136. *An X-Ray Study of the Structure of the Phthalocyanines. Part I.*
The Metal-free, Nickel, Copper, and Platinum Compounds.

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THE phthalocyanines, recently described by Linstead and his collaborators (J., 1934, 1016),
form a series of beautifully crystalline compounds which are remarkable for their great
stability, the copper derivative subliming unchanged at 580°. Phthalocyanine itself,
containing only carbon, hydrogen, and nitrogen, is hardly less stable. Further interest
attaches to these compounds, as Linstead has pointed out, on account of their value as
pigments, their structural relationship with the natural porphyrins, and finally, in con-
nexion with the stereochemistry of the metals with which they combine. X-Ray analysis
is undoubtedly the most powerful method for dealing quantitatively with the last aspect.

Owing to the great size and complexity of the molecules, it has not yet been possible to
locate all the individual atoms in the crystal unit. Such a task would require the precise
measurement of many hundreds of reflexions and involve the determination of 60 para-
meters for the carbon and nitrogen atoms alone. By a fortunate circumstance, however,
the crystal structures of the parent phthalocyanine and many of the metallic derivatives
are dimensionally so similar that direct comparisons can be made between the intensities
of corresponding reflecting planes in the different compounds. By this means the main
outlines of these structures are already clear. It is best, therefore, to commence by making
a comparative study of the various compounds. The way is then cleared for complete
structure determinations by quantitative intensity measurements.

Crystal Data.—The writer is greatly indebted to Dr. Linstead and Dr. Dent for supplying
well-formed crystals of phthalocyanine and its copper, nickel, and platinum derivatives.
By low-pressure sublimation in a current of carbon dioxide at temperatures above 500°,
these were obtained as long needles or laths. The crystals are all monoclinic, the needle
axis corresponding with the b axis in the following description. The cross section was
usually small, especially in the platinum compound, but in the other three compounds fine
laths were obtained, measuring 0·1 by 0·3 or 0·4 mm., and sometimes 1 cm. or more in
length, which were very suitable for the X-ray work. No definite end faces were observed,
the growth of the crystal being generally terminated by fracture across the lath. In the
metal-free compound the $(20\bar{1})$ and the (001) face were developed, the latter being especially
prominent. Apart from the somewhat phenomenal elongation along the b axis, the habit
is very similar to that of many organic crystals, with some tendency to cleavage in the

(001) and (20$\bar{1}$) planes. The most perfect natural faces were observed in copper phthalocyanine, where the (001), (100), (20$\bar{1}$), and (10$\bar{1}$) planes were found, as in Fig. 1. Some specimens of this compound were twinned on (001).

The X-ray work was carried out by means of rotation, oscillation, and moving-film photographs, with copper radiation. The absorption of rays of this wave-length ($\lambda = 1\cdot54$) by the metal compounds is somewhat high, but by employing small specimens (0·005—0·01 mg.) excellent results were obtained. The cell dimensions and other constants are collected in Table I. The linear measurements should be accurate to about 0·5%. The observed halvings of {*h0l*} when *h* is odd and of {010} were obtained from long-exposure moving-film photographs (compare Plate I). Between 100 and 200 {*h0l*} reflexions were observed from each crystal, without yielding any exception to the general halving. To establish the {010} halving, only a few reflexions are available ($d_{010} = 3\cdot81$—4·79 Å.). Prolonged exposures were taken about the *a* and *c* axes, and this halving was established for phthalocyanine and the copper and the nickel compound up to the (050), and for the platinum compound up to the (030). The (020) and (040) reflexions are definite, but weak.

FIG. 1.

Copper phthalocyanine.

FIG. 2.

