tempts were made to grow mixed crystals with R = n-C_4H_9, X = H. In this case the Zn(II) complex is known from crystal structure analysis[8] to be tetrahedral. The Ni(II) complex is planar both in solid and in a solution of noncoordinating solvents[8]—the steric factors necessary for a tetrahedral geometry cannot be provided by a straight-chain R group. The phenomenon of forced configuration and anomalous isomorphism (mixed crystal formation) occurs only when the steric factors are potentially present in the Ni(II) complex.

Acknowledgment.—Thanks are due to Professor R. H. Holm. Financial support was provided by the National Science Foundation.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO

Dichloro(phthalocyanino)silicon[1]

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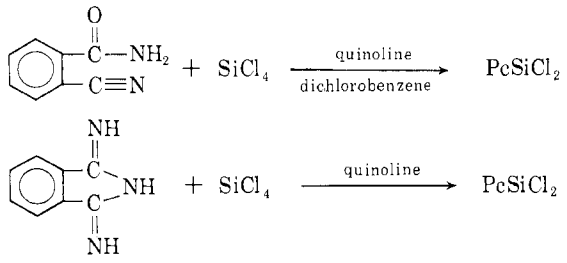
Received August 17, 1964

In the originally reported syntheses of dichloro(phthalocyanino)silicon, $PcSiCl_2$, *o*-phthalonitrile was allowed to react with either silicon tetrachloride or hexachlorodisiloxane in quinoline.[2,3] These syntheses proved to be experimentally quite inconvenient, and their deficiencies have impeded work on the silicon phthalocyanines, since for this series the chloro complex is the key compound.

Two convenient syntheses for $PcSiCl_2$ are now reported which are based on the use of *o*-cyanobenzamide and 1,3-diiminoisoindoline, respectively. These are



In addition techniques are given for the recrystallization of $PcSiCl_2$ and for its facile conversion to $PcSi(OH)_2$.

Experimental

***o*-Cyanobenzamide.**[4]—To prepare this compound, 472 g. of phthalimide was stirred with 1 l. of concentrated ammonium hydroxide for 24 hr. The phthalamide thus produced, after being filtered off, washed with water and ethanol, and dried at 100°, weighed 500 g. (95% yield). A mixture of 164 g. of this, 567 ml. of acetic anhydride, and 114 ml. of acetic acid was refluxed for 45 min. and the resultant solution filtered, allowed to cool to 41°, and refiltered. This yielded a crystalline product which, after being washed with acetic acid, water, and ethanol and dried at 110°, weighed 63.5 g. (43% yield); m.p. 180° dec. Acetic anhydride was used to doubly recrystallize 10 g. of this *o*-cyanobenzamide; m.p. 180° dec., lit.[4] 172°.

Anal. Calcd. for $C_8H_6N_2O$: C, 65.60; H, 4.14. Found: C, 65.86; H, 4.35.

Dichlorophthalocyaninosilicon from *o*-Cyanobenzamide.—A mixture of 21.9 g. (0.15 mole) of *o*-cyanobenzamide, 17.2 ml. (0.15 mole) of silicon tetrachloride, 220 ml. of quinoline, and 110 ml. of *o*-dichlorobenzene was heated, with mechanical stirring in a flask fitted with a condenser, to 205°, held at this temperature for 5 min., cooled to 180°, and filtered. The $PcSiCl_2$ thus isolated was washed with quinoline, benzene, pyridine, acetic acid, ethanol, and ether and dried at 110°. It weighed 8.2 g. (35% yield based on *o*-cyanobenzamide) and was identified by infrared spectra.[5]

1,3-Diiminoisoindoline.[6]—Ammonia was bubbled into a stirred mixture of 320 g. of *o*-phthalonitrile, 4.0 g. of sodium methoxide, and 1 l. of methanol at a moderate rate for 40 min. The mixture was then brought to reflux and maintained at this temperature for 3.2 hr. with continued stirring and addition of ammonia. Upon being cooled and filtered the product yielded a crop of greenish crystals which, after being washed with ether and dried, weighed 101 g. A second crop weighing 54 g. was obtained the following day, for a total yield of 43%. Recrystallization of some of the product with methanol and ether (charcoal) yielded colorless crystals, m.p. 195–196° dec., lit.[7] 196° dec. Repetition of the synthesis with the same mother liquor gave additional product.

Dichloro(phthalocyanino)silicon from 1,3-Diiminoisoindoline.—In a flask equipped with a water condenser, a mechanically stirred mixture of 36.5 g. (0.25 mole) of 1,3-diiminoisoindoline, 41.5 ml. (0.36 mole) of silicon tetrachloride, and 415 ml. of quinoline was brought slowly to reflux (219°). It was maintained at this temperature for 30 min. and then cooled to 184° and filtered (Whatman No. 541). The purple crystalline product, after being washed with quinoline, benzene, methanol, and acetone and dried at 110°, weighed 27.4 g. (71% yield based on 1,3-diiminoisoindoline). It was identified by infrared spectra.[5]

Purification.—1-Chloronaphthalene was used as a solvent for the recrystallization of $PcSiCl_2$. From 63.5 ml. of the solvent 10.5 ml. was distilled off and to the remainder, after brief cooling, 481 mg. of $PcSiCl_2$ was added. The resultant mixture was refluxed, filtered, cooled, and refiltered. This yielded 309 mg. of product (64% yield).

Hydrolysis.—A sample of 1.59 g. of $PcSiCl_2$ together with 8.00 g. of $NaOCH_3$ was mixed with a solution prepared by diluting 5 ml. of water to 100 ml. with 95% ethanol. This suspension was refluxed 60 min., cooled, and filtered. The resultant $PcSi(OH)_2$, after being washed with water and dried, weighed 1.23 g. (83% yield). It was identified by infrared spectra.[8]

(1) This work was supported initially by the Air Force Office of Scientific Research under Contract AF 49(638)-773 and the National Science Foundation under Grant NSF G-15833; further support was provided by the Office of Naval Research under Contract Nonr-1141(18).

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(6) Dr. J. A. Elvidge suggested that 1,3-diiminoisoindoline could be prepared in this fashion and the authors wish to express their thanks to him for this suggestion.

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