213. *Phthalocyanines and Associated Compounds. Part XIV. Further Investigations of Metallic Derivatives.*

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In a continuation of the general investigation of phthalocyanine as a co-ordinating group the following new metallic derivatives are now described (Pc = $C_{32}H_{16}N_8$) : *Dilithium* ($PcLi_2$), *lithium hydrogen* (PcHLi), *silver* (PcAg or ? PcHAg), *mercuric*, (PcHg), *diantimony* ($PcSb_2$), *chloroantimony* (PcSbCl), *chloroferric* (PcFeCl) *phthalocyanines* and *palladium chlorophthalocyanine* ($C_{32}H_{15}N_8ClPd$).

The reactions and structures of these substances are discussed. The dilithium compound is soluble in cold alcohol and acetone, and can be used for the preparation of other metallic phthalocyanines by double decompositions at room temperature.

The additive compounds of ferrous phthalocyanine with bases (reminiscent of those of hæmin) have been investigated. A *hexa-aniline* and *hexa-*o*-toluidine* compound and a *dipyridine* compound have been isolated.

The work described in this paper falls into two parts. (1) A number of new metallic phthalocyanines, mainly of a reactive kind, are now described. (2) The iron phthalocyanines and their additive compounds, which are related to hæmin and the hæmochromogens, have been further examined.

(1) The metallic phthalocyanines now described are the derivatives of lithium, silver, mercury, antimony, and palladium. The most interesting of these is the lithium compound, which is easily prepared by the action of lithium amyloxide on phthalonitrile, a method analogous to that used for the preparation of disodium phthalocyanine (Barrett, Dent, and Linstead, J., 1936, 1719; compare Linstead and Lowe, J., 1934, 1022). When an excess (over 2 mols.) of lithium amyloxide is used, the product is *dilithium phthalocyanine*, $PcLi_2$ (Pc represents the bivalent phthalocyanine group, $C_{32}H_{16}N_8$). When the nitrile is used in considerable excess, the product is *lithium hydrogen phthalocyanine*, PcHLi. Both these compounds are readily obtained crystalline and are easily distinguished, the dilithium compound being of the normal phthalocyanine type, blue with a purple reflex, and the lithium hydrogen compound nearly black with a silver reflex. They are both converted into phthalocyanine by sulphuric acid, and the metal is completely eliminated from the dilithium compound by the action of aqueous alcohol. The lithium hydrogen compound yields the dilithium compound on treatment with lithium amyloxide. Attempted crystallisation of the dilithium compound from chloronaphthalene results in its conversion into the lithium hydrogen derivative, possibly owing to the presence of traces of water or similar reagent in the solvent.

Dilithium phthalocyanine is remarkably soluble in organic solvents in the cold, for example, in absolute alcohol, amyl alcohol, and acetone. The solubility is greater than any yet encountered in the group, although several metallic phthalocyanines are soluble in bases, and a few other abnormalities have been noticed (*e.g.*, the solubility of α-magnesium naphthalocyanine in ether, and that of chloroaluminium chlorophthalocyanine in alcohol). In this high solubility, lithium phthalocyanine falls into line with many other organo-lithium compounds.

The combination of solubility in alcohol with lability of the central metal makes dilithium phthalocyanine a most useful reagent, and it has become possible for the first time to prepare metallic phthalocyanines by double decomposition at room temperature. Thus when alcoholic solutions of anhydrous cupric chloride and dilithium phthalocyanine are mixed, copper phthalocyanine is immediately precipitated; the phthalocyanine derivatives of calcium, zinc, lead, manganese, and cobalt have been prepared similarly. The reaction is, however, not general, for stannous chloride converts dilithium phthalocyanine into free phthalocyanine and not its tin derivative, doubtless owing to alcoholysis of the stannous chloride. Thorium and bismuth chlorides and tungsten oxychloride bring about the same result, but here there is no evidence that the corresponding metallic phthalocyanines are capable of existence.