End view of phthalocyanine molecules.
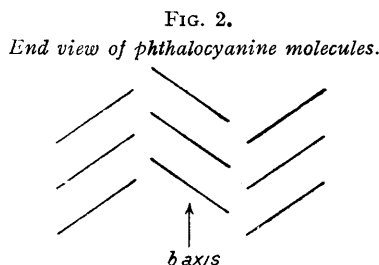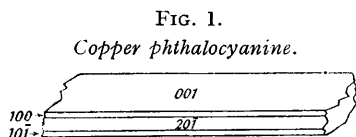
These results definitely establish that the space group is $P2_1/a$ and, consequently, that the molecule has a centre of symmetry. It may be noted that with the above halvings it is not possible to relegate the crystal to a lower symmetry class which does not require the centre of symmetry. Owing to the important deductions concerning the structure which follow from the centro-symmetry, it seemed worth while to make additional tests of the presence or absence of pyro-electric or piezo-electric effects in the crystal. Some well-formed crystals of copper phthalocyanine were selected for the test, measuring about 0·5 by 0·1 mm., and 12 mm. long. Two such crystals were attached to fine silk fibres and immersed in liquid air. No attraction between the crystals was observed while the temperature was thus falling rapidly, or upon removal while the temperature was rising. As a control, two small crystals of resorcinol gave a very large effect, while two small crystals of *s*.-triphenylbenzene, which is weakly polar, gave a smaller but quite definite effect. The negative result for copper phthalocyanine is in conformity with the X-ray evidence.

TABLE I.

	Phthalo-cyanine.	Nickel deriv.	Copper deriv.	Platinum deriv.
a, Å.	19·85	19·9	19·6	23·9
b, Å.	4·72	4·71	4·79	3·81
c, Å.	14·8	14·9	14·6	16·9
β	122·25°	121·9°	120·6°	129·6°
Space group	$C_{2h}^5(P2_1/a)$	$C_{2h}^5(P2_1/a)$	$C_{2h}^5(P2_1/a)$	$C_{2h}^5(P2_1/a)$
Mols. per cell	2	2	2	2
Molecular symmetry	Centre	Centre	Centre	Centre
Vol. of unit cell	1173 Å.³	1186 Å.³	1180 Å.³	1186 Å.³
d (found)	1·44	1·63	1·63	1·98
d (calc.)	1·445	1·59	1·61	1·97
M	514	571	576	707
No. of electrons per unit cell, F (000)	532	584	586	684

General Structural Considerations.—The dimensional similarity of the first three crystals indicates at once that the molecule must consist of a large rigid framework which suffers no appreciable distortion by the entrance of the metal atom. One must assume that in the
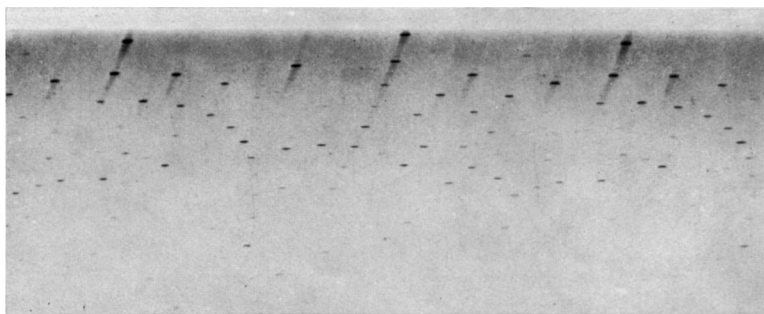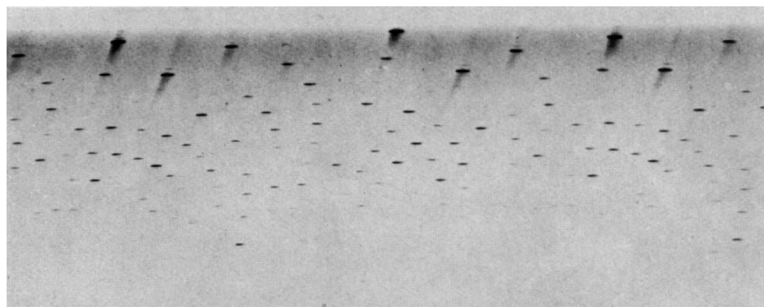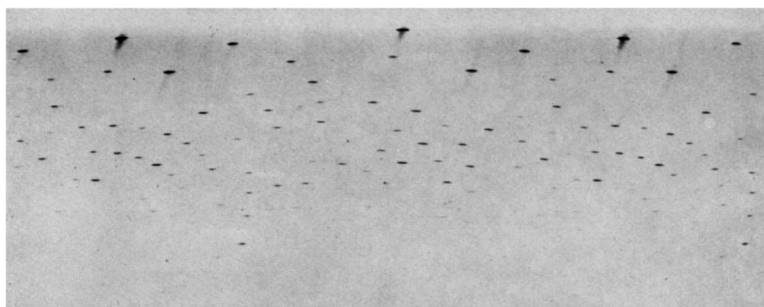
PLATE I.

