the tetrahedral angle (probably[29] between 140 and 150°) and examination of molecular models reveals that $POBr_3BBr_3$ is considerably more sterically strained, with respect to POB angle distortion than $POBr_3BCl_3$. This explanation is not entirely satisfactory in that the $POCl_3$ complexes exhibit the usual order. However, with the present limited evidence, it is probably the most realistic.

Acknowledgments.—The authors wish to thank Messrs. Albright and Wilson Ltd., for a research grant to K. K. S. G. and the Central Research Fund of the University of London for a grant to purchase a recorder.

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[29] I. Lindqvist, "Inorganic Adduct Molecules of Oxo-Compounds," Springer-Verlag, Berlin, 1963, p 96.

CONTRIBUTION FROM THE OLIN MATHIESON
RESEARCH CENTER, NEW HAVEN, CONNECTICUT

Complexes Derived from 1,3-Diiminoisoindoline-Containing Ligands. II. The Stepwise Formation of Nickel Phthalocyanine

BY THOMAS J. HURLEY, MARTIN A. ROBINSON, AND SAMUEL I. TROTZ

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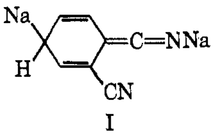
The stepwise formation of nickel phthalocyanine is traced through the initial complexation of 1,3-diiminoisoindoline with nickel chloride, its condensation with 2 additional moles of 1,3-diiminoisoindoline, and the formation of a unique six-membered isoindolinenine complex. This latter compound readily converts to the metalated phthalocyanine upon heating.

Introduction

Since the discovery of phthalocyanine, in 1907,[1] this molecule and its metalated analogs have been the subject of extensive investigation. In spite of the fact that many preparative methods have been uncovered and the physical and chemical properties of these compounds elucidated, the mechanisms of formation are less clearly defined. A pertinent example involves the preparation of sodium phthalocyanine by the action of sodium metal, sodamide, or sodium hydride on a solution of phthalonitrile in butyl alcohol.[2-4] Sander[5] postulated that phthalonitrile and sodium metal react to form the labile addition product I, which then polymerizes with the addition of three phthalonitrile molecules to form the stable tetramer ring system. However, Borodkin[6] was not in agreement with the formulation of the intermediate since the phthalocyanine molecule was not produced in the absence of alcohol. He theorized that, in the example under discussion, it is the sodium butylate that reacts with phthalonitrile, forming an unstable addition product (II), which gives the phthalocyanine derivative either by reaction with other phthalonitrile molecules or through the intermediate isoindolinenine species (III). The course of the reaction in methanol was also studied. When a mixture of sodium metal and phthalonitrile was refluxed in methanol, the metalated phthalocyanine formed. If, however, the temperature was maintained at 40°, then colorless crystals deposited. Isolation and purification of these crystals followed by elemental analyses indicated that the substance was the sodium derivative of methoxyiminoisoindolinenine (IV).[6]



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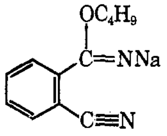

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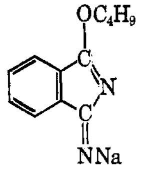

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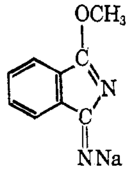

IV

In the work reported here, the stepwise formation of nickel phthalocyanine from nickel(II) chloride and

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[1] A. Braun and J. Tcherniac, *Ber.*, **40**, 2709 (1907).
[2] R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1022 (1934).
[3] I. G. Farbenindustrie A.G., British Patent 468,292 (July 2, 1937).
[4] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1157 (1938).
[5] S. Sander, *Die Chemie*, **55**, 255 (1942).
[6] V. F. Borodkin, *Zh. Prikl. Khim.*, **31**, 813 (1958).

TABLE I

Complex[a]	Yield, %	Analytical data, % Theory C	H	N	Ni	Reported C	H	N	Ni	Molecular weight Theory	Reported	Molar conductivity, mhos cm^{-1} Acetone	Methanol	Magnetic moment, BM
Ni(PrIII)$_2$	50	66.2	4.4	16.3	8.6	66.0	4.9	15.8	8.4	689	695	<0.5	...	~0
Ni(BuIII)$_2$	70	66.9	4.8	15.6	8.2	66.7	4.9	15.4	8.2	717	689	<0.5	...	~0
Ni(*i*-BuIII)$_2\cdot 3H_2O$	30	62.3	5.2	14.5	7.7	62.4	5.2	14.5	8.0	771	...	...	...	...
Ni(AmIII)$_2$	80	67.7	5.1	15.0	7.9	67.6	5.4	15.3	8.0	745	723	<0.5	...	~0
Ni(DII)$_2$Cl$_2\cdot{}^3/_4H_2O$	80	44.4	3.6	19.4	13.6	44.4	4.4	19.4	14.0	434	...	...	61	2.81