In the case of palladous chloride the two reactions proceed simultaneously with the formation of a mixture of free phthalocyanine and a palladium derivative. Of particular interest are the reactions of dilithium phthalocyanine with silver nitrate and mercuric chloride in alcohol, which give *silver* and *mercury phthalocyanines* respectively.

Dilithium phthalocyanine also reacts readily with organic halogen compounds with elimination of the metal. The product in all cases is metal-free phthalocyanine, there being no fixation of either alkyl or acyl groups. The reaction with methyl iodide does not proceed in the absence of alcohol and in its presence follows the course:

$$\mathrm{PcLi_2 + 2MeI + 2EtOH \longrightarrow PcH_2 + 2LiI + [2MeOEt]}$$

and not the alternative:

$$\mathrm{PcLi_2 + 2MeI \longrightarrow PcMe_2 + 2LiI}$$

Very similar results had already been obtained from parallel experiments on disodium phthalocyanine (Barrett, Dent, and Linstead, *loc. cit.*), but the present results are more convincing, owing to the solubility of the substance under investigation.

As has been pointed out in previous papers, a bivalent tetraco-ordinate metal in its phthalocyanine derivative is regarded as equally attached to each of the four *iso*indole nitrogen atoms, the central ring being a resonating system. Similarly the acidic hydrogen atoms of free phthalocyanine are regarded not as combined solely with any one of these nitrogen atoms but rather as equally shared between two (see Robertson, J., 1936, 1195). (An equivalent arrangement is presumably present in the true salts of phthalocyanine, in which the metals are held by electrovalencies, although representation is more difficult.) The important point for the present purpose is that any atom or group covalently attached to one of these nitrogen atoms will be chelated with at least one of the other three. Otherwise resonance of the great ring is no longer possible and the peculiar aromatic-like stability disappears. Alkyl groups are not capable of co-ordination in this way. Hence it is to be expected that *N*-alkyl phthalocyanines and similar compounds, if capable of existence at all, will have much lower stabilities than those of free phthalocyanine and its normal metallic derivatives. Another factor tending to prevent such substitution will be the small amount of space available for the substituents, but it seems unlikely that this would be decisive because of the possibilities of adjustment latent in the molecule. We regard the resistance to alkylation as valuable chemical evidence of the resonance of the great ring.

Of the other new metallic phthalocyanines, the mercury derivative (PcHg) was a normal electrovalent compound. It resembled cadmium phthalocyanine (Barrett, Dent, and Linstead, *loc. cit.*), being insoluble in organic solvents and easily decomposed to free phthalocyanine by acid. Elimination of mercury is actually more easy than that of cadmium, being achieved by boiling with chloronaphthalene.

Silver phthalocyanine was prepared by double decomposition of silver nitrate and dilithium phthalocyanine in alcohol, or of silver sulphate and lead phthalocyanine in boiling chloronaphthalene. Analysis of the beautifully crystalline product corresponded with the monosilver phthalocyanine structure (PcAg), but the possibility that it is a silver hydrogen compound, PcAgH, cannot be excluded. In the second of these the silver would be in the usual argentous condition; the former would be an interesting addition to the rare class of compounds in which silver is bivalent. We endeavoured to settle the point by quantitative oxidation with ceric sulphate (cf. Dent, Linstead, and Lowe, J., 1934, 1033), but the oxygen uptake was much too high for either formulation, indicating some catalytic decomposition of the oxidising agent. The question must therefore be left open. Silver phthalocyanine is soluble in chloronaphthalene, but tends to decompose in the boiling solvent with the formation of phthalocyanine and metallic silver. The metal is readily removed by concentrated sulphuric acid. The compound may be sublimed under reduced pressure with partial decomposition. The indications are therefore that the metal is in covalent union.

