## **213.** *Phthalocyanines. Part II. The Preparation of Phthalocyanine and some Metallic Derivatives from* o-*Cyanobenzamide and Phthalimide.*

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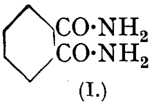
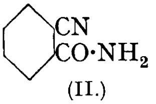
The results reported in Part I (preceding paper) suggested the possibility of preparing the iron pigment and similar substances by the action of metals on the dehydration products of phthalamide (I), namely, *o*-cyanobenzamide (II) and phthalonitrile (III).

After a few comparative experiments, attention was concentrated on the cyanoamide. The dinitrile appeared to be less reactive, a fact attributed at the time to the absence of a pseudo-acidic hydrogen atom available for the fixation of the metal. Subsequent work (Part III) showed this decision to have been premature.


(I.)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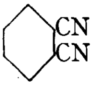
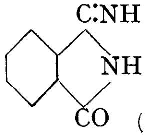

(III.)


(IV.)

*o*-Cyanobenzamide reacted readily with many metals (p. 1021) at about 250° to yield strongly coloured substances of the same type as the original iron pigment. The real precursor of these complex compounds is iminophthalimidine (IV), a derivative of *iso*indole, which is readily formed by isomerisation of *o*-cyanobenzamide above its melting point (Braun and Tcherniac, *Ber.*, 1907, **40**, 2709; compare Posner, *Ber.*, 1897, **30**, 1693). The metals used in the preparation could often be replaced by their oxides, sulphides, or carbonates without affecting the nature of the product. The most promising results were obtained by the use of magnesium (metal or oxide), iron (metal, oxide, or sulphide), cobalt, nickel, and antimony. The reactions were exothermic and yielded phthalocyanines of the same general type, together with phthalimide and ammonia as by-products. The phthalocyanines resembled one another in their blue colour, insolubility, and stability, but differed in their reaction with concentrated sulphuric acid.

The reaction between cyanobenzamide and magnesium (or its oxide) produced some 40% of a bright blue compound which after purification yielded a macrocrystalline *magnesium phthalocyanine*, $C_{32}H_{20}O_2N_8Mg$ or $(C_8H_4N_2)_4Mg,2H_2O$. A number of associated magnesium compounds have since been isolated (Part III), but this is the most stable form and has been repeatedly prepared by a number of different methods. The results of analysis leave no doubt as to the presence of oxygen in the molecule (p. 1023).

Magnesium phthalocyanine bore a general resemblance to the original iron compound, but differed in its stability to acids. When its solution in cold concentrated sulphuric acid was poured on ice, a blue solid was obtained which contained no metal. The eliminated magnesium could be isolated nearly quantitatively from the solution. When special precautions were taken (p. 1020), this substance separated from boiling quinoline in a crystalline condition. The crystals differed in form and translucency from those of the magnesium compound. The metal was also eliminated by the action of concentrated hydrochloric acid at 90°, but more slowly, presumably owing to the insolubility of the magnesium compound in this acid.

The product of both these reactions is *phthalocyanine*, the parent substance of the group, which has since been obtained by a number of other methods. It possesses the peculiar stability and insolubility of the metallic derivatives. It has a greenish-blue colour and a beautiful purple reflex. The solution in sulphuric acid decomposes very slowly in the cold, rapidly on being heated. Nitric acid converts it into phthalimide and ammonium nitrate, and under controlled conditions approximately half the total nitrogen is eliminated as ammonium salt in this manner. Distillation with soda-lime yields benzonitrile and ammonia. There is thus a close resemblance with the original iron pigment.

Free phthalocyanine can be reconverted into the magnesium compound by treatment with the pure metal in boiling quinoline or benzophenone. The product is indistinguishable from that obtained directly from cyanobenzamide.

