Macromolecular Platinum Metals Chelates

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In this review the advances in and problems associated with the preparation, structure and practical applications of macromolecular platinum metals chelates (MPMC) are presented and assessed. The terminology, classification and nomenclature of MPMC are considered and special attention is paid to their preparation and structural features. Some applications of MPMC are described.

During the last two decades the chemistry of macromolecular platinum metals chelates (MPMC) has received much attention. The chelation of platinum metals by polymeric ligands is widely used, for example, for the preparation of efficient polymeric catalysts (1), for membrane filtration of solutions containing low concentrations of platinum metals (2, 3), and in ion exchange (4, 5). Important theoretical problems in the polymeric and co-ordination chemistry of MPMC, such as macromolecular reactivity, the nature of bonding in metal chelates and the distortion of ligands have also been investigated.

Terminology, Classification and Nomenclature of the MPMC

High molecular weight homo- and heterochain compounds with pendant metal chelates (I) (6) or where the chelates form crosslinks (II) (7) to the chain are usually called macromolecular metal chelates, as shown below. Here the symbol ~ denotes a polymeric chain.

In contrast to co-ordination polymers which are described in detail elsewhere (8, 9) MPMC do not contain metal in the polymer backbone, thus the metal can be easily removed or substituted by other metals without breaking the main chain of the macromolecule. Similarly other platinum metals complexes with chelates which act as ion-exchange resins (3 – 5, 10) should also be related to macromolecular platinum metals chelates.

The parameters used in MPMC classification, the classes and typical examples of MPMC (11 – 21) are listed in Table I. It should be noted that pendant type MPMC may be formed when low molecular weight platinum metals chelates
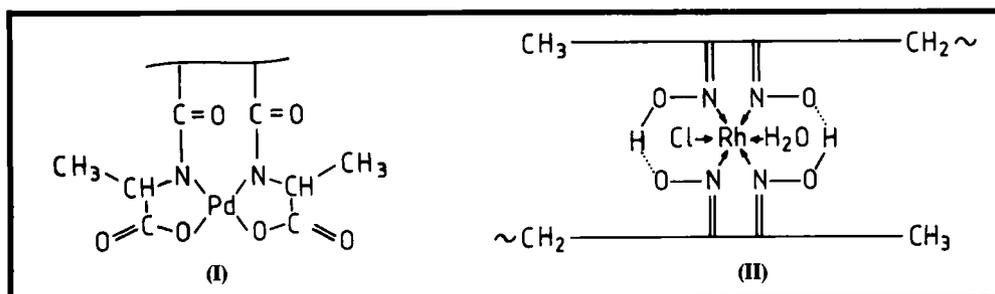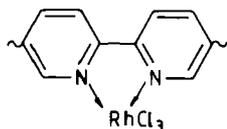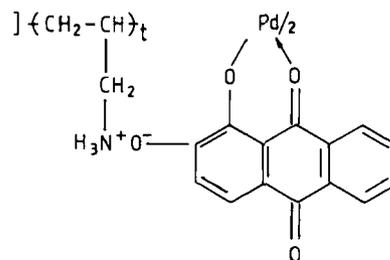

(I)   (II)

Table I

Macromolecular Platinum Metals Chelates Classification

1. Parameter: nature of metal-ligand bonding
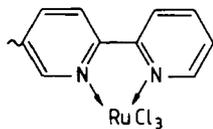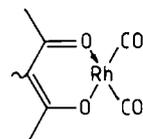
a. Molecular chelates

b. Intramolecular compounds
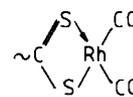
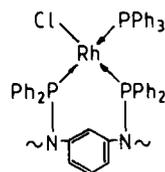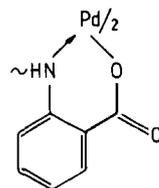### 2. Parameter: chelate node nature

a. N,N-chelates

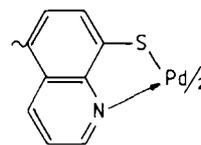**b. O,O-chelates**

c. S,S-chelates

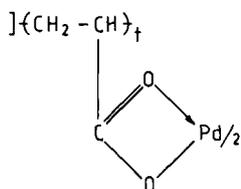**d. P,P-chelates**
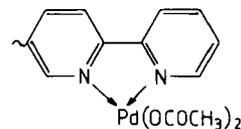
e. N,O-chelates

f. N,S-chelates

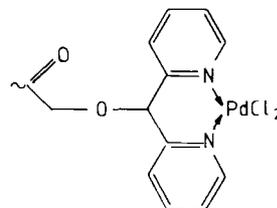### 3. Parameter: number of atoms in metal cycles
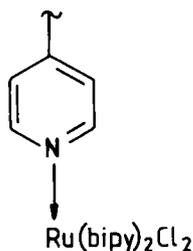
a. four-member chelates

b. five-member chelates

c. six-member chelates

] is a polymeric carrier surface

are bound with polymers, an example of which is this ruthenium chelate (22):

Ru(bipy)$_2$Cl$_2$

where bipy is 2,2'-bipyridyl.

