7. *An X-Ray Study of the Phthalocyanines. Part IV. Direct Quantitative Analysis of the Platinum Compound.*

By J. MONTEATH ROBERTSON and IDA WOODWARD.

By substituting an atom of high atomic number at some point in a complex organic structure a very direct method of *X*-ray analysis becomes available. This has often been utilised, but rarely in a fully quantitative manner. The possibilities of the method are discussed, and it is concluded that it may have almost unlimited application. At the same time there are serious practical difficulties. A critical test of the method is made in the analysis of platinum phthalocyanine, $C_{32}H_{16}N_8Pt$, with quantitative intensity measurements, corrections for absorption, diffraction effects, etc. The positions of all the atoms (except hydrogen) in this structure are determined with an average accuracy of about ± 0·05 A. A double Fourier series of 302 terms is employed for this purpose.

The molecular structure, as expected, is closely similar to that of the other members of the phthalocyanine series, although certain small changes in dimensions, due to the presence of the platinum atom, are noted. The crystal structure, however, is different, because the molecules are arranged in a different way, their planes being inclined at a much smaller angle to the (010) plane (26·5° instead of 44·2°). The structure may be regarded as a polymorphic modification of those already described in this series.

THE work now described has two objects, the first being a complete structure determination of platinum phthalocyanine. The crystals of this compound are not isomorphous with those of the other members of the phthalocyanine series whose structures have already been determined (J., 1935, 615; 1936, 1195; 1937, 219) and new problems are encountered. It is now shown that the changes in the cell dimensions of platinum phthalocyanine, amounting to as much as 4 A. when compared with other members of the series, are not caused by any large changes in the dimensions or shape of the phthalocyanine molecule itself, although some minor changes in the molecular framework due to the central platinum atom are noted. The change in crystal structure is due to a different arrangement of the molecules, which are now inclined at a smaller angle to the (010) plane. The new structure may therefore be regarded as a polymorphic modification of those already described, although no actual transition for any one compound has yet been observed. Such transitions may, however, be possible.

The second aspect of this work is to present a critical test of what is probably the most direct method of *X*-ray analysis which has fairly general application to complex organic structures, *viz.*, that depending on the presence of a heavy atom. This method has often been utilised in *X*-ray work, although rarely in a fully quantitative manner. It was suggested in the paper on nickel phthalocyanine (J., 1937, 219) and discussed in connection with the insulin structure (*Nature*, 1939, **143**, 75), and has recently been applied to the elucidation of a number of structures (see, *e.g.*, Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169; Powell and Ewens, J., 1939, 286).

In outline, the method is simple. If we place one or more heavy atoms of high scattering power for *X*-rays (high atomic number) at certain points in the structure, then the contributions which these atoms make to the *X*-ray reflections from certain planes will dominate the combined contributions from the other, lighter, atoms (carbon, nitrogen, etc.). To a first approximation the lighter atoms may be neglected, and the positions of the heavy atoms determined from the intensities by trial or by an application of the Patterson method. A subsequent Fourier analysis of all the intensity data, with origin and phase constants referred to the positions of the heavy atoms, may then reveal the presence of the lighter atoms.

When the heavy atoms occupy centres of symmetry in the structure, as in platinum phthalocyanine, the analysis is simplified. An origin being taken at the centre of symmetry, the structure amplitude due to the heavy atom is always positive (phase constant $+\pi$) and that due to the remaining light atoms may be positive or negative ($\pm\pi$). If the contribution from the heavy atom is sufficiently large, the total structure amplitude will always be positive. In effect, unknown differences of phase are converted into differences of amplitude which can be measured. A direct Fourier synthesis may therefore be carried out, which then becomes equivalent to a Patterson synthesis. Regarding it as a Patterson synthesis, we only obtain the vectors connecting each of the light atoms to the heavy atom, the vectors between the light atoms themselves becoming second order quantities and unimportant. The result is a direct picture of the structure, instead of its vector map.

In applying the method to a complex organic structure it is not necessary that the atomic number of the heavy atom should equal the sum of the atomic numbers of the light atoms present, for two reasons. First, the scattering factor, or atomic *f*-curve, for the heavy atom will decrease much more slowly, especially at large glancing angles, than the *f*-curves for the light elements present; for this reason the heavy atom may be two or even three times as effective as its atomic number would indicate. Secondly, and more important, is the fact that the contributions from the various light atoms in the structure tend to cancel each other out. In a molecular structure there is in general no integral relation between the co-ordinates of the atoms and the cell dimensions. As the molecule gets larger there is consequently less and less chance of all the atoms being in phase for a given reflection, and the average value of the structure amplitude, the heavy atom being excluded, departs further from its possible maximum. The contribution of the heavy atom to the structure amplitude does not fall off in this way and hence its swamping power on the reflections may be just as effective in the case of a very large molecule as in a small one. For this reason the method appears to have almost unlimited application.