[a] Abbreviations are: Ni(PrIII)$_2$ = Bis[1-imino-3-(1′-imino-3′-propoxyisoindoleninone-1′)isoindolinato]nickel(II); Ni(BuIII)$_2$ is the butoxy derivative; Ni(*i*-BuIII), the isobutoxy derivative; Ni(AmIII), the pentoxy derivative.

1,3-diiminoisoindoline, in an appropriate alcoholic solvent, is traced through the various intermediate products. It is found that an alkoxyiminosioindolinenine–nickel complex is one of these intermediates.

Experimental Section

Materials.—1,3-Diiminoisoindoline was synthesized by the method of Elvidge and Linstead.[7] Anhydrous nickel chloride was prepared from the reagent grade hydrate by heating at 150°. All other chemicals employed were standard reagents and used without further purification.

Synthesis. Preparation of Dichloro-1,3-diiminoisoindolinenickel(II)–0.75-Water.—Nickel(II) chloride–6-water (2.37 g, 0.01 mole) was dissolved in 150 ml of anhydrous ethanol. To this was added a solution of 1,3-diiminoisoindoline in 200 ml of anhydrous ethanol. The temperature of the reactants must be held below 30° to prevent further condensation of the organic molecule. The yellow-green product which immediately precipitated out of solution was filtered, washed with ether, and dried *in vacuo* over P_4O_{10}.

Preparation of Bis[1-imino-3-(1′-imino-3-pentoxyisoindoleninone-1′)isoindolinato]nickel(II).—Anhydrous $NiCl_2$ (3.0 g, 0.0225 mole) and 90 ml of amyl alcohol were placed in a 300-ml round-bottom flask equipped with a magnetic stirrer and reflux condenser. The slurry was heated to reflux and to it was added a boiling solution of 1,3-diiminoisoindoline (11.6 g, 0.08 mole) in 110 ml of amyl alcohol. This reaction mixture was refluxed for 12 min and quickly filtered while hot. The product which crystallized as red platelets was filtered, washed with pentane, and air dried.

Other alkoxy derivatives were obtained as red crystalline solids in a similar manner. Analytical results are listed in Table I.

Alternatively, the product was synthesized by refluxing dichloro-1,3-diiminoisoindolinenickel(II) and 1,3-diiminoisoindoline in pentanol. The stoichiometric ratio of reactants was 1:2. The isolation and purification methods were analogous to that described in the previous method.

Conversion of Bis[1-imino-3-(1′-imino-3-pentoxyisoindoleninone-1′)isoindolinato]nickel(II) to Nickel Phthalocyanine.—A small amount of the nickel complex was placed in a glass tube which was then cooled in liquid nitrogen, evacuated, and attached to a vacuum line. The vessel was then heated whereupon the color of the material changed from red to blue. Some colorless liquid formed and was collected in a cold finger. The colorless liquid was chromatographed and identified by mass spectrometry as a mixture of 1-pentanol and 1-pentanal. The blue solid was removed and identified by infrared spectroscopy and elemental analyses as nickel phthalocyanine.

Molecular Weight Determinations.—Molecular weights were obtained with a Microlab osmometer. Benzene was employed as the solvent medium. The results are listed in Table I.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were obtained at 21° by the Gouy method. Nickel(II) chloride–6-water and ferrous ammonium sulfate–6-water were used as standards. Magnetic moment values were calculated by the spin-only formula. Diamagnetic corrections were made for the ligands and anions so that the reported moments (Table I) are attributable solely to the metal ion.

Conductivity Measurements.—Molar conductances (Table I) were obtained by the use of an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 0.500 cm^{-1}. The measurements were made at 25° using 10^{-3} *M* solutions and a bridge frequency of 1000 cps.

Spectra.—The spectra in the visible and near-infrared regions were obtained on a Cary Model 14 recording spectrophotometer. For solution spectra matched cells with fused-quartz windows were used. Solid spectra were obtained using a thick Nujol mull between two quartz plates. A variable screen was used in the reference beam. Results are listed in Table II.

