382. *Phthalocyanines. Part VII. Phthalocyanine as a Co-ordinating Group. A General Investigation of the Metallic Derivatives.*

By P. A. Barrett, C. E. Dent, and R. P. Linstead.

In its power of forming stable derivatives with a wide variety of metals, phthalocyanine can be ranked with acetylacetone. Twenty elements whose phthalocyanine derivatives have been studied are given in the table. This includes representatives of each group (1—8) of the periodic table.

| Group 1. (Hydrogen)	2.	3.	4.	5.	6.	7.	8.
Sodium	Beryllium	Aluminium	Tin	Vanadium	Chromium	Manganese	Iron
Potassium	Magnesium		Lead				Cobalt
Copper	Calcium						Nickel
	Zinc						Platinum
	Cadmium						
	Barium						

A number of other metallic compounds are still under study, but it seems desirable to indicate the main results which have so far been achieved. Developments in the purely organic chemistry of the group will be described separately.

In one respect the metallic phthalocyanines differ from other organic co-ordination compounds; they are not usually prepared from the parent metal-free compound but from the dinitrile or nitrile-amide of phthalic acid, the metal being fixed at the same time as the phthalocyanine unit is formed (*e.g.*, $4C_8H_4N_2 + \text{Met} \longrightarrow C_{32}H_{16}N_8\text{Met}$). There is a great tendency, particularly in the case of phthalonitrile, for this to occur and the reactions are exothermic. Metallic reagents suffer an interesting variety of changes in their efforts to provide the metal necessary for phthalocyanine formation. These are illustrated in the summary which follows. A classification based on the valency of the central element has been used.

(1) *Univalent Elements* (H,Na,K).—Free phthalocyanine, $C_{32}H_{16}N_8H_2$ (Byrne, Linstead, and Lowe, J., 1934, 1017), has now been prepared by the decomposition by means of acids or water of the following metallic derivatives : beryllium, sodium, magnesium, potassium, calcium, manganese, cadmium, tin, barium and lead. It is also formed when phthalonitrile is heated at high temperatures either alone or with such catalysts as silica gel or platinum. It has been shown (Dent, Linstead, and Lowe, J., 1934, 1033) that the formula for phthalocyanine is $(C_8H_4N_2)_4H_2$ and not $(C_8H_4N_2)_4$, and independent and conclusive evidence in support of this is given later in this paper. The preparation from phthalonitrile $(C_8H_4N_2)$ over platinum in the absence of an obvious reducing agent might appear to favour the second of these formulæ. This objection is not serious because the reaction is accompanied by gross decomposition and deposition of carbon.

The suggestion made in Part III that the formation of free phthalocyanine from phthalonitrile and sodium amyloxide proceeded through the intermediate formation of a sodium compound has been verified. These compounds react in boiling amyl alcohol to yield *disodium phthalocyanine*, which is converted into free phthalocyanine slowly by hot water,

rapidly by dilute acids. The preparation of phthalocyanine from phthalonitrile by this route thus involves the processes :

$$4C_8H_4N_2 + 2NaO\cdot C_5H_{11} \longrightarrow C_{32}H_{16}N_8Na_2 \longrightarrow C_{32}H_{16}N_8H_2$$
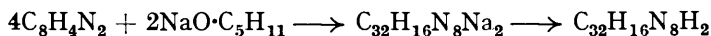
Experiments designed to determine the fate of the amyloxide residues ($2C_5H_{11}\cdot O$) in the first of these reactions were inconclusive.

In attempts made to prepare *N*-methylphthalocyanine from the disodium compound and methyl iodide, no reaction occurred even at 220°. The sodium was rapidly eliminated by a mixture of methyl iodide and ethyl alcohol, but the organic product from the sodium compound was pure unmethylated phthalocyanine. The reaction presumably proceeds as follows :

$$PcNa_2 + 2MeI + 2EtOH \longrightarrow PcH_2 + 2NaI + 2MeOEt$$
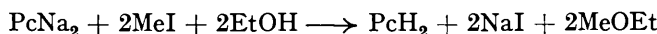
[Pc represents the bivalent phthalocyanine group ($C_{32}H_{16}N_8$)].

Potassium amyloxide and phthalonitrile yield a *dipotassium phthalocyanine* similarly but less readily. The metal appears to be more easily removed than is sodium ; for example, the salt yields phthalocyanine on treatment with methyl iodide at 170°.

(2) *Elements normally Bivalent* (Be, Mg, Ca, Ba, Pb, Cu, Zn, Cd, Ni, Co).—Massive beryllium is rapidly dissolved by boiling phthalonitrile,* provided that the surface of the metal has first been etched with acid. The product gives on sublimation in a vacuum anhydrous *beryllium phthalocyanine* (PcBe), which yields a *dihydrate* in moist air. Beryllium phthalocyanine is converted into free phthalocyanine when it is dissolved in concentrated sulphuric acid and the solution diluted with water. Magnesium phthalocyanine dihydrate (J., 1934, 1023) has now been dehydrated by careful vacuum sublimation. The *anhydrous* compound is hydrated rapidly and in a characteristic manner in moist air, but can be kept indefinitely in a dry atmosphere. These results confirm the structure previously advanced for the magnesium compound.
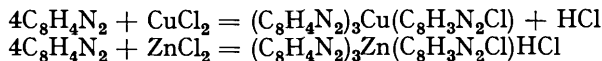
Calcium phthalocyanine is conveniently prepared by the action of calcium oxide or ethoxide on phthalonitrile. The reaction with quick-lime presumably involves the oxidation of a small proportion of the nitrile, *e.g.*, by the reaction $73C_8H_4N_2 + 18CaO \longrightarrow 18Ca(C_8H_4N_2)_4 + 8CO_2 + 2H_2O + N_2$ or an equivalent process. The product is a green insoluble substance which cannot be sublimed and is converted into phthalocyanine by the action of acids. Barium phthalocyanine is formed similarly but less readily from baryta and phthalonitrile. The metal is more easily removed by acids than is calcium.

Copper phthalocyanine may be taken as the prototype of the stable metallic phthalocyanines of normal structure. In addition to the methods already described (Dent and Linstead, J., 1934, 1027), it has been prepared by the action of anhydrous cupric chloride on phthalocyanine in boiling quinoline. This process gave the cupric derivative (PcCu) and there was no indication of the formation of a cuprous compound, $PcCu_2$. Careful fractional crystallisation failed to show the presence of more than one form of the cupric compound. The action of metallic salts on free phthalocyanine is valuable for the preparation of less accessible compounds of the group containing other metals. The smooth formation of cupric phthalocyanine from equivalent amounts of the metal-free compound and cupric chloride confirms the presence in the former of two replaceable atoms of hydrogen.

Zinc phthalocyanine, prepared from the metal and phthalonitrile, resembles the copper compound in many respects. It has the normal structure, PcZn. The substance itself is blue, but when precipitated from its sulphuric acid solution by the addition of water a greenish-blue sulphate is formed, which regenerates the original substance on treatment with alkali. There is no elimination of metal. A similar salt formation occurs during the reaction between zinc chloride and phthalonitrile. The product contains two atoms of chlorine to the molecule, *i.e.*, to each atom of zinc, and *one* of these is lost as hydrogen chloride on treatment with sulphuric acid. Dilution of the solution in this acid and

---

* Thus phthalonitrile, although it contains neither an acidic nor a pseudo-acidic hydrogen atom, dissolves metals to form compounds in which the metallic atoms are held by primary valencies. This is possible because a ring is formed under the conditions of reaction.

neutralisation yields *zinc monochlorophthalocyanine* (which contains one nuclear halogen) and the first product appears to be essentially the *hydrochloride* of this. The original reaction therefore simulates that between cupric chloride and phthalonitrile (Dent and Linstead, J., 1934, 1027), the only difference being that in one case the hydrogen chloride formed by the nuclear halogenation escapes and in the other is fixed as a salt :

$$4C_8H_4N_2 + CuCl_2 = (C_8H_4N_2)_3Cu(C_8H_3N_2Cl) + HCl$$
$$4C_8H_4N_2 + ZnCl_2 = (C_8H_4N_2)_3Zn(C_8H_3N_2Cl)HCl$$

Cadmium phthalocyanine resembles the zinc compound in the method of formation, but differs from it in that it is insoluble and non-volatile, and by the fact that the metal is removed by acids. This significant difference is discussed later.

Nickel phthalocyanine is conveniently prepared from *o*-cyanobenzamide and the metal, but the *cobalt* compound is most easily made by dissolving the etched massive metal in boiling phthalonitrile. These products are normal compounds of the type PcMe; they are stable to concentrated sulphuric acid and sublime well. Cobaltous chloride reacts smoothly with phthalonitrile with the formation of hydrogen chloride and *cobalt mono-chlorophthalocyanine.* The product yields a mixture of phthalimide and a chloro-phthalimide on oxidation and no chloride ion is liberated : hence the chlorine is nuclear. The original reaction thus resembles that between phthalonitrile and cupric chloride.
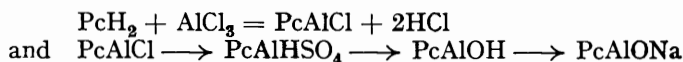
Lead phthalocyanine is abnormal in many respects. It can readily be prepared by the violently exothermic reaction between litharge and phthalonitrile. The mechanism is probably similar to that suggested above for the reaction between quick-lime and phthalonitrile. The yield is almost theoretical on the basis that one nitrile molecule in 73 is used up in the reduction of the litharge. The product after purification, by either sublimation or crystallisation, corresponds to PcPb and is easily converted into phthalo-cyanine by the action of mineral acids. It differs from the other normal metallic phthalo-cyanines in colour (it is bright green) reflex and crystalline form. A mixture of lead sulphate and metal-free phthalocyanine heated under reduced pressure gave a sublimate of lead phthalocyanine, together with a little unchanged free phthalocyanine. This remarkable reaction, which involves the liberation of sulphuric acid or sulphur trioxide, illustrates once more the stability of the phthalocyanine unit. The many peculiarities of lead phthalocyanine are not due to the high atomic weight of the central atom, for the platinum compound is normal.

Other phthalocyanines in which the central metal exhibits bivalency are described below under " elements of variable valency."