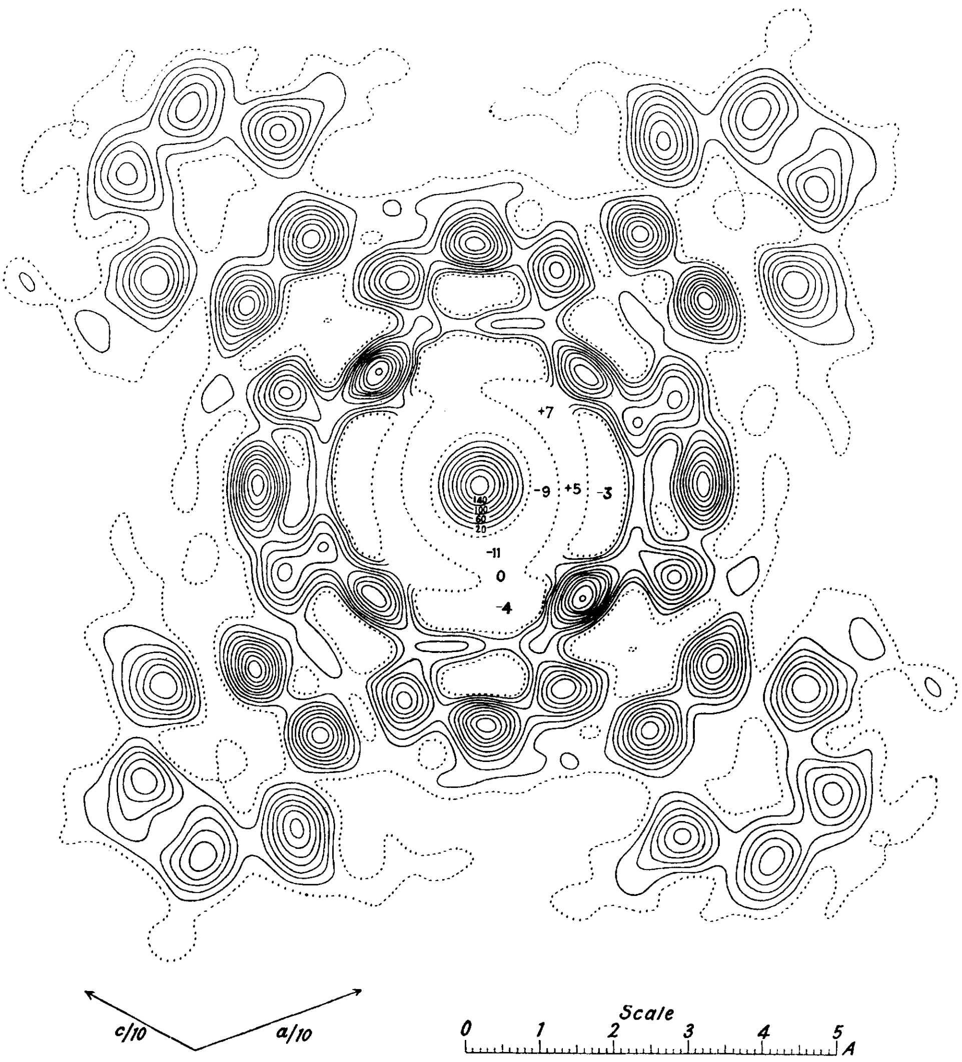
The difficulties of the method are of a practical nature and have often been pointed out (*e.g.*, Cox, *Ann. Reports*, 1937, **34**, 188). For most of the reflections the larger part of the intensity is derived from the known contribution of the heavy atom, and we are primarily interested in the small residual increase or decrease due to the unknown remainder of the structure. To obtain results of corresponding accuracy it would become necessary to measure the intensities with an accuracy several times as great as in the case of ordinary structures consisting only of light atoms; but at the same time the difficulty of making the measurements is increased by the presence of a highly absorbing atom.

Even more important than the accuracy of measurement is the range of reflections covered, on which depends the convergency of the series. As noted above, the scattering curve for the heavy atom tends to decrease slowly with increasing glancing angle, and so the range covered should be increased, otherwise spurious diffraction effects will be introduced owing to the series being incomplete.

On account of these difficulties the results obtained hitherto from compounds containing heavy atoms have not been very satisfactory. The presence of the lighter atoms is usually indicated on the electron-density maps only by a very hazy outline, and their positions are correspondingly uncertain. In some cases carbon atoms are not resolved at all.

To test the possibilities of the method we have accordingly studied the *b* axis projection of the platinum phthalocyanine structure as carefully as possible, making use of quantitative intensity measurements, applying corrections for absorption, and including a sufficient number of terms to make the series reasonably convergent. The results, summarised in the contour map of Fig. 1, show that with suitable precautions a fairly high degree of accuracy can be attained. The maximum uncertainty in the positions of the light atoms is about ± 0·1 A., and this figure can be greatly improved in most parts of the structure when allowance is made for diffraction effects and false detail.

FIG. 1.



Projection of platinum phthalocyanine along the b *axis, on the* (010) *plane, which makes an angle of* 26·5° *with the molecular plane. Each contour line represents a density increment of one electron per* A.^{2}, *except in the central portion where the increment is* 20 *electrons per* A.^{2} *for each line. The one-electron line is dotted.*

Analysis of Platinum Phthalocyanine.—The crystal data for this compound,

$C_{32}H_{16}N_8Pt$, are: space group C_{2h}^5 ($P2_1/a$), $a = 23{\cdot}9$, $b = 3{\cdot}81$, $c = 16{\cdot}9$ A., $\beta = 129{\cdot}6°$, with two centrosymmetrical molecules per unit cell of volume 1186 A.^{3}, d(found) = 1·98, (calc.) = 1·97, $M = 707$, $F(000) = 684$.

The atomic number of platinum is 78, and the sum of the atomic numbers of the other atoms in the molecule is 264. The scattering factor decreases so much more slowly for platinum than for the other atoms, however, that if we take the values given for the Hartree scattering factor for sin $\theta = 0{\cdot}5$ the structure factor for the whole molecule will be positive unless the sum of the geometrical structure factors for the atoms other than platinum is greater than 65% of its maximum value. For free phthalocyanine this quantity never exceeds 46% of its maximum. These figures, as well as the signs determined for the structure factors for nickel phthalocyanine (J., 1937, 129), justify us in ascribing positive signs to all the structure factors for platinum phthalocyanine, an assumption fully confirmed later by direct calculations of the structure factors from the atomic co-ordinates.

The measured structure factors derived from intensities in the ($h0l$) zone are given in Table I, and this provides a double Fourier series of 302 terms which was summed at 1800 points on the asymmetric unit (half the molecule) to give the contour map shown in Fig. 1. This is drawn at unit electron intervals, except in the central portion where the increment is increased to 20 electrons per A.^{2}, the peak value at the centre of the platinum atom being 174 electrons per A.^{2}, as against peak values of 7 or 8 for the other atoms. (A better idea of the vertical scale is obtained from the section in Fig. 7.)

TABLE I.