Analysis indicates that phthalocyanine has the formula $C_{32}H_{18}N_8$ or $(C_8H_4N_2)_4H_2$. There is no analytical deficiency corresponding to the presence of oxygen. Its structure and that of the magnesium compound are discussed in Part VI. Their preparation and interconversion may be expressed empirically as follows:

$$\begin{aligned}
&\text{(i)}\ \ 4C_8H_6ON_2 + Mg = (C_8H_4N_2)_4Mg + 4H_2O \\
&\text{(ii)}\ \ (C_8H_4N_2)_4Mg + H_2SO_4 = (C_8H_4N_2)_4H_2 + MgSO_4 \\
&\text{(iii)}\ \ (C_8H_4N_2)_4H_2 + Mg = (C_8H_4N_2)_4Mg + H_2
\end{aligned}$$

[The water which is present in the molecule of the magnesium compound (see p. 1023) is neglected in these equations for the sake of simplicity.]

The reaction between elementary antimony and *o*-cyanobenzamide is exceptional in that the coloured substance initially produced contains only a trace of metal. After crystallisation from quinoline, pure phthalocyanine is obtained, free from antimony.

Iron, nickel, and cobalt, on the other hand, yield stable metallic phthalocyanines. The products contain combined metal which resists the action of cold concentrated sulphuric acid, the metallic complexes being reprecipitated on dilution of their solutions in the acid. The iron compound has not yet been obtained in a state of known homogeneity; when freed as far as possible from organic impurities and casual metal, it bears a close resemblance to the iron pigment of Part I and gives similar analytical figures (Found: C, 62·6; H, 3·0; N, 18·5; Fe, 11·1%).

*Preparation from Phthalimide.*—The reaction between phthalimide, ammonia, and metals was next investigated in the light of the experience gained with *o*-cyanobenzamide. Here again magnesium was found to be the most convenient metal for the production of a substance of the desired type; only the metal itself, however, and not the oxide, was effective. The new process required a much more careful control of temperature than that utilising cyanobenzamide and gave only some 20% of magnesium phthalocyanine under the optimum conditions. The product was identical in every way with that obtained from the cyanoamide and yielded the same free phthalocyanine on treatment with sulphuric acid.

## EXPERIMENTAL.

Phthalamide (Aschan, *Ber.*, 1886, **19**, 1399) was conveniently made in quantity by stirring phthalimide (2 kg.) for 24 hours with 6 l. of ammonia (*d* 0·880). The microcrystalline cake of the diamide was filtered off and dried at 100° [yield, 2 kg.; m. p. 220° (decomp.)] (Found: N, 17·1. Calc.: N, 17·1%).

Following the method of Braun and Tcherniac (*loc. cit.*), a mixture of phthalamide (164 g.) and acetic anhydride (590 g.; nearly 6 mols.) was heated as rapidly as possible to the boiling point and boiled till clear (1 hour). The almost pure cyanobenzamide which separated on cooling was washed with cold alcohol and dried at 100° (yield, 38%); m. p. 172°. The following process is less wasteful and gives a better yield, but the product is slightly contaminated with phthalimide. The diamide (1 mol.) was boiled with a mixture of acetic acid (3 mols.) and anhydride (2 mols.) until clear (1 hour); the cooled solution deposited a 65% yield of crude cyanobenzamide, m. p. 168—171°. Higher proportions of acid, a smaller bulk of total liquid, and slower reaction all led to increased production of phthalimide.

*Magnesium Phthalocyanine.*—The reaction of *o*-cyanobenzamide with magnesium oxide is convenient for the preparation in quantity and over 300 g. of the magnesium compound have been prepared by its use. Naphthalene was the best of the diluents tried. There is little reaction below 230° and most of the preparations were carried out at 240—250°, but considerably higher temperatures have no obviously bad effects. The naphthalene slowly volatilises, but it is not advisable to allow it to escape completely, as the cooled mass is then very hard. In a typical experiment, 40 g. of crude *o*-cyanobenzamide (prepared by the acetic acid–anhydride method and containing some phthalimide), 15 g. of naphthalene, and 10 g. of magnesium oxide were heated for 2 hours at 230—240° in an enamelled iron pot fitted with a short air reflux and heated by an oil-bath. The hard residue was powdered and extracted in a Soxhlet apparatus with hot acetone until free from naphthalene, phthalimide, and a small amount of a soluble green impurity. It was then freed from excess of magnesia with dilute acid, washed with water, and dried. Yield, 18 g. of a blue solid.