(3) *Tervalent Element* (Al).—We expected that the bivalent phthalocyanine complex and an exclusively tervalent atom such as aluminium would interact to form substances of the type Pc·AlX, where X is a univalent atom or group. This was borne out in practice. Aluminium chloride reacted readily with phthalonitrile to yield a metallic phthalocyanine, but as the product is comparatively complex, it will be convenient to con-sider first the simpler substance obtained from the chloride and free phthalocyanine. These react in boiling quinoline to yield *chloroaluminium phthalocyanine* * (PcAlCl), a blue solid which can be purified by crystallisation but decomposes slightly on sublimation. It shows no tendency to hydration but is appreciably soluble in alcohol (abnormal). It dissolves in sulphuric acid with evolution of hydrogen chloride; dilution with water then

---

* *Note on nomenclature.* Three types of halogen (chlorine in the examples given below) must be distinguished, the chemical differences between which are illustrated in the text. (1) *Nuclear.* When the chlorine atom is substituted in a benzene ring, " chloro " is prefixed to " phthalocyanine " in the name; *e.g.*, the compound from phthalonitrile and cupric chloride is copper chlorophthalocyanine $(C_{32}H_{15}N_8Cl)Cu$. (2) *Central.* When the chlorine is attached to the central metallic atom, " chloro " is prefixed to the name of the metal; *e.g.*, the compound from phthalocyanine and aluminium chloride is chloroaluminium phthalocyanine, $(C_{32}H_{16}N_8)AlCl$. (3) *Salt-like.* When the chlorine is attached as hydrogen chloride (presumably to a nitrogen atom), " hydrochloride " is added to the name of the compound; *e.g.*, the compound from phthalonitrile and zinc chloride is zinc chlorophthalocyanine hydrochloride, $(C_{32}H_{15}N_8Cl)Zn,HCl$. The nomenclature of other substituted phthalocyanines follows directly from this.

precipitates a greenish-blue sulphate, there being no elimination of metal. Ammonia reacts with this to form *hydroxoaluminium phthalocyanine* (PcAlOH), isolated as a *trihydrate* and a stable *monohydrate*. This substance is amphoteric; it regenerates the sulphate on treatment with sulphuric acid and forms a salt with sodium hydroxide. The reactions involved are :

$$PcH_2 + AlCl_3 = PcAlCl + 2HCl$$
$$\text{and} \quad PcAlCl \longrightarrow PcAlHSO_4 \longrightarrow PcAlOH \longrightarrow PcAlONa$$
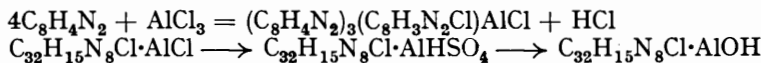
The formation of the monochloroaluminium compound is strong independent evidence for the presence of two reactive hydrogen atoms in free phthalocyanine.

The water of the monohydrate of the hydroxo-compound can be removed only at very high temperatures; the hydroxyl groups of two molecules then also interact to yield what appears to be *aluminium phthalocyanine oxide* :

$$2PcAlOH,H_2O \longrightarrow (PcAl)_2O + 3H_2O$$
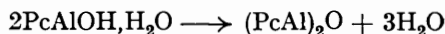
This sublimes in fine needles and shows no tendency to recombine with water. The stable monohydrate appears to illustrate the tendency for aluminum to assume the stable 6-co-ordinate state [PcAl(OH)H$_2$O], but the hydration of other aluminium compounds of the group is irregular.

Aluminium chloride reacts vigorously with phthalonitrile at 250° with evolution of heat and hydrogen chloride to yield *chloroaluminium chlorophthalocyanine*, which readily forms a *dihydrate* and a *trihydrate*. This substance contains chlorine of two dissimilar types. One atom resembles that present in the product from phthalocyanine and aluminium chloride discussed above : it is eliminated by sulphuric acid, and treatment of the product with ammonia yields *hydroxoaluminium chlorophthalocyanine*. The other atom is nuclear and cannot be eliminated. When the molecule is broken up by acid oxidising agents, a mixture of phthalimide and a chlorophthalimide of unknown orientation is produced. The central chlorine atom is not held by an electrovalency, for an alcoholic solution only gives a precipitate very slowly with alcoholic silver nitrate. These compounds are formed by the reactions :

$$4C_8H_4N_2 + AlCl_3 = (C_8H_4N_2)_3(C_8H_3N_2Cl)AlCl + HCl$$
$$C_{32}H_{15}N_8Cl \cdot AlCl \longrightarrow C_{32}H_{15}N_8Cl \cdot AlHSO_4 \longrightarrow C_{32}H_{15}N_8Cl \cdot AlOH$$

The first equation represents the *main* reaction between aluminium chloride and phthalonitrile. The experimental yield of hydrogen chloride was 80% of that required by this equation, but estimation was difficult.

(4) *Elements of Variable Valency* (Sn, Pt, Fe, Mn, Cr, V).—The derivatives of tin provide the only example so far realised in the phthalocyanine group in which the central metal can exhibit both its ordinary states of valency. They have therefore been examined in detail, the reactions which have been studied being shown in the following scheme :
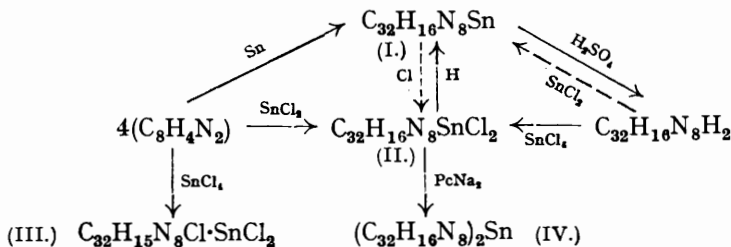
A full arrow indicates that the reaction was realised; a broken arrow that it was realised but that some complication occurred.

Phthalonitrile and metallic tin react slowly at 300° to yield dark blue *stannous phthalocyanine* (I), which is of the normal type, PcSn. Although yielding a blue vapour when heated, it cannot be sublimed satisfactorily. When it is treated with sulphuric acid, the metal is eliminated with the formation of phthalocyanine, but this happens so slowly

that side reactions occur and the yield is poor. Stannous phthalocyanine, unlike other phthalocyanines, gives a bright green colour on treatment with nitric acid or nitrogen dioxide corresponding to the conversion of the tin into the stannic state.

The reaction between stannous chloride and phthalonitrile is violently exothermic and gives rise to the green *dichlorotin phthalocyanine* (II) in excellent yield. No hydrogen chloride is evolved and the process involves a unique direct addition. The two chlorine atoms of dichlorotin phthalocyanine are attached to the metal, because (i) oxidative fission yields unchlorinated phthalimide and chloride ion, (ii) caustic alkali and ammonia eliminate the halogen completely, and (iii) if the dichloro-compound were stannous phthalocyanine dihydrochloride, alkali would liberate the parent compound, whereas dichlorotin phthalocyanine would be converted into a dihydroxotin phthalocyanine or an alkali salt of this. The reaction realised was :

$$PcSnCl_2 + 4KOH \longrightarrow PcSn(OK)_2 + 2KCl + 2H_2O$$

so the second alternative is correct.

The action of alkali in alcoholic solution and of sodium ethoxide on the dichloro-compound gave rise to interesting colour changes and gross decomposition of the molecule. Successive treatments with ammonia under pressure and boiling quinoline led to the formation of stannic oxide and free phthalocyanine. The compound is therefore much less stable to alkali than most phthalocyanines.

The interchange between the stannous and the dichlorostannic form is readily effected. When hydrogen is passed through a solution of dichlorotin phthalocyanine in boiling quinoline, reduction to the stannous compound occurs. The reverse reaction is brought about by dry chlorine gas, but is complicated by some nuclear chlorination occurring, and crystallisation of the product yields substantially pure dichlorotin chlorophthalocyanine (III).

When dichlorotin phthalocyanine is boiled with disodium phthalocyanine in chloronaphthalene, sodium chloride is eliminated and *stannic phthalocyanine* (IV) formed. For this compound, which is free from chlorine and oxygen, no other formula seems possible. It is unique in containing two phthalocyanine units attached to a metal. It is more soluble than most phthalocyanines, but the other properties are normal.

By analogy with the reactions already described, it was expected that free phthalocyanine would react with stannous and stannic chlorides in a suitable solvent to yield respectively the stannous and the dichlorostannic derivative. The second of these reactions was realised. The first was complicated by the fact that, although a fixation of tin occurred, the product contained chlorine. Analysis indicated that it might be stannous phthalocyanine hydrochloride, but this awaits confirmation. Stannic chloride reacts with phthalonitrile at 300° to yield the expected *dichlorotin chlorophthalocyanine* (III) :

$$4C_8H_4N_2 + SnCl_4 = C_{32}H_{15}ClN_8 \cdot SnCl_2 + HCl$$

The reaction resembles that between aluminium chloride and phthalonitrile.

In the hope of obtaining dialkyl tin phthalocyanines the reactions between dimethyl-stannic chloride * and free phthalocyanine was examined. The main product was dichlorotin phthalocyanine, methane presumably being eliminated. The reaction between dimethylstannic iodide and phthalonitrile led to gross decomposition.

Platinous chloride combines readily with phthalonitrile to yield *platinum phthalocyanine* (ous), PcPt. This remarkable compound, which contains over a quarter of its weight of platinum, sublimes at about 550° and is stable to sulphuric acid. No nuclear chlorination, either of the product or of the unreacted phthalonitrile, is involved in its formation, hence the chlorine presumably emerges as such or as platinic chloride. There appears to be no reaction between phthalocyanine and platinum metal or platinous chloride.

Iron phthalocyanine, which was the first member of the group studied in these labor-

* For the preparation of these dialkylstannic halides we found the original method of Cahours (*Annalen*, 1860, **114**, 367), *viz.*, the direct interaction of tin and methyl iodide, much preferable to that involving the decomposition of methylstannoxylic acid.

atories (J., 1934, 1016; compare B.P. 322,169), could not be obtained pure until the technique of sublimation had been perfected. Material prepared from o-cyanobenzamide and metallic iron, after sublimation, gave analytical figures corresponding to *ferrous phthalocyanine*, PcFe. The original iron compound of Part I yielded the same material on sublimation. On oxidation with ceric sulphate (Dent, Linstead, and Lowe, *loc. cit.*) ferrous phthalocyanine takes up oxygen equivalent to $1\frac{1}{2}$ atoms per molecule. This corresponds with the usual oxidation of the complex and the conversion of the iron into the ferric state. Cobalt phthalocyanine behaves similarly, the metal passing into the cobaltic state. Attempts to prepare a chloroiron phthalocyanine (ferric), which would be the " hæmin " of the series, are still in progress. Anhydrous ferric chloride reacts readily with phthalocyanine to form a mixture of the ferric and the ferrous compound, from which the latter was sublimed in good yield.