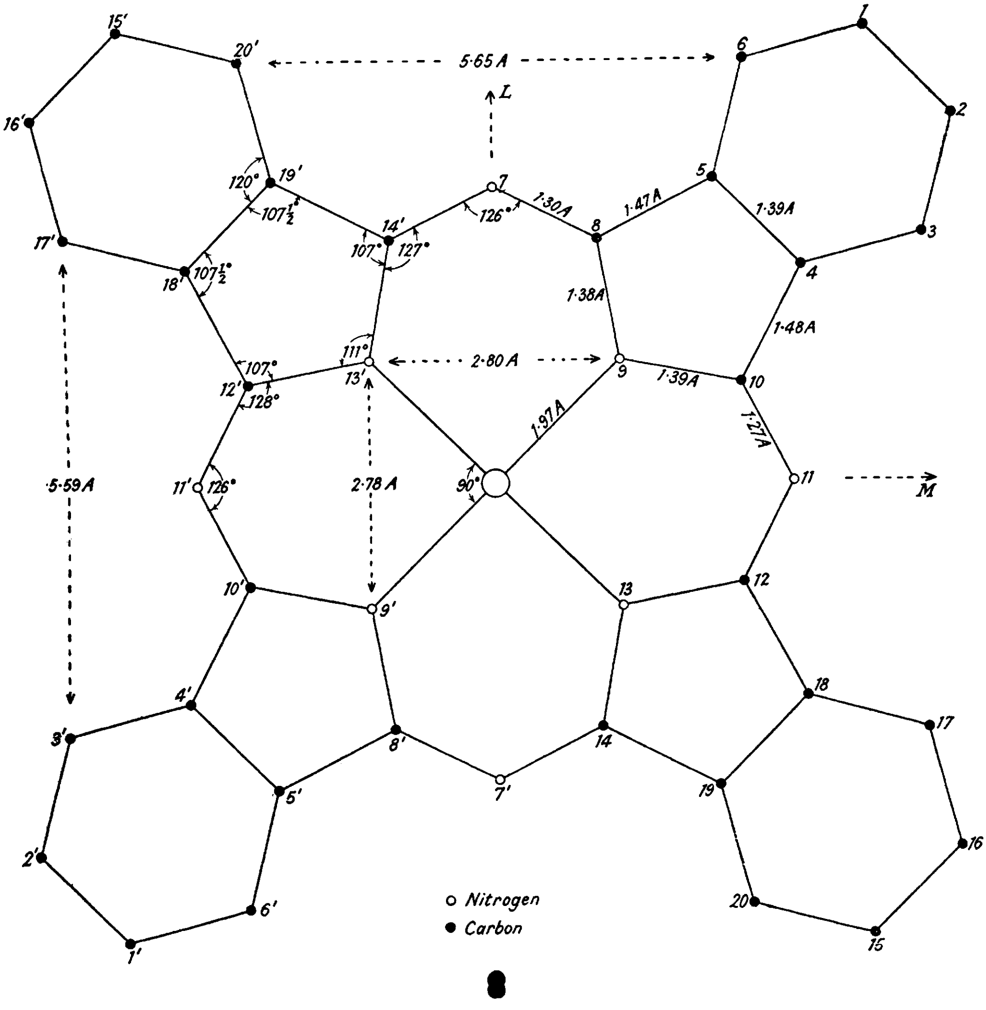
Values of $F(h0l)$. All signs positive.

						h.							
l.	0.	2.	4.	6.	8.	10.	12.	14.	16.	18.	20.	22.	24.	26.
14	32	—	—	—	—	—	—	—	—	—	—	—	—	—
13	59	34	—	—	—	—	—	—	—	—	—	—	—	—
12	84	62	33	—	—	—	—	—	—	—	—	—	—	—
11	78	38	57	—	—	—	—	—	—	—	—	—	—	—
10	76	32	52	38	—	—	—	—	—	—	—	—	—	—
9	81	83	48	53	39	—	—	—	—	—	—	—	—	—
8	87	98	61	89	56	25	—	—	—	—	—	—	—	—
7	163	136	97	114	78	43	33	—	—	—	—	—	—	—
6	115	168	127	109	100	75	42	—	—	—	—	—	—	—
5	120	66	103	122	80	48	51	38	—	—	—	—	—	—
4	205	152	54	128	104	66	42	59	—	—	—	—	—	—
3	127	143	171	67	129	92	77	70	48	—	—	—	—	—
2	79	170	157	56	152	76	70	68	89	39	—	—	—	—
1	234	59	129	132	134	115	89	35	60	56	—	—	—	—
0	684	160	104	165	139	148	112	77	32	33	40	—	—	—
$\bar{1}$	234	210	200	97	154	180	132	90	67	43	42	—	—	—
$\bar{2}$	79	142	49	83	130	147	112	82	97	37	34	—	—	—
$\bar{3}$	127	214	78	109	164	169	101	59	87	78	69	46	—	—
$\bar{4}$	205	97	95	142	146	132	181	111	58	107	61	72	—	—
$\bar{5}$	120	182	122	139	131	106	127	135	88	108	53	82	—	—
$\bar{6}$	115	177	145	178	145	160	65	118	100	89	71	79	44	—
$\bar{7}$	163	190	182	194	98	132	47	134	91	86	77	43	64	—
$\bar{8}$	87	140	185	176	180	93	42	101	73	77	56	35	44	—
$\bar{9}$	81	114	157	104	183	176	129	90	126	82	60	46	41	35
$\bar{10}$	76	92	110	114	122	147	132	139	125	87	88	68	66	27
$\bar{11}$	78	45	98	93	60	101	105	103	103	99	62	55	95	51
$\bar{12}$	84	47	61	113	84	84	120	89	111	103	90	45	52	64
$\bar{13}$	59	80	36	58	117	125	97	70	123	64	109	83	46	42
$\bar{14}$	32	63	50	30	50	82	90	66	78	59	91	84	55	41
$\bar{15}$	—	33	55	52	74	70	53	46	42	73	29	74	49	—
$\bar{16}$	—	—	35	49	51	82	93	48	34	94	39	58	28	—
$\bar{17}$	—	—	—	—	38	60	54	71	48	65	76	57	44	—
$\bar{18}$	—	—	—	—	—	34	33	49	40	46	58	27	—	—
$\bar{19}$	—	—	—	—	—	—	—	—	31	31	31	—	—	—

In spite of strongly marked diffraction rings surrounding the central platinum atom, all the atoms can be identified, and those forming the outlying benzene rings are specially well resolved. It is obvious that the molecule is very closely similar to that of nickel phthalocyanine, but it appears to be much broader, which means that it is inclined at a much smaller angle to the plane of the projection. This angle is in fact found to be 26·5°, as compared with 44·2° for the nickel and the metal-free compound.

It is seen from Table I that the Fourier series is, in spite of the large number of terms included, much less convergent than that employed in, *e.g.*, the synthesis of nickel phthalocyanine, the range of values of F being here 8·4 to 1 as compared with 14·5 to 1. This lack of convergence is responsible for the strong diffraction pattern surrounding the platinum atom, which is studied in detail below and is shown to be the cause of the main distortions in its neighbourhood. The irregularities in other parts of the diagram are due mainly to the difficulty already mentioned of measuring the intensities to the same degree of absolute accuracy as has been attained in the case of other compounds studied, owing to the presence throughout of the large contribution due to the platinum atom.

