nent in air, and forms a closely adhering coat like that which is produced upon the surface of zinc or lead, protecting the metal beneath from further change.

In many points the chemical reactions of thallium resemble those of silver, to which metal it is also further approximated by the circumstance that the atomic heat of the metal, like that of silver, is double that of the series to which lead belongs. Although therefore in other physical properties thallium differs greatly from silver, it seems to be more closely allied to that metal than to any other.

January 22, 1863.

Major-General SABINE, President, in the Chair.

The following communications were read:—

I. "Researches on some of the Artificial Colouring Matters.—
No. I. On the Composition of the Blue Derivatives of the Tertiary Monamines derived from Cinchonine." By A. W. HOFMANN, LL.D., F.R.S. Received December 18, 1862.

The chemical visitors of the International Exhibition will not easily forget the magnificent collection of products displayed in the French court by M. Menier of Paris. Among these compounds, equally remarkable for their variety and beauty, the large crystals of cyanine, rivalling in splendour and purity Mr. Nicholson's acetate of rosaniline, have attracted general attention. M. Menier, who has produced this new dye on a very large scale, has most liberally placed at my disposal some of the finest of these crystals for examination, hoping that their more minute investigation might perhaps lead to a method of giving solidity to this new colour, which in brilliancy and purity of tint is second to none of the several blues lately derived from coal-tar. The composition of cyanine and its mode of formation having hitherto remained unknown, I have gladly availed myself of this opportunity of performing some experiments with this interesting compound. I am sorry to say that, in a practical point of view, these experiments have failed entirely; but my studies have led me to some observations on this substance which, as a contribution to the history of cyanine, deserve to be recorded, and which I beg leave to communicate to the Royal Society.
The discovery of the blue compounds from chinoline and its homologues dates as far back as 1856. In that year Mr. G. Williams engaged in a renewed examination of the base extracted by Runge from coal-tar and obtained by Gerhardt from the alkaloids of the cinchona bark, the identity in composition of which I had established in one of my earlier researches. Among the numerous compounds of these bases most carefully examined by Mr. G. Williams on this occasion, were also their methylated and ethylated derivatives, one of which, the iodide of methyl-leucolylammonium, I had discovered when studying the action of iodide of methyl upon ammonia and its analogues. It was in preparing this compound from the chinoline obtained by the distillation of cinchonine, and in separating the ammonium-base corresponding to the iodide by means of oxide of silver, that Mr. Williams first observed the splendid coloration which has led him to the discovery of the new dye now commercially known under the name of cyanine. Precisely similar phenomena were subsequently (in 1857) observed by M. von Babo, who produced them by treating chinoline with the sulphates of methyl and ethyl, and described the coloured substances thus obtained as methylirisine and ethylirisine. Mr. Williams was inclined to attribute the formation of the blue compounds, in which he recognized distinctly basic properties, to a process of oxidation; M. von Babo represents his methyl- and ethylirisine, although with very great reserve, by the formulæ

\[ C_{11}H_{14}N_2O_2 \quad \text{and} \quad C_{13}H_{16}N_2O_2. \]

No attempt has since been made to establish the composition of these singular compounds by a more minute examination. In fact several years elapsed without any further notice being taken of them, until the development of the aniline industry revived the memory of these remarkable colour phenomena, which have since attracted the general attention of dyers and printers. Mr. G. Williams showed that, among the several coloured compounds produced by the action of iodides of alcohol radicals upon chinoline bases, the one obtained by means of iodide of amyl is particularly rich in tinctorial power; he has given a very interesting account of this new dye, and accurately described the mode of manufacture of this body, which, under the name of cyanine, soon became an article of commerce.

Unfortunately the tint produced by cyanine is less fast than beautiful, and the hopes entertained of the industrial future of the new
compound has not been realized; nevertheless the importance attached by dyers to Mr. Williams's discovery is well marked by the fact of a gold medal, together with a prize of 10,000 francs, having been proposed for the discovery of a means of rendering stable the beautiful colours dyed by cyanine.

The crystals submitted to me for examination by M. Menier were distinct prisms, sufficiently well formed for crystallographical determinations. They are at present in the hands of Quintino Sella. Their substance possesses a beautiful green metallic lustre with a golden tint, by which, as well as by crystalline form, they are readily distinguished from acetate of rosiniline, which they in other respects much resemble. The crystals are insoluble in anhydrous ether, difficultly soluble in water, but dissolve readily in alcohol. The solution has a magnificent blue colour, with a coppery iridescence on its surface. Addition of acids destroys this colour. Ammonia and the fixed caustic alkalies leave the colour apparently untouched; but it is now produced by a finely divided deep-blue precipitate suspended in the liquid, which may be filtered off, the filtrate separated from it being colourless.