Black substances of the phthalocyanine class, but of uncertain constitution, are obtained by the interaction of manganese dioxide and phthalonitrile, and of manganese metal and o-cyanobenzamide. Both these give *manganese phthalocyanine* (MnPc) on sublimation, and free phthalocyanine on treatment with sulphuric acid. Chromium gives phthalocyanine derivatives with some difficulty and we have not yet obtained substances of certain constitution. Both o-cyanobenzamide and phthalocyanine yield compounds of the general type when treated with anhydrous chromous chloride. Vanadium pentoxide reacts with phthalonitrile to yield *vanadyl phthalocyanine*, PcVO, which is stable to sulphuric acid and can be sublimed. As expected on general grounds, no phthalocyanine derivatives of silicon could be obtained from the interaction of silicon tetrachloride with free phthalocyanine. Boron trichloride gave an unstable green compound when heated with phthalocyanine to 300°, which was probably an addition compound. The sharp contrast with aluminium chloride is in agreement with the requirements of the covalency rule, from which it can be predicted that boron cannot give a covalent compound of the type PcBCl.

DISCUSSION.

The question whether the metal atoms of the metallic phthalocyanines are held to the *iso*indole nitrogen atoms by covalencies or electrovalencies may be examined by applying the tests of volatility and solubility in organic media (Sidgwick, " The Electronic Theory of Valency," 1927, Chapter 6). Sodium, potassium, calcium, barium, and cadmium phthalocyanines differ from the other compounds of the series in being quite insoluble, even on continuous extraction with chloronaphthalene or quinoline above 200°, and incapable of sublimation. The metal–nitrogen link in these compounds must therefore be presumed to be electrovalent and that of all the other metallic derivatives to be covalent. A similar distinction is found among the corresponding metallic acetylacetonates. The five electrovalent metallic phthalocyanines readily liberate metallic ions on treatment with acids or, in some cases, water alone.

The fact that the metal in zinc phthalocyanine is held by covalencies, whereas the corresponding cadmium compound is electrovalent, is in keeping with Fajans' principle that in the same periodic group of metals the tendency to form covalent compounds decreases with rise in atomic number. It is also of interest that, where comparison is possible between pairs of metals in the same group, a metal of higher atomic number enters the phthalocyanine complex more reluctantly and leaves it more readily. This is shown by comparing sodium with potassium, beryllium with magnesium, calcium with barium, and tin with lead.

The stability of metals in metallic phthalocyanines towards acids is not, however, determined only by the tendency of the metal to become ionised, but also by its stability in the planar 4-co-ordinate state and by considerations of molecular dimensions. Robertson (J., 1935, 615; this vol., p. 1195) finds that the distance from the centre of the *iso*indole nitrogen atoms to the centre of the molecule is 1.91 ± 0.03 A. in free phthalocyanine, and the dimensions are not materially affected by the entry of a metal atom. If we deduct 0.55 as the radius of the nitrogen, there remains a hole in the centre of the molecule of radius about 1.35 A., into which the metal must fit. All the metallic phthalocyanines
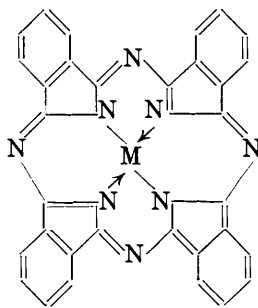
which resist attack by concentrated sulphuric acid actually contain metals whose normal effective radii (as neutral atoms) are of about this order. This is shown in the table, where the atomic radii are those given by Sidgwick (" The Covalent Link in Chemistry," p. 83) :

Metal	Cu	Zn	Fe	Co	Ni	Pt	Al (as AlX)	V (as VO)
Radius, A.	1·28	1·32	1·27	1·25	1·24	1·38	1·43	1·30

On the other hand, larger or smaller covalent metals, such as manganese (1·18) and lead (1·75) are displaced by acids. These considerations provide an independent verification of the effective dimensions of the metals given in the table from a novel standpoint.

Klemm and Klemm have recently (*J. pr. Chem.*, 1935, **143**, 82) dealt with the magnetic properties of certain metallic phthalocyanines. They conclude from their experiments (i) that the metal atoms in nickel, cobalt and iron phthalocyanines are not held by electro-valencies and (ii) that the metal in the nickel compound is attached to all the *iso*indole nitrogen atoms. This is in agreement with the views advanced in the present paper, but we do not agree with Klemm and Klemm's suggestion that the metals of magnesium and manganese phthalocyanines are held by electrovalencies because of their com-parative lability to acids. Both of these compounds and the beryllium derivative (anhydrous), which also contains a labile metal, are similar in volatility, solubility, and crystalline form to undoubtedly covalent metallic phthalocyanines and we believe their metal–nitrogen links to be covalencies, more easily broken than those of the copper or nickel compounds.

Co-ordination.—As a basis for the discussion of the co-ordination of the metal atoms, we may take the general formula (V) (see *J.*, 1934, 1035; formula XVI) of the normal metallic phthalocyanines, where M is a bivalent metal such as copper, platinum or zinc. There is no chemical evidence incompatible with this formula and it has been strikingly confirmed by the X-ray investigations of J. M. Robertson (*loc. cit.*) and the absolute determination of molecular weights (Robertson, Linstead, and Dent, *Nature*, 1935, **135**, 506).

It has been proved that the metal is held to two *iso*indole nitrogen atoms by primary valencies; its co-ordination with the other two to form four chelate rings (cf. Part VI) is reasonably certain for the following reasons : (*a*) The stability of most of the metallic phthalocyanines towards heat and reagents, par-ticularly mineral acids. There are analogies for this among other compounds recognised as co-ordinated, *e.g.*, cobalt glycine is precipitated un-changed by dilution of its solution in concentrated sulphuric acid (Ley and Winkler, *Ber.*, 1909, **42**, 3894; 1912, **45**, 372). (*b*) The fact that very few metallic phthalo-cyanines tend to become solvated during crystallisation. If, for example, the platinum or copper were dicovalent in their phthalocyanine derivatives and not co-ordinated, we should expect them to pass readily into the tetraco-ordinate (or higher) state by combination with two (or more) molecules of a base. These phthalocyanines, however, crystallise unsolvated from bases. (*c*) The existence of metals in so stable a form in the lower state of valency (Fe, Mn) would be remarkable unless the metal were co-ordinated. (*d*) The molecular conditions necessary for co-ordination and chelation are present, namely, lone pairs of electrons on two nitrogen atoms and incomplete outer shells in the central atoms. These atoms are so placed as to permit (one might almost say, to force) ring formation; the four chelate rings are all six-membered, contain one or two double bonds and hence are strainless or practically so (cf. Sidgwick, *op. cit.*, Chapter 14).

Phthalocyanine is therefore a quadridentate chelating unit, capable of occupying four positions in the co-ordination sphere of a metal. This type of four-fold chelation, in which the metal is completely enclosed in an outer ring and the whole molecule thereby knit together, clearly leads to structures of great stability. As usual, this stability is not influenced by the electronic completeness of the core of the metallic atom : zinc phthalo-

cyanine has a rare-gas arrangement (2) (8) (18) **4,4,** but the very stable copper compound contains a typical incomplete core, (2) (8) (17) **4,4,** as in the cupric ion.

The normal metallic phthalocyanines, Metal Pc, are simply related to the corresponding derivatives of acetylacetone, MetalAc$_2$. Vanadyl phthalocyanine, VOPc, may be compared with vanadyl acetylacetone, and PcSnCl with Ac$_2$SnCl. On the other hand, there are no counterparts of AlAc$_3$ and VAc$_3$. Metals do not exhibit their maximum covalency in their phthalocyanine derivatives, except in the simplest cases, for stereochemical reasons.

Fine Structure.—The general formula (V) for covalent metallic phthalocyanines is not regarded as completely correct, for it implies a distinction between the four nitrogen atoms which hold the metal. We believe that no such distinction exists and that, in Robertson's words, " the *o*-quinonoid ring does not possess a definite location in the molecule." This follows from Robertson's demonstration of the centrosymmetry of metallic phthalocyanines and from the non-existence of isomerides of the types represented by (A) and (B). Free
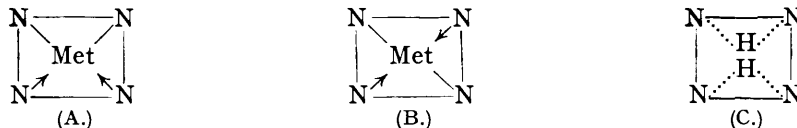
phthalocyanine also is centrosymmetrical, and on classical stereochemistry the two hydrogen atoms should be on opposite sides of the great ring (*trans*). It is preferable to assume that the molecules of phthalocyanine exist in a state of resonance and that each hydrogen atom is co-ordinated with two nitrogen atoms in the manner crudely represented by (C). Independent chemical evidence in support of this has recently come to hand. A similar condition is to be attributed to the metallic derivatives.

Phthalocyanine thus resembles the aromatic type in stereochemistry,* in the loss of unsaturated characteristics and in the very high stability. It appears highly probable that this resemblance originates in a similar, although more complex, resonance in the molecule. A further partial analogy is with the enolic derivatives of unsymmetrical β-diketones and associated substances, which also do not exist in the expected number of isomeric forms and have an abnormal stability (Wheland, *J. Chem. Physics*, 1933, **1**, 731; Sidgwick, *op. cit.*). A resemblance between these compounds, including their metallic derivatives, and the aromatic type was recognised 22 years ago by Morgan and Moss (*J.*, 1914, **105**, 189).

The considerations advanced here may also be applied to the compounds of the porphyrin group, on the very probable assumption that the Küster–Hans Fischer formula for the fundamental ring structure is correct (compare *Ann. Reports*, 1935, **32**, 361).

<div align="center">EXPERIMENTAL.</div>

General Notes on Purification and Analysis.—The methods of crystallisation and sublimation are described below in detail, as it appears that they may be generally useful for the purification of solids only soluble to a small extent in high-boiling liquids and of those capable of sublimation at high temperatures.