Up to now the MPMC nomenclature has been inadequately described; basically the two approaches shown below have been used:

(i) the addition of the prefix "poly" to the substance name, for example, polydioximate palladium(II) of type III (23);

(ii) separate descriptions of the metal ion (or its compound MX$_n$) and ligand, for example, the complex of RhCl$_3$ with the condensation product of 2,2'-bipyridyl-4,4'-dicarbonylchloride and 2,6-diaminopyridine of type IV (11).

Methods of MPMC Preparation

Common methods and principles for the synthesis of complex compounds are widely used in the preparation of MPMC. A description of these methods, with appropriate examples, is given in Table II. Depending upon the characteristics of the polymer the chelation may be carried out in the homogeneous phase (soluble linear homo- and copolymers) or in a heterogeneous mixture (cross-linked polymers, grafted polymers and gels). In the case of soluble polymers solutions of ligand in organic solvents or mixed media, and aqueous, organic or aqueous-organic solutions of MX$_n$ are used. In the case of insoluble polymers reactions have to be carried out with the polymer

in suspension, but there are drawbacks with this method: the synthesis of complexes takes from one hour (29) to several days (24), and as a rule, a rise in temperature results in higher yields of the complex; reaction conditions including pH, intermixing intensity, and ratios of the reagents greatly affect the chelation process, although these conditions of MPMC synthesis have not yet received serious systematic study.

MPMC Structure

The characteristics of the chelation of platinum metals with polymeric ligands have been analysed previously (1, 30). It should be noted that as a rule intramolecular chelates of type I are formed in dilute solutions and that intermolecular chelates of type II are formed in concentrated solutions and polymeric matrices. The stereochemistry of co-ordination in MPMC is determined by the nature of the metal complex in the case of soluble polyligands, and the structural arrangement of the ligands in the case of cross-linked polymers. In the majority of cases, the chelating fragments of macroligands behave in the same way as their low molecular weight analogues; therefore metal chelates of similar composition and structure are formed. Binding of MX$_n$ by polymer matrices has some features in common with reactions involving low molecular weight reactants. Thus, for example, if the polymeric chain imposes steric hindrance towards chelate formation then monodentate MX$_n$ fixing of type V is observed (31). The chloromethylated copolymer of styrene and divinylbenzene, modified by 1,2-bis(diphenylphosphino)ethane, forms mononuclear MPMC of type VI (32) with RhH(CO)(PPh$_3$)$_3$, while low molecular weight

(III)   (IV)

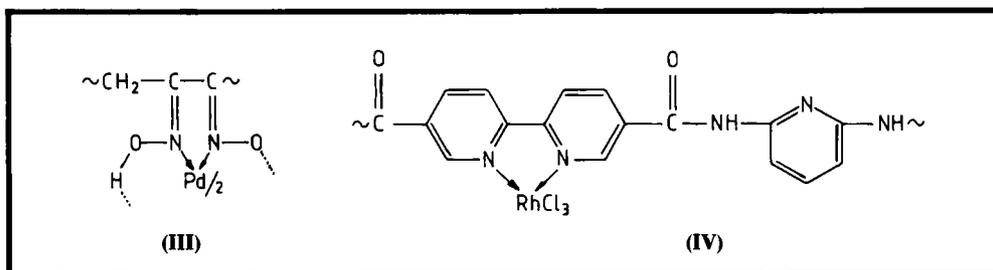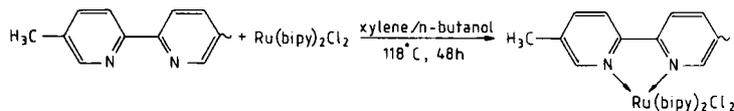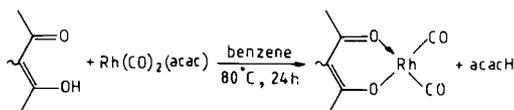# Methods of Macromolecular Platinum Metals Chelates Preparation

1. Synthesis on the base of chelating macroligands
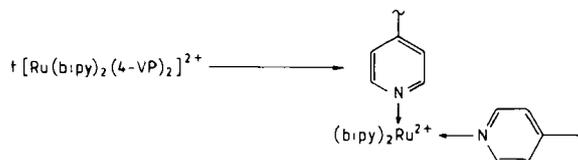a. Interaction of MX_n —chelating macroligand (24)

