

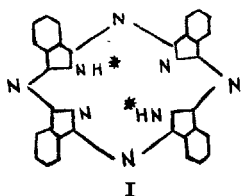
STUDIES ON PHYSICO-CHEMICAL PROPERTIES OF PHTHALOCYANINES.

DETERMINATION OF MOLECULAR WEIGHTS OF FREE PHTHALOCYANINE AND SOME OF ITS METALLIC DERIVATIVES.

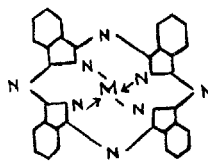
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Phthalocyanines, since their discovery in 1928, and synthetic preparations in the pure state by Linstead and his school have been materials of such absorbing interest to the chemist as well as to the industrialist that it was considered worthwhile to investigate some of their physico-chemical properties. Phthalocyanines combine the complexity of organic structure with the stability of inorganic compounds, resulting in a new chromophore with a splendid resonance and a unique resistance to light, heat, acids and alkalis and to most of the organic solvents. The structure of free phthalocyanine, as given in I, has been finally accepted as correct.



I



II (*M* = Divalent metal)

The structure consists of four corners with iso-indole nuclei which are bound through nitrogen atoms, so that the middle part consists of a 16-membered ring. Within this ring are found two imino-hydrogen atoms (marked with asterisk) which are replaceable by metal. This structure was assigned by Robertson and established with certainty with the help of X-ray investigations. It has been proved by Linstead *et al.* (1936) that the metal is held to the two iso-indole N atoms by primary valencies and is co-ordinated with the other two N atoms to form four-chelate rings, this sort of chelation leading to greater stability (Structure II).

Phthalocyanine derivatives with 26 elements are known so far. Their solubilities are anomalous. Though they exhibit general similarity, there exist distinct differences depending on the constituent metallic atom and they can be classified into three groups:—

- (a) Derivatives of Na, Ca, Hg, etc., are amorphous powder, insoluble in organic solvents and do not sublime. The metal can be removed by dilute acids and some organic solvents.
- (b) Stable covalent co-ordination compounds, like Cu, Ni, Zn, Pt, etc., derivatives. They are stable towards cold concentrated sulphuric acid and hot alkalis and the metal cannot be separated without disrupting the whole molecule. They are soluble in high boiling organic solvents, crystallise in monoclinic crystals and sublime at 500–600°C.
- (c) Labile covalent co-ordinating compounds, like those of Mg, Mn, Sn, etc. They cannot be crystallised or sublimed. The metal is easily removed by the acids.

Of the various physico-chemical properties of phthalocyanines studied so far, reference may be made to their oxidisability studied by Linstead *et al.* (1934); their halogenation studied by Linstead *et al.*; their catalytic activities studied by Cook and by Tamamusha and Tohonatsu; their absorption spectra studied by Linstead *et al.* in a number of organic solvents like chloronaphthalene, bromonaphthalene, pyridine, quinoline, ethyl alcohol, acetone, and in an inorganic solvent like absolute sulphuric acid. As regards the determination of molecular weights of phthalocyanines, the only reference available in literature (other than X-ray method) is the determination of the molecular weight of magnesium phthalocyanine in naphthalene as a solvent, by ebullioscopic method studied by Linstead and Lowe, who have found that the experimental value is in good agreement with the theoretical value.

The object of the present investigation was to determine (a) the molecular weights of free phthalocyanine and its derivatives of copper, lithium, chloro-chloro-aluminium and silver in sulphuric acid by the cryoscopic method; (b) the molecular weight of dilithium phthalocyanine by the ebullioscopic method in absolute ethyl alcohol as the solvent.

Sulphuric acid has been found to be very suitable for this purpose as it is a good solvent for the phthalocyanines. It has a high dielectric constant—greater than 84. The complications due to inter-ionic forces and ion-association are of considerably smaller magnitude. In this connection references may be made to the valuable work done by Hantzsch, Oddo and Scandola, Conant and Werner, and by Hamet *et al.* on the determination of molecular weights of a large number of organic and inorganic substances by cryoscopic methods with sulphuric acid as a solvent.

Section A deals with the determination of molecular weights of free phthalocyanine, copper phthalocyanine, dilithium phthalocyanine, silver phthalocyanine and chloro-aluminium chloro-phthalocyanine by the cryoscopic method in sulphuric acid.