1. *Extraction and crystallisation.* The apparatus † is shown in Fig. 1a in a size suitable for the extraction of 2 g. of substance with about 200 c.c. of solvent. The solvent is contained in a 500 c.c. flask of Pyrex glass (A) with a broad fused-on neck, 13″ × 2″. The solid is placed in an inner vessel of Pyrex glass (B) (6″ × 1$\frac{3}{8}$″), resembling a drying tube in shape, which contains a layer (C), $\frac{1}{4}$″ thick, of Gooch asbestos held between two filter discs. The vessel (B) is held vertically in the neck of the flask by means of four indentations at (D) and can be lowered into or removed from the flask by means of a hook inserted in a hole (E). The liquid is boiled in (A), the vapour passes round (B) and is condensed by means of a condenser (F) mounted in the neck of the flask by a cork carrying a safety tube. The condenser consists of a tube of Pyrex glass terminated by a bulb the end of which is bent at an angle. If chloronaphthalene

---

* See Linstead and Robertson, following paper.

† We gratefully acknowledge Dr. A. R. Lowe's assistance in the development of the technique of crystallisation.

(b. p. 250°) is used as the extracting liquid, decalin (b. p. about 190°) is used as the liquid in (F). This is boiled by the condensing chloronaphthalene and itself condenses at the top end of (F). The condensed chloronaphthalene drops off the point of (F) and percolates through the solid in (B), which slowly passes into (A). By turning the cork carrying (F) from time to time, the condensing liquid is directed down a different side of (B). The extraction is generally stopped when the separated solid in (A) causes bad bumping. (It was often possible to extract three 2 g. batches of solid with the same solvent before this occurred.) When a lower-boiling solvent is used, the condensing liquid has to be altered to one of suitable b. p., *e.g.*, water for aniline. A water-condenser is then used to cool the top of (F). Direct heating by means of a flame is the most satisfactory. The phthalocyanine crystallises in (A), often from the boiling solution.

This extractor is preferable to one of the Soxhlet type, which is difficult to operate with a high-boiling liquid. Extraction proceeds practically at the boiling point and there is no attack of the cork by solvent vapour.

2. *Sublimation.* The apparatus, shown in Fig. 1b, is made from the hardest Jena glass (Supremax). The phthalocyanine is introduced through (B) into the pocket (A), and the tube is then assembled as shown. A stream of dry carbon dioxide enters through a drawn-out capillary at C and escapes to a pump and gauge at B. This prevents sublimation up the vertical arm towards C. The tube at D is kept at about 400° by means of a gauze heated

Fig. 1a.—*Apparatus for constant extraction with high-boiling liquid.*

Fig. 1b.—*Apparatus for sublimation at high temperatures.*

by a small flame. The pressure is suitably adjusted and the phthalocyanine is heated to red heat by a second burner. Volatile impurities pass beyond the gauze towards B, inorganic impurities remain in A, and the phthalocyanine collects at D. At the end of the experiment the sublimate is freed from the glass by means of a bent wire (inserted at C) and carefully removed down the side arm C. For *X*-ray investigation, crystals over 1 cm. long were prepared in this apparatus.

Phthalocyanines do not melt. Their purity was assessed and they were characterised by microscopic examination (the reflex against a dark ground is often characteristic) and by analysis.* In macro-combustions for carbon and hydrogen all the sublimable substances could be burnt completely in 15 minutes. Nitrogen was estimated by the macro-Kjeldahl method for the aluminium compounds and by macro-Dumas for the remainder. Total chlorine was estimated by fusion with Kahlbaum lime by Liebig's method, a blank determination being necessary. The estimation of metals, where it differs from standard practice, is described under the individual compounds. A few asterisked micro-analyses are by Schoeller.

Phthalocyanine.†—The preparation from the metallic derivatives is described under the individual metals, and the "catalytic" preparation under platinum. Chloronaphthalene is the most convenient solvent for its crystallisation. A sample purified by sublimation had C, 74·6; H, 3·5; N, 22·05 (Calc. for $C_{32}H_{18}N_8$: C, 74·7; H, 3·5; N, 21·8%). Quantitative oxidation of sublimed material with ceric sulphate (J., 1934, 1038) confirmed the presence of 2 atoms of oxidisable hydrogen per molecule.

* Measurements of absorption spectra will be described shortly.

† The preparation of free phthalocyanines and of various metallic derivatives from phthalonitriles and *o*-cyanobenzamides respectively has been described in B.PP. 410,814 and 389,482 as well as in the papers already cited. The coloured substances containing iron, nickel and copper made from phthalic anhydride, etc., and ammonia, as described in B.P. 322,169, are now seen to consist of or contain the corresponding phthalocyanines (cf. also B.P. 390,149).
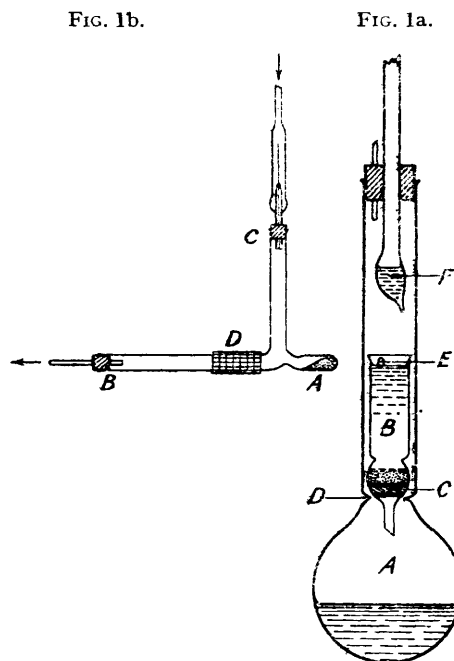
Sodium. 10 G. of phthalonitrile were added to a solution of 1·8 g. of sodium in 100 c.c. of amyl alcohol, and the mixture refluxed gently for 10 minutes. Some ammonia was evolved at first. The product was filtered hot and washed with absolute alcohol and dry ether. *Disodium phthalocyanine* remained as a dull greenish-blue powder with a purple reflex. Yield, 70% (Found : Na, 7·95, 8·0. $C_{32}H_{16}N_8Na_2$ requires Na, 8·2%). It decomposed on being heated under reduced pressure and no appreciable amount of product was removed by extraction with boiling quinoline. A similar preparation was carried out in which only 17 c.c. of amyl alcohol were used. No vapours condensable at − 20°˙ were given off. The amyl alcohol residues yielded impure phthalimide and a trace of (?) *iso*valeric acid insufficient for identification.

Sodium phthalocyanine on treatment with water at 90° for 15 hours yielded a product containing about 2·5% of sodium. After a further 3 days' treatment the value fell to Na, 0·52, 0·3% and the product yielded phthalocyanine on sublimation. Disodium phthalocyanine did not react with methyl iodide in the cold or at 220° (sealed tube, 4 hours). 5 G. were warmed overnight with 10 c.c. of methyl iodide and 10 c.c. of absolute alcohol. The filtered solid was metal-free phthalocyanine and readily attacked copper in boiling quinoline [Found for sublimed material : C, 75·0; H, 3·6; N, 21·8 (Dumas), 21·7 (Kjeldahl). Calc. : C, 74·7; H, 3·5; N, 21·8%]. Sodium phthalocyanine also yielded free phthalocyanine with mineral acids.

Potassium. The preparation of free phthalocyanine through a potassium compound has already been described (B.P. 410,814). The potassium compound was conveniently isolated by refluxing 20 g. of powdered phthalonitrile for an hour with a solution of 5 g. of potassium in 200 c.c. of amyl alcohol. The mixture rapidly became green, but the formation of pigment was slower than in the case of sodium. The product was filtered, washed with dry ether, and dried in a vacuum desiccator. Crude *dipotassium phthalocyanine* was obtained as a blue powder (10 g.) which was insoluble in all solvents and could not be sublimed (Found : K, 11·0, 11·2. $C_{32}H_{16}N_8K_2$ requires K, 13·2%). Prolonged treatment with boiling absolute alcohol led to conversion into free phthalocyanine (ash, 0·3%). 3 G. of the potassium compound were heated at 170° for 6 hours with 5 c.c. of methyl iodide. The product, washed with alcohol and crystallised from chloronaphthalene, was free phthalocyanine (Found : C, 75·0; H, 3·6. Calc. : C, 74·7; H, 3·5%).

Calcium. A mixture of 10 g. of phthalonitrile and 10 g. of quick-lime was heated slowly with mechanical stirring to 275—280°. After 15 minutes the solid mass was exhaustively extracted with boiling alcohol and freed from lime with ice-cold hydrochloric acid. *Calcium phthalocyanine* (70% yield) remained as a dull green pigment almost without lustre. It was insoluble in the usual solvents and could not be sublimed (Found : C, 70·4; H, 2·9; Ca, 5·8. $C_{32}H_{16}N_8Ca$ requires C, 69·6; H, 2·9; Ca, 7·2%). The high carbon and low calcium figure indicate the presence of an impurity of the approximate composition of phthalonitrile, probably the insoluble polymeride previously reported (J., 1934, 1035). A mixture of 20% of $C_8H_4N_2$ and 80% of $C_{32}H_{16}N_8Ca$ requires C, 70·7; H, 2·9; Ca, 5·8%. Extraction with boiling glacial acetic acid, by which the polymeride is slowly dissolved, led to a gradual elimination of calcium. No phthalimide or phthalonitrile was eliminated from the compound by heating at 300° in a vacuum. The calcium content was not lowered by treatment with dilute hydrochloric acid at 0°, but when the compound was dissolved in concentrated sulphuric acid and the solution poured into ice and water, phthalocyanine was precipitated. After crystallisation from chloronaphthalene this had C, 74·4; H, 3·1 (Calc. : C, 74·7; H, 3·5%). The metal was also eliminated when the calcium compound was boiled for 6 hours with 2 vols. of 15% hydrochloric acid (Found : C, 74·1; H, 3·0%). The overall yield of phthalocyanine from phthalonitrile varied from 60 to 68%.

The impure calcium compound was also obtained by refluxing phthalonitrile (10 g.) for 2 hours with a solution of 5 g. of calcium in 50 c.c. of absolute alcohol. After similar purification the product had C, 69·6; H, 3·1; Ca, 5·4%.