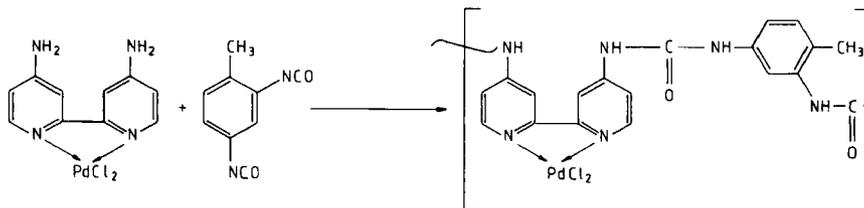b. Method of ligand exchange (14, 15)

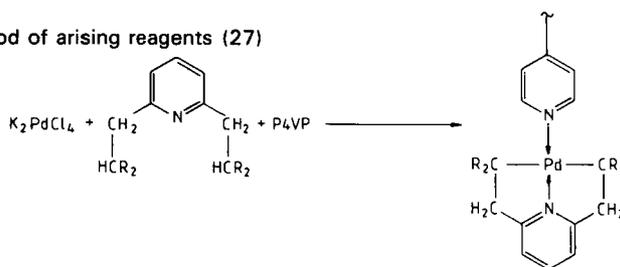2. Methods of assemblage
a. Polymerisation of metal chelate monomers (25)

b. Polycondensation (26)

c. Method of arising reagents (27)

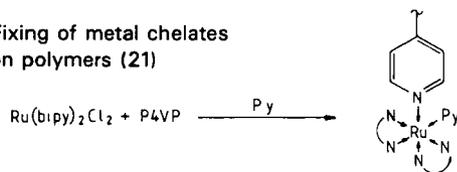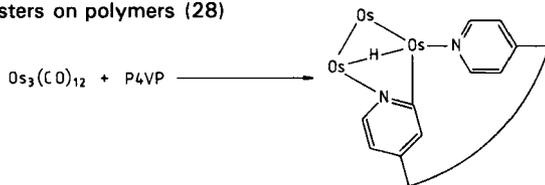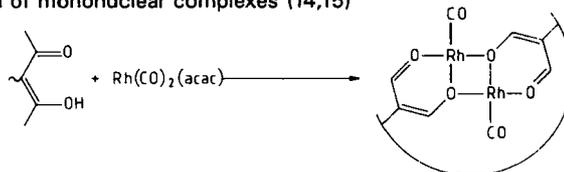d. Fixing of metal chelates
on polymers (21)

3. Synthesis of polynuclear chelates
a. Fixing of clusters on polymers (28)

$Os_3(CO)_{12}$ + P4VP $\longrightarrow$

b. Dimerisation of mononuclear complexes (14,15)

+ $Rh(CO)_2(acac)$ $\longrightarrow$

acac is acetylacetonate anion, 4-VP is 4-vinylpyridyne, P4VP is poly-4-vinylpyridyne, Py is pyridine, $\overset{\frown}{N\quad N}$ is 2,2'-dipyridyl

ligands, such as 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane, form rhodium dimer complexes (32), below.

It should be pointed out that co-ordination of MX_n by chelating polymers leads to the formation of rather more stable complexes than formed from the corresponding low molecular weight chelates. The chelates formed are often stable to the reduction of the transition metal (such as during catalysis). This can be demonstrated by two examples: first, the reduction of Rh(III), fixed on polyamides with bipy groups, to Rh(I) by hydrogen proceeds in two steps (11): at first step Rh(I) is formed, see page 190, but at second step autocatalytic reduction of Rh(III) by Rh(I) proceeds according to the rate equation:

$$d[Rh(I)]/dt = k[Rh(III)]^2[Rh(I)]$$

The immobilised Rh(I) is stable only in a hydrogen atmosphere. Second, in a similar way, the reduction of Pd(II) occurs as (26):

$$\int bipy.Pd(II)(OCOCH_3)_2 \xrightarrow{\text{LiAlH}_4} \int bipy.Pd(0)$$
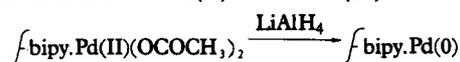
In the macromolecular complex, Pd(0) can be reoxidised by dilute nitric acid or by $(NH_4)_2Ce(NO_3)_6$.