10 G. of pure *o*-cyanobenzamide were heated for 15 minutes at 230—240° with 2 g. of magnesium metal (pure turnings such as are used in the Grignard reaction were found most reactive). The melt was powdered, extracted successively with dilute caustic soda solution, 10% sulphuric acid (over-night), and hot water. After prolonged extraction with boiling alcohol, 4 g. of a bright blue solid remained. Magnesium carbonate gave results very similar to those obtained with the oxide.

The compound dissolves in boiling quinoline (3·7 parts in 100) to yield a deep greenish-blue solution, which on cooling deposits blue needles with a purple lustre. The substance can also be crystallised from boiling pyridine and is slightly soluble (0·4%) in boiling naphthalene. (A conical aluminium funnel fitted with a specially turned detachable perforated disc of the same metal was used for the filtration of boiling quinoline solutions, which tended to crack porcelain funnels. Ordinary dull aluminium has the advantage for this purpose that it does not appear to react with phthalocyanine.)

Twice crystallised *magnesium phthalocyanine* contained C, 67·7; H, 3·7; N, 19·5; Mg, 4·3 ($C_{32}H_{20}O_2N_8Mg$ requires C, 67·1; H, 3·5; N, 19·6; Mg, 4·2%). The carbon and hydrogen figures were unaltered when the sample was mixed with potassium dichromate in the combustion boat. The analysis for magnesium was carried out by very slow ashing, sublimation (green vapour) being avoided as far as possible. The ash was pure magnesium oxide: two samples, corresponding to Mg 4·27 and 4·19%, were dissolved in hydrochloric acid, and the magnesium was twice precipitated as magnesium ammonium phosphate and weighed as pyrophosphate in the usual way (Found: Mg, 4·19, 4·19%).

The magnesium compound (1 g.) was boiled with 32 c.c. of 30% nitric acid for 2 minutes. From the clear brown solution obtained, continuous extraction with ether (24 hours) removed 0·35 g. of phthalimide slightly contaminated with phthalic acid. Other reactions of the magnesium compound are described in Part III.

*Phthalocyanine.*—(i) *From the magnesium compound.* The following method was adopted after many trials. The magnesium compound, carefully freed from traces of metal or oxide, was slowly sifted in very small quantities into 10 times its weight of 96% sulphuric acid, stirred mechanically and kept at about − 3°. The solution was filtered through a coarse sintered-glass funnel, which was washed with more acid. The liquid was then slowly run on ice made from distilled water. The blue precipitate was collected, washed free from acid, and dried. In one series of experiments 25 g. of *phthalocyanine* were thus obtained from 42 g. of the magnesium derivative. Phthalimide could be isolated from the mother-liquors: fission to this compound is presumably caused by the local evolution of heat on liberation of the metal, for free phthalocyanine can be precipitated from its solution in sulphuric acid with little or no loss. If ordinary crushed ice is used for the precipitation, the phthalocyanine leaves an appreciable ash containing iron.

The precipitated material, without crystallisation, contained C, 73·5; H, 3·2; N, 21·1%. Another sample which had been precipitated a second time contained C, 73·6; H, 3·6; N, 21·6%. After crystallisation from pure quinoline the material was obtained as lustrous needles (Found: C, 74·8; H, 3·6; N, 21·5; deficiency, 0·1. $C_{32}H_{18}N_8$ requires C, 74·7; H, 3·5; N, 21·8%).

1·7 G. of the magnesium compound were heated on the steam-bath for 2 days with 100 c.c. of 10% hydrochloric acid. The blue solid was removed (1·45 g.), and ether extracted 0·2 g. of phthalic acid from the filtrate. The solid after crystallisation from quinoline left no ash on ignition (Found: C, 74·0; H, 3·7%).