Barium. A mixture of 15 g. of phthalonitrile and 7·5 g. of anhydrous baryta was heated at 290° for 2 hours. The reaction was not so vigorous as in the case of quick-lime. The green pigment was freed from excess of nitrile with boiling alcohol but, as it was decomposed by ice-cold dilute hydrochloric acid, the excess of baryta could not be removed. The yield of crude barium compound was 16·5 g.; it was insoluble and could not be sublimed. 10 G. boiled for an hour with dilute hydrochloric acid yielded 7·5 g. of free phthalocyanine (overall yield, 50% from nitrile. Found : C, 74·3; H, 3·4%).

Beryllium. Massive beryllium metal does not react appreciably with phthalonitrile, even after 3 hours' boiling, unless it has first been etched with dilute acid, which presumably removes a film of oxide. Microscopic examination of a lump of metal after reaction shows definite

surface pitting. After 2 days a pitted sample again becomes unreactive. 20 G. of phthalonitrile were boiled gently (nitrate bath) with 3 g. of the etched metal. The melt was semisolid in 30 minutes, and after an hour the product was cooled, the excess metal removed, and the powdered residue washed with alcohol (5·8 g.). On sublimation at about 5 mm. this gave a blue vapour depositing long flattened needles. The lustre appeared more blue and less bronze than that of the metal-free and the copper compound. The main opposite faces of the needle had a bluish lustre and the two less conspicuous faces a bronze lustre (Found : C, 73·8; H, 3·5. $C_{32}H_{16}N_8Be$ requires C, 73·7; H, 3·1%). The crystals broke up in moist air owing to hydration, but less rapidly than those of the magnesium compound. Long crystals of beryllium phthalocyanine become curved and then hook-shaped before finally fracturing to a blue powder. Large crystals sometimes remain intact for as long as 5 hours. The *dihydrate* was a blue powder (Found : C, 69·3; H, 3·5; N, 20·0; Be, 1·6; increase in weight, 6·6. $C_{32}H_{16}N_8Be,2H_2O$ requires C, 68·9; H, 3·6; N, 20·1; Be, 1·6, 1·65; increase in weight, 6·6%.) The original material was soluble to 2·8% in boiling quinoline and to nearly 1% in boiling pyridine. The crystals obtained from these solutions were solvated, as with the magnesium compound (J., 1934, 1026). On treatment with sulphuric acid and dilution in the usual way the beryllium compound yielded phthalocyanine. The elimination of metal was not complete, successive treatments yielding material with Be 0·6 and 0·3%.

[The metal was estimated by slow ashing in an open crucible and weighing as BeO. Microdeterminations gave results about 0·25% too high. High ash values were also obtained by weighing the residue left in the boat after the macro-determinations of carbon and hydrogen. It was first thought that a metallic carbide or nitride was formed under these conditions, but a " wet " carbon analysis of the ash (with chromic anhydride and phosphoric acid) showed the absence of carbon, and a micro-Kjeldahl estimation the absence of nitrogen. The high ash must be due to the presence of a stable hydroxide or peroxide.]

Magnesium. The yield of magnesium phthalocyanine from phthalonitrile and magnesium was improved to 79% and the process quickened by the use of the metal in the form of lightly etched turnings. The product was washed with alcohol and sublimed at 5 mm. There was some decomposition, but the *anhydrous* compound was obtained as lustrous blue needles in 20% yield [Found : C, 71·2 (" wet analysis "). $C_{32}H_{16}N_8Mg$ requires C, 71·6%]. The hydration of crystals of the magnesium compound resembled that of the beryllium, but was almost complete in 1 hour in moist air. The product was the dihydrate (Found : C, 66·8; H, 3·3; N, 19·7 ; Mg, 4·5; increase in weight, 6·0. Calc. : C, 67·1; H, 3·5; N, 19·6; Mg, 4·3; increase in weight, 6·3%). The following experiment proves conclusively that the increase in weight is due to the addition of water and not oxygen. Freshly sublimed magnesium phthalocyanine was sealed in an evacuated tube with two side-arms, one containing phosphoric oxide, the other connected to a reservoir containing water but separated from this by a thin glass diaphragm. The crystals remained in their original state for some days; the limb containing the phosphoric oxide was then sealed off and removed, and the glass diaphragm broken. Within an hour the crystals began to break up in the characteristic manner.

Zinc. Phthalonitrile (10 g.) and zinc dust (1·3 g.) were heated slowly to 245°, by which time the melt had solidified. After 20 minutes at 260—270°, the product was cooled, ground, and washed with alcohol, 9·1 g. of a blue lustrous mass remaining. This sublimed in good yield, the sublimate of *zinc phthalocyanine* resembling the copper compound in appearance (Found : C, 66·8; H, 2·9; N, 19·5; Zn, 11·4. $C_{32}H_{16}N_8Zn$ requires C, 66·5; H, 2·8; N, 19·4; Zn, 11·3%). 1 G. of the unsublimed material was dissolved in sulphuric acid and precipitated in the usual manner. After having been washed with boiling water and alcohol, 1·02 g. of a dull green solid were obtained which turned blue and yielded sodium sulphate when boiled with sodium hydroxide solution. When a similar product was washed with dilute aqueous ammonia, boiling water, and alcohol, blue, substantially pure zinc phthalocyanine (0·87 g.) was obtained (Found : C, 65·8; H, 2·8; Zn, 11·4%).

A mixture of 10 g. of phthalonitrile and 2·7 g. of fused zinc chloride gave a purple-red melt at 150—210°, which turned blue at 240° and soon set to a solid, some hydrogen chloride being evolved. After 20 minutes at 260—270°, the mass was cooled, ground, and washed with alcohol (in which the pigment was slightly soluble). Yield, 9·75 g. (Found : Cl, 9·2. $C_{32}H_{15}N_8ClZn,HCl$ requires Cl, 10·9%). 2·5 G. of this product were dissolved in sulphuric acid (hydrogen chloride was evolved). The green solid precipitated by dilution was washed with alkali and water and dried. 2·08 G. of blue *zinc chlorophthalocyanine* were obtained, which could be crystallised from chloronaphthalene but not sublimed (Found : Cl, 4·6. $C_{32}H_{15}N_8ClZn$ requires Cl, 5·8%). Both this substance and zinc phthalocyanine were slightly soluble in ether.

5 s

Cadmium.† 10 G. of phthalonitrile and 2·5 g. of cadmium filings yielded a phthalocyanine readily at 290°. After 2 hours, the product was boiled with alcohol, which removed nitrile and a pink impurity, and was freed from excess of cadmium by repeated flotation in alcohol. *Cadmium phthalocyanine* is dull green, with a purple reflex most noticeable when the substance is moist with organic liquids. It is insoluble in all solvents and cannot be sublimed (Found : C, 62·2; H, 2·5; Cd, 17·6. $C_{32}H_{16}N_8Cd$ requires C, 61·6; H, 2·6; Cd, 18·0%). On treatment with sulphuric acid it yields free phthalocyanine (Found : C, 74·5; H, 3·5%).

Nickel. Phthalonitrile yielded a phthalocyanine (not yet examined) when heated with nickel chloride. 30 G. of *o*-cyanobenzamide were heated in a nitrate bath with 6 g. of nickel foil previously etched with hydrochloric acid. After 3 hours at 270°, the mass was semi-solid and no more ammonia was evolved. The product was cooled, freed from excess of metal, ground, freed from phthalimide with warm 20% sodium hydroxide solution (overnight), and washed with water and boiling alcohol. Yield, 6—8 g. of lustrous crystals. Sublimation gave pure *nickel phthalocyanine* in needles with an extremely bright red lustre. The powder is dull greenish-blue (Found : C, 67·3 *; H, 3·0 *; N, 19·6 *; Ni, 10·5, 10·5. $C_{32}H_{16}N_8Ni$ requires C, 67·3; H, 2·8; N, 19·6; Ni, 10·3%). The unsublimed material passed substantially unchanged through sulphuric acid (Recovery, 92%. Found : C, 66·7; H, 3·0; Ni, 9·5%). [For the determination of nickel, the compound (0·15 g.) was destroyed by the action of 1 c.c. each of concentrated nitric and sulphuric acids; the solution was diluted, nearly neutralised with sodium hydroxide, and the nickel estimated with ammoniacal dimethylglyoxime in the usual way.]

Cobalt. 10 G. of phthalonitrile and 3 g. of etched massive cobalt were refluxed for 4 hours. The product was cooled, freed from metal, boiled with alcohol, and dried (30% yield). *Cobalt phthalocyanine* was unusually soluble in quinoline and chloronaphthalene, giving green-blue solutions, and crystallised readily from pyridine in blue micro-crystals containing combined pyridine, which were washed with ether and dried at 100° (Found : C, 67·1; H, 2·8; N, 18·8; Co, 10·4. $C_{32}H_{16}N_8Co$ requires C, 67·3; H, 2·8; N, 19·6; Co, 10·3%). This sublimed to beautiful blue needles with a reddish-purple lustre (Found : C, 66·7; H, 2·7%). It gave a dark green solution in sulphuric acid, from which it was precipitated unchanged by dilution (Recovery, 70%. Found : C, 66·9; H, 2·8; N, 19·9%). Material which had been treated with sulphuric acid was oxidised quantitatively with ceric sulphate, 1 g.-mol. requiring 1·50, 1·49 g.-atoms of oxygen. Oxidation with boiling nitric acid yielded phthalimide, m. p. 230°.

The same product was obtained from *o*-cyanobenzamide and etched cobalt metal, but the reaction between phthalonitrile and tricobalt tetroxide appeared less satisfactory.

10·2 G. of phthalonitrile were heated to 200° with 2·6 g. of anhydrous cobalt chloride. Pigment was at once formed, the temperature rose rapidly to 250°, and hydrogen chloride was evolved. When the melt had solidified, it was cooled, broken up, and boiled with alcohol. Yield, 85% of a blue powder with a purple lustre, giving green-blue solutions in quinoline and chloronaphthalene and a deep blue solution in pyridine. 3 G. were extracted during 6 hours with 80 c.c. of chloronaphthalene. The solution deposited *cobalt chlorophthalocyanine* (2 g.) in long blue needles with a purple lustre (Found : C, 63·2; H, 2·2; Cl, 6·1. $C_{32}H_{15}N_8ClCo$ requires C, 63·4; H, 2·5; Cl, 5·9%). Crystallisation from pyridine gave a solvated product. Oxidation of the pure compound with boiling nitric acid gave a mixture of imides containing chlorine and melting indefinitely at 200—210°. The mother-liquor gave no reaction for chloride. (Analyses for cobalt were carried out by ashing with nitric acid, then with sulphuric acid, heating to dull redness, and weighing as $CoSO_4$.)