{20Ī} {200} {001} {20Ž} {20Ī}
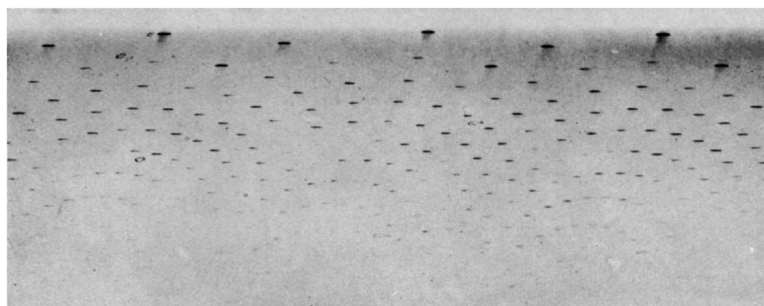

Phthalocyanine {h0l}.

Nickel phthalocyanine {h0l}.

Copper phthalocyanine {h0l}.

Platinum phthalocyanine {h0l}.

metal-free phthalocyanine there exists some cavity, perhaps sparsely occupied by two imino-hydrogen atoms, which can accommodate the various metallic elements. The small alteration in the dimensions of the copper compound, and the more abrupt change in the platinum compound, are more probably accounted for by a change in the *orientation* than by any change in the molecular dimensions. In the platinum compound, for example, the *b* axis decreases in length by 1 Å., but the area of the *ac* face increases in proportion, so the volume of the cell remains constant.

The figures show that one molecule is contained in a space of $\frac{1}{2}abc \sin \beta$ or about $9.9 \times 12.5 \times 4.7$ Å.^{3} for the first three compounds, and of about $12.0 \times 13.0 \times 3.8$ Å.^{3} for the last. This at once points to large, square, and probably flat molecules, well spread out in the *ac* plane. The platinum phthalocyanine molecules are obviously flattened out still more in this plane. Molecules of identical orientation recur at intervals of 4.7 or 3.8 Å. along the *b* axis. Now the minimum distance of approach between aromatic hydrocarbon rings in the solid state is known to be about 3.6—3.7 Å. (Report of International Conference on Physics, 1934, Part II, p. 46), a value which may be taken as a measure of the " thickness " of such molecules. Hence, although the molecules of the first three compounds may be inclined to the *ac* plane at angles up to 35° or 40°, and platinum phthalocyanine at 10—20°, yet there is no possibility of any of these molecules being interleaved by the adjacent (reflected) molecules. When viewed end-on, the molecules are probably arranged in a manner such as is shown in Fig. 2, the lines indicating their mean planes. Thus a projection of the structure along the *b* axis, on the (010) plane, will give a complete picture of the molecule and all its component atoms. The possibility of such a simple projection is rarely encountered in organic crystal structures, for, even in such comparatively simple examples as naphthalene and anthracene, many of the individual atoms are obscured by overlap, either from within the molecule, if it is viewed from a high angle, or from interleaving molecules, if they are more nearly normal to the projection axis.