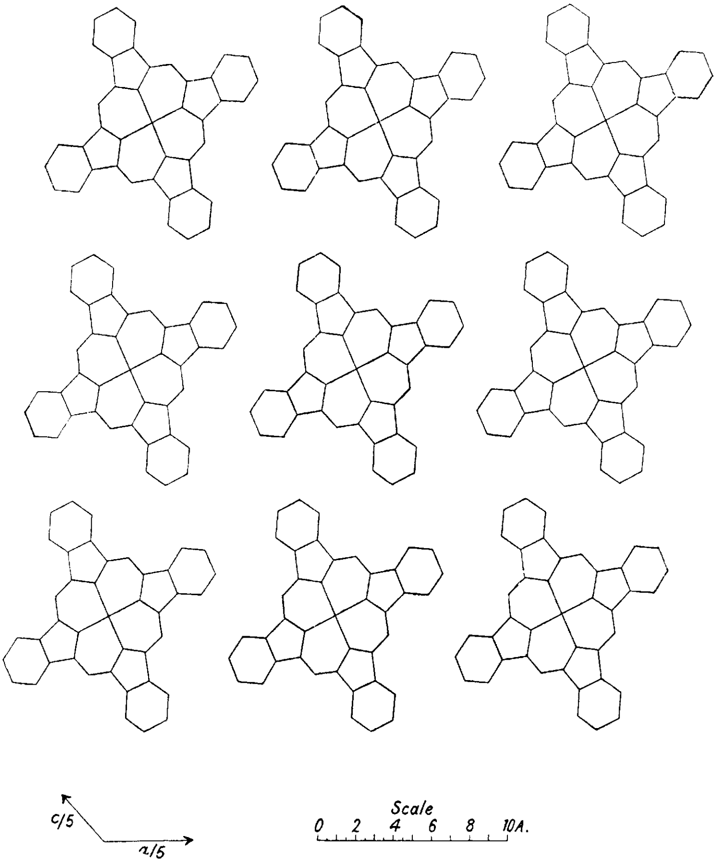
FIG. 2.



Dimensions of the platinum phthalocyanine molecule. Average uncertainty about ±0·05 A.

Dimensions of the molecule. In deducing the molecular model shown in Fig. 2 from the contour map the method used was similar to that employed for free phthalocyanine, with certain modifications necessitated by the impossibility of locating accurately the atomic centres of the 16-membered inner ring of atoms. The bond lengths and angles involving these are liable to considerable error, amounting in the case of atoms 9, 10, 12 and 14 to as much as 0·1 A. For atoms 9 and 13 it was found possible to make a quantitative correction for the diffraction effect, subtracting from the electron density that found at the same distance from the origin in regions where no atom was situated. The distance, 1·97 A., of these atoms from the central platinum atom can probably be relied upon to within 0·06 A. At a later stage, when the diffraction effect was considered in more detail, a revised correction gave a value of 2·01 A. It is interesting to compare these results with the values 1·92 A. and 1·83 A. found in the metal-free and the nickel compound. The increase in the platinum compound corresponds to the increased radius of the metal atom.

FIG. 3.



Group of molecules of platinum phthalocyanine in b*-axis projection.*

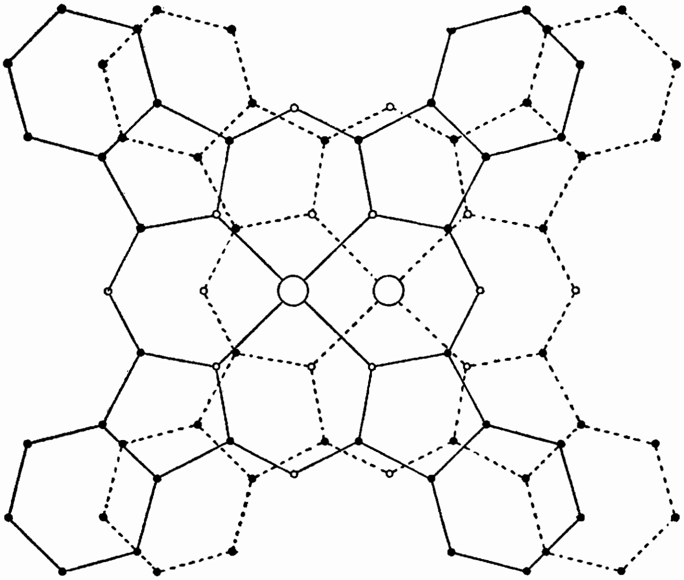
The distortion in the bond lengths and angles of the 16-membered ring is in the direction which would be expected from the increase of distance between the platinum atom and the nitrogen atoms nearest to it, but little weight can be attached to this on account of the large margin of error in the values assigned to these quantities.

Apart from these effects the general features of the structure are almost identical with those of nickel phthalocyanine. The over-all dimensions and the tetragonal symmetry of the molecule are retained, and the lengths of the bonds connecting the benzene rings to the inner nucleus again indicate only a relatively small amount of double-bond character.

Intermolecular distances. An extension of the *b* axis projection is given by the skeleton drawing in Fig. 3, which shows one molecule completely surrounded by its neighbours. The method of packing is seen to be similar to that of metal-free and of nickel phthalocyanine; but in the stacking of the molecules along the *b* axis there is a striking difference, due to the smaller angle of inclination which the molecular plane of platinum phthalocyanine makes with the (010) projection plane (26·5° instead of 44·2°). This is shown by making a normal projection of the molecule in the plane of the adjacent molecule vertically below it on the *b* axis, as in Fig. 4. The dotted lines connect the atoms of the lower molecule. The diagram should be compared with the corresponding one for nickel phthalocyanine (J., 1937, 224). Unlike the nickel atom, the platinum atom gives as much clearance as possible to the nearest atoms in the parallel molecules, and it will be seen that in no case are the atoms vertically over each other. The closest approaches found between atoms in these parallel molecules are those between the nitrogen atom **9** and the carbon atom **10**, 3·44 A.; and between the carbon atoms 3 and 4, and 5 and 6, 3·45 A. in both cases. The vertical distance between the molecular planes is 3·41 A.

No distances as low as these are found between atoms in other molecules, the least being 3·55 A. between the carbon atoms 6 of the standard molecule and 15 of the reflected molecule at $(a/2, b/2, c)$.

FIG. 4.



Normal projection of two parallel molecules.

EXPERIMENTAL.