Lead. 10 G. of pure litharge were added in small portions to 20 g. of phthalonitrile at 200°. The mixture frothed and heat was evolved after each addition so that it was advisable to remove the mixture from the heating bath in the early stages. After the addition, heating was continued for 10 minutes and the hard mass was cooled, ground, and washed thoroughly with alcohol. Yield, 29 g. containing about 2 g. of litharge. *Lead phthalocyanine* could be purified by crystallisation from quinoline (Found : C, 53·3; H, 2·2; Pb, 29·2%) or by sublimation, which gave a green vapour. The crystals were fragmented parallelepipeds, pure green by transmitted light; the lustre was dark red and not so evident as that of other metallic phthalocyanines (Found : C, 53·4; H, 2·2; N, 15·9; Pb, 28·5. $C_{32}H_{16}N_8Pb$ requires C, 53·4; H, 2·2; N, 15·6; Pb, 28·8%). (The lead was determined by decomposing the compound with nitric and sulphuric acids and weighing as lead sulphate or by direct ashing with sulphuric acid.)

---

† Cadmium and vanadyl phthalocyanines have also been prepared by Dr. J. S. H. Davies of Imperial Chemical Industries, Ltd. (private communication).

Treatment of lead phthalocyanine with concentrated sulphuric acid in the usual way gave a mixture of phthalocyanine and lead sulphate, from which most of the sulphate could be removed with ammonium acetate solution. Extraction of the mixture with chloronaphthalene gave pure phthalocyanine in 65% overall yield (Found : C, 74·7; H, 3·6. Calc. : C, 74·7; H, 3·5%). When heated strongly, the mixture regenerated lead phthalocyanine, which sublimed together with a little of the metal-free compound. Crystals of both types could be detected in the sublimate, which contained 22·7% of lead. Crystalline lead phthalocyanine (20 g.) was not apparently affected by concentrated hydrochloric acid, but the addition of an equal volume of water caused the crystals to turn blue immediately without altering in form. The elimination of metal was completed by warming, 14 g. of phthalocyanine being obtained after removal of lead chloride with boiling water.

Treatment of lead phthalocyanine at room temperature for a minute with dilute nitric acid (1 : 1) gave a blue product, from which only free phthalocyanine could be obtained by sublimation. A 25% yield of phthalocyanine could be obtained by successive treatments of the lead compound, contained in a Gooch crucible, with a little concentrated nitric acid, the acid being drawn rapidly by means of a pump into a large volume of water. The nitric acid solution was purple; the precipitate obtained on dilution was first purple, but rapidly changed to the blue of phthalocyanine. When moist nitrogen peroxide was passed over lead phthalocyanine, a similar purple product was formed which subsequently changed to blue. We hope to examine these intermediate products further.

Aluminium. No metallic phthalocyanine was formed by the action of aluminium on phthalocyanine in boiling quinoline.

A mixture of 20 g. (4·8 mols.) of phthalonitrile and 5 g. (1 mol.) of crushed aluminium chloride was heated slowly in a bath to 250°; a sudden reaction then occurred. The internal temperature rose to 300° and the melt solidified and evolved hydrogen chloride. (In a controlled experiment this was led by a current of nitrogen into silver nitrate and was found to be equivalent to 0·8 g.-atom of chlorine per g.-mol. of phthalocyanine formed.) The product was cooled, ground, and washed with benzene. Yield, 20·3 g. 8 G. were crystallised from 400 c.c. of chloronaphthalene, which deposited 5·0 g. of *chloroaluminium chlorophthalocyanine* as a hygroscopic blue powder. Samples once and twice crystallised severally and dried at 115° were analysed [Found : (i) C, 59·4; H, 2·9; N, 17·4; Al, 4·4. (ii) C, 59·7; H, 2·9; N, 17·3. $C_{32}H_{15}N_8Cl\cdot AlCl,2H_2O$ requires C, 59·6; H, 2·9; N, 17·4; Al, 4·2%]. The total chlorine was determined by the Liebig lime method; the " labile " (non-nuclear) chlorine by oxidation with ceric sulphate, filtration of the imides and estimation of the chloride in the filtrate gravimetrically (Found : total Cl, 11·5; labile Cl, 5·7, 6·1. Calc., 11·0 and 5·5% respectively). Oxidation with nitric and sulphuric acids gave a mixture of phthalimide and a chlorophthalimide, m. p. about 205°, and chloride ion.

Chloroaluminium chlorophthalocyanine was soluble in absolute alcohol (1·6% at room temperature) and also in pyridine, chloronaphthalene, nitrobenzene, acetone and methyl alcohol, but was insoluble in amyl alcohol, ethyl acetate, chlorobenzene and hydrocarbons. Sublimation gave hard blue octahedra in poor yield. These contain labile chlorine, but the composition is uncertain. The dihydrate (above) took up one additional molecule of water from moist air at room temeprature, and lost this at 115° (Found : gain in weight, 2·3. Calc., 2·55%). A sample dried at 260° took up 8·2% of water from moist air ($3H_2O$ requires 8·15%) and lost 3·1% (calc., 2·55%) of this at 115°; it then gave the analytical figures required for the dihydrate. The dihydrate *gained* in weight in a calcium chloride desiccator.

An alcoholic solution of the compound gave a precipitate only after 5 hours with alcoholic silver nitrate, but addition of ammonia or alkali removed the labile chlorine and the corresponding hydroxo-compound was precipitated in a finely divided state. This substance was best prepared as follows : 5 G. of the chloro-compound were dissolved in sulphuric acid in the usual way, hydrogen chloride being evolved. Dilution gave a blue-green precipitate (3·8 g.) which contained sulphuric acid. Treatment of this suspension with an excess of aqueous ammonia yielded *hydroxoaluminium chlorophthalocyanine* (3·1 g.). When sodium hydroxide was used, the product contained sodium (Found : Na, 2·1%) removable with difficulty. The hydroxo-compound is blue, insoluble in the usual solvents and in hot concentrated alkali solution, and contains no labile chlorine (Found : C, 64·4; H, 2·7; N, 18·5, 18·6; Al, 4·7. $C_{32}H_{15}N_8Cl\cdot AlOH$ requires C, 65·0; H, 2·7; N, 19·0; Al, 4·5%).

Chloroaluminium phthalocyanine. 20 G. of phthalocyanine were boiled with 40 g. of aluminium chloride in 150 c.c. of quinoline for 20 minutes. The original greenish-blue colour rapidly changed to a pure blue. An equal bulk of alcohol was then added, the solution was

boiled and filtered, and the residue washed thoroughly with alcohol. The product, which contained alumina, was extracted in four 11-g. batches with the same 150 c.c. of boiling chloro-naphthalene. It was comparatively soluble, each extraction requiring only about $2\frac{1}{2}$ hours. Combined yield, 17·6 g. of blue octahedra (Found : C, 66·3; H, 2·8; N, 19·0; Al, 5·1%). From 12·6 g. of this, 120 c.c. of boiling chloronaphthalene extracted 11·2 g. of analytically pure material in 4 hours (Found : C, 67·2; H, 2·8; Al, 5·0; Cl, 5·9. $C_{32}H_{16}N_8AlCl$ requires C, 66·9; H, 2·6; N, 19·5; Al, 4·7; Cl. 6·2%). This compound showed no tendency to hydrate in moist air.

On treatment with sulphuric acid, hydrogen chloride was evolved, and dilution yielded a bluish-green precipitate. This was filtered off, neutralised with excess of aqueous ammonia, again filtered, washed with boiling alcohol, and dried at 100°. Sintered-glass funnels were essential for these filtrations. *Hydroxoaluminium phthalocyanine* (*monohydrate*) resembled the corresponding compound containing nuclear chlorine. It was blue, and insoluble in the usual solvents (Found : C, 66·7, 67·2; H, 3·3, 3·3; N, 19·5, 19·6; Al, 5·1, 4·8. $C_{32}H_{16}N_8 \cdot AlOH,H_2O$ requires C, 66·8; H, 3·3; N, 19·5; Al, 4·7%). It was free from chlorine. Sodium hydroxide was taken up immediately from $N/10$-solution, but not in an equivalent amount. In moist air the monohydrate took up a further two molecules of water (Found : gain in weight, 6·1. Calc., 5·9%), which were lost at 100°.

Strong heating of the monohydrate led to the sublimation of *aluminium phthalocyanine oxide* as a blue vapour depositing needles of the usual type. This showed no tendency to combine with water (Found : C, 70·25, 70·05; H, 2·6, 2·8; N, 20·4 *; Al, 4·7. $C_{64}H_{32}ON_{16}Al_2$ requires C, 70·2; H, 2·9; N, 20·5; Al, 4·9%).

The ash left in the boat after the combustion of all the compounds of this group approximates in composition to AlO·OH or Al_2O_3,H_2O (compare the mineral diaspore) and the figures for aluminium given above are calculated on this basis. Thus, four combustions of hydroxo-aluminium chlorophthalocyanine (Calc.: Al, 4·5%) gave ashes equivalent to Al, 5·5, 5·5, 5·6 and 5·9% if the ash were taken as Al_2O_3; or to Al, 4·7, 4·7, 4·7, 5·0% if the ash were AlO·OH. Three combustions of aluminium phthalocyanine oxide (Calc.: Al, 4·9%) gave ashes equivalent to 5·6, 5·6, 5·7 (if Al_2O_3) or 4·7, 4·8, 4·9 (if AlO·OH). The ash from each of the latter was treated with nitric acid, ignited in air, and again weighed. Each then gave a value of Al, 4·9% (ash as Al_2O_3), corresponding to the conversion of the oxide into the anhydrous form. Neither of the chloroaluminium phthalocyanines gave satisfactory figures on quantitative oxidation with ceric sulphate.