It was found by Byrne, Linstead, and Lowe (J., 1934, 1017) that *o*-cyanobenzamide gave with antimony a substance which yielded free phthalocyanine on crystallisation from quinoline; and a reaction between antimony and phthalonitrile has also been observed.

The latter reaction has now been further examined and from the product we have isolated *diantimony phthalocyanine* ($PcSb_2$) practically pure. This compound is much less stable than most members of the group. It yields free phthalocyanine on treatment with sulphuric acid, or on being heated with high-boiling solvents. When boiled with alcoholic potash, it yields a little free phthalocyanine and there is much fission to phthalic acid. It is decomposed by heat.

It is difficult to reconcile the formula $PcSb_2$ with ordinary valency requirements, and it is impossible to find room in the centre of the phthalocyanine ring for two antimony atoms (effective radii 1·45 A.) or ions. The compound may have a complex structure such as $Pc\colon Sb\cdot Sb\colon Sb\cdot Sb\colon Pc$. In this the two terminal antimony atoms are located in the centre of phthalocyanine rings and are joined by a chain of two antimony atoms in the manner shown.

An antimony phthalocyanine of more conventional type is obtained by the action of antimony trichloride on free phthalocyanine in boiling chloronaphthalene. This material is *chloroantimony phthalocyanine*, PcSbCl, resembling the chloroaluminium compound, PcAlCl (Barrett, Dent, and Linstead, *loc. cit.*). It can be sublimed and crystallised from chloronaphthalene without decomposition, which shows the compound to be covalent. The action of boiling quinoline or cold sulphuric acid produces free phthalocyanine, which proves that the chlorine atom is attached to the antimony and not substituted in a benzene nucleus.

Phthalonitrile reacts with palladium chloride to yield *palladium chlorophthalocyanine* $(C_{32}H_{15}N_8Cl)Pd$. Hydrogen chloride is eliminated owing to the substitution in one benzene ring. In so far as the lower chloride reacts with phthalonitrile, palladium resembles platinum; but in the fact that nuclear substitution occurs, the reaction resembles that between the nitrile and cupric chloride (Dent and Linstead, J., 1934, 1027).

(2) *Iron Phthalocyanines.*—Barrett, Dent, and Linstead (*loc. cit.*) isolated ferrous phthalocyanine (PcFe), but could not obtain *chloroferric phthalocyanine* (PcFeCl) in a state of purity. This has now been achieved by warming the ferrous compound with concentrated hydrochloric acid in a vessel open to the air. The green chloroferric compound is easily turned blue by successive treatment with sulphuric acid and alkali, including ammonia, and the halogen is completely eliminated, but we have not been able to isolate hydroxyferric phthalocyanine (PcFeOH) in a state of purity.

It has been shown that ferrous phthalocyanine is extremely soluble in aniline to give a green solution depositing macrocrystals of an *additive compound* (Linstead, J., 1934, 1016). Further investigation of this shows it to contain six molecules of aniline ($PcFe,6C_6H_7N$). These are eliminated quantitatively by the action of either heat or warm hydrochloric acid. The former regenerates ferrous phthalocyanine, the latter yields the chloroferric compound. *o*-Toluidine gives a similar crystalline *compound*, containing six molecules of base, but the corresponding *pyridine addition compound* contains only two molecules of pyridine.* The pyridine compound is considerably more stable than those containing the aromatic bases. The tendency of ferrous phthalocyanine to combine with aromatic bases appears to be general (for example, it readily yields a green solution with ethereal β-naphthylamine), but no other solid additive compounds could be isolated.

EXPERIMENTAL.

(The general methods of purification and analysis were those described in J., 1936, 1719.)