From the cell dimensions, space group, measured density, and metal content of these compounds, it is possible to calculate the molecular weights to within about 5% (*Nature*, 1935, **135**, 506). The results agree with those required by Linstead's formulæ, (I)—(IV), but it is impossible to determine the number of hydrogen atoms in the molecule by this method. It is, however, clearly established that the unit cell contains two centro-symmetric molecules. An important deduction immediately follows regarding the symmetry of the central group. *The metal atom and the four surrounding* iso*indole nitrogen atoms must all lie strictly in one plane.* For the metal atom, being unique, must coincide with the centre of symmetry. If a straight line be drawn from the centre of one of the nitrogen atoms to the centre of the metal atom and produced an equal distance beyond, it will touch the centre of the opposite nitrogen atom, by the definition of a centre of symmetry. The metal atom and the other two nitrogen atoms must similarly lie on another straight line. Hence it is possible to describe a plane containing these two straight lines and the five atom centres situated on them.

There is as yet no direct experimental evidence from the *X*-ray work that the whole molecule is planar. We may, of course, choose any two pairs of centro-symmetric points, *e.g.*, on the extracyclic nitrogen atoms, or at the centres of the benzene rings, and show that they lie on a plane containing the central metal atom; but these various planes need not coincide.

Linstead has shown (J., 1934, 1037) that the chemical evidence is in favour of formula (I) for phthalocyanine and (III) for the metal derivatives, the metal displacing the two imino-hydrogen atoms and being bound by covalencies to the two *iso*indole nitrogen atoms, and probably co-ordinated to the other two. He also points out that from general stereochemical considerations " the cyclic framework of phthalocyanine (I) should exist in one plane, and the only possibility of deviation lies in the ability of ring A to rotate about the two single links connecting it to the extracyclic nitrogen atoms." We have just seen, however, from the crystal evidence, that any two pairs of centro-symmetrical points and the centre itself are necessarily coplanar. Hence, in the crystal, ring A cannot deviate from the great plane of the molecule. It would seem to follow from the stereochemistry (Linstead, *loc. cit.*) that the two imino-hydrogen atoms in (I) must lie out of the great plane,

S S

giving rise to the possibility of a *cis-* and a *trans-*form.   Only the latter is strictly compatible with the centre of symmetry.
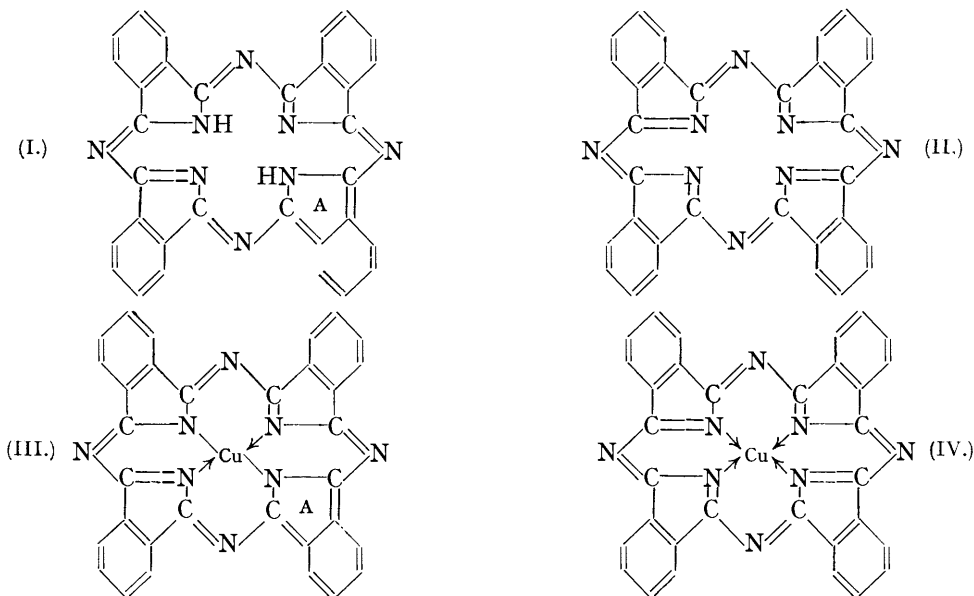
A few difficulties remain with regard to the fine structure.   Formulæ (II) and (IV), which contain no imino-hydrogen and represent the metal atom as bound by four co-ordinate links, are perfectly centro-symmetrical and thus completely satisfy the crystal evidence; but Linstead shows that the chemical evidence and the physical properties of the copper compound are rather definitely in favour of (I) and (III), which necessitate one *o*-quinonoid and three benzenoid rings.   The difficulty of reconciling these formulæ with the centro-symmetry displayed in the crystal is not, however, very great.   The problem is analogous to that encountered in reconciling the ordinary Kekulé formula for benzene to the centro-symmetry displayed by symmetrically substituted benzene derivatives in the crystalline state.   In the phthalocyanine structure we must regard the whole molecule as one continuously conjugated system, so that the *o*-quinonoid ring does not possess a definite location in the structure.   This is not in conflict with the chemical evidence.