Tin. A mixture of phthalonitrile (10 g.) and tin (4 g.) was heated at 300° for 3 hours, with mechanical stirring to keep the molten metal in contact with the nitrile. Little phthalo-cyanine was formed in the first 90 minutes, but the mass then rapidly thickened. The product was cooled, separated from the excess of metal, and exhaustively extracted with alcohol (Soxhlet), a 70% yield of dark blue powder being left. Extraction of this with boiling quinoline first removed a dark impurity, and then *stannous phthalocyanine* was rapidly extracted. It crystallised in dark blue micro-parallelepipeds with a dark violet lustre (Found : C, 60·8; H, 2·5; N, 18·1; Sn, 18·6. $C_{32}H_{16}N_8Sn$ requires C, 60·9; H, 2·5; N, 17·8; Sn, 18·8%). (Tin was estimated by ashing the compound with a drop of concentrated nitric acid, followed by ignition and weighing as stannic oxide.) The dull blue rubbing of this substance changed to bright green when exposed to nitrogen dioxide vapour. Vacuum sublimation gave a deep blue vapour, but only a skin of solid was formed and none of the usual monoclinic needles.

The brown solution of 3 g. of stannous phthalocyanine in 50 c.c. of concentrated sulphuric acid was filtered on to 300 g. of pure crushed ice. A green precipitate was formed which turned blue on the addition of alkali. After 3 hours it was filtered off, washed free from acid, and dried. Recovery, 1·0 g. containing 8·5% of tin. When a solution of the tin compound in sulphuric acid was kept for 4 days before dilution, the elimination of metal was practically complete but the yield of free phthalocyanine (ash, 0·4%) was small.

A mixture of 10 g. of phthalonitrile and 5 g. of powdered anhydrous stannous chloride was heated to 210°. The melt turned green and a violent exothermic reaction occurred, the rise in temperature being 100°; no hydrogen chloride was evolved. The product was cooled, ground, and exhaustively extracted with alcohol. Yield, 90% of a green powder with a fine purple lustre. 3 G. were extracted with boiling quinoline (80 c.c.). The dark earlier extracts were rejected; the pure green solution subsequently obtained deposited *dichlorotin phthalocyanine* (1 g.) as bluish-green plates with a faint purple lustre (Found : C, 54·9; H, 2·2; N, 16·0; labile Cl, 9·9; Sn, 16·5. $C_{32}H_{16}N_8Cl_2Sn$ requires C, 54·8; H, 2·3; N, 15·9; Cl, 10·0; Sn, 16·9%). [Labile chlorine was estimated as follows : a known weight (about 0·2 g.) of the finely powdered

pigment was boiled under reflux in an all-glass apparatus for 24 hours with a solution of 3 g. of potassium hydroxide (chlorine-free) in 50 c.c. of distilled water. The liquid was diluted, the residual pigment filtered off (52 Whatman paper), and the filtrate acidified with nitric acid. After a trace of silica had been filtered off, the chlorine was estimated gravimetrically.] Dichlorotin phthalocyanine dissolved with decomposition in warm concentrated nitric acid; the solution deposited phthalimide (m. p. 230°) and the filtrate contained chlorine ions. The compound dissolved in concentrated sulphuric acid with evolution of hydrogen chloride. A green precipitate was formed on dilution which was turned blue by alkali, the metal being partly eliminated (Found : Sn, 12·0%).

Phthalonitrile reacted readily with stannous iodide at 210°, the temperature rising to 270° and some iodine being evolved. The green product, after extraction with alcohol, appeared to be a mixture of stannous and *di-iodotin phthalocyanine* (Found : I, 25·3. $C_{32}H_{16}N_8I_2Sn$ requires I, 29·0%). This substance lost iodine when boiled with chloronaphthalene or when heated alone.

Dichlorotin phthalocyanine (4 g.) was refluxed for 24 hours with 20 g. of potassium hydroxide in 100 c.c. of water. The product was filtered off, washed free from alkali, and dried. Yield, 3·4 g. of a lustreless blue powder, free from chlorine, mainly the *potassium* salt of *dihydroxotin phthalocyanine* (Found : C, 51·5; H, 2·4; K, 8·5. $C_{32}H_{16}O_2N_8K_2Sn$ requires C, 51·7; H, 2·2; K, 10·8%). When this was boiled with dilute sulphuric acid, it formed a green sulphate, presumably impure $PcSnSO_4$ (Found : SO_4'', 9·6. Calc., 13·2%).

Dihydroxotin phthalocyanine could not be obtained in a pure condition. When the dichloro-compound was heated under pressure with aqueous ammonia (*d* 0·88), a dark powder was formed which, when boiled with quinoline, yielded stannic oxide, and free phthalocyanine. Attempts to reduce the dichloro-compound in alkaline media led to the following colour changes : (i) Benzyl alcohol + sodium, faint pink changing to green, stannic oxide deposited. (ii) Ethyl alcohol + sodium, transitory pink changing to bright blue, decolorised by air; stannic oxide deposited, acidification of the filtrate gave phthalic acid (extracted with ether and identified as the anhydride). (iii) Sodium ethoxide and alcoholic potassium hydroxide behaved similarly. Stannous phthalocyanine gave a similar colour change with alcoholic potassium hydroxide, but the pink (magenta) intermediate stage was more clearly marked.

A current of hydrogen was passed for 48 hours through a boiling solution of dichlorotin phthalocyanine (2 g.) in quinoline. The cooled solution deposited stannous phthalocyanine as a crystalline powder with a violet lustre (Found : C, 60·5; H, 2·3%). When hydrogen was passed over the dichloro-compound heated cautiously by means of a free flame, hydrogen chloride was evolved but the residue was partly charred.

Chlorine, dried by means of sulphuric acid and phosphoric oxide, was passed intermittently over a weighed quantity of stannous phthalocyanine. After 3 days the gain in weight was 12·7% (calc. for 2Cl, 11·1%) and the dark crystals had changed to an amorphous green powder. This crystallised from quinoline, in which it was moderately easily soluble, in green plates with a faint lustre (Found : C, 52·8; H, 2·2; labile Cl, 9·7. $C_{32}H_{15}N_8Cl\cdot SnCl_2$ requires C, 52·2; H, 2·0; labile Cl, 9·7%). The analysed compound is therefore essentially *dichlorotin chloro-phthalocyanine*, but the gain in weight indicates that the uncrystallised product must have contained some less chlorinated material. Fission of the crystallised product yielded an imide, m. p. 217°, containing chlorine.

Stannic phthalocyanine. 0·5 G. of dichlorotin phthalocyanine and 0·4 g. of disodium phthalocyanine were refluxed in chloronaphthalene for 90 minutes. The colour changed rapidly to a strong dark blue. The solution was kept overnight and filtered. The insoluble portion (discoloured salt) was extracted with water, and yielded 0·19 g. of silver chloride (91%). The chloronaphthalene solution after 5 days' standing deposited a blue crystalline solid, which contained solvent of crystallisation. Extraction for 4 days with boiling benzene removed this and left *stannic phthalocyanine* as greenish-blue crystals (Found : C, 67·7; H, 2·9; N, 19·5; Sn, 10·5. $C_{64}H_{32}N_{16}Sn$ requires C, 67·2; H, 2·8; N, 19·6; Sn, 10·35%). This compound sublimes substantially unchanged to give a microcrystalline deposit. It is sufficiently soluble in benzene, xylene and pyridine to give a blue colour in the cold, but it is insoluble in ether, alcohol, acetone, ethyl acetate and light petroleum. Unlike the stannous compound, stannic phthalocyanine gives a normal purple colour with nitrogen dioxide.

A mixture of 5 g. of powdered phthalocyanine, 3 g. of anhydrous stannous chloride, and 50 c.c. of quinoline were refluxed for 12 hours. The cooled solution deposited a solid, which was filtered off and washed with hot alcohol, 3·5 g. of plates with a blue-green lustre being obtained (Found : C, 56·0; H, 2·4; Sn, 18·2%). This contained chlorine. It was boiled for

15 minutes with diluted aqueous ammonia, the appearance being unchanged [Found : C, 57·8; H, 2·5; Cl (total) 5·8%]. Crystallisation from quinoline (blue solution) gave small cubes with a reddish lustre (Found : C, 58·0; H, 2·5. $C_{32}H_{16}N_8Sn,HCl$ requires C, 57·5; H, 2·6; Cl, 5·3; Sn, 17·8%). Analysis suggests that this is *stannous phthalocyanine hydrochloride* or *stannous chlorophthalocyanine*. The former constitution is favoured by the method of preparation, the latter by the stability of the halogen.

Free phthalocyanine did not react with boiling stannic chloride (12 hours) and reaction was incomplete after 5 hours at 300°, the product being blue, turned purple by nitrogen dioxide. 5 G. of phthalocyanine were heated for 12 hours at 300° with 5 c.c. of stannic chloride and 5 c.c. of chloronaphthalene. Considerable pressure (hydrogen chloride) was developed in the tube. The green product was washed thoroughly with carbon tetrachloride and ether; crystallisation from quinoline then yielded pure dichlorotin phthalocyanine (Found : C, 55·0; H, 2·4; total Cl, 9·6%). The reaction between phthalocyanine and stannic chloride also appeared to be complete after 24 hours at 300° in the absence of a solvent, for the product was pure green and was not turned purple by nitrogen dioxide.

Phthalonitrile (10 g.) was heated at 300° for 12 hours with 5 c.c. of stannic chloride. The product was partly crystalline but contained a brown impurity, removed by 5 days' extraction with boiling alcohol. The residue was crystallised from quinoline (green solution), which yielded *dichlorotin chlorophthalocyanine* as green crystals with a purple lustre (Found : C, 52·6; H, 2·1; labile Cl, 9·9; total Cl, 14·7. $C_{32}H_{15}N_8Cl·SnCl_2$ requires C, 52·2; H, 2·0; labile Cl, 9·7; total Cl, 14·4%).

Experiments with Dimethyltin Dihalides.—The method of Cahours (*loc. cit.*) for the preparation of dimethyltin di-iodide was modified as follows : tin foil (18 g.) was heated with methyl iodide (20 c.c.) at 160° in a sealed tube for 12 hours; the metal had then almost all dissolved and a brown liquid and some needle crystals remained. The product distilled as a pale yellow liquid at 150°/8 mm. The distillation was stopped when a darker brown material began to pass over. The distillate solidified rapidly and, after 3 hours out of contact with air, was dried by means of the pump and on a porous tile. Yield, 40 g. of white crystalline solid, m. p. 42°, crude; 43°, after crystallisation from light petroleum. The mixture of alcohol and ether used by Cahours for crystallisation leads to darkening.