Lithium Phthalocyanines.—60 G. of phthalonitrile were added to a solution of lithium (4 g.) in amyl alcohol (300 c.c.). A green colour appeared, and when the mixture was warmed, a vigorous exothermic reaction took place, the colour changing to deep blue and some lithium phthalocyanine separating. The mixture was boiled for 30 minutes, cooled, diluted to 1 l. with benzene, and kept for 3 hours. After filtration, the residue of dull blue lithium phthalocyanine (36 g.) was extracted (Soxhlet) with acetone, previously dried over sodium sulphate. Basic lithium compounds were left in the extractor. Evaporation under reduced

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* The stability of the pyridine addition compounds of the phthalocyanines of the iron group increases in the order: [nickel]<cobalt<iron. Nickel phthalocyanine does not appear to form an isolable compound. The cobalt compound (compare J., 1936, 1730) contains one mol. of pyridine.

pressure left *dilithium phthalocyanine* as a crystalline deposit with a purple lustre (yield, 30 g.; 50%). For analysis a sample was heated at 300° for 3 hours under reduced pressure (Found: C, 72·9, 73·2; H, 3·1, 3·2; Li, 2·5, 2·6. $C_{32}H_{16}N_8Li_2$ requires C, 73·0; H, 3·0; Li, 2·7%).

The dilithium compound is freely soluble in alcohol, amyl alcohol, and acetone, but not in ether or benzene. On cautious addition of benzene to a hot alcoholic solution it separates in plates or needles with a purple lustre, which are solvated and lose alcohol at 250—300°. The unsolvated compound is completely soluble in alcohol. The powder is greenish-blue. The absorption spectrum is given in Part XIII (preceding paper).

The dilithium compound (2 g.) was continuously extracted with 80 c.c. of boiling chloronaphthalene for 9 hours. The green solution obtained became dark grey on cooling and after 12 hours 0·4 g. of *lithium hydrogen phthalocyanine* was deposited as black needles with a silver lustre and a black rubbing (Found: C, 74·0; H, 3·3; Li, 1·3. $C_{32}H_{17}N_8Li$ requires C, 73·8; H, 3·3; Li, 1·35%). When the crystalline material was dissolved in boiling chloronaphthalene, it again gave a green solution, going grey on cooling. The solution in concentrated sulphuric acid was brown, and gave a blue precipitate of phthalocyanine when poured into water. The same compound was obtained by adding 52 g. of phthalonitrile to a solution of 0·7 g. of lithium in 300 c.c. of amyl alcohol. The solution became brownish-red and then grey, and after 25 minutes the black precipitate of lithium hydrogen phthalocyanine was collected and crystallised from chloronaphthalene.* The lithium hydrogen compound dissolved in lithium amyloxide to give a blue solution containing the dilithium derivative.

Reactions. Water (2 c.c.) was added to a solution of dilithium phthalocyanine (3 g.) in absolute alcohol (25 c.c.). The blue precipitate of free phthalocyanine which formed immediately was collected after 3 hours and crystallised from chloronaphthalene (Found: C, 74·5; H, 3·5. Calc.: C, 74·7; H, 3·5%). The dilithium compound was hydrolysed similarly by dilute acids.

A solution of anhydrous cupric chloride (1 g.) in absolute alcohol (15 c.c.) was added gradually with shaking to dilithium phthalocyanine (2 g.) dissolved in 20 c.c. of the same solvent. A bright blue precipitate of copper phthalocyanine separated immediately. This was collected after 3 hours, washed free from cupric chloride with alcohol, dissolved in sulphuric acid, and precipitated with water. Yield, 1·8 g. (Found: Cu, 10·8. Calc.: Cu, 11·1%).

Similar double decompositions were carried out between dilithium phthalocyanine (2 g.) and the following anhydrous salts (50% excess) in absolute alcohol. The chlorides were dehydrated before use at 150° in a current of hydrogen chloride. The order given below follows the periodic table, Group I coming first.

