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Macromolecular Metal Complexes in Nature and Laboratory: A Survey through the Field

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Summary: Based on a very recently published monograph a short overview on macromolecular metal complexes (metal complexes and metals in macromolecules) is given. The understanding of biological system is fundamentally important to construct artificial macromolecular metal complexes. A classification for the various up to now synthesized systems is given, and properties and potential applications are pointed out.

Keywords: classification; macromolecular metal complexes; metal complexes; metals in macromolecules; properties

Introduction

One of the most important trends in the future process of macromolecular chemistry will be the wide-scale employment of elements of the Periodic Table for the synthesis of macromolecules. Among the around 109 elements of the Periodic Table only the six noble gases and eleven elements of the groups IA and VIIA (including H), which are univalent and can only play the role of terminating groups, are incapable of producing stable macromolecules in solution (although for some elements, especially those of high atomic number, formation of macromolecules is not known). But some of them can contribute to weak chain- or network-forming interactions in the solid state. The remaining around 80 elements are principally capable of functioning as chain- or network-forming elements. The expected and practically unlimited structural possibilities offered by this approach provide an enormous potential to improve greatly the capacity of structural macromolecular materials. Products with new static, dynamic, thermal, electronic, electrical, photoelectrical properties, etc. can be developed. Also there appear to be highly interdisciplinary possibilities for both fundamental studies and applications. A great number of macromolecules involving practically all metals of the Periodic

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Table of elements have been synthesized, the kinetic and thermodynamic characteristics of complex formation have been obtained and several aspects of the structural or supramolecular organization of macromolecular metal complexes have been elucidated.

An understanding of the structure and reactivity of biological reaction centers is important for the construction and optimization of artificial systems. Research has shown that the combination of a specific metal in a specific ligand surrounding and in combination with a specific macromolecule is the fundamental prerequisite for activity and selectivity.

Systematic studies on artificial combinations of metal ions, metal complexes and metals with macromolecules began only around sixty years ago. Now this field has reached the first advanced state in detailed synthesis, structure investigation and first optimization of structure–property relationships. A recent monograph describes in detail synthesis, structure and properties of metal complexes and metals in macromolecules (also called macomolecular metal complexes (MMC)).[1] This article gives a short overview on natural and synthetic MMC.

Macromolecular Metal Complexes and Metal in Biological Systems

The variety of metals used by biological systems is very large, ranging from the alkali metals to the transition metals. They play an essential role in living systems, in both growth and metabolism. Some metal ions are necessary in gram quantities, others are trace elements and essential beneficial nutrients at low levels but metabolic poisons at high levels, and some metal ions are called detrimental metal ions because they are toxic and impair the regular course of life functions in all concentrations. A look at the Periodic Table shows that almost every group is represented in living matter (Figure 1). Some selected references for metals in biological matter are given.[2-8]

In living organisms metal ions can coordinate to a variety of biopolymers in ionic, coordinative and also covalent bonds:

- In proteins at the (C=O) or (N–H) bonds and especially at N, O, S donor atoms of side chains.
- In nucleic acids at basic N atoms or at phosphate groups.
- In carbohydrates and lipids at (C–O) and (P–O) groups.
- In solid bones, teeth and kidney stones.

Metal ion interactions also play an important role in the binding of nucleic acids with proteins, influencing denaturation stability and protein synthesis and thus keeping the inherited information.

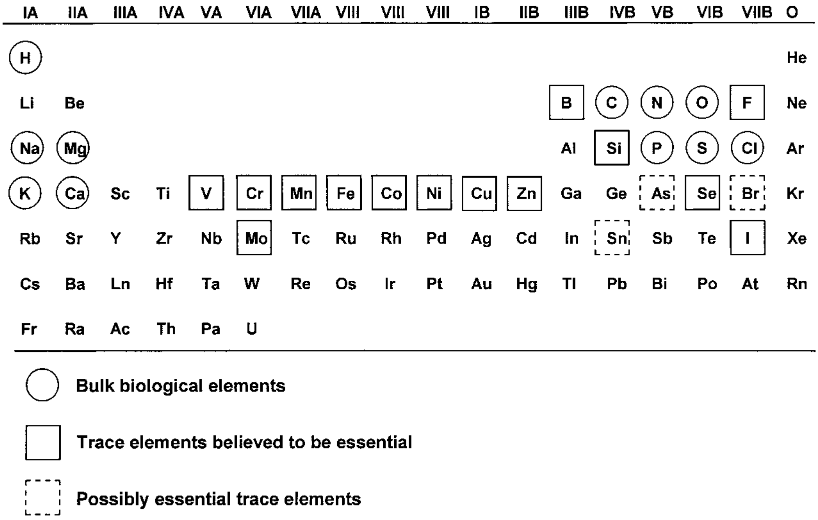


Fig. 1. Elements essential for life.[5]

Metal complexes are involved in various processes essential for life:

- Metals as cofactors in proteins and metalloproteins: oxygen binding and transport, electron transfer, energy transfer followed by electron transfer, and several regulating functions.
- Metalloenzymes: hydrolytic enzymes, redox enzymes, redox reactions with several electron pairs, rearrangements.
- Interference of detrimental metal ions with normal cell metabolism: metabolic poisons.
- Communicative functions of metals: magnetic compass, initiator of cell functions, regulation of gene expressions.
- Interaction with nucleic acids: stabilization of DNA and RNA.