The green crystals were found to be the iodide of a peculiar basic compound. The iodine is rather firmly held in this compound; but it may be precipitated from the alcoholic solution by oxide of silver, and exchanged for bromine or chlorine by treatment of this solution with bromide or chloride of silver, when the bromide or chloride corresponding to the iodide are produced. The analysis of the crystals gave results indicating unequivocally the formula

$$C_{29}H_{33}N_2I,$$

which received a close confirmation by the examination of a fine platinum-salt crystallizing in rhombic tablets, which is obtained by precipitating the chloride corresponding to the iodide, strongly acidulated with hydrochloric acid, by dichloride of platinum. Nevertheless slight discrepancies between the theoretical values of the formula and the results obtained led me to assume the existence in the crystals of a compound containing less carbon and hydrogen, indeed of a homologous iodide,

$$C_{29}H_{32}N_2I.$$

This hypothesis, not countenanced at first by the remarkable constancy which the composition of the iodide presented even after three
or four crystallizations, was fully confirmed when the chloride was submitted to a systematic partial precipitation by dichloride of platinum. After several repetitions of the process, the partially precipitated platinum-salt being decomposed by sulphuretted hydrogen and the chlorides again partially precipitated, two platinum-salts were obtained, one of which, the less soluble one, proved to be the pure platinum-salt corresponding to the iodide with 30 equivalents of carbon, whilst the other one was sufficiently pure to show that it belonged in reality to the homologous iodide with 2 equivalents of carbon less.

The amount of the iodide

\[ \text{C}_{28} \text{H}_{42} \text{N}_2 \text{I}, \]

which contaminated (if the term may be applied to so beautiful a substance) the iodide

\[ \text{C}_{30} \text{H}_{49} \text{N}_2 \text{I}, \]

is, however, so small that its presence did not materially influence the analytical results obtained in the further examination of the compound.

The explanation of the formation of the iodide presents no difficulty; this substance obviously derives from lepidine,

\[ \text{C}_{19} \text{H}_9 \text{N}, \]

whilst only the slight admixture is due to the presence, in the original bases submitted to the action of iodide of amyl, of a small quantity of chinoline,

\[ \text{C}_9 \text{H}_7 \text{N}. \]

In fact Mr. Williams, in describing the preparation of his dye, distinctly states that the chinoline by no means requires to be pure for the purpose. M. Menier has moreover kindly furnished me with a considerable quantity of the crude material from which the green crystals are obtained. This proved to be a mixture of several bases, in which the presence of lepidine and chinoline was traced without the slightest difficulty, by the analyses of platinum-salts.

In the genesis of the new iodide two different phases have to be distinguished, viz., 1, the transformation of lepidine into iodide of amylepidyl-ammonium,

\[ \text{C}_{10} \text{H}_9 \text{N} \quad + \quad \text{C}_5 \text{H}_{11} \text{I} \quad = \quad \text{C}_{15} \text{H}_{20} \text{N} \text{I}; \]

2, the condensation under the influence of potash of two molecules of the compound into one molecule of a higher order,

$$2\left\{C_{15}H_{20}NI\right\} + KH_2O = C_{30}H_{39}N_2I + KI + H_2O.$$  


It became indispensable to verify these reactions by the analysis of additional compounds.

The green crystals dissolve with facility in boiling dilute hydriodic acid; the colourless solution deposits on cooling yellow needles of remarkable beauty, the analysis of which has furnished the values of the formula

$$C_{30}H_{40}N_2I_2 = C_{30}H_{39}N_2I, HI.$$  

These crystals are isomeric with iodide of amyl-lepidyl-ammonium, from which, however, they are distinguished by all their properties. They dissolve in cold water without decomposition, but on addition of alcohol they immediately assume a blue coloration, the original monacid compound being reproduced. The same change takes place at 100°; so that in preparing the compound for analysis it was necessary to dry it in vacuo. In the facility with which the diacid compounds are converted into the monacid salts, this substance resembles rosaniline, which, as I have pointed out in a recent paper, forms likewise colourless acid salts of little stability.