Section B deals with the determination of molecular weight of dilithium phthalocyanine in absolute alcohol by ebullioscopic method.

Section A.

EXPERIMENTAL.

Reagents.

Sulphuric acid: Sulphuric acid (A.R. quality) was distilled in an all-pyrex distillation set under a stream of dry CO_2 . The acid distilled over without decomposition at 318°C .– 319°C . at atmospheric pressure (690 mm. of Hg). The distillate was stored in an air-tight bottle in a desiccator. The fuming sulphuric acid was prepared by heating 33% oleum in the distillation flask and absorbing the evolved SO_3 into distilled H_2SO_4 . This fuming acid was also preserved in an air-tight bottle inside a desiccator.

Free phthalocyanine and its various derivatives were prepared according to the methods of Linstead *et al.*

KHSO_4 : Merck's A.R. quality KHSO_4 was used in this investigation.

Apparatus and Experimental Procedure.

For determining the freezing point Beckmann apparatus was used with the following modifications to prevent absorption of moisture: (1) The rubber and cork stoppers were replaced by ground joints *A* and *B* as shown in Fig. 1; (2) For stirring the following simple arrangement was made. A rubber tube is placed over the side tube *C* and another glass tube passed through it. A slightly thinner glass rod is introduced into the latter tube and connected to the platinum stirrer by means of a flexible wire as shown in Fig. 1. The stirrer was operated by hand. There is little friction and the sealing was almost complete. This was further protected by

another glass tubing whenever stirrer was not in operation. For recording the freezing point a Beckmann thermometer reading to $1/100^\circ$ was used. The thermo-

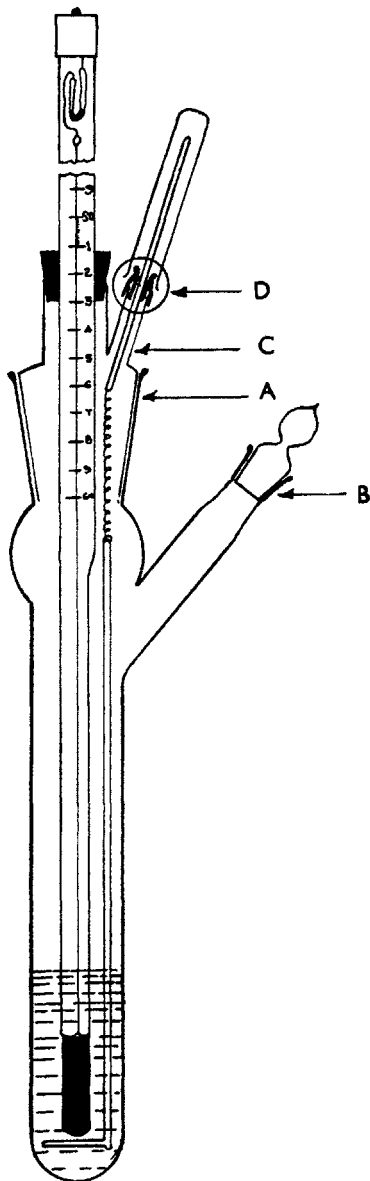


FIG. 1.

meter was first of all set at about 10.5°C . to approximate to the freezing point of absolute sulphuric acid.

During the cryoscopic measurements, (a) the temperature of the cooling was not allowed to exceed 2° to 3° ; (b) the stirrer was operated as uniformly as possible; (c) the thermometer was always tapped before taking a reading.

Stock sulphuric acid was prepared by mixing fuming acid with the distilled acid in a ratio calculated to give slightly less than 100% H_2SO_4 and it was stored in an automatic sealing tube of the type used by Oddo and Scandola (Fig. 2). This