TABLE II

SPECTRAL ABSORPTIONS IN THE 400–1500-mμ REGION

Complex	Absorption, mμ	ε	Assignment
Ni(BuIII)$_2$[a,b]	570	3600	Metal–ligand transition
	540 sh	2500	Metal–ligand transition
	462	7000	Metal–ligand transition
Ni(DII)$_2$Cl$_2$[c]	795	50	d–d transition
	605	430	d–d transition

[a] The spectra in the visible and infrared regions for the other alkoxy derivatives are the same. [b] In benzene. [c] In methanol and verified in Nujol.

Infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics. Potassium bromide pellets were utilized and the results were checked out by employing mulls of Fluorolube and Nujol.

The nmr spectra were obtained on a Varian Associates Model A-60 spectrometer employing deuteriochloroform as the solvent medium. Tetramethylsilane was the standard.

Discussion

If permitted to proceed for a long enough duration, the reaction between nickel chloride and 1,3-diiminoisoindoline (abbreviated DII) in an appropriate alcoholic solvent will yield nickel phthalocyanine. By carefully controlling the reaction conditions, we are able to report on the isolation of several of the intermediate products that are formed on the way to nickel phthalocyanine. The reaction is pictured in Scheme I.

When the reaction between nickel chloride–6-water and DII (I-A) is carried out at room temperature, a green-tan solid of the formula $[Ni(DII)_2Cl_2]\cdot{}^3/_4H_2O$ (I-B) is obtained. Variations in the stoichiometry of the initial reactants does not cause alterations in the final product indicating that there is a preference for the complexation of only two organic molecules. Further, a study of molecular models demonstrated that DII can only complex in a monodentate manner, and, as will be seen later, the coordinating atom is the ring

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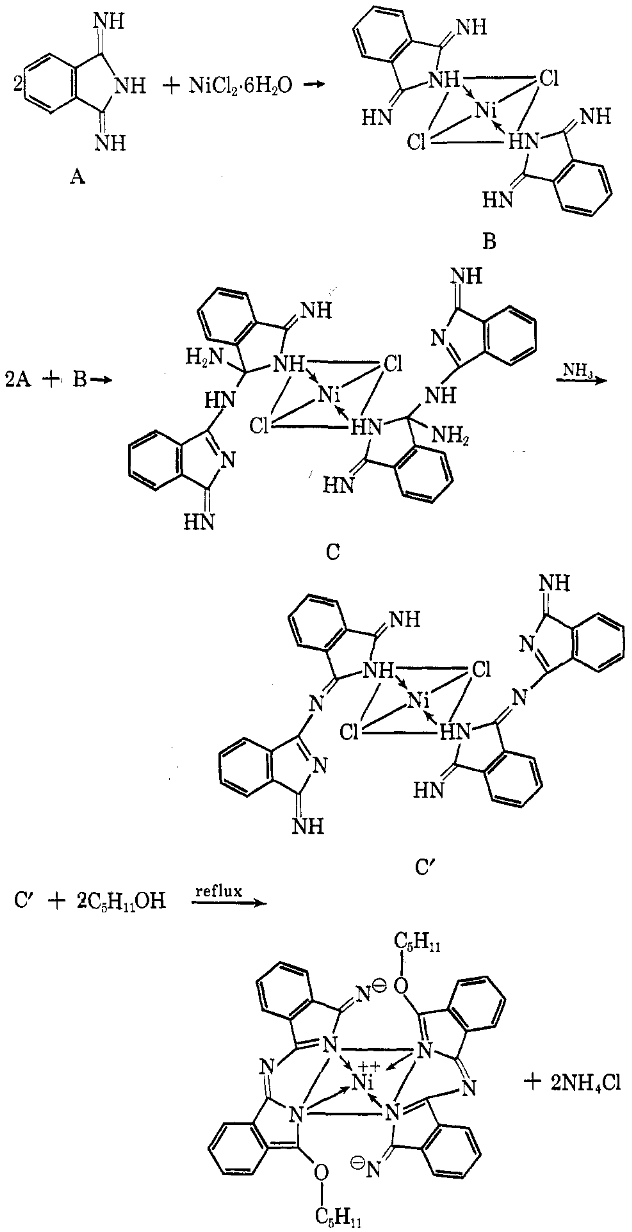
[7] J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5000 (1952).