MPMC Applications

Three different ways of looking at MPMC lead to diverse applications: (i) the effect of the metal on the operational parameters of polymers, (ii) the effect of the macromolecular chain on metal properties, and (iii) the synthesis of new polymeric materials, which differ substantially in their properties from the initial reactants, see

(V)

MX_n

(VI)

$RhH(CO)PPh_3$
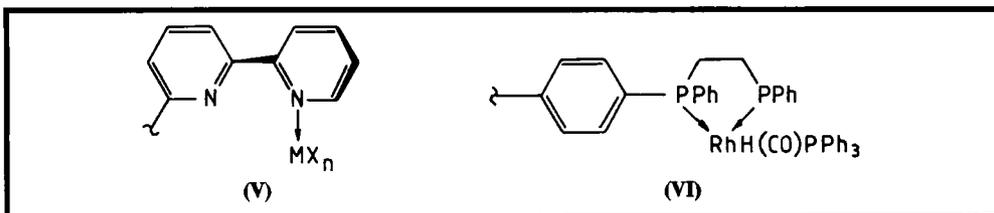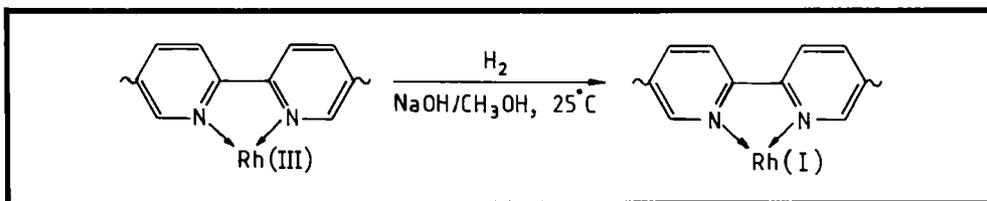
Table III. This information has been concentrated mainly in the patent literature (33). One of the most interesting examples involve platinum-containing polymers showing inhibitory activity with respect to tumour cells L929, HeLa, Detroit, WISH (34). The mechanism of the activity of this preparation is probably based on the slow release of the active component, which provides the prolonged action of the anti-tumour preparation.

During recent years a new direction in catalysis has developed, whereby the chemistry of immobilised catalysts combines the advantages of homogeneous (high activity and selectivity) and heterogeneous (technologically practical) catalytic systems (1). Chelation is one of the most simple ways of overcoming the basic shortcoming of fixed metal complex catalysts, which is the relatively low stability of the metal-polymer bond during the catalytic reaction. Thus, for example, the catalyst for olefin hydrogenation, which is

based on rhodium complexes with cross-linked polystyrene containing bipy fragments, was effective for more than 300 cycles (31).

The chelation of platinum metals is important for analytical purposes (3 – 5, 10). As a rule, the selective uptake of metal ions is achieved by using polymeric ligands where the structure of the ligands is determined by the co-ordination chemistry of the specific metal. The uses of MPMC for the preparation of electroactive coatings (25), electroconducting (35), photoconducting materials (25), and in systems for the photochemical storage of energy (35), are also of interest.

Thus, analysis of the methods of preparation, structures and the applications of MPMC indicate substantial progress in MPMC chemistry has been achieved. There are still important problems to be solved however, which would enable the basic principles of MPMC chemistry to be formulated. Further work needs to be done on:

Table III

Fields of MPMC Applications

Applications	Metal chelate
Metal complex catalysis	Pt, Pd, Rh, Ir, Os, Ru
Improvement of thermal properties of polymers	Pt, Pd, Rh, Ir, Os, Ru
Selective binding and separation of metal ions	Pt, Pd, Rh, Ir, Os, Ru
Electroconducting polymers	Pd, Os, Ru
Photoconducting polymers	Os, Ru
Electroactive coatings	Os, Ru
Energy storage systems	Ru
Biological preparations	Pt

(i) the elaboration of new methods of MPMC preparation; (ii) a detailed analysis of the influence of the metal and polymeric chain in the early stages of the chelation process and the role of the participating chelating macroligands; (iii) an investigation of the stereochemistry of chelates in MPMC; and (iv) problems of stereoregulation and supramolecular structure of MPMC.

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Surface Studies of Osmium Alloy Coatings

The thermionic emission from a surface coated with a binary alloy has been shown to be superior to that from a pure tungsten surface, or one coated with a pure metal. As far as emission enhancement is considered, surface chemistry may have a more important effect than the substrate. It has been reported that addition of a small amount of a rare earth metal to a binary alloy coating leads to a reduction in work function. For this reason a study has been made of osmium-rhenium-tungsten coatings on impregnated tungsten cathodes (C. S. Ares Fang and C. E. Maloney, *J. Vac. Sci. Technol.*, 1990, **8**, (3), 2329–2332).

Measurements from an uncoated area of the cathode surface were compared to those from three areas coated with different alloy compositions, and showed that the effective work function of a surface coated with 40 osmium-40 rhenium-20 per cent tungsten was 1.76 eV.