Silver nitrate gave a blue precipitate of *silver phthalocyanine* (Found: Ag, 16·5. $C_{32}H_{16}N_8Ag$ requires Ag, 17·4%; see below). Calcium chloride gave a dull green precipitate of calcium phthalocyanine, insoluble in quinoline and chloronaphthalene (Found: Ca, 7·4. Calc. for $C_{32}H_{16}N_8Ca$: Ca, 7·25%). This material is purer than that obtained from phthalonitrile and quick-lime or calcium ethoxide (Barrett, Dent, and Linstead, *loc. cit.*, p. 1728). Zinc chloride gave a blue precipitate of zinc phthalocyanine, which sublimed in purple needles (Found: C, 66·8; H, 2·7; Zn, 11·0. Calc.: C, 66·5; H, 2·8; Zn, 11·3%). Mercuric chloride gave a dull green precipitate of *mercuric phthalocyanine*, very difficult to filter (Found: C, 53·6; H, 2·3; Hg, 28·5. $C_{32}H_{16}N_8Hg$ requires C, 54·0; H, 2·3; Hg, 28·2%; see below). Thallium hydroxide gave a bright green precipitate, not further investigated. Thorium chloride gave a voluminous precipitate, which yielded free phthalocyanine on crystallisation from chloronaphthalene (Found: C, 74·7; H, 3·3%). Stannous chloride, stannic chloride, dimethylstannic chloride and dimethylstannic iodide gave similar voluminous precipitates, none of which contained tin. The product from stannic chloride was crystallised from quinoline and identified as phthalocyanine (Found: C, 74·3; H, 3·5%). Lead acetate gave a grass-green precipitate of lead phthalocyanine, which crystallised from chloronaphthalene in rectangular prisms (Found: Pb, 28·5. Calc.: Pb, 28·8%). Bismuth trichloride gave a voluminous precipitate of free phthalocyanine, which after crystallisation had C, 74·6; H, 3·6%. Tungsten oxychloride similarly gave a blue precipitate containing no metal. Manganous chloride gave a nearly black precipitate of manganous phthalocyanine, which sublimed in greenish-black needles (Found: Mn, 9·5. Calc.: Mn, 9·7%). Cobalt chloride gave a voluminous precipitate of the corresponding phthalocyanine, which crystallised from chloronaphthalene in stout needles (Found: Co, 10·3. Calc.: Co, 10·3%). Palladium chloride gave a blue precipitate, which crystallised from chloronaphthalene in purple needles,

* This method of preparation was discovered by Dr. C. E. Dent.

but was not homogeneous (Found, in two samples: Pd, 5·2, 8·2. $C_{32}H_{16}N_8Pd$ requires Pd, 17·5%).

No precipitation occurred when methyl iodide (5 c.c.) was added to a solution of dilithium phthalocyanine (2 g.) in absolute alcohol (15 c.c.). After the mixture had stood for 7 days in a securely stoppered bottle, a considerable quantity of free phthalocyanine had separated (Found: C, 74·4; H, 3·5%). The absence of *N*-methyl groups was confirmed by fission with ceric sulphate; an amount of the reagent equivalent to 1·08 atoms of oxygen per molecule was then taken up, and a theoretical yield of pure phthalimide (m. p. and mixed m. p. 228°) obtained.

The same reagents were refluxed for 7 days in dry ether (20 c.c.) in place of alcohol as a solvent, moisture being excluded. The residual pigment was completely soluble in dry acetone and hence was the unchanged lithium compound.

Dilithium phthalocyanine (2 g.) was completely converted into free phthalocyanine by 3 hours' refluxing with acetyl chloride (5 c.c., distilled over sodium) and pure ethyl acetate (10 c.c.). The product, crystallised from chloronaphthalene, had C, 74·4; H, 3·4%. The action of benzyl chloride in boiling absolute alcohol gave the same result (Found: C, 74·5; H, 3·3%).

Other New Metallic Phthalocyanines.—The preparation and analysis of the mercuric compound are described above. The analytical sample was washed for several days with hot alcohol, until free from mercuric chloride. When crystallised from chloronaphthalene, the mercuric compound yielded free phthalocyanine (Found: C, 74·7; H, 3·7%), and the same result was achieved on treatment with sulphuric acid (Yield, 70%. Found: C, 74·2; H, 3·2%).