Intensity Measurements.—Some finely crystalline specimens of platinum phthalocyanine, obtained by vacuum sublimation, were supplied by Professor Linstead. On account of the high absorption ($\mu = 120$ per cm. for Cu-$K\alpha$ radiation), special precautions were necessary. The corrections were reduced as far as possible by the use of extremely small crystal specimens. That used for the intensity measurements was in the form of a lath about 0·02 mm. by 0·085 mm., and weighing about 0·01 mg. This was completely immersed in a beam of filtered copper radiation, and the reflections recorded photographically by means of a moving-film camera. The great number of intensities to be measured rendered a rapid method desirable, and that described by Dawton (*Proc. Physical Soc.*, 1938, **50**, 919) was adopted. Certain difficulties in the correlation of the positive and negative films used in this method of photometry impair its accuracy in this case, especially in certain parts of the film. The results were checked in some cases by the integrating photometer (Robinson, *J. Sci. Instr.*, 1933, **10**, 233).

The measurements were put on an absolute scale by correlation with determinations of the absolute values of the reflections from the $(20\bar{1})$ and (001) planes by the ionisation spectrometer, both Mo-$K\alpha$ and Cu-$K\alpha$ monochromatic radiations being used. The weight of the crystal specimen used in these experiments was 0·0095 mg., determined on a magnetic balance and checked by careful measurement of its dimensions.

Corrections were made for absorption by determining the path length of the mean ray through the crystal for each reflection. These correction factors varied from 1·4 to 2·8.

Fourier Analysis, Molecular Orientation, and Co-ordinates.—The values of $F(h0l)$, all assumed positive for the reasons already given, are shown in Table I. The electron density given by

$$\rho(x, z) = \frac{1}{ac \sin \beta} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(h0l) \cos 2\pi(hx/a + lz/c)$$

was computed by the three-figure strip methods described by Robertson (*Phil. Mag.*, 1936, **21**, 176), the a axis being divided into 120 parts (intervals of 0·199 A.) and the c axis into 60 parts (intervals of 0·281 A.). The contour maps were prepared in the usual way by drawing sections in the two directions given by the rows and columns of the summation totals and dropping perpendiculars at the contour levels.

The projections of regular hexagons of sides 1·39 A. were imposed on the benzene rings of the contour map, and the inclination to the b axis of the molecular axis M (see Figs. 1 and 2) was obtained, exactly as for free phthalocyanine (J., 1936, 1195), the results being

Ring 1, $\psi_M = 62{\cdot}9°$
Ring 1′, $\psi_M = 64{\cdot}2°$
Ring 15, $\psi_M = 63{\cdot}4°$
Ring 15′, $\psi_M = 65{\cdot}2°$

The mean of these values, 63·9°, was adopted for ψ_M (the inclination of M to the b axis).

In determining the other inclinations of the molecular axes L and M, by averaging the directions of the lines joining certain atoms, as in free phthalocyanine, only the atoms in the benzene rings were used, with the addition of 7,7′ for L and 11,11′ for M. Adjustments were then applied to give the best average positions for all the atoms. The projections of L and M, thus determined, are inclined at an angle of 92·1°, and if we assume that these axes are at right angles and proceed as before (J., 1936, 1202) we obtain the following values for their direction cosines :

$\chi_L = 71{\cdot}4°$ $\cos \chi_L = 0{\cdot}3197$ $\chi_M = 32{\cdot}9°$ $\cos \chi_M = 0{\cdot}8395$
$\psi_L = 85{\cdot}7°$ $\cos \psi_L = 0{\cdot}0747$ $\psi_M = 63{\cdot}9°$ $\cos \psi_M = 0{\cdot}4399$
$\omega_L = 19{\cdot}2°$ $\cos \omega_L = 0{\cdot}9446$ $\omega_M = 108{\cdot}6°$ $\cos \omega_M = -0{\cdot}3189$

$\chi_N = 116{\cdot}1°$ $\cos \chi_N = -0{\cdot}4393$
$\psi_N = 26{\cdot}5°$ $\cos \psi_N = 0{\cdot}8949$
$\omega_N = 85{\cdot}5°$ $\cos \omega_N = 0{\cdot}0781$

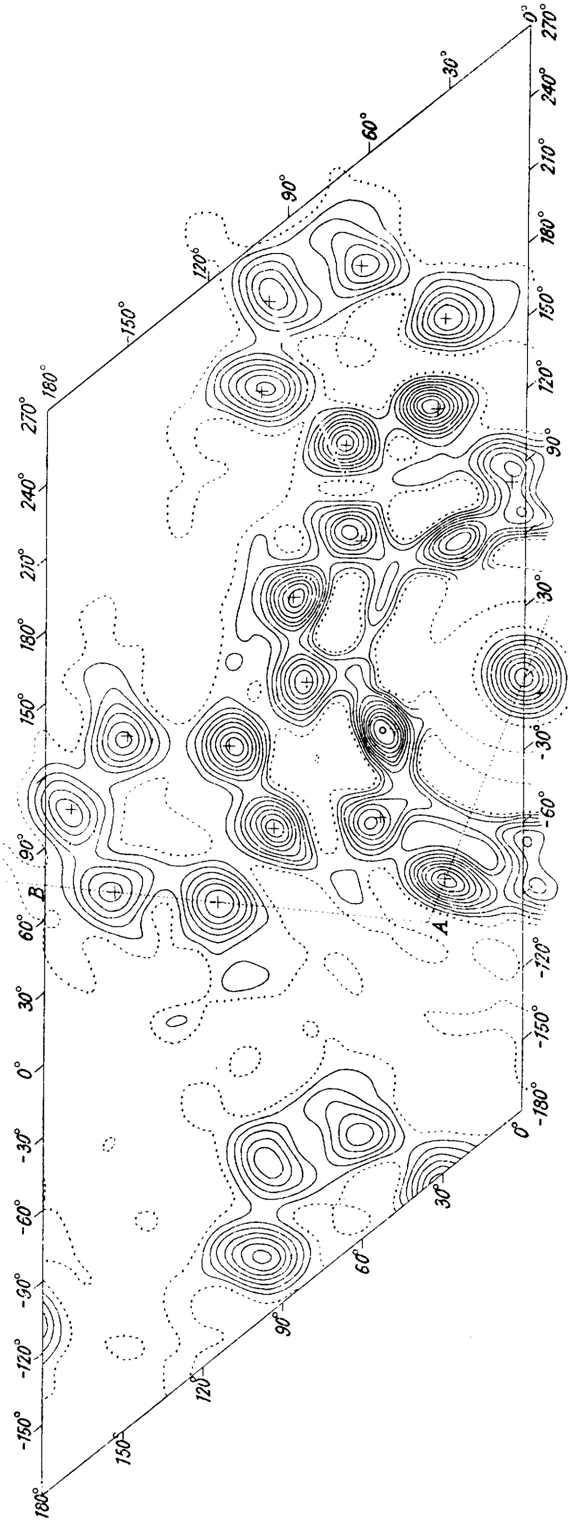
The co-ordinates of the atoms are given in Tables II and III, and the final positions assigned are indicated by crosses in Fig. 5.