The dimethylstannic oxide, obtained from 10 g. of the iodide by treatment with sufficient aqueous ammonia, was suspended in 25 c.c. of alcohol and a current of hydrogen chloride was passed until solution was complete. Evaporation left 5 g. of dimethyltin dichloride as white needles, m. p. 107°, identical with material prepared in poor yield by the method of Pfeiffer and Lehnardt (*Ber.*, 1903, **36**, 3027) and Pope and Peachey (*Proc. Roy. Soc.*, 1903, **72**, 7). The m. p.'s of both the dimethyltin dihalides agree with those given by Pfeiffer (*Z. anorg. Chem.*, 1910, **68**, 112), Cahours's values being low.

A mixture of 10 g. of phthalocyanine, 4 g. of dimethyltin dichloride and 10 c.c. of chloronaphthalene was heated for 12 hours at 300°. The finely crystalline product (11 g.), after having been washed with ether, consisted of cubes with a steely-blue lustre and a small amount of material with a purple lustre. The cubes were separated by hand-picking and after being washed with boiling alcohol and benzene yielded dichlorotin phthalocyanine, the lustre changing to purple. The rubbing was green (Found : C, 55·4; H, 2·2; labile Cl, 10·0%).

Phthalonitrile (5 g.) reacted rapidly with dimethyltin di-iodide (2 g.) at 220°, but the product appeared to be badly charred. A little methyl iodide but no iodine or ethane was evolved.

Platinum. A mixture of 1·8 g. of platinous chloride and 20 g. of phthalonitrile was heated to 280° during 20 minutes. Pigment was first formed at about 180° and the melt began to solidify at 230°; some hydrogen chloride was then evolved. The cooled product was ground and thoroughly washed with alcohol. The recovered phthalonitrile was free from chlorine. Yield of residue, 4·2 g., which gave 2·75 g. of crystalline *platinous phthalocyanine*, blue needles with a bronze lustre from chloronaphthalene. It sublimed readily in small needles [Found : (for crystallised material) C, 54·7; H, 2·5; N, 15·9; Pt, 27·0; (for sublimed) C, 54·4; H, 2·3. $C_{32}H_{16}N_8Pt$ requires C, 54·3; H, 2·2; N, 15·8; Pt, 27·6%]. No chlorine could be detected. Great care was necessary in ashing this compound owing to the ease with which it sublimed. Platinum phthalocyanine is the most resistant member of the group towards oxidation, being comparatively stable to cold nitric acid.

Phthalocyanine failed to react with reduced platinum during 28 hours in boiling quinoline, or with platinous chloride during 6 hours in boiling quinoline. Neither did it react when heated with platinous chloride alone at various temperatures from 300° to 500°. Phthalonitrile reacted with platinous hydroxide (19 hours, 340°) to give a 35% yield of free phthalocyanine (Found :

C, 74·6; H, 3·4; N, 22·0.   Calc.: C, 74·7; H, 3·5; N, 21·8%).   Heating of 3 g. of phthalo-nitrile with 0·25 g. of platinum (prepared by ignition of the oxide) for 45 hours at 360° produced some charring and a 79% yield of crystalline phthalocyanine (after extraction with boiling acetic acid).   After sublimation, this was ash-free.

Iron. Ferrous phthalocyanine was best prepared from *o*-cyanobenzamide, the reaction between phthalonitrile and iron being slow.   20 G. of the cyano-amide were heated at 250° for 6 hours with 4 g. of a pure iron wire, previously etched.   The cooled product was freed from phthalimide with concentrated sodium hydroxide solution, the excess of wire removed, and the product filtered off and washed with water and alcohol.   Yield, 2·2 g. of lustrous crystals. Crystallisation from quinoline or aniline gave additive compounds, but sublimation gave long needles of the pure ferrous derivative.   Both the colour (blue-green) and the lustre are duller than those of the nickel compound (Found: C, 67·4; H, 2·8; N, 19·8. $C_{32}H_{16}N_8Fe$ requires C, 67·6; H, 2·8; N, 19·7; Fe, 9·8%).   The same substance was obtained by subliming the product first crystallised from quinoline, solvent of crystallisation being liberated.   The sublimed compound was oxidised by ceric sulphate in the manner already described (J., 1934, 1038).   0·1040, 0·1281 G. required 10·75, 13·31 c.c. of $N/20 \times 1·002$-ceric sulphate; whence Fe = 9·7, 9·7% on the basis of the equation

$$2(C_8H_4N_2)_4Fe + 16H_2O + 3O = 8C_8H_5O_2N + Fe_2O_3 + 8NH_3$$
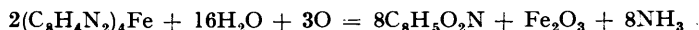
Ferric chloride (A.R., anhydrous) reacted readily with phthalonitrile at 210°, hydrogen chloride being evolved and a good yield of a dark green pigment formed.   Although this could be crystallised from chloronaphthalene, no homogeneous product could be isolated and the analytical figures were low for $C_{32}H_{15}N_8Cl \cdot FeCl$.   It could not be sublimed.   Ferric chloride reacted rapidly with phthalocyanine in boiling quinoline.   Analysis indicated that the product was a mixture of ferrous phthalocyanine and chloroferric phthalocyanine.   It was non-homogeneous under the microscope (Found: C, 65·1; H, 2·8; N, 18·1; Cl, 2·4; Fe, 8·9.   A mixture of 50% FePc and 50% FePcCl requires C, 65·6; H, 2·7; N, 19·1; Cl, 2·9; Fe, 9·5%). The chlorine was labile to alkali.   Sublimation of the mixture gave a good yield of ferrous phthalocyanine free from chlorine (Found: C, 66·7; H, 2·7; Fe, 9·6%).

Manganese.   (i) 30 G. of phthalonitrile and 6 g. of manganese dioxide were heated for 6 hours at 270°.   The black amorphous product was ground and washed with benzene (24·3 g.). Extraction of 9·2 g. in small quantities with 110 c.c. of chloronaphthalene gave a deep brown solution, which deposited 5·3 g. of amorphous black solid.   (ii) Manganese metal reacted more readily with *o*-cyanobenzamide than with phthalonitrile.   30 G. of the cyano-amide and 8 g. of metallic manganese were heated for 5 hours at 270°.   The product was ground and washed with sodium hydroxide solution and alcohol, leaving 18·5 g. of a black solid.   Extraction of 10·9 g. with 110 c.c. of chloronaphthalene during 9 hours yielded 4·9 g. of crystalline solid.

The constitution of these products is uncertain.   Both gave on sublimation a greenish-black vapour depositing a poor yield of *manganous phthalocyanine* in fine lustrous black needles giving a greenish-black powder (Found: C, 67·2; H, 2·8; N, 19·9. $C_{32}H_{16}N_8Mn$ requires C, 67·7; H, 2·8; N, 19·7; Mn, 9·7%).   If the ash left in the combustion boat be taken as Mn_3O_4, the manganese content was 9·7%.   Both crude products and the pure manganous compound gave free phthalocyanine on treatment with sulphuric acid, but the yield was comparatively low (25—40%), apparently owing to fission.   The free phthalocyanine gave the usual beautiful product on sublimation [Found: C, 74·4; H, 3·5; N, 22·2; (ash, 0·2).   Calc.: C, 74·7; H, 3·5; N, 21·8%].

Chromium.   No chromium phthalocyanine was formed in the following experiments: phthalocyanine heated in boiling chloronaphthalene with metallic chromium, chromium sesquioxide, phosphate, chromous acetate or with hydrated chromous or chromic chloride; phthalocyanine heated in boiling quinoline with chromous acetate or anhydrous chromic chloride; phthalocyanine sublimed with a mixture with chromium metal, chromium sesquioxide, and chromous acetate.

Anhydrous chromic chloride, prepared by passing chlorine over the finely divided metal at red heat, was converted into chromous chloride by heating in a stream of dry hydrogen until the product was greyish-white and no more hydrogen chloride was evolved.   The material was used as soon as possible, as it deliquesced and was oxidised in air.

3 G. of phthalocyanine and 1 g. of chromous chloride were heated in 20 c.c. of boiling quinoline for ½ hour; the liquid was then green.   After standing overnight, the solid was filtered off, washed with alcohol (yield, 3·8 g.), and extracted with 120 c.c. of chloronaphthalene.   The material extracted in the first 3 hours contained unchanged phthalocyanine and was rejected.

A further 38 hours' extraction removed only 1·55 g. of crystalline material, which corresponded approximately to $C_{32}H_{15}N_8ClCr$. The structure of this is uncertain. It dissolved in sulphuric acid with evolution of hydrogen chloride. Dilution gave a dull green solid, which after neutralisation with aqueous ammonia contained chromium but no sulphur or chlorine, and behaved on analysis approximately as a dihydrate or a hydroxy-monohydrate of chromium phthalocyanine.

o-Cyanobenzamide reacted readily with anhydrous chromous or chromic chloride at 260—270° to give dull green compounds not yet investigated.

Vanadium. A mixture of 2 g. of vanadium pentoxide and 10 g. of phthalonitrile was kept at 240—250° for 30 minutes and then cooled, powdered, and boiled with alcohol (yield, 6 g.). Two successive extractions and crystallisations, chloronaphthalene being used, gave *vanadyl phthalocyanine* as a microcrystalline, blue, lustreless powder (Found : C, 66·6; H, 2·8; N, 19·6; V, 8·5. $C_{32}H_{16}ON_8V$ requires C, 66·4; H, 2·8; N, 19·4; V, 8·8%). The crude product yielded the same substance on sublimation, cubical masses of crystals being deposited from a deep blue vapour (Found : C, 66·1 *; H, 2·6 *; N, 19·6; V, 9·0%). Vanadyl phthalocyanine gave an orange-brown solution in concentrated sulphuric acid, from which it was precipitated unchanged on dilution (Found : V, 9·2%).

Boron, Silicon. 10 G. of disodium phthalocyanine were heated in a pressure tube with 5 g. of boron trichloride. The product, after being washed with carbon tetrachloride, was a bright green powder and was presumably an additive compound, as after 5 minutes in the air of the laboratory or 2 hours in a vacuum desiccator it had changed in colour to a dull blue. Crystallisation of the green product from quinoline gave free phthalocyanine (Found : C, 74·7; H, 3·3%). Elementary boron failed to react with phthalonitrile at 300°. Phthalocyanine did not react with silicon tetrachloride at 300° (Found : C, 74·4; H, 3·7% in recovered material).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.