Recrystallised lead phthalocyanine (3 g.) and silver sulphate (3 g.) were refluxed in chloronaphthalene (30 c.c.) for 3 hours. The initial grass-green colour changed quickly to greenish-blue and silver phthalocyanine (? silver hydrogen phthalocyanine) separated from the cooled product in fine needles with a red lustre. Inorganic impurities were removed by flotation in ether (Found: C, 63·0; H, 2·6; Ag, 16·2. $C_{32}H_{16}N_8Ag$ requires C, 62·0; H, 2·6; Ag, 17·4%). Another method of preparation is described above. In an endeavour to remove the last traces of impurity, the substance was crystallised from chloronaphthalene. Metallic silver was, however, deposited on the walls of the extraction vessel as a grey film, and the product contained only 14·0% of silver. When heated under reduced pressure, the original pigment melted and a small portion sublimed to give blue needles containing 14·5% of silver. On treatment with sulphuric acid metal-free phthalocyanine was formed. Fission with ceric sulphate gave results corresponding to an oxygen uptake of 1·55 and 1·60 atoms of oxygen per molecule.

Phthalonitrile (20 g.) was mechanically stirred with 7 g. of finely powdered antimony at 300°; the mixture slowly turned dark blue and after 4 hours was nearly solid. Boiling alcohol removed the excess of nitrile and left 22 g. (75%) of a dull blue, amorphous powder with a dull green rubbing. The same reaction occurred when atmospheric oxygen was excluded by a current of nitrogen. The crude product was purified by repeated flotations in alcohol; the excess of antimony sank and the lighter phthalocyanine could be poured off with the supernatant liquid. Eventually a solid was obtained which microscopic examination showed to be almost entirely amorphous blue *diantimony phthalocyanine*, contaminated with a few lustrous needles of free phthalocyanine and a few particles of antimony (Found: C, 51·5; H, 2·3; N, 15·0, 15·3; Sb, 29·2. $C_{32}H_{16}N_8Sb_2$ requires C, 50·9; H, 2·1; N, 14·9; Sb, 32·2%). No further purification of this substance could be effected. When it was heated under reduced pressure, it decomposed, giving no trace of vapour. When crystallised from chloronaphthalene, it gave a good yield of free phthalocyanine (Found: C, 74·4; H, 3·4%), and the antimony remained as a sludge on the asbestos filter of the extractor. Crystallisation from quinoline and α-methylnaphthalene gave the same result. 5 G. of the crude reaction product on treatment with sulphuric acid in the usual manner gave 3 g. of phthalocyanine. The metal was also removed by 24 hours' boiling with concentrated hydrochloric acid or aqueous potash. Boiling alcoholic potash dissolved the reaction product (2 g.) to give a bright green solution, which was decolourised by cooling and admission of air. A mixture of basic antimony compounds and a little free phthalocyanine separated and from the filtrate 1 g. of phthalic acid was recovered (m. p. 202°; anhydride, m. p. 128°).