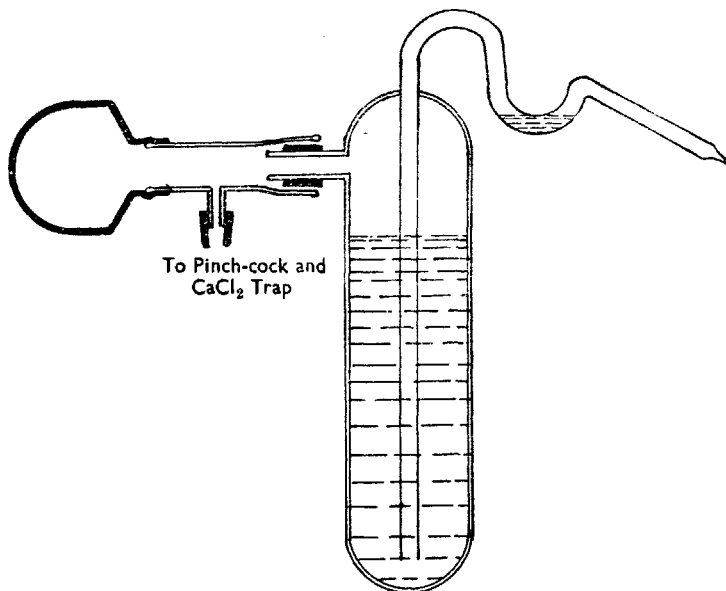


FIG. 2.

acid was then forced out into the freezing point tube up to a definite mark. The freezing point of the acid was next adjusted to the desired point by adding to it small quantities of fuming H_2SO_4 by means of a pipette. The total quantity of H_2SO_4 was found out by weighing the freezing point tube before and after addition of acid.

There is a marked change in the freezing point of H_2SO_4 on either side of the maximum point which corresponds to absolute H_2SO_4 with freezing point of 10.5°C . The freezing point of sulphuric acid of composition, either more or less than 100%, is less than 10.5°C . After determining the freezing point (F.P.) of the solvent the phthalocyanine or its derivative was added, and the lowering of the freezing point produced was measured.

Determination of the cryoscopic constants of the solvents used.

In the present investigation two types of solvent were used:—

- (a) Sulphuric acid containing about 0.1% water, the freezing point being 0.11°C . less than the maximum.
- (b) Sulphuric acid containing about 1% water, the freezing point being 4.15°C . less than the maximum.

Before determining the molecular weights of the phthalocyanines, the cryoscopic constant K was determined for the solvents by observing freezing point depressions of KHSO_4 at different dilutions. Taking Vant Hoff's factor $i = 2$, the molecular weight of KHSO_4 comes down to 68. Assuming this value of the molecular weight

of KHSO_4 in solution, the cryoscopic constants K were calculated from the formula

$$K = \frac{M \cdot \delta t \cdot W}{\omega}$$

where $M = 68$, $\delta t =$ observed freezing point depression, $W =$ amount of sulphuric acid in grams, and $\omega =$ amount of KHSO_4 in grams.

Graphs were drawn taking K as ordinates and the concentrations of KHSO_4 as abscissae (Fig. 3) and from the graphs, K for zero concentration of KHSO_4 was extrapolated. The results are tabulated in Tables I and II.

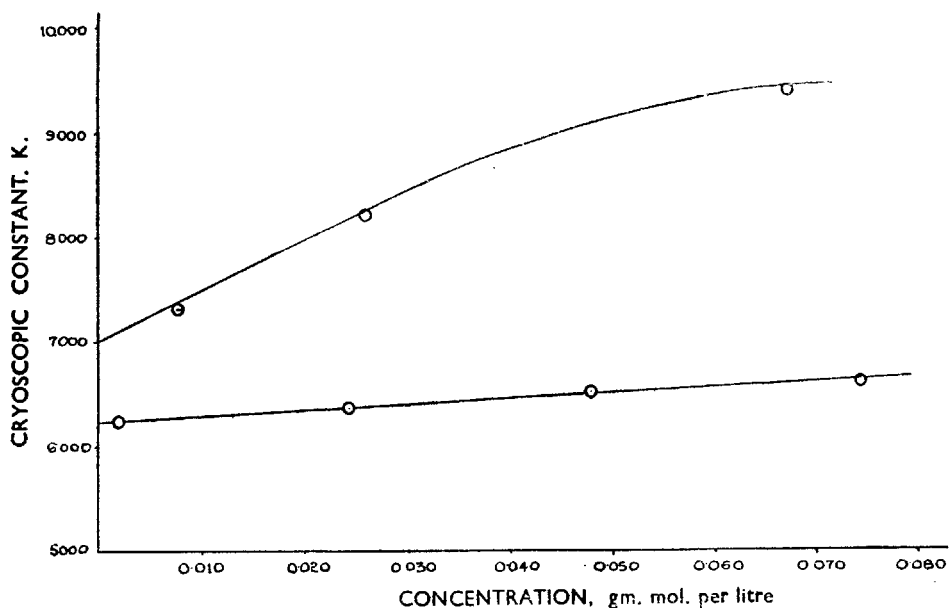


FIG. 3.