Scheme I



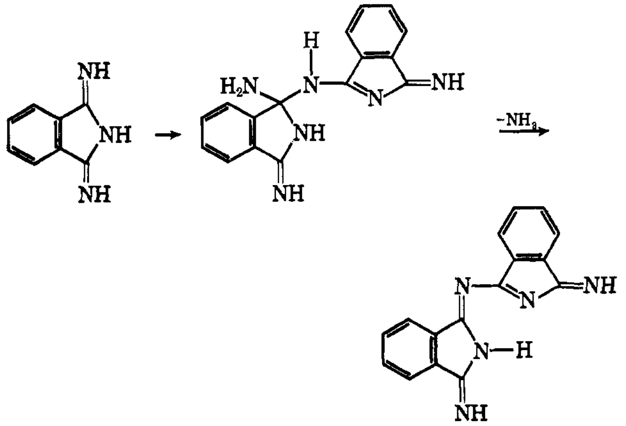
$$\mathrm{D} \xrightarrow{\text{heat}} \text{nickel phthalocyanine} + C_5H_{11}OH + C_4H_9CHO$$

amino nitrogen. Structural elucidation of this compound has not been completed.

In refluxing amyl alcohol, the nickel complex condenses with 2 moles of DII, splitting out ammonia and, presumably, passing through intermediates I-C and I-C′. However, the reaction does not stop here; rather, the solution takes on a deep red color owing to the formation of bis[1-imino-3-(1′-imino-3-pentoxyisoindoleninone-1′)isoindolinato]nickel(II) (structure I-D). Alternatively, this compound can be synthesized directly from nickel chloride and DII in refluxing amyl alcohol.

Analogs containing other alkoxy groups have also been prepared. Only the structural characterization of the pentoxy derivative will be discussed, but the procedures apply equally to the other alkoxy analogs.

Elemental analyses and molecular weight determinations (Table I) established the molecular formula as $Ni(C_{21}H_{19}N_4O)_2$. The nonconductive nature, diamagnetic behavior, and visible spectrum exhibited by this complex indicated that the divalent nickel ion was surrounded by a square-planar array of ligand molecules. At this point, elucidation of the nature of the organic chelating agent was necessary. The empirical formula of the ligand, $C_{21}H_{19}N_4O$, was quite different from that of the starting material, DII, which is $C_8H_7N_3$. Part of this transformation could be explained in terms of the known condensation of DII.[8]



This, however, still did not account for the total change in the ratios. Fortunately, the diamagnetic nature of the complex permitted facile utilization of nuclear magnetic resonance methods. Three important pieces of information were obtained from this study. First, the aromatic:aliphatic proton ratio was 8:11. Second, the aliphatic protons appeared in four groupings, the ratios of which were 3:6:1:1. Finally, there were no exchangeable protons. It was, therefore, concluded that there were two isoindoline rings to one amyl group, the latter being bonded to an oxygen atom. The one apparently anomalous factor was that, for the amyl group, it would be expected that the protons should appear in three groupings with the ratios being 3:6:2 arising from one methyl group, three methylene groups, and a methylene group contiguous to the oxygen atom, respectively. The observed behavior was resolved by a proton decoupling experiment where it was demonstrated that the two methylene protons on the carbon contiguous to the oxygen atom, though chemically equivalent, were magnetically inequivalent. Further, the lack of replaceable hydrogens indicated that the imine protons, present in the original molecules, had been lost during the condensation reaction. This was corroborated by infrared spectroscopy in which it was shown that the NH stretch was absent. It is assumed that one of the imine groups was replaced by the alkoxy moiety and the other proton removed in conjunction with the chloride ion, resulting formally in a negative charge on the terminal nitrogen. The other coordination site is satisfied by

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[8] J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5008 (1952).

the formation of a dative bond between the isoindoline ring nitrogen and the nickel ion. This results in a relatively strain-free six-membered isoindolenine ring in which the terminal imino nitrogen comes into close proximity to the ring carbon atom of the other coordinating ligand, to which the alkoxy group is bonded. Consequently, ring closure should be effected in a facile manner. This is found to be the case. Heating Ni($C_{21}H_{19}N_4O$)$_2$ (I-D) results in the splitting off of the alkoxy groups and the rearrangement of bonds involving ring closure resulting in the formation of nickel phthalocyanine. The other products, identified by mass spectrometry, are 1-pentanol and 1-pentanal.

Acknowledgment.—We wish to thank Mr. D. Vickers for ably assisting us in obtaining and interpreting the nuclear magnetic resonance spectra. In addition, we acknowledge the microanalytical group at Olin Mathieson for the expert handling of the samples reported herein.