The green iodide dissolves with equal facility in hydrochloric and hydrobromic acid, yielding perfectly colourless solutions, and giving rise to the formation of well-crystallized compounds, which contain, in addition to iodine, respectively bromine and chlorine.

On submitting the green iodide in alcoholic solution to the action of chloride of silver, the whole of the iodine is separated in the form of iodide of silver, a blue solution being obtained from which the monacid chloride crystallizes, on slow evaporation, in green metallu- lustrous sharply-defined prisms of surpassing beauty. This salt was found to contain

$$C_{30}H_{39}N\text{ Cl.}$$

Dissolved in hydrochloric acid, this salt furnished a diacid compound which, on evaporation in vacuo, separates in long straw-coloured needles. The highly deliquescent character of this substance has
hitherto prevented me from analysing it; but if there was the slightest doubt of this compound having the composition

\[ \text{C}_{30} \text{H}_{40} \text{N}_2 \text{Cl}_2 = \text{C}_{30} \text{H}_{39} \text{N}_2 \text{Cl}, \text{HCl}, \]

it would be dispelled by the analysis of a fine-yellow difficulty soluble platinum-salt crystallizing in small well-defined rhombic plates, which falls directly on addition of dichloride of platinum to the alcoholic solution of the diacid chloride, containing a considerable amount of hydrochloric acid, and which, by analysis, was found to be represented by the formula

\[ \text{C}_{30} \text{H}_{40} \text{N}_2 \text{Cl}_2, 2 \text{PtCl}_2. \]

The gold-salt is obtained by precipitating the solution of the acid chloride with trichloride of gold, when a yellow, scarcely crystalline precipitate is formed, which, dried in vacuo, contains

\[ \text{C}_{30} \text{H}_{40} \text{N}_2 \text{Cl}_2, 2 \text{AuCl}_3. \]

I have, moreover, prepared the monacid bromide, which forms beautiful metal-lustrous prisms easily crystallizable; the diacid nitrate as a crystalline network, on evaporating a solution of the base in nitric acid in vacuo; and, lastly, the acid sulphate, which crystallizes in white, well-formed rhombic tables, very soluble in water, but insoluble in alcohol, by which it is not decomposed like the other diacid compounds.

I have refrained from multiplying the analytical evidences by the minute examination of these salts, because I was happy enough to observe a reaction which supported the interpretation of the results of analysis in an unequivocal manner. Remembering the simple scission which I had formerly accomplished by exposing the iodide of tetrethylammonium to the action of heat, when the compound splits into iodide of ethyl and triethylamine, I was induced to submit the green iodide to distillation. The green crystals rapidly fuse into a blue liquid, the surface of which presents a peculiar coppery lustre. On raising the temperature, decomposition takes place, and in the receiver is condensed a mixture of lepidine and iodide of amyl, the reunion of which to iodide of amyl-lepidyl-ammonium may be prevented by collecting them in hydrochloric acid; at the same time a gas is evolved, burning with a brilliant flame and readily absorbed by bromine, and which could easily be condensed by passing it through a serpentine surrounded with ice. I was thus enabled to collect
enough of the volatile hydrocarbon to determine its boiling-point, which proved it to be pure amyylene. If the heat be carefully regulated, the amount of charcoal remaining in the retort is comparatively small. The interpretation of the phenomena observed is given in the following equation:—

\[ C_{30}H_{39}N_2I = 2C_{10}H_2N + C_5H_{11}I + C_5H_{10} \]

Green iodide. Lepidine. Iodide of Amylene.

Here, again, I have had an opportunity of proving the presence in the crystals of a small quantity of the homologous chinoline compound; for on submitting, after separating the iodide of amylen, the hydrochlorate of the volatilized base to distillation with potassa, and collecting apart the first quantity of the basic liquid which came over with the vapour of water, this substance proved by the platinum determination to be chiefly chinoline, while the portion of the base distilling last proved by the same mode of analysis to be pure lepidine.

The results obtained in these experiments furnish new illustrations of the tendency to molecular accumulation by which the ammonias and their derivatives are distinguished. Only a few weeks ago I had the honour of submitting to the Royal Society a short account of this class, which is obtained as a secondary product in the manufacture of aniline. The coloured derivatives of the bases of the chinoline series present in their composition considerable analogy with paranilne.

