212. *Phthalocyanines. Part I. A New Type of Synthetic Colouring Matters.*

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THIS series of papers describes a new class of coloured organic compounds which comprises a parent substance, named *phthalocyanine* from its origin and deep blue colour, and a series of complex metallic derivatives which are of great beauty of appearance and unusual stability. The mode of formation and the reactions of these substances indicate that they are of a new structural type which may be exemplified by the formula (XIV) on p. 1035 of the parent substance.* The central ring of this formula has a striking resemblance to that of the natural porphyrins.

The present paper is concerned with the discovery and preliminary investigation of the first member of the class. This is followed by a description of preparative methods and properties (Parts II, III, and IV), molecular-weight determinations (Part V), and a general discussion of structure (Part VI).

The first phthalocyanine was discovered by chance in 1928 during the course of the industrial production of phthalimide in the Grangemouth works of Messrs. Scottish Dyes, Ltd. The process consists in passing ammonia into molten phthalic anhydride in iron vessels and it was found that during certain preparations traces of a dark blue substance were formed in the molten imide. This material was stable, crystalline, and contained iron which was not eliminated by treatment with concentrated sulphuric acid.† As it appeared that the substance might prove of academic interest, its study was taken up in 1929 through the kindness of Professor J. F. Thorpe, F.R.S., and the Research Committee of the Dyestuffs Group of Imperial Chemical Industries, Ltd.

This iron compound (crude *iron phthalocyanine*) was insoluble in the usual organic media and in water, dilute acids and alkalis. It could, therefore, easily be freed from simple impurities, but absolute purification was made difficult and it could not be determined whether the substance was a chemical individual or a mixture of compounds of a similar type. Preliminary experiments were carried out on the material purified as far as possible by suitable extraction. This product gave the mean analytical figures: C, 62·4; H, 2·9; N, 19·2; Fe, 12·6%, leaving a deficiency (? oxygen) of some 3%. No other elements could be detected. These values correspond to an atomic ratio of 4C : 1N, which indicates that two atoms of nitrogen are combined with a phthalic residue.

Hot nitric acid or aqua regia decomposed the compound into phthalimide and the iron separated as ferric salt. The same fission could be effected by cold acid permanganate. Concentrated sulphuric acid at 100° yielded phthalic acid and phthalimide together with

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* This formula was arrived at on the basis of the chemical evidence described in Part VI (compare *Brit. Assoc. Reports*, 1933). An *X*-ray investigation by Dr. J. M. Robertson of the Royal Institution, which will shortly be published, has since confirmed the structures advanced in these papers.

† The preliminary examination of the iron compound was carried out by Messrs. S. W. Dunworth and H. A. E. Drescher of Scottish Dyes Ltd.

ferrous and ammonium sulphates. Distillation with soda–lime formed benzonitrile and ammonia.

These results made it probable that the substance was formed by a process of dehydration and amination of phthalimide, accompanied by fixation of metal, and that the molecule contained either an *iso*indole skeleton or a unit capable of yielding this skeleton with ease.

EXPERIMENTAL.

The iron pigment was a dark powder with a purple lustre; individual needle crystals could be observed. When rubbed on paper, it gave a Prussian-blue streak. It was insoluble in water and the usual organic solvents, but dissolved in hot aniline and its homologues to give intensely green solutions which contained complex additive compounds. It was very stable at high temperatures, but just below a dull red heat it slowly burnt with a slight evolution of a green vapour, to leave first a pyrophoric residue of ferrous oxide and finally ferric oxide.

The substance was unaffected by boiling concentrated hydrochloric acid. In cold concentrated sulphuric acid it gave a brown solution which on being poured on ice yielded the apparently unchanged material as a Prussian-blue precipitate. The iron content of the substance always fell slightly on this treatment; the significance of this is not yet known. The solution in cold sulphuric acid was stable and yielded the colour on dilution after several days' standing.

A solution of 1 g. in 30 c.c. of concentrated sulphuric acid was warmed at 120° for a few minutes; the brown colour then faded. No blue precipitate was formed on dilution with ice, and addition of ammonia in excess precipitated ferrous hydroxide. The filtrate from this on evaporation left a residue, from which acetone extracted phthalic acid (0·5 g.), identified by conversion into the anhydride. Warm concentrated nitric acid or aqua regia rapidly dissolved the pigment to give a clear yellow liquid which showed the usual tests for ferric iron. Dilution of this with an equal bulk of water yielded phthalimide as a grey precipitate. After crystallisation, this was identified by its m. p. 230—231° (unchanged by admixture with authentic phthalimide, or by sublimation) and general properties. A further quantity was isolated from the mother-liquor. The iron pigment, suspended in 10% sulphuric acid, was treated with a 3% solution of potassium permanganate. Decoloration was rapid. The solution, after being left over-night, yielded phthalimide (m. p. and mixed m. p. 231°) on extraction with ether.

The iron compound was unaffected by aqueous alkali and floated unchanged on molten potash. Alcoholic potash or sodium ethoxide yielded a greenish-blue solution, but only if there was free access of air. The colour disappeared when the solution was boiled under reflux and reappeared on removal of the condenser. Very little solid was dissolved and nothing definite could be isolated from the solution. On fusion with soda–lime the iron pigment evolved ammonia and, more reluctantly, benzonitrile, identified by hydrolysis to benzoic acid.

The iron pigment was boiled with aniline, and the intensely green solution filtered and left over-night. The separated solid was washed rapidly with benzene and dried. For analysis, the crystals were powdered, again washed with benzene, and dried (Found : C, 72·7; H, 5·3; Fe, 5·3%). The *aniline* compound forms prisms with a fine purple reflex giving a bright green powder. It gives a crystalline sublimate on being heated and is appreciably soluble in benzene. The carefully washed material gave a carbylamine reaction and yielded aniline sulphate with sulphuric acid. The combined base could be removed by trituration with concentrated hydrochloric acid or by heating to 180°. The residue was a dark blue powder, insoluble in benzene and giving no carbylamine reaction.

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