Cryoscopic constant K for sulphuric acid containing about 0.1% water.

TABLE I.

Volume of acid taken = 20.4 c.c. $W = 37.4$ grams.

ω (grams).	C. 10^5 (Mols.)	F.P. (Beckmann reading).	δt ($^{\circ}\text{C}.$)	K	K (extrapolated).
0.0049	177	0.220
0.00670	2420	0.232	0.012	6230
0.01326	4780	0.388	0.168	6380	6200
0.02072	7450	0.559	0.339	6500
		0.758	0.538	6610

Cryoscopic constant for sulphuric acid containing about 1% water.

TABLE II.

Volume of acid taken = 29.8 c.c. $W = 54.4$ grams.

w (grams).	C. 10 ⁵ (Mol.)	F.P. (Beckmann reading).	δt (°C.)	K	K (extrapolated).
.....	4.279
0.0283	713	4.335	0.056	7320
0.1663	4104	4.697	0.418	9290	7000
0.2737	6740	4.977	0.698	9450

The experimental results on the molecular weights of free phthalocyanine and its various derivatives are recorded in Tables III and IV. The molecular weight was calculated from the relation $M = \frac{K.w}{\Delta t.W}$.

TABLE III.

F.P. of acid used = 0.11° below the maximum F.P. of absolute sulphuric acid; cryoscopic constant $K = 6,200$ (extrapolated). M = Molecular weight calculated according to the formula; M_{obs} = Molecular weight found experimentally.

Substance.	M_{calc}	W gms.	w gms.	C. 10 ⁵ (Mol.)	t (°C.)	M_{obs}	i
Free Phthalocyanine (C ₃₂ H ₁₈ N ₈) ..	514	33.25	0.1002	1074	0.177	105.5	4.9
do. do. ..	514	33.05	0.1098	1176	0.199	102.9	5.0
Copper Phthalocyanine (C ₃₂ H ₁₆ N ₈ Cu) ..	576	32.65	0.1108	1078	0.170	123.8	4.7
do. do. ..	576	32.45	0.1254	1228	0.196	122.3	4.7
Silver Phthalocyanine (C ₃₂ H ₁₆ N ₈ Ag) ..	619	30.00	0.1578	1549	0.500	64.9	9.5
do. do. ..	619	32.90	0.1476	1326	0.452	61.5	10.0
Chloraluminium Chloro- phthalocyanine (C ₃₂ H ₁₅ N ₈ Cl.AlCl. 2H ₂ O)	644	37.25	0.1316	1005	0.543	40.3	16.0

TABLE IV.

F.P. of acid used = 4.15° below the maximum F.P. of absolute sulphuric acid; cryoscopic constant $K = 7,000$ (extrapolated).

Substance.	M_{calc}	W grams.	w grams.	$C. 10^5$ (Mol.)	t ($^\circ\text{C}.$)	M_{obs}	i
Free Phthalocyanine ($\text{C}_{32}\text{H}_{18}\text{N}_8$) ..	514	38.7	0.1068	988	0.285	67.8	7.6
do. do. ..	514	38.7	0.1137	1076	0.291	70.7	7.3
Copper Phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$) ..	576	36.4	0.0886	778	0.222	76.7	7.5
do. do. ..	576	36.5	0.0980	858	0.252	74.6	7.7
Dilithium Phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{N}_8\text{Li}_2$) ..	526	37.6	0.0995	908	0.470	39.4	13.4
do. do. ..	526	37.3	0.1176	1108	0.542	40.7	13.0
Silver Phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{N}_8\text{Ag}$) ..	619	38.8	0.1178	902	0.353	60.2	10.3
do. do. ..	619	39.0	0.1334	1016	0.381	62.8	9.9
Chloraluminium Chloro- phthalocyanine ($\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cl}.\text{AlCl}.\text{H}_2\text{O}$) ..	644	36.7	0.1122	874	0.550	39.0	16.5
do. do. ..	644	36.8	0.0922	700	0.451	38.7	16.6

Section B.