Were the *o*-quinonoid ring fixed in the molecule, the distortion of interatomic distances produced would be sufficient to destroy the exact centre of symmetry,* unless this centre were not a true one, but a statistical centre derived from a random distribution of molecules in the crystal.   The structure and general condition of the crystal seem too perfect for this latter supposition to be a likely one.

Evidence from Intensities.—The intensities of the *X*-ray reflexions are in general agreement with the structures deduced by Linstead.   This evidence is of a much more searching and detailed character than the general considerations of dimensions and symmetry with which we have so far dealt; if successfully completed, it should furnish accurate information regarding the exact situation of every atom in the molecule; but owing to the great complexity of the molecules only a qualitative survey and comparison of the different compounds is attempted below.

The {*h*0*l*} zone, which corresponds to a projection of the structure on the (010) plane, contains by far the greatest range of reflecting planes.   This zone was studied by means of moving-film photographs of crystals rotated about the *b* axis.   Typical exposures for the four compounds are shown in Plate I, all taken with copper radiation.   When we pass from phthalocyanine to the nickel derivative, the *intensity* of many of the reflexions is seen to change abruptly; many planes which were absent or too weak to be visible now appear

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* See analysis of benzoquinone (*Proc. Roy. Soc.*, 1935, *A*, in the press).

owing to the extra contribution which the central nickel atom (atomic number 28) makes to the scattering. The *position* of corresponding reflecting planes, however, is almost identical, because the lattice dimensions are so similar. The photograph obtained from the copper derivative is practically identical with that of the nickel derivative, as regards both dimensions and intensities.* This is to be expected, because copper (atomic number 29) has practically the same scattering power for X-rays as nickel. In the photograph obtained from the platinum compound, however, there is a striking alteration. Almost every possible reflecting plane is represented, and the intensity distribution is very uniform. Platinum (atomic number 78) is equal to 13 carbon atoms in scattering power for X-rays, and the effect of this concentration of scattering matter at the centre of the molecule is to swamp all the reflexions, and produce a nearly uniform distribution of intensity. To a rough first approximation, this structure may be considered as an open lattice of platinum atoms 12—13 Å. apart. Occasionally, a number of the other atoms combine to reinforce or diminish the reflexions, a possibility which becomes of more frequent occurrence as the higher orders are reached.