(ii) *From* o-*cyanobenzamide and antimony.* 40 G. of cyanobenzamide, 10 g. of powdered metallic antimony, and 20 g. of naphthalene were heated at 260° for 1 hour. The powdered product was extracted successively with boiling acetone, caustic soda solution, and hot water, until free from naphthalene and phthalimide. Yield, 11 g. of a lustrous purple powder. The bulk of the antimony was removed by repeated flotations in ethyl iodide, in which it sank. On ignition the pigment left 1% of ash. (The ashing of products prepared by the use of antimony was carried out after the material had been moistened with concentrated sulphuric acid.) The product dissolved in quinoline much less readily than did the magnesium compound and the solution was slightly greener in shade. A boiling saturated solution was filtered and allowed to cool very slowly during 48 hours in a Dewar flask, placed in an insulated furnace previously heated to about 230°. Beautiful long needles with a purple lustre were deposited, giving an ash of 0·4%. These were decomposed with warm nitric acid, the solution evaporated to dryness, and the residue dissolved in hydrochloric acid. No antimony sulphide was precipitated from this solution by hydrogen sulphide. Further extractions of the residue with boiling quinoline yielded smaller crystals with a higher ash content (over 1%). The material of low ash content contained C, 73·4; H, 3·6; N, 21·7%. The results suggest that a small amount of an antimony compound is present in the crude product. In subsequent preparations of phthalocyanine by this method the product was freed from naphthalene in the usual manner, and the pigment was then extracted from the excess of antimony with boiling quinoline in a specially constructed Soxhlet extractor of Pyrex glass fitted with an air reflux condenser, all connections being ground in. The extracted material was fractionally crystallised from quinoline. The purest material obtained contained C, 74·3;* H, 3·7;* N, 20·9%.* The nitrogen analyses given above were determined by the Dumas method. It was subsequently found that accurate results could be obtained by both the

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* Asterisked analyses throughout these papers were made by Dr-Ing. A. Schoeller of Berlin.

macro- and the micro-Kjeldahl method: the sample of phthalocyanine just referred to gave N, 21·6, 21·6% ($C_{32}H_{18}N_8$ requires C, 74·7; H, 3·5; N, 21·8%).

The phthalocyanine obtained by both these processes is a bright, rather greenish-blue solid, with a strong purple lustre. Under the microscope the crystals appear as slender translucent needles, often fragmented, whereas the prismatic needles of the magnesium compound appear opaque. Phthalocyanine does not melt, but at 550° under reduced pressure * it sublimes without decomposition as a bluish-green vapour yielding lustrous needles.

Apart from quinoline and its derivatives, the only organic substances which have been found to dissolve phthalocyanine appreciably at the boiling point are benzophenone, naphthalene, and alicyclic alcohols such as *cyclo*hexanol and menthol, which yield blue solutions containing very little of the pigment; and aniline and its homologues, which give green solutions, presumably with compound formation. No crystallisation has been observed from these solutions.

*Reactions.* Phthalocyanine was completely converted into its magnesium derivative by the following process: 3·8 g. of the substance (prepared by the antimony method) and 0·15 g. of magnesium turnings were heated in boiling benzophenone at 307° for 2 hours. The purified and recrystallised product contained Mg, 3·5%. After a further day's boiling with more magnesium, and recrystallisation, the beautifully crystalline product contained C, 67·8; H, 3·6; Mg, 4·5%. A similar result was obtained starting with phthalocyanine prepared from the magnesium compound.

From 3·45 g. of phthalocyanine, after treatment with concentrated sulphuric acid by the method used in the preparation, 3·3 g. of unchanged material were recovered. After such a solution had been heated, no colour was produced on dilution.