Reagents.—Pure dilithium phthalocyanine prepared according to the method described before, and pure and crystallised benzoic acid were used. As a solvent absolute alcohol distilled over metallic calcium, and diethyl phthalate was used.

Apparatus and Method of Experimental Procedure.

For the determination of boiling point Landsberger's method, as modified by Walker and Lumsden, was used. The thermometer used in these experiments was graduated to $1/100^\circ$. When the thermometer registered a constant temperature, the reading was taken as the boiling point of the pure solvent. Next the molecular weight of a simple substance, like benzoic acid, was determined in absolute alcohol to test the accuracy of the method.

The molecular weight of dilithium phthalocyanine was determined in the same way and the results are recorded in Table V.

TABLE V.

$k' = 1560.0$.

Substance.	θ ($^\circ\text{C}.$)	ω gms.	θ_1 ($^\circ\text{C}.$)	e ($^\circ\text{C}.$)	v (c.c.)	M	
						Obs.	Calc.
Benzoic acid ..	75.50	0.5	76.10	0.60	11.0	118.2	122.0
Dilithium phthalocyanine ..	75.50	0.5	75.67	0.17	9.25	496.1	525.9
" "	75.50	0.5	75.64	0.14	11.5	484.0	525.9

θ = boiling point of absolute alcohol; θ_1 = boiling point of solution; ω = weight of the solute; e = elevation of the boiling point; v = volume of the solution; M_{obs} = molecular weight found experimentally; and M_{calc} = molecular weight calculated according to the formula.

From the above table we can see that the molecular weight, as determined by experiment in the solvent of absolute alcohol, is in good agreement with the theoretical value.

DISCUSSION.

Section A.

The cryoscopic measurement of Hantzsch in sulphuric acid as a solvent with compounds, organic as well as inorganic, containing \bar{N} atoms not linked to oxygen atoms, led him to the following conclusions:—

The nitrogen-bearing compounds will dissolve in sulphuric acid with complete salt formation and forming a polyvalent ion depending on the number of \bar{N} atoms in the compound. This is demonstrated by the lowering of the freezing point and the molecular weight corresponding to an increase in the number of ions in the solution.

Thus

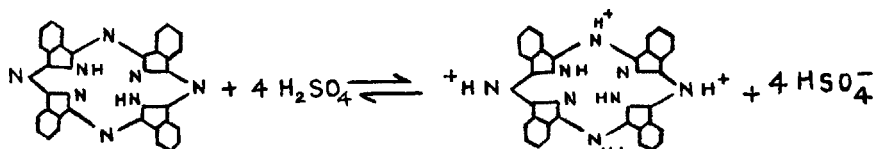
No. of \bar{N} atoms in the compound ..	1	2	3	4	5
Maximum No. of ions 2	3	4	5	6

Accordingly the number of ions formed in sulphuric acid solution can be estimated and thus one can know how many \bar{N} atoms of the compound take part in salt formation. Hantzsch has studied many compounds including basic, neutral and even acidic substances like NH_3 , HNO_2 , HNO_3 , and benzoic acid.

The experimental results of Tables III and IV may be explained schematically as outlined below:

(1) *Free Phthalocyanine* :

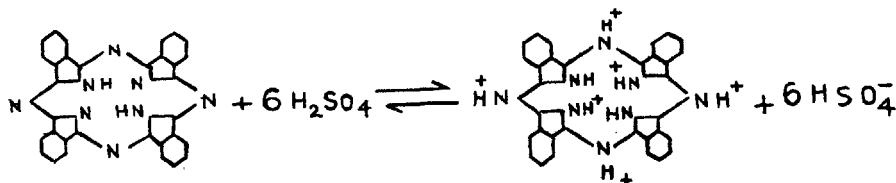
(a) With sulphuric acid containing 0.1% water:



It follows from the scheme that $n = 5$ which is in good agreement with experimental values. If we assume complete dissociation as, we could do logically, at such low concentration in a solvent with so high a dielectric strength, i which is equal to $1 + (n-1)\alpha$ becomes $1 + (n-1)$, that is, $i = n$.

