been pumped away, was maintained at 0° during a study of the decomposition process. Shortly after bringing the sample to 0°, decomposition was detected by a sudden increase in pressure which scattered material throughout the system. At this point the system was quenched to −196° and the hydrogen gas produced (7 mmoles) was measured volumetrically and identified mass spectrometrically. Upon warming the system to 0°, $(CH_3)_2S$ and B_2H_6 which were produced in the initial decomposition reaction were distilled away and identified mass spectrometrically. An additional 7 mmoles of H_2 plus B_2H_6 and $(CH_3)_2S$ were formed very slowly at 0° over a period of about 1 week. The solid residue from the decomposition was shown to be B_2O_3 from analysis and by converting it to H_3BO_3, which was identified by X-ray powder diffraction.

Spectroscopic Equipment.—Raman spectra at −40 to −50° of the solid product and of a solution of the product (*ca.* 5 *M*) in dichloromethane were obtained through the courtesy of Dr. A. J. Dahl and Dr. R. C. Taylor of the University of Michigan using a spectrograph and light source which have been described previously.[12]

B^{11} n.m.r. at −40 to −50° of a solution (*ca.* 5 *M*) of the product in dichloromethane were obtained at 19.25 Mc. through the courtesy of Dr. D. Gaines of Indiana University and Dr. William Richey of the Sohio Oil Company.

Acknowledgment.—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation. S. G. S. wishes to thank The Ohio State University for assigned research duty.

[12] G. L. Vidale and R. C. Taylor, *J. Am. Chem. Soc.*, **78**, 294 (1956).

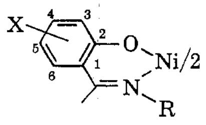
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

A Case of Anomalous Isomorphism

BY A. CHAKRAVORTY[1]

Received August 13, 1964

It has been convincingly proven[2-4] that bis(N-alkylsalicylaldimine)nickel(II) (A) exhibits a planar–tetrahedral equilibrium in a solution of noncoordinating solvents when R is a secondary or tertiary alkyl group. However in the solid phase the compounds are either diamagnetic and hence planar or fully paramagnetic (μ_{eff} = 3.30 B.M.) and pseudotetrahedral depending on the nature of R and X. Thus the intramolecular steric factors[2a] that are responsible for planar–tetrahedral equilibria in solutions are favored or disfavored to one extreme by the static crystal forces. In the



A

R = *i*-C_3H_7 series,[2b] X = H is paramagnetic and tetrahedral,[5] X = 5-CH_3 is diamagnetic, X = 5-C_2H_5 is paramagnetic, and X = 5-*n*-C_3H_7 is again diamagnetic. Only the tetrahedral Ni(II) complexes are isostructural with the corresponding Zn(II), which in all probability are tetrahedral irrespective of R and X.[2a,6] The interesting sequence mentioned above clearly indicates that the favored form in the crystalline phase is determined by a delicate balance of crystal forces and steric effects. This suggested that the planar diamagnetic compounds though not isostructural with Zn(II) complexes in their pure solid phases might still be introduced into the Zn(II) lattice to assume a tetrahedral structure. In other words, there is a possibility that two compounds having completely different individual crystal structures might still form mixed crystals due to the forced change in the molecular geometry of one of the components.

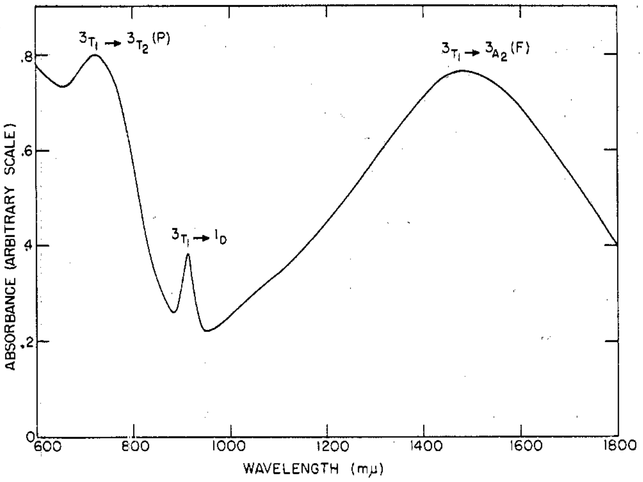


Figure 1.—Ligand field spectrum of R = *i*-C_3H_7, X = 5-CH_3 (25% Ni and 75% Zn) taken in Nujol mull.

In fact the above-mentioned R = *i*-C_3H_7, X = 5-CH_3, diamagnetic in its pure solid phase, could be grown in the corresponding Zn(II) lattice. The Ni(II) content can be made 25% and probably more. The mixed crystals are strongly paramagnetic. Since the Zn(II) complex is tetrahedral,[2a] this paramagnetism arises from isomorphous replacement of Zn(II) by Ni(II). Convincing evidence for the presence of tetrahedral Ni(II) in these crystals is obtained from their crystal field spectrum taken in Nujol mull on a Cary Model 14 recording spectrophotometer. The band at 1460 mμ is characteristic of all tetrahedral Ni(II)–salicylaldimines; this band is absent in all planar complexes in this series[2a,4] including pure R = *i*-C_3H_7, X = 5-CH_3. The spectrum and assignment are shown in Figure 1. Similar paramagnetic mixed crystals were grown in other cases, *e.g.*, R = *i*-C_3H_7, X = 5-C_6H_5; here again the pure Ni(II) complex is diamagnetic in the solid phase. Undoubtedly the situation could be achieved in many more cases. Similar examples of forced configuration have also been observed in pyrrole-2-aldimine complexes.[7] Unsuccessful at-

---

[1] Correspondence should be addressed to the Department of Chemistry, Indian Institute of Technology, Kanpur, India.

[2] (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); (b) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

[3] L. Sacconi, P. Paoletti. and M. Ciampolini, *ibid.*, **85**, 411 (1963).

[4] A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964).

[5] M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1104 (1963).

[6] E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961).

[7] A. Chakravorty, L. J. Theriot, and R. H. Holm, to be published.

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[6] 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.

(8) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

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

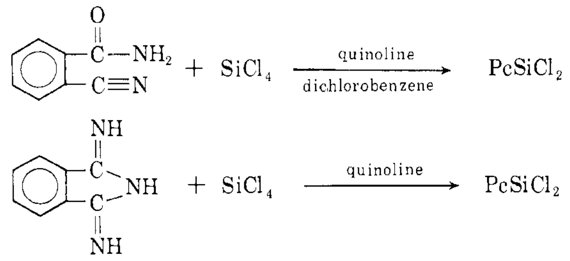
Dichloro(phthalocyanino)silicon[1]

BY MICHAEL K. LOWERY, ALBERT J. STARSHAK, S.J.,
JOHN N. ESPOSITO, PAUL C. KRUEGER, AND
MALCOLM E. KENNEY

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).

(2) R. D. Joyner, J. Cekada, Jr., R. G. Linck, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **15**, 387 (1960).

(3) R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, **1**, 236 (1962).

(4) G. T. Byrne, R. P. Linstead, and A. R. Lowe, *J. Chem. Soc.*, 1017 (1934).

(5) P. C. Krueger, Ph.D. Thesis, University Microfilms, No. 64-14, p. 114.

(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.

(7) J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5000 (1952).

(8) Reference 5, p. 118.