### Aniline series.

- \( C_6H_7N \) Aniline.
- \( C_6H_7N, HCl \) Chloride.
- \( C_9H_7N \) Paraniline.
- \( C_9H_7N, HCl \) Monacid chloride.
- \( C_6H_7N, HCl \) Diacid chloride.

### Lepidine series.

- \( C_{15}H_{19}NH_2O \) Hydrated oxide of amylylepidyl-ammonium.
- \( C_{15}H_{19}N, HCl \) Chloride.
- \( C_{15}H_{19}NH_2O \) Free blue base.
- \( C_{15}H_{19}N, HCl \) Green iodide, monacid.
- \( C_{15}H_{19}N, HCl \) Yellow iodide, diacid.

I have written the formulae of the coloured compounds so as to bring out their analogy with the paranilne salts—in fact, so as to
characterize them as para-compounds of the amyl-lepidyl-ammonium salts, but I am far from attributing to these formulæ any other value. In fact the molecular construction of this new class of compounds remains to be established by further experiments.

The theory which (in 1852) satisfactorily represented the constitution of the nitrogen bases then examined, requires an expansion to include the tinctorial ammonias added to our knowledge during the last decade. The time for the enunciation of this amplified theory has not yet arrived.

Here only a few experiments may still be mentioned, which were made with the oxide corresponding with the salts described.

The action of oxide of silver upon the iodide dissolved in alcohol liberates the base, which, on evaporation of the alcohol, separates as an indistinctly crystalline deep-blue mass, moderately soluble in water, less soluble in anhydrous ether, easily soluble in alcohol. Ether precipitates the base from its alcoholic solution; I have not examined it.

Submitted to distillation, the free oxide gives rise to an oily base, which I naturally expected to be lepidine; but the experiments which I have hitherto made with this substance appear to negative this assumption. I have undertaken a more minute examination of the compound, because, if it be different, its study will probably throw some light upon the still uncertain constitution of the tertiary bases of the chinoline series, which I have frequently attempted to decipher.

It remained now only for me to examine the mode of formation of the remarkable compound the nature of which I have endeavoured to clear up. With this view I have studied the action of iodide of methyl and amyl upon chinoline and lepidine, large quantities of which were kindly placed at my disposal by my friend Mr. David Howard. The products obtained in this reaction I have not submitted to a minute examination, having satisfied myself that their principal phases are well illustrated by the equations which I have given for the formation of the substances produced by the action of iodide of amyl upon lepidine. Nor have I followed out in detail the complicated secondary changes, and more especially the generation of the red colouring matter which is abundantly formed in these reactions. I have nothing to add to the perfect description of these phenomena by the distinguished discoverer of this pigment.
In conclusion I may be allowed to express my best thanks to M. Menier: without the magnificent crystals furnished by his ateliers, I could not have even attempted to clear up this question.

Though proud of her office as guide of industry, science acknowledges without blushing that there are territories on which she cannot advance without leaning on the strong arm of her powerful companion. Joint labours of this kind cannot fail to seal the pledge of alliance between industry and science.

II. "On some new Compounds obtained by Nitrogen-substitution, and new Alcohols derived therefrom." By Peter Griess, Esq. Communicated by Dr. Hofmann. Received December 18, 1862.

In the beginning of this year (1862) I pointed out* that diazoamidobenzol, when submitted to the action of nitric acid containing nitrous acid in solution, is transformed into a new compound according to the equation

\[
C_{12}H_{11}N_3 + 2 HNO_2 + HNO_3 = 2(C_6H_4N_2, HNO_3) + 2H_2O.
\]

Diazo-amidobenzol. New compound.

I have now found that this remarkable compound, the nitrate of diazobenzol, can be much more easily produced by the action of nitrous acid upon nitrate of aniline,

\[
C_6H_7N, HNO_3 + HNO_2 = C_6H_4N_2, HNO_3 + 2H_2O.
\]

Nitrate of aniline. Nitrate of diazobenzol.

This process has furnished me a considerable number of similarly constituted nitrogen-substituted derivatives, not only of monacid monamines, but also of diamines; and it is to some of the bodies generated by means of the latter that I beg leave to call the attention of the Royal Society.

If a current of nitrous acid be passed into a cold solution of the nitrate of benzidine, a base which, by the researches of P. W. Hofmann, has been characterized as a well-defined diacid diamine, a new compound is produced, crystallizing from water in white needles,

* Ann. Chem. Pharm.