Calculation of Structure Factors.—The co-ordinates for the nitrogen and carbon atoms as given in Table III were used for the calculation of their contributions to the structure factors for the 302 reflections measured. The average scattering curve for hydrocarbons was used (*Proc. Roy. Soc.*, 1935, *A*, **150**, 110), nitrogen atoms being weighted in the ratio 1·2 to 1, as in the corresponding calculations for free phthalocyanine.

These structure factors (F_M) were subtracted algebraically from the measured values (F, meas.), and the difference (F, meas. $- F_M$) is attributable to the two platinum atoms in the cell, the geometrical structure factors of which are unity. These differences were halved, and plotted against sin θ, and the points were found to be grouped about a curve, the experimental scattering curve for platinum. It was found that the points lay more closely on a curve if the structure factors F were multiplied by a factor 1·165, which should be compared with a similar factor, 1·33, used to obtain the best agreement between the measured and calculated structure factors for free phthalocyanine. The scattering curve for platinum finally adopted is shown in Fig. 6. It is seen that it rises to a value of over 80 at $\sin \theta = 0$, which is slightly greater than the number of electrons in the platinum atom. From this we conclude that the scale of the intensity measurements is slightly too high, but the random errors are too large for any real certainty on this point.

The experimental curve is seen to fall away much more rapidly for values of sin θ greater than 0·5 than Brindley's scattering curve for platinum, the ratio being only about 2 to 3 for $\sin \theta = 0{\cdot}7$. This effect is much more marked than in the case of nickel (J., 1936, 119).

FIG. 5.



Co-ordinates assigned to atomic centres in platinum phthalocyanine $\mathfrak{b}$ *axis projection.*

TABLE II.

Co-ordinates with respect to molecular axes, L and M.

Atoms.	L, A.	M, A.	Atoms.	L, A.	M, A.	Atoms.	L, A.	M, A.
Pt	0	0	4, 18	±2·44	3·45	8, 14	±2·75	1·16
1, 15	±5·12	4·18	5, 19	±3·43	2·47	9, 13	±1·39	1·40
2, 16	±4·13	5·15	6, 20	±4·77	2·82	10, 12	±1·13	2·76
3, 17	±2·79	4·80	7	±3·34	0	11	0	3·34

TABLE III.

Co-ordinates with respect to monoclinic crystal axes. Centre of symmetry as origin.

Atom.	x, A.	$2\pi x/a$.	y, A.	$2\pi y/b$.	z, A.	$2\pi z/c$.
Pt	0	0°	0	0°	0	0°
1CH	8·04	121·2	2·22	209·7	4·55	96·9
2CH	7·52	113·3	2·58	243·4	2·94	62·5
3CH	5·84	87·9	2·32	219·1	1·44	30·6
4C	4·67	70·3	1·70	160·3	1·56	33·3
5C	5·19	78·2	1·34	126·7	3·18	67·7
6CH	6·88	103·6	1·60	151·0	4·68	99·6
7N	3·68	55·4	0·25	23·5	4·10	87·2
8C	3·70	55·7	0·72	67·6	2·89	61·6
9N	2·34	35·2	0·72	68·0	1·13	24·0
10C	2·83	42·7	1·30	122·6	0·24	5·2
11N	1·92	29·0	1·47	138·8	−1·38	− 29·4
12C	0·34	5·2	1·13	106·8	−2·53	− 53·9
13N	−0·72	−10·9	0·51	48·4	−2·28	− 48·6
14C	−2·36	−35·5	0·30	28·7	−3·85	− 82·1
15CH	−3·24	−48·7	1·45	137·4	−8·01	−170·5
16CH	−1·59	−23·9	1·96	185·0	−7·20	−153·4
17CH	−0·31	− 4·7	1·90	179·6	−5·41	−115·2
18C	−0·70	−10·6	1·33	125·9	−4·42	− 94·1
19C	−2·35	−35·4	0·83	78·3	−5·22	−111·2
20CH	−3·62	−54·6	0·89	83·7	−7·01	−149·4

TABLE IV.

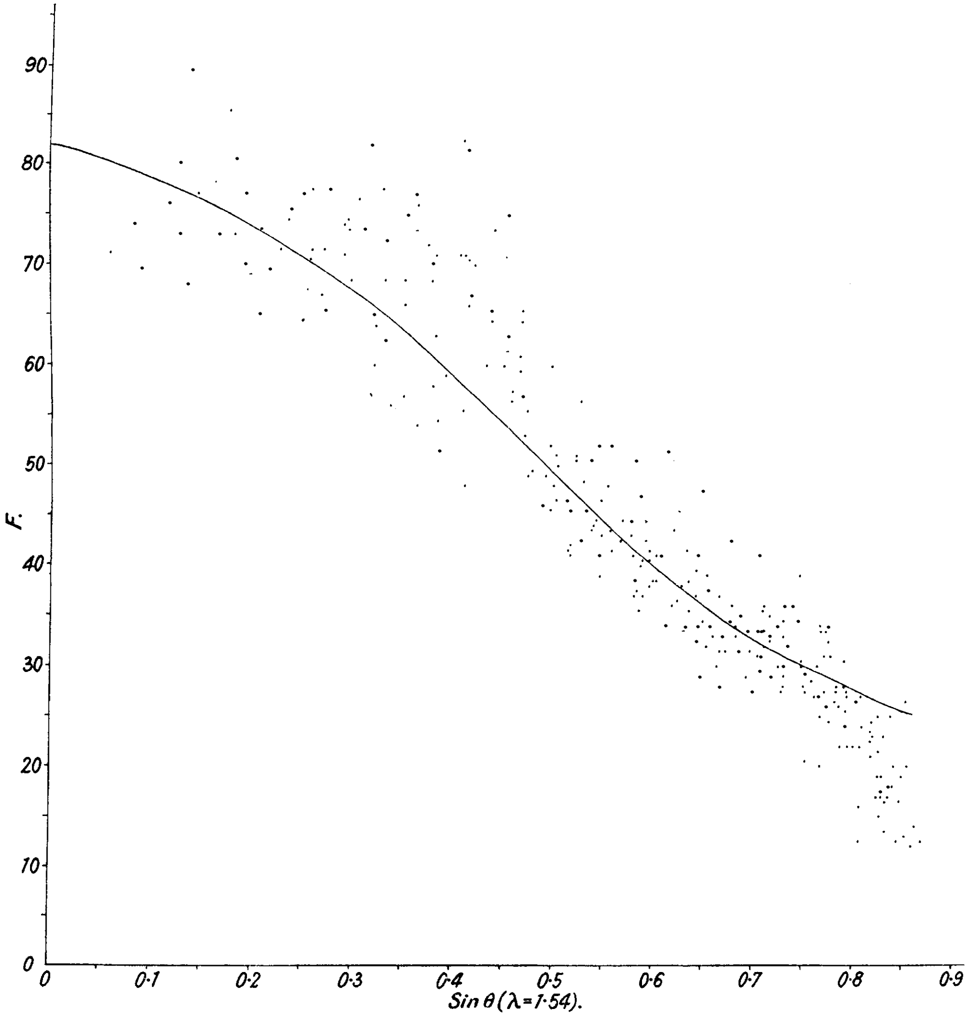
Measured and calculated values of the structure factor.

