalonitrile in refluxing 1-chloronaphthalene. A reaction mixture consisting of 0.87 g. of PbO and 2.00 g. of phthalonitrile (1:4 mole ratio) suspended in 1-chloronaphthalene was refluxed 80 min. and filtered. The product, 1.0 g. of PcPb mixed with PbO, was recrystallized extractively from quinoline. The blue-black crystalline PcPb obtained weighed 0.44 g. after being washed with benzene and vacuum dried at 110° (a 16% yield). It was composed of microscopic transparent green needles.

Anal. Calcd. for C$_{32}$H$_{16}$N$_8$Pb: C, 53.40; H, 2.24; Pb, 28.8. Found: C, 53.65; H, 2.12; Pb, 29.0.

Discussion

A summary of the preparative relationships between the compounds dealt with in this paper is



Because oxidation–reduction reactions based on PcSn as well as replacement reactions based on PcSnCl$_2$ can be used for the preparation of tin phthalocyanines, the choice of synthetic routes for these compounds is greater than that for comparable germanium and silicon phthalocyanines, where ordinarily only the replacement route can be used.

From the data gathered on the conditions leading to the formation of the α and the β polymorphs of Pc_2Sn from solution it is concluded that the β form is the thermodynamically more stable form, although the difference in the stabilities is probably not great. Correlating with this is the fact that the DTA thermograms of the α and β forms show similar peaks at similar temperatures and that they furnish no evidence for polymorphic transformations below the peaks at 600°.

These peaks are attributable to the reaction

$$Pc_2Sn \longrightarrow PcSn + PcH_2$$

Hydrogen for the reaction must come from the decomposition of some of the phthalocyanine rings. The large peak which follows the doublet in each case is assignable to the gross decomposition of the $PcSn$–PcH_2 mixture. It is interesting to note that the thermogram for pure PcSn shows that it decomposes at about this same temperature.

In viewing the DTA data it must be remembered that the decomposition temperatures obtained do not represent equilibrium processes and that variations in conditions can be expected to lead to differing decomposition temperatures. Thus it is not surprising that a PcH_2–$PcSn$ sublimate begins to appear on the DTA apparatus chamber walls at about 525° in the Pc_2Sn experiments and that a PcH_2–$PcSn$ residue is left when Pc_2Sn is heated at 560° for 45 min. Similarly it is not unexpected that PcH_2–$PcSn$ sublimates form at even lower temperatures in sealed tube sublimations of Pc_2Sn carried out over long periods of time.

Since the Pc_2Sn 1-chloronaphthalene solvate is converted to the β polymorph by very mild conditions and the α–β conversion in solvents is slow, it seems probable that the arrangement of the Pc_2Sn molecules in the crystals of the solvate and the β polymorph are closely interrelated.

Contrasting with the α–β polymorphism of Pc_2Sn and the polymorphism of the divalent transition metal phthalocyanines[9] is the apparent lack of polymorphism in PcSn. An interpretation of this will have to await structural data on PcSn, but it does suggest that the crystal structure of PcSn differs from the structures of the transition metal phthalocyanines.

The solubilities and hydrolytic stabilities of the four $PcSnX_2$ halides are in accord with expectations. Thus, the increase in solubility of the halides in refluxing 1-chloronaphthalene in progressing from $PcSnF_2$ to $PcSnI_2$ (roughly 0.4 to 3.4 mg./ml.) is consistent with the increase in the covalent character of the Sn–X bond. Similarly, the increasing ease of hydrolysis of the halides in the series $PcSnF_2$ to $PcSnI_2$ can be correlated with the Sn–X bond energies. (In refluxing aqueous ammonia $PcSnF_2$ is not detectably hydrolyzed in 3 days, $PcSnCl_2$ is hydrolyzed in 45 hr., and $PcSnI_2$ is hydrolyzed in 45 min.)

The successful isolation of $PcSn(OH)_2$ from the hydrolysis of the halides fits in with the general pattern observed for diorganotin dihydroxides and oxides. In the latter compounds oxides generally are found when the organic group is small.[10a] When the organic group is large hydroxides can be isolated.

During the work with PcPb no evidence of a Pb^{IV} phthalocyanine was found. Even attempted oxidations of PcPb with Br_2 in 1-chloronaphthalene gave PcH_2 as the only new phthalocyanine. Similarly $PbCl_2$ and phthalonitrile in 1-chloronaphthalene gave no phthalocyanine. Pb^{II} is clearly stabilized by the ring, a situation which contrasts strongly with the stabilization of Pb^{IV} in organolead compounds.[10b]

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(9) A. N. Sidorov and I. P. Kotlyar, *Opt. Spectry.*, **11**, 92 (1961).

(10) G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956: (a) p. 188; (b) p. 212.