

The Platinum Metal Phthalocyanines

THE PREPARATION AND CHARACTERISTICS OF THE PURE COMPOUNDS

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The likelihood that the platinum metal phthalocyanines might prove to be of commercial importance as homogeneous catalysts as well as of academic interest prompted an investigation into the preparation of these compounds and their subsequent characterisation.

Phthalocyanine is a deep blue-green pigment in which it has long been known that it is possible to replace two hydrogen atoms by a metal to form compounds having a similar distinctive colour. Iron phthalocyanine was discovered in 1928 at the Grangemouth works of Scottish Dyes Ltd, where it had been formed accidentally during the preparation of phthalimide from phthalic anhydride and ammonia in an iron vessel. Its structure was elucidated by Professor R. P. Linstead and his co-workers (1) between 1929 and 1934, and they coined the name now accepted. Copper phthalocyanine, the first dye of this type to be made commercially, is better known as Monastral Fast Blue BS. Greener shades of this dye may be produced by chlorinating the phthalocyanine skeleton. Some of the metal phthalocyanines have been found to have interesting catalytic applications as well as semi- and photo-conducting properties. There is thus a possibility that the platinum metal phthalocyanines might be of significant commercial as well as academic interest and the Johnson Matthey Research Laboratories have been investigating the preparation of these compounds in a pure form.

Pt (II) phthalocyanine is readily made by the process described by Linstead and his co-workers by reacting platinumous chloride PtCl_2 with *o*-dicyanobenzene, $\text{C}_6\text{H}_4(\text{CN})_2$ at 280 to 300°C. The resulting compound can be recrystallised from hot 1-chloronaph-

thalene and is readily soluble in and recoverable from concentrated sulphuric acid. In this way crystals of the pure compound can be grown and made available for study.

The structure (2) of this compound is shown in Fig. 2. This should be compared with Fig. 1, which represents the structure of phthalocyanine, $\text{C}_{32}\text{H}_{18}\text{N}_8$ (or PcH_2 where Pc is equivalent to $\text{C}_{32}\text{H}_{18}\text{N}_8$). It will be seen that a platinum atom replaces the two imino-hydrogen atoms (*). The inner square (side 2.7 Å, diameter 3.82 Å) of nitrogen atoms can accommodate the largest of metal atoms, e.g. platinum (diameter 2.8 Å) without undue strain.

When palladous chloride is reacted in a similar way, however, palladous monochlorophthalocyanine PdPcCl is formed. In this compound, the palladium atom (like the platinum atom considered above) replaces the two imino-hydrogen atoms in the molecule; but in addition a chlorine atom attaches itself to the phthalocyanine skeleton. PdPcCl can be recrystallised to yield a pure product.

The position with regard to the other platinum metals is more complex and the literature on their structure is confusing (3). Recent work in these laboratories has, however, thrown considerable light on the nature of the reactions.

When rhodium trichloride RhCl_3 is treated with *o*-cyanobenzamide at about 280°C the

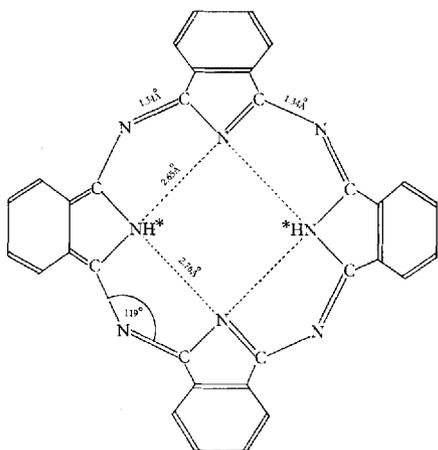


Fig. 1 Metal free phthalocyanine

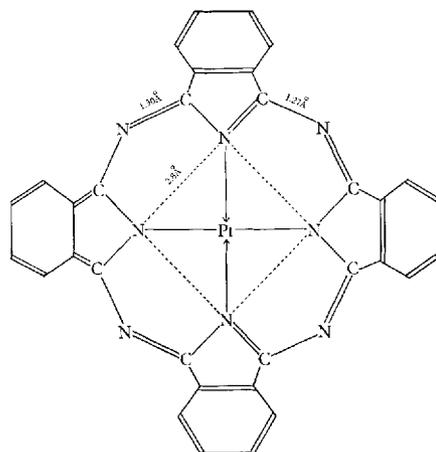


Fig. 2 Platinum (II) phthalocyanine

product is a chlor-rhodium phthalocyanine PcRhCl , the chlorine being directly bound to the metal in its normal valence state. This compound cannot be crystallised but can be purified by extracting impurities consecutively with alcohol, benzene and acetone.

The other three platinum metals, iridium, ruthenium and osmium, do not appear to form metal chlorphthalocyanines. When the chlorides of these metals are treated with either *o*-cyanobenzamide or *o*-dicyanobenzene at about 280°C the products after extraction with alcohol, benzene and acetone are of a "solvated" type and have the compositions $\text{PcIrClC}_6\text{H}_4(\text{CN})_2$, $\text{PcRuClC}_6\text{H}_4(\text{CN})_2$ and $\text{PcOsCl}_2\text{C}_6\text{H}_4(\text{CN})_2$ respectively. The complex character of these compounds is confirmed by the fact that the dicyanobenzene can only be removed by strong heating below about 500°C and that it can be replaced with aniline by boiling in that solvent.

These solvated iridium, ruthenium and osmium phthalocyanines are sparingly soluble in such common solvents as acetone, alcohol, benzene and ether and yield intensely coloured solutions having characteristic visible absorption maxima.

It has been reported by Russian workers that the osmium tetroxide-*o*-dicyanobenzene

reaction gives a dark blue pigment whose extraction with and reprecipitation from concentrated sulphuric acid yields a polymer $(\text{PcOs}(\text{IV})\text{O}\cdot\text{SO}_2\text{O})_n$.

Re-examination of the main reaction product in our research laboratories has shown, however, that it is a derivative of osmyl phthalocyanine, $\text{PcOs}(\text{VI})\text{O}_2\cdot\text{C}_6\text{H}_4(\text{CN})_2$. Boiling aniline converts this to the ammine, $\text{PcOsO}_2\cdot 3\text{C}_6\text{H}_6\text{NH}_2$. Treatment of either derivative with concentrated sulphuric acid could give $(\text{PcOs}(\text{VI})\text{O}\cdot\text{SO}_4)$. Full details of all this work will shortly be published elsewhere.

Now that methods of making these organo-metallic compounds reproducibly have been worked out and their properties have been established, it is hoped that more investigators will be encouraged to make use of their peculiar characteristics in a wide field of chemical research.

References

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