(b) With sulphuric acid containing 1.0% water:

The two central nitrogen atoms (which are not imino), with one pair of electrons, take up two more protons under changed condition of the solvent as:

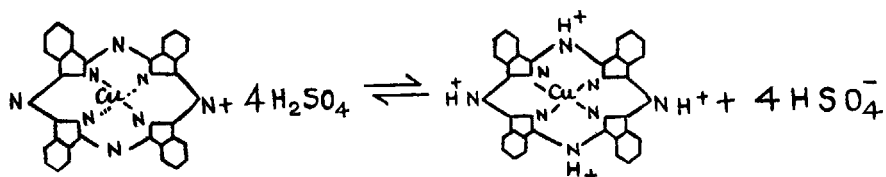


Hence i should be 7 which has been experimentally observed. From this it seems evident that the inner two co-ordinating nitrogen atoms also take up protons

in the presence of small quantities of water, whose function is difficult to explain at present.

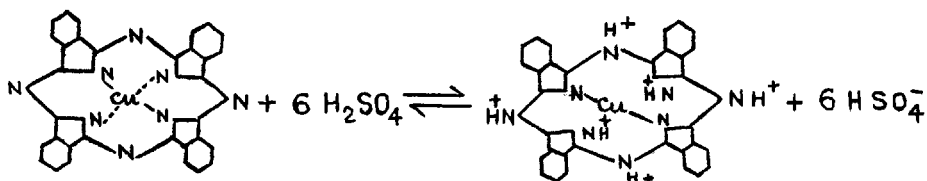
(2) *Copper Phthalocyanine* :

(a) With 0.1% water in the solvent :



Hence i should be 5 which has been experimentally observed.

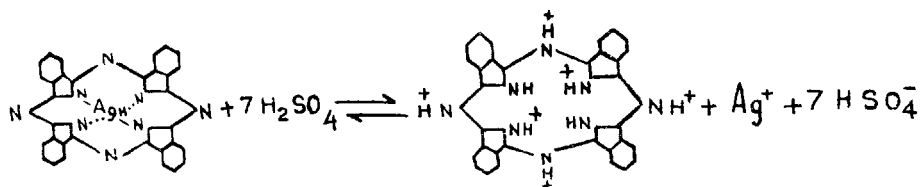
(b) With 1.0% water in the solvent :



Here also we observe similar results as in the case of free phthalocyanine, that is, $i = 7$.

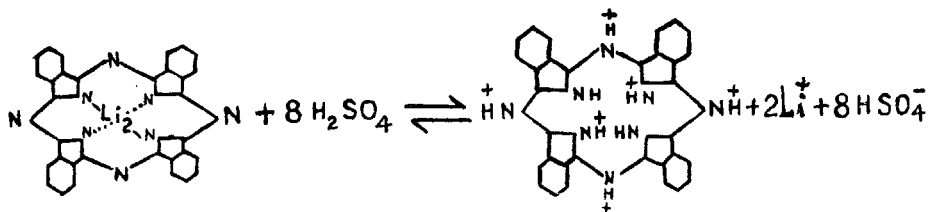
In other cases the same reaction scheme may be postulated with sulphuric acid containing 0.1% as well as 1.0% water.

(3) *Silver Phthalocyanine* :

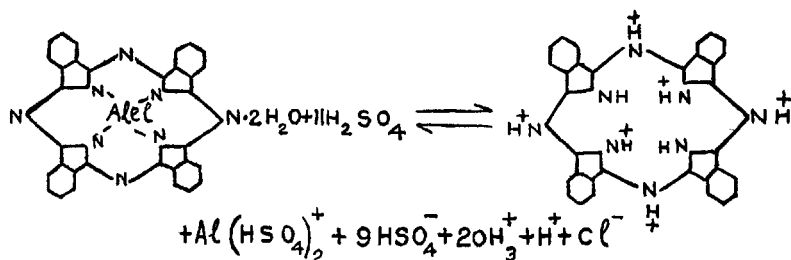


which should give $i = 9$, which has been found to agree fairly well with the experimental value.

(4) *Dilithium Phthalocyanine* :



Here $i = 11$ whereas the experimental values are in the neighbourhood of 13. This discrepancy may be due to experimental error.

(5) *Chloro-aluminium Chloro-phthalocyanine* :

Here $i = 15$ which is in fair agreement with the experimental value of 16.

Section B.

The agreement between the theoretical and the observed value is quite satisfactory and evidently the molecule of dilithium phthalocyanine remains undissociated in absolute alcohol.

Our thanks are due to Dr. T. L. Rama Char for carrying out some preliminary experiments.

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