hkl.	sin θ (λ = 1·54).	F_M.	$2F$ Pt (all +ve).	F, calc. (all +ve).	F, meas.
200	0·084	+12	158	170	160
400	0·168	−42	151	109	104
600	0·251	+26	142	168	165
800	0·335	+14	130	144	139
10,00	0·419	+14	115	129	148
12,00	0·502	+16	99	115	112
14,00	0·586	+ 2	83	85	77
16,00	0·669	−24	70	46	32
18,00	0·753	− 8	60	52	33
20,00	0·837	+ 6	53	59	40
001	0·059	+92	160	252	234
002	0·119	−73	156	83	79
003	0·178	−44	150	106	127
004	0·237	+12	144	156	205
005	0·296	−29	136	107	120
006	0·355	−35	127	92	115
007	0·414	+21	116	137	163
008	0·473	−19	104	85	87
009	0·533	−16	92	76	81
00,10	0·592	+ 2	82	84	76
00,11	0·651	+ 9	73	82	78
00,12	0·701	+29	66	95	84
00,13	0·769	+ 9	59	68	59
00,14	0·828	+ 2	53	55	32
20,13	0·825	0	54	54	34
20,12	0·767	+ 8	59	67	62
20,11	0·706	− 24	66	42	38
20,10	0·647	− 33	74	41	32
209	0·588	+ 12	82	94	83
208	0·529	+ 13	93	106	98
207	0·470	+ 10	105	115	136
206	0·411	+ 3	117	120	168
205	0·353	− 48	127	79	66
204	0·297	+ 5	136	141	152
203	0·240	− 8	143	135	143
202	0·184	+ 9	149	158	170
201	0·130	−101	155	54	59
$20\bar{1}$	0·065	+ 91	160	251	210
$20\bar{2}$	0·092	+ 3	158	161	142
$20\bar{3}$	0·140	+ 35	154	189	214
$20\bar{4}$	0·195	− 57	148	91	97
$20\bar{5}$	0·251	+ 28	142	170	182
$20\bar{6}$	0·306	+ 24	135	159	177
$20\bar{7}$	0·364	+ 36	125	161	190
$20\bar{8}$	0·423	0	114	114	140
$20\bar{9}$	0·481	+ 15	103	118	114
$20,\bar{1}\bar{0}$	0·540	+ 5	92	97	92

The structure factor for each reflection was now obtained by adding to the already calculated structure factor F_M the contribution from the two platinum atoms, as obtained by doubling the value of the scattering factor given by Fig. 6. This whole structure factor is shown in Table IV under the heading *F*, calc. Only the axial and a few of the (*h*0*l*) results are shown in the table, but these may be taken as typical. (The complete list of measured values is given in Table I.)

The agreement between the measured and the calculated values of *F*, as assessed in the usual way by expressing the sum of the discrepancies between the measured and the calculated values as a percentage of the sum of the measured values, is 11·3 for the complete set of 302 planes. This compares well with the figures obtained (J., 1937, 226) for metal-free and for nickel phthalocyanine, but such a good result is due in part to the fact that the position of the platinum atoms, with their large contribution to the scattering, is perfectly known. A detailed examination of the figures leads to the conclusion that the measured values of *F* for the small spacing planes are too small, an error attributable to the practical difficulty of including the whole of the diffuse reflections in this region of the film in the field of the photometer used.

FIG. 6.