A mixture of 5 g. of phthalocyanine, 5 g. of antimony trichloride, and 5 c.c. of chloronaphthalene was heated in a sealed tube at 300° for 6 hours. The liquid was filtered, and the dark green residue washed with ether, stirred with water, heated to boiling, and allowed to settle. The crystalline phthalocyanine derivative sank to the bottom and basic antimony compounds, formed by the hydrolysis of the excess of reagent, remained in suspension. This was cleared by the addition of hydrochloric acid in drops. The product was then collected and washed with water and alcohol. Yield, 5 g. It dissolved easily in hot chloronaphthalene, containing a little antimony trichloride, to give a pure green solution, which deposited *chloroantimony phthalocyanine* in cigar-shaped needles, with a blue-green lustre and a green rubbing. The material for analysis was washed with dilute hydrochloric acid (1 : 1) and dried (Found : C, 57·2; H, 2·4; Cl, 5·2; Sb, 17·9. $C_{32}H_{16}N_8ClSb$ requires C, 57·4; H, 2·4; Cl, 5·3; Sb, 18·2%). The substance could be prepared more conveniently by refluxing the same reagents in chloronaphthalene; the blue-green colour changed to pure green after 30 minutes. The solution was cooled and filtered, and the chloroantimony compound (6·2 g. from 5 g. of phthalocyanine) washed with benzene. When heated under reduced pressure, chloroantimony phthalocyanine sublimed unchanged as a deep green vapour, which deposited green plates with a dark green lustre (Found : C, 57·25; H, 2·7%). On crystallisation from quinoline the compound yielded free phthalocyanine (Found : C, 74·7; H, 3·3%). This was also formed by treatment with sulphuric acid.

When phthalonitrile (5 g.) was heated at 280—290° with 1 g. of palladous chloride, the melt rapidly turned deep blue and hydrogen chloride was evolved. After 2 hours an 80% yield of a blue chlorine-containing substance was obtained, which dissolved in chloronaphthalene with a bluish-green colour and deposited *palladium monochlorophthalocyanine* as an amorphous blue solid (Found : Pd, 16·3. $C_{32}H_{15}N_8ClPd$ requires Pd, 16·3%). Like other nuclear-halogenated phthalocyanines, this could not be sublimed.

Iron Phthalocyanines and their Addition Products.—Ferrous phthalocyanine was obtained from *o*-cyanobenzamide and pure iron wire by the method of Barrett, Dent, and Linstead (*loc. cit.*). The product was ground, washed with sodium hydroxide solution and hydrochloric acid, and extracted (Soxhlet) successively with acetic acid and alcohol. Yield, 35% (Found : C, 67·8; H, 2·45; Fe, 10·5. Calc. : C, 67·6; H, 2·8; Fe, 9·8%).

Chloroferric phthalocyanine was first made by decomposing the aniline addition compound of ferrous phthalocyanine with hydrochloric acid (see below), but was most conveniently prepared as follows : Ferrous phthalocyanine was warmed on the steam-bath for an hour with a large excess of concentrated hydrochloric acid. The liquid was filtered and the solid was washed free from acid and dried, by washing with alcohol and finally at 100°. Yield, theoretical (Found : C, 63·2, 63·3; H, 3·0, 2·8; Cl, 5·6; Fe, 10·0. $C_{32}H_{16}N_8ClFe$ requires C, 63·6; H, 2·7; Cl, 5·9; Fe, 9·4%). Chloroferric phthalocyanine was a dull green solid, with a yellowish-green rubbing. It dissolved in sulphuric acid with evolution of hydrogen chloride to give a purplish-red solution. When poured on ice and water, this yielded a green solid, turned blue by the addition of caustic alkali or ammonia. In spite of a number of attempts we were unable to obtain from this product a hydroxyferric phthalocyanine giving satisfactory analytical figures. A typical product, dried at 100°, had C, 61·7; H, 3·2; Fe, 10·7% ($C_{32}H_{16}N_8Fe{\cdot}OH$ requires C, 65·6; H, 2·7; Fe, 9·6%). The product contained no sulphur or halogen and may have been hydrated. Drying to constant weight at 200°, however, resulted in a further fall in the carbon and hydrogen figures, so that some decomposition into volatile organic material (? phthalimide) probably occurred.