Notes

CONTRIBUTION FROM THE OLIN MATHIESON
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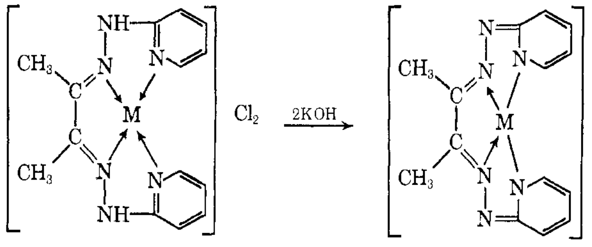
Complexes Derived from 1,3-Diiminoisoindoline-Containing Ligands. I. Deprotonation of 1,3-Bis(2-Pyridylimino)isoindoline Complexes

BY MARTIN A. ROBINSON, SAMUEL I. TROTZ,
AND THOMAS J. HURLEY

Received August 30, 1966

In 1958, Lions and Martin[1] first reported on the phenomenon of deprotonation of cationic complexes. In this unique and isolated incident, a diamagnetic complex was isolated from the reaction between cobalt(II) bromide and 2-pyridinal (2-pyridyl)hydrazone. The spin multiciplicity of the complex arose as a result of the oxidation of the cobalt(II) ion to the trivalent state accompanied by the reduction of one of the ligand molecules through the loss of a proton. Other experimenters[2-4] have shown that the deprotonation process is quite general and need not necessarily be associated with an oxidation–reduction reaction. In most cases, deprotonation can be brought about by treatment of the cationic complex with alkali, resulting in the formation of the neutral species with no alteration in the number of coordinating sites on the ligand molecule due to deprotonation. For example, the nickel chloride complex of butane-2,3-dione bis(2′-pyridylhydrazone) (I) is doubly deprotonated by the action of potassium hydroxide to yield the neutral complex (II).[5] There are some instances, however, where the number of coordinating positions have been altered by deprotonation.[2] Thus, in neutral solutions benzilmono(2-pyridyl)hydrazone acts as a tridentate chelating agent (III), whereas, in acid solution where the deprotonation can be prevented, the molecule appears then to function only as a bidentate ligand (IV).



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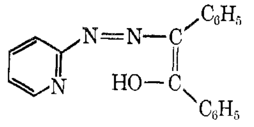

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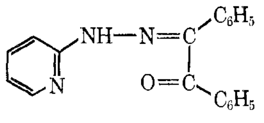

IV

In the work reported herein, deprotonation, in addition to being induced in the usual manner, can also be facilitated by altering the anionic component of the transition metal salt.

Experimental Section

Syntheses. 1,3-Bis(2-pyridylimino)isoindoline.—A solution of 2-aminopyridine (37.6 g, 0.4 mole) in hot butanol was added quickly to a butanol solution of 1,3-diiminoisoindoline (29.0 g, 0.2 mole). The solution was held at reflux for 4 hr and then cooled to room temperature. A yellow solid formed. It was filtered, washed with ether, recrystallized from methanol, and dried under vacuum at 60° for 8 hr; mp 189–192°. *Anal.* Calcd for $C_{18}H_{13}N_5$: C, 72.2; H, 4.4; N, 23.4. Found: C, 72.3; H, 4.4; N, 23.5.

Metal Perchlorate Complexes of 1,3-Bis(2-pyridylimino)isoindoline.—These complexes were synthesized by allowing a methanol solution of the metal perchlorate to react with a methanol solution of the ligand in a 1:2 stoichiometric ratio. The complexes formed immediately and were filtered, washed with methanol and ether, and dried under vacuum at 60°.

Preparation of Complexes from the Metal Chloride Salts.—These complexes were prepared from methanol in a manner analogous to that previously described for the perchlorate complexes but were recrystallized from nitrobenzene.

Preparation of Complexes from the Metal Acetate Salts.—These complexes were isolated out of methanol and recrystallized from nitrobenzene. Alternatively, formamide may be employed as the solvent. If the ratio of reactants is 1:1, a large amount of the bis complex still precipitates out, but evaporation of the solvent results in the isolation of a complex whose stoichiometry

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[1] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3855 (1958).
[2] J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962).
[3] J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).
[4] B. Chiswell and F. Lions, *ibid.*, **3**, 490 (1964).
[5] B. Chiswell, F. Lions, and M. L. Tomlinson, *ibid.*, **3**, 492 (1964).