Phthalocyanine (2 g.) was boiled with 20% nitric acid (30 c.c.) for about 15 minutes. The hot solution was filtered and, on cooling, deposited phthalimide, m. p. 232°, after recrystallisation from hot water (0·5 g.). The mother-liquor, on evaporation, yielded phthalic acid, identified as the anhydride. From the nitric acid solution, made alkaline, ammonia was immediately liberated. A weighed amount of phthalocyanine was boiled with the minimum amount of nitric acid necessary for decomposition, boiling being stopped as soon as a clear solution was obtained. The liquid was then extracted constantly with ether for 50 hours, the aqueous layer made alkaline, and the liberated ammonia estimated by the Kjeldahl method (Found: N, 8·0, 10·7, 8·5, 8·7. Calc. for half of the total nitrogen present: N, 10·9%). A blank experiment with phthalimide gave no ammonia under the same conditions.

The resistance of phthalocyanine to alkali is remarkable. 4·2 G. of the pure compound were heated with soda–lime until the containing glass softened. A small amount of benzonitrile (identified by hydrolysis to benzoic acid) distilled over and ammonia was freely evolved. The residue, after being washed with ether, boiling dilute acid, and water, was bright blue, apparently unchanged, material (1·8 g.) containing only a trace of inorganic matter.

*Reaction of Other Metals with Cyanobenzamide.*—The reaction with iron (metal, ferric oxide, or ferrous sulphide) was most conveniently carried out exactly as with magnesium at 240°. When the metal was used, the yield of lustrous purple pigment was 40—45%. This product has already been described (p. 1019). Very similar substances were obtained by the use of nickel and its oxide (NiO) or of cobalt oxide ($Co_3O_4$), and positive indications were given by the following reagents: chromium, bismuth oxide, manganese carbonate, cerium, manganese, tin, aluminium, stannous oxide, copper, cupric oxide, molybdenum, tungsten, calcium oxide, and antimony oxide. No definite evidence of the formation of a compound of the phthalocyanine type was obtained when the following substances were heated with *o*-cyanobenzamide: aluminium oxide, titanium oxide, manganese dioxide, cadmium oxide, mercury and alkali metals or their derivatives.

*Reaction of Phthalimide and Magnesium.*—Colour was produced when liquid phthalimide and magnesium were heated in a stream of ammonia at 250—280°, but not when phthalimide was sublimed over the metal in a stream of ammonia at 250°. Magnesium oxide gave no reaction, presumably because its basicity prevented the fixation of ammonia.

500 G. of phthalimide and 20 g. of magnesium were melted in a wide glass tube heated by an oil-bath. The internal temperature was kept at 240—250° and a vigorous stream of dry ammonia passed, the molten mass being stirred mechanically. A considerable quantity of phthalimide sublimed. After 8 hours' heating, the viscous melt was cooled, broken up, and treated with a large bulk of 5% caustic soda solution, the vessel being steamed out to remove the last traces of pigment. The product was treated with hydrochloric acid to remove the excess of metal,

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* This temperature was measured by Mr. C. E. Dent in the course of attempted vapour-density determinations.

and extracted with boiling acetone in a Soxhlet apparatus, a small amount of a bright green substance being removed and 80 g. of a blue powder remaining. On continuous extraction of the latter with boiling quinoline the pigment was dissolved, leaving rather less than 20% of a chocolate-brown impurity.

Pure magnesium phthalocyanine was isolated in the usual way by careful crystallisation of the quinoline-soluble material. A sample which had been crystallised four times contained C, 67·6; H, 3·6; N, 19·4%. 2 G. of this, after treatment with sulphuric acid with the usual precautions, yielded 1·4 g. of phthalocyanine with an ash content of 0·2% (Found : C, 73·3; H, 3·6; N, micro-Kjeldahl, 21·1%). These substances had the general properties of those already mentioned.

The chocolate-brown impurity contained magnesium and was formed in greater amount at temperatures above 250°, particularly with a deficiency of ammonia. In one preparation a violent exothermic reaction occurred between phthalimide and magnesium before ammonia had been admitted into the melt and a large amount of this material was formed. It dissolved in concentrated sulphuric acid with an intense crimson colour, and on dilution the original material was precipitated. The use of high-boiling diluents such as mineral oil, naphthalene, and ethyl phthalate in the phthalimide reaction led to exclusive formation of this substance.

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[*Received, May* 22*nd*, 1934.]