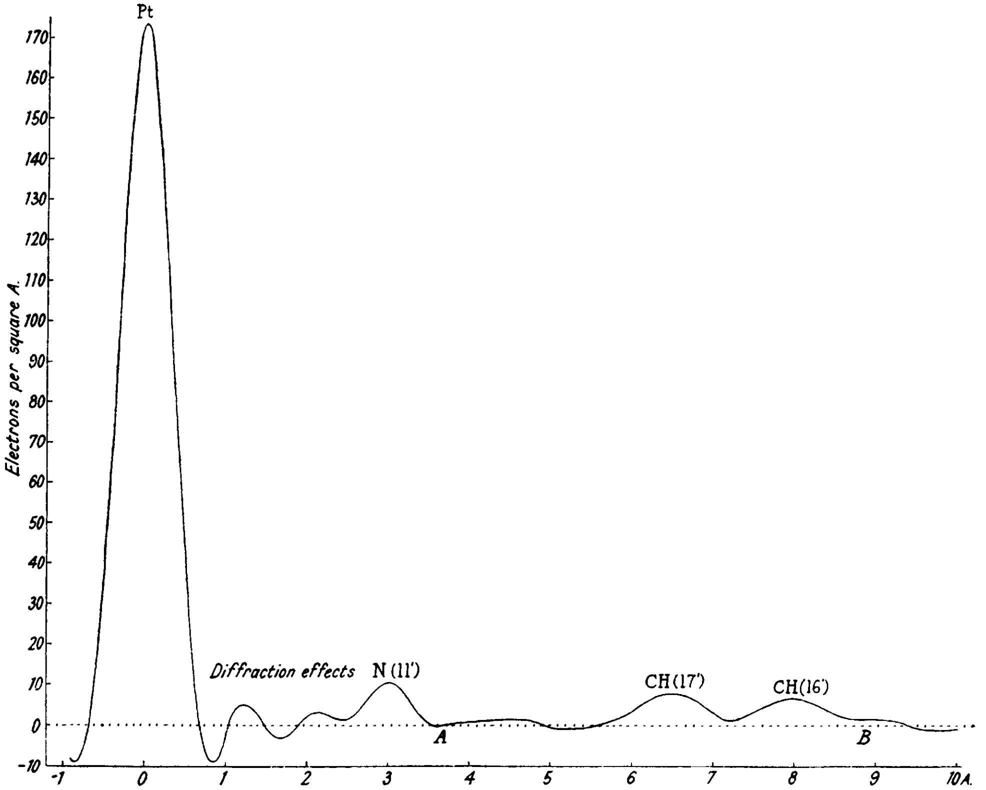


Experimental scattering curve for platinum.

Study of Diffraction Effects.—The scattering curve for platinum was now employed in the calculation of the diffraction effects due to the incompleteness of the series summed. It is clear that this incompleteness is due mainly to the presence of the platinum atom in the structure, because in the similar synthesis of metal-free phthalocyanine no serious diffraction effects are observable, in spite of the fact that the summation range was less. The values of F for two platinum atoms, for each of the reflections included in the original summation, were now used in a new summation. This was carried out in exactly the same way as that for platinum phthalocyanine, except that the summation totals were found along one line only, the a axis, and only such terms in the preliminary summation as were necessary for this were calculated. As the scattering centres are assumed to be symmetrical, and as they are now sufficiently far apart to be free from any appreciable overlapping, this is sufficient to give us a new contour map. A section of this map is shown in Fig. 8, covering one platinum atom and its diffraction effects.

A corresponding section of the original map on the same scale is given in Fig. 7. It follows the dotted line *OAB* in Fig. 5, cutting the platinum, a nitrogen, and two benzene carbon atoms.

FIG. 7.



A scale section of typical atoms (along the line OAB *in Fig.* 5).

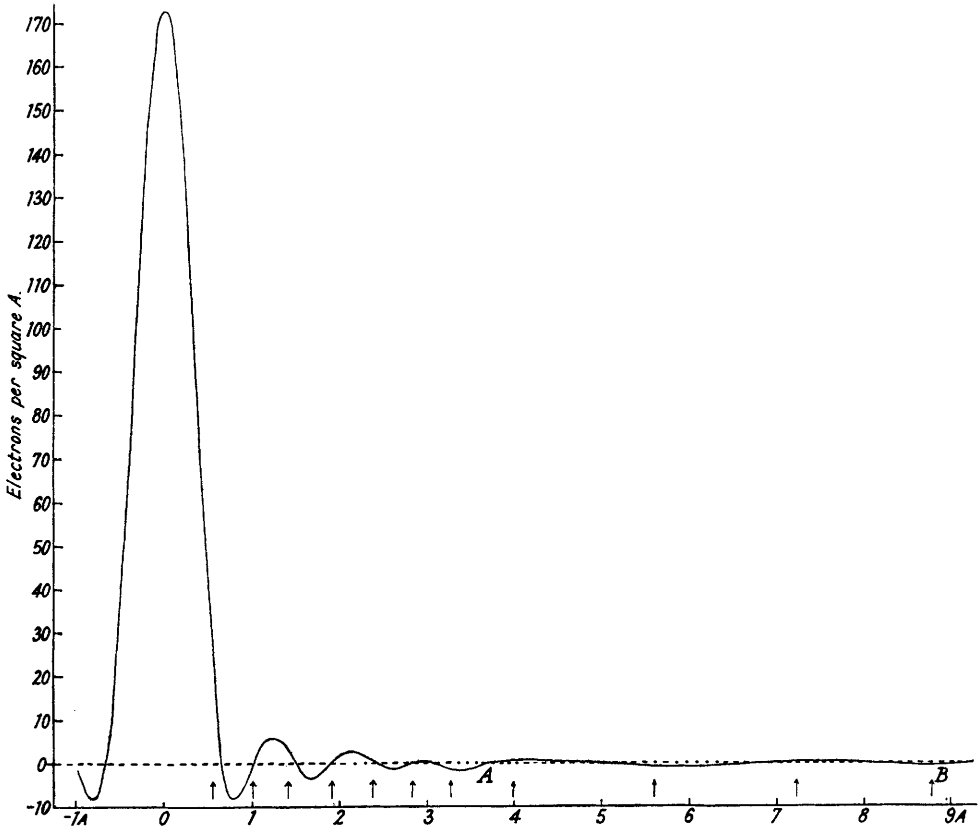
Comparison with Fig. 8 will show that the diffraction produces no appreciable distortion of the benzene rings, and the atoms of the inner rings present an appearance strikingly different from that of the diffraction effects in their neighbourhood.

It is of interest to compare the dimensions of these diffraction rings with those obtained by calculation (Bragg and West, *Phil. Mag.*, **1930**, **10**, 823). The positions of the calculated maxima and minima are shown by arrows on Fig. 8, and it will be seen that the agreement is good.

By reference to the contour map in Fig. 1, it is obvious at once that the main distortions of the contours are accounted for by these diffraction effects in the neighbourhood of the platinum atom. The splitting of the peak due to atom 10 into two parts by the incidence of a diffraction trough very near to its maximum, and the crowding of the contours of atom 9 by the ridge falling on it, are conspicuous examples. The position of the centre of the peak of atom 9 was calculated with an allowance for the diffraction effect, as noted earlier.

An approximate electron count for the platinum atom, regarded as a cone, and extending only as far as the first zero contour, gives a value of 79·0 electrons, the atomic number of platinum being 78. As it is probable (Bragg and West, *loc. cit.*) that a higher value would be obtained if we included the diffraction rings, this result confirms the conclusion previously reached that the scale of intensity measurements is slightly too high.

Fig. 8.



The section of Fig. 7 showing only the platinum atom and its diffraction effects (arrows indicate calculated *zero values).*

We wish to thank Professor Linstead for crystal specimens, and the Royal Institution for laboratory facilities.

The University, Sheffield.
The Royal Institution, London.

[*Received, October 4th,* 1939.]