Table II gives some observations on the intensities of certain reflexions which help to settle the orientations of the molecules in the crystals. Fig. 3 shows the positions of the
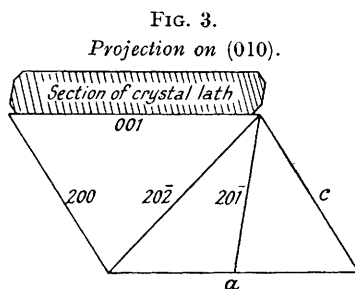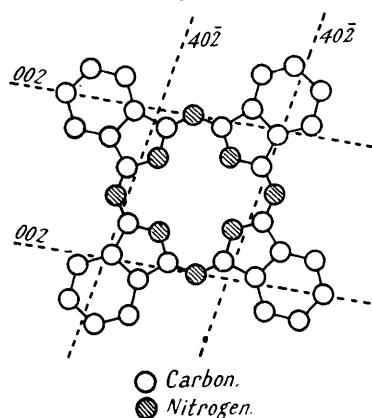
FIG. 3.

Projection on (010).

FIG. 4.

Symmetrical model of phthalocyanine molecule.

○ *Carbon.*
◕ *Nitrogen.*

trace of some of these planes on the (010) projection of nickel, copper, and metal-free phthalocyanine. It will be observed that the (001) and (20$\bar{1}$) are nearly perpendicular to each other (80°); so also are the (200) and (20$\bar{2}$) (76°). Now, from Table II, it will be seen that the intensity distribution in the successive orders of the (001) and the (20$\bar{1}$) series shows a very marked correspondence. The same is true of the successive orders of the (200) and the (20$\bar{2}$) series. This applies to all four compounds, and is most pronounced in the platinum derivative. The intensity of the successive orders of any given plane depends upon the average distribution of atoms normal to the plane. Hence the above results show that this average distribution is very similar in directions (arbitrarily chosen) which are nearly 90° apart. In other words, the molecule at least approximates to four-fold symmetry in its detailed structure.

If we make a symmetrical model based on the chemical structure, it is possible to explain a number of the observed intensities qualitatively. The (002) and the (40$\bar{2}$) planes, seen edge-on, probably occupy roughly the positions shown in Fig. 4 with respect to this model, which may, however, be foreshortened by 10—20% in some direction depending upon the precise inclination of the molecular planes to the (010). Now it can be seen that there is a considerable concentration of atoms near to these planes, and we should

* The size of the crystal specimens and the exposure times necessarily vary a little from one compound to another.

TABLE II.

hkl.	sin θ. λ = 1·54. Phthalo-cyanine.	Phthalo-cyanine.	Ni deriv.	Cu deriv.	Pt deriv.	hkl.	sin θ. λ = 1·54. Phthalo-cyanine.	Phthalo-cyanine.	Ni deriv.	Cu deriv.	Pt deriv.
001	0·062	v.s.	v.s.	v.s.	v.s.	200	0·092	abs.	s.	s.	v.s.
002	0·123	v.s.	m.	m.	m.	400	0·183	s.	abs.	abs.	m.s.
003	0·184	m.	v.w.	v.w.	m.s.	600	0·275	m.s.	s.	s.	s.
004	0·246	v.w.	s.	s.	s.	800	0·367	abs.	m.	m.	s.
005	0·307	m.s.	v.v.w.	v.v.w.	m.	1000	0·458	v.w.	m.	m.	m.s.
006	0·369	m.s.	v.w.	v.w.	w.m.	1200	0·550	v.w.	w.m.	w.m.	m.
007	0·430	w.	m.s.	m.s.	m.s.	20$\bar{2}$	0·107	w.	s.	s.	v.s.
20$\bar{1}$	0·079	v.s.	v.s.	v.s.	v.s.	40$\bar{4}$	0·214	s.	abs.	abs	m.s.
40$\bar{2}$	0·157	v.s.	m.	m.	w.m.	60$\bar{6}$	0·322	m.	m.s.	m.s.	s.
60$\bar{3}$	0·236	m.	v.w.	v.w.	m.s.	80$\bar{8}$	0·427	m.s.	m.s.	m.s.	s.
80$\bar{4}$	0·314	abs.	m.	m.	s.	100$\overline{10}$	0·536	v.v.w.	w.m.	w.m.	m.s.
100$\bar{5}$	0·393	v.w.	w.	w.	m.	120$\overline{12}$	0·643	abs.	w.	w.	m.
120$\bar{6}$	0·471	m.s.	w.	v.v.w.	w.m.	020	0·326	w.	m.	m.	m.s.
140$\bar{7}$	0·549	v.v.w.	w.m.	w.m.	m.s.	040	0·652	v.w.	w.m.	w.m.	—