Additive compounds. Ferrous phthalocyanine (1 g.) was boiled with 10 c.c. of aniline, and the intensely green solution filtered hot. A little pigment was undissolved, and the filtrate deposited the *hexa-aniline addition compound* as a mass of purple prismatic needles, resembling potassium permanganate. These were collected, washed with benzene, and dried by suction and in a vacuum desiccator. Analyses had to be carried out on freshly prepared material owing to the tendency for the base to be eliminated on standing (Found : C, 72·0, 72·0; H, 5·1, 5·2; N, 17·9; Fe, 4·6. $C_{32}H_{16}N_8Fe,6C_6H_5{\cdot}NH_2$ requires C, 72·5; H, 5·2; N, 17·4; Fe, 5·0%). These figures agree satisfactorily with those previously obtained (C, 72·7; H, 5·3; Fe, 5·3%). The aniline compound gives a bright green rubbing on paper, but this rapidly becomes dull owing to loss of aniline, even in a corked tube. Re-analysis of the original 1929 sample revealed a partial loss of aniline from the crystalline solid.

The early work (*loc. cit.*) showed that the base was removed by cold acid or by heating at 180°. These decompositions have now been examined quantitatively. At 180°, in a stream of carbon dioxide, the weight became constant after 90 minutes, the loss corresponding to 49·6% of aniline ($6C_6H_5{\cdot}NH_2$ requires loss, 49·6%). The liberated base was identified by conversion into acetanilide, and the residue as ferrous phthalocyanine (Found : C, 68·1; H, 2·7%). A weighed quantity of the additive compound was warmed with hydrochloric acid, the liquid filtered, and the aniline in the filtrate and washings estimated by titration with standard sodium nitrite solution (Found : 50·0, 50·4% aniline). The residue was dried and weighed. It amounted to 51·5% of the original pigment, contained chlorine, and was identical in properties with chloroferric phthalocyanine (Found : C, 63·7; H, 2·7; Fe, 9·5. Calc. for $C_{32}H_{16}N_8ClFe$: C, 63·6; H, 2·7; Fe, 9·4%).

The *hexa*-o-*toluidine addition compound* of ferrous phthalocyanine was made in a similar manner to the aniline compound. It was very readily dissociated even by washing with solvents. It formed small purple prisms with a bright green smear, rapidly turning dull (Found : C, 72·3, 72·4; H, 5·7, 6·0; N, 16·1; Fe, 5·2. $C_{32}H_{16}N_8Fe,6C_7H_7{\cdot}NH_2$ requires C, 73·4; H, 5·8; N, 16·2; Fe, 4·6%).

The *dipyridine compound* was best prepared by extracting ferrous phthalocyanine in a Soxhlet apparatus with dry pyridine and allowing the extract to crystallise. It separated in very small, purple crystals with a bright green smear, and could be washed with water or alcohol and dried at 100° without decomposition (Found : C, 68·5, 69·0; H, 3·9, 3·7; N, 19·6; Fe, 7·5, 7·7. $C_{32}H_{16}N_8Fe,2C_5H_5N$ requires C, 69·4; H, 3·6; N, 19·3; Fe, 7·7%). When it was heated at 150° for an hour in a stream of carbon dioxide, the loss in weight was only 0·33%; at 200°, the loss in weight in 4 hours was 21·2% and in 6 hours 24·3% (Calc. for $2C_5H_5N$, 21·7%). There were indications of gross decomposition by the longer heating. The loss of weight on treatment with hydrochloric acid also agreed approximately with the presence of two molecules of base.

Bright green solutions, undoubtedly containing similar additive compounds, were formed when ferrous phthalocyanine was treated with the following reagents : solutions of β-naphthylamine in ether, benzene, acetone, and xylene (but not in petroleum); similar solutions of *p*-toluidine and also the molten base; phenylhydrazine. In no case, however, could a crystalline solid be isolated.

It was not found possible to separate aniline from pyridine, or aniline from *p*-toluidine, by taking advantage of the difference in the stabilities of their additive compounds with ferrous phthalocyanine.

We thank the Dyestuffs Group of Imperial Chemical Industries, Ltd., for grants and gifts of chemicals.

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[*Received, May* 14*th*, 1938.]