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 platinous chloride
PtCl₂ with o-dicyanobenzene, C₆H₄(CN)₂
at 280 to 300°C. The resulting compound
can be recrystallised from hot 1-chloronaph-
thalene and is readily soluble in and recover-
able 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 phthalo-
cyanine, C₃₂H₃₆N₈ (or PcH₈ where Pc is
equivalent to C₃₄H₁₈N₈). 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 mono-
chlorophthalocyanine PdPcCl is formed. In
this compound, the palladium atom (like
the platinum atom considered above) re-
places the two imino-hydrogen atoms (*).
Because of the smaller size of the palladium
atom it cannot fit into the inner square
without undue strain. 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, how-
ever, thrown considerable light on the nature
of the reactions.

When rhodium trichloride RhCl₃ is treated
with o-cyanobenzamide at about 280°C the
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 PcIrClC₂H₄(CN)₂, PcRuClC₂H₄(CN)₂ and PcOsCl₂C₂H₄(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 (PcOs(IV)O₂S₂O₄)ₖ.

Re-examination of the main reaction product in our research laboratories has shown, however, that it is a derivative of osmyl phthalocyanine, PcOs(VI)O₂C₂H₄(CN)₂. Boiling aniline converts this to the ammine, PcOsO₃C₂H₄NH₂. Treatment of either derivative with concentrated sulphuric acid could give (PcOs(VI)O₆S₂O₄). Full details of all this work will shortly be published elsewhere.

Now that methods of making these organometallic 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
4 W. Herr, Z. für Nattürforsch, 1964, 9a, 180