v.s. = very strong.	w. = weak.
s. = strong.	v.w. = very weak.
m.s. = medium strong.	v.v.w. = just visible.
m. = medium.	abs. = absent.
w.m. = weak medium.	— = beyond experimental limits.

therefore expect strong reflexions. These are actually observed in the metal-free compound, but in the copper and the nickel compound these strong reflexions become weak and are replaced by strong second-order reflexions, (004) and (80$\bar{4}$). This is just what would be expected if the metal atom goes in at the centre of the molecule, because the copper or nickel atom is nearly as effective as 5 carbon atoms in scattering power for X-rays, and so the (002) and (40$\bar{2}$) planes become interleaved with scattering matter. This orientation of the molecule with respect to the crystal planes is further supported by the way in which adjacent molecules are found to fit together when the structure is extended, a gap of 3—4 Å. existing between atoms on neighbouring molecules. The orientation given is comparatively rough at present, however, so that a rotation of the molecule by 10°, which would be equivalent to interchanging the indices of the (40$\bar{2}$) and (002) planes in Fig. 4, might be possible.

These observations on the intensities can be extended in a more general form. The phase constant of the contribution to the structure factor made by the metal atom must always be positive, because the metal atom is situated at the centre of symmetry. Now if the phase constant of a given reflexion from metal-free phthalocyanine is also positive, *i.e.*, if it corresponds to an average sinusoidal distribution of scattering matter with a maximum at the centre of symmetry, then the corresponding reflexion in the metal compounds will be of greater intensity; but if the reflexion from metal-free phthalocyanine is negative, corresponding to a minimum at the centre of symmetry, then the corresponding reflexion from the metal compounds will show a decrease in intensity, provided that the structure factor of the metal-free reflexion is in this case of greater magnitude than one-half the contribution made by the metal atom alone. Representing the structure factors of phthalocyanine, the metal atom alone, and of metal phthalocyanine by S_P, S_M, and S_{MP} respectively, we have $S_P + S_M = S_{MP}$. As S_M is always positive, we can usually determine the sign of S_P by observing the relative magnitudes of S_P and S_{MP}. To what extent this method can be applied in quantitative work will depend on how closely similar are the orientations of the phthalocyanine and metal phthalocyanine molecules in the crystals.

SUMMARY.

Phthalocyanine and its nickel, copper, and platinum derivatives form a series of closely similar monoclinic crystals, space-group $P2_1/a$, with two centro-symmetrical molecules per unit cell. The dimensions indicate large, square, and probably flat molecules. It is shown that the central metal atom and the four surrounding *iso*indole nitrogen atoms are necessarily coplanar. The bearing of these facts upon the chemical structure is discussed. In particular, the X-ray evidence, in conjunction with the stereochemical considerations

mentioned by Linstead, shows that the whole molecule, with the possible exception of the two central imino-hydrogen atoms, should exist in one plane.

A general consideration of the intensities of the reflexions shows that the molecules possess at least approximately four-fold symmetry, with concentrations of atoms about where they would be expected from Linstead's structure. The approximate orientations of the molecules in the crystals have been determined. By comparing corresponding reflexions from the metal-free and from the metal compounds, a direct determination of the phase constants of some of the reflexions can be made.