Also metal or metal compound clusters fulfill necessary functions as catalysts or for electron transfer in living systems. Two examples are:

- Mn clusters for the four electron oxidation of water to oxygen in the mechanism of photosynthesis.
- Electron-rich Fe–S clusters for electron transport in the respiratory chain.

Metals also play an important role in non-living nature. Humic acids consist of a polycyclic cross-linked backbone with bound polysaccharides, proteins and phenols. Metal ions of, for example, iron, copper, zinc or manganese are bound at carboxylic acid and carbonyl groups. The complexation of humic acids with metal ions is involved in many biological, biochemical and geochemical processes. For example, the interaction of humic acids with metal compounds is a necessary part of soil formation. The interaction of metal ions with natural inorganic sorbents influences the redistribution of some elements in geological deposits and soils. Sorption of metal ions, especially iron, copper, manganese and gold by microorganisms are examples.

Synthetic Metal Complexes and Metals in Macromolecules

Systematic studies of metal complexes and metals in macromolecules have a short history of about sixty years. During World War II, the United States Air Force established a research program to develop polymers which were stable up to 600 °C.[9] Undoubtedly, this promoted studies in the field of metals in polymers. The first publication of the results obtained in terms of the program appeared in the late Fifties and early Sixties.[10,11] About this time investigations of chelate-forming resins and their metal complexes were started[12] in connection with aspects of the nuclear-power industry and hydrometallurgy, and also including analytical aspects and the separation of metals, especially rare elements and isotopes. It should be mentioned that the initiatives for intensive studies of metals in polymers were always determined by the demands of some branches of industry. Thus, in the early Seventies an increasing number of studies were concerned with the catalytic properties of polymer-bound metal complexes with the aim of heterogenizing homogeneous catalysts for various chemical reactions.[13,14] As early as 1975 British Petroleum and Mobil Oil Corporation had received about 2000 patents on immobilized catalysts for hydrolysis, carbonylation, isomerization, polymerization and other reactions.[15]

At the end of the Seventies and beginning of the Eighties the results of the first intensive studies of the binding of small molecules and the conversion of solar energy using polymer metal complexes were published.[16,17] Also around this time reviews and the first books summarized the developing interest in the field of metal complexes and metals in macromolecules.[16-21]

Today several summarizing reports exist in this field covering such themes as macromolecular metal complexes, organometallic polymers, metal-containing monomers, metal-containing polymeric materials, polymer-immobilized metal complexes, macromolecular complexes and macromolecular metal chelates in different ways.[1,22-30] In addition, International Conferences on Macromolecular Metal Complexes (MMC) initiated in 1985 by E. Tsuchida (Waseda University, Tokyo) have been held regularly every second year since 1985 under the sponsorship of the IUPAC (for MMC IX see [31]). Since the Seventies/Eighties the field has increasingly developed. Now in several countries scientific groups are active to develop this field further in many directions for the future. A great number of macromolecules involving practically all metals of the Periodic Table of elements have been studies. The most recent development is the formation and stabilization of metal nanoparticles/clusters (size 1–100 nm) in macromolecules. This aspect is extensively developed now and has led to new composite materials with several interesting properties. Thus, the field of metals in macromolecules covers all aspects of chemistry, especially polymer chemistry, analytical chemistry, coordination chemistry, theoretical chemistry and bioinorganic/organic chemistry, and overlaps with biology, physics, medicine and engineering science.

This time various combinations of metal complexes or metals with organic, inorganic and semiorganic macromolecules exist. Therefore a strict and clear classification is necessary. Metal complexes or metals can be part of a macromolecular chain/network as follows: binding at a macromolecule; part of a macromolecule via the ligand; part of a macromolecule via the metal; physically incorporated into a macromolecule. This classification, first given in 1996[22] and taken over in [1] is used because from the numerous possibilities a metal complex or metal is easily classified by the kind of interaction it has with a macromolecule.

Type I: A metal ion, metal complex or metal is bound to a chain of a linear or cross-linked organic or inorganic macromolecule via a covalent (at the metal or ligand), a coordinative (at the metal), a complex (at the ligand of a complex), an ionic or a π-bond (Figure 2). Additional possibilities exist for different kinds of binding at the surface of a carrier or the end group of a macromolecule.

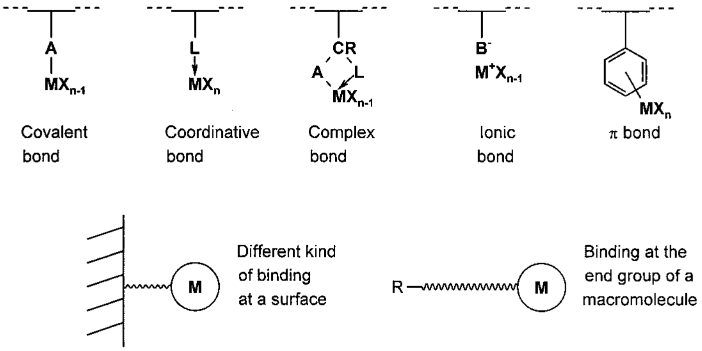
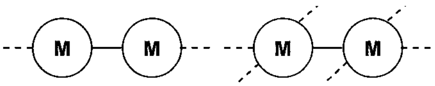


Fig. 2. Type I: Metals bound at macromolecules.

Type II: The ligand of a metal complex is part of a macromolecular chain or network (Figure 3). Besides the direct synthesis of macromolecular metal complexes from low molecular precursors, a macromolecular ligand can be prepared first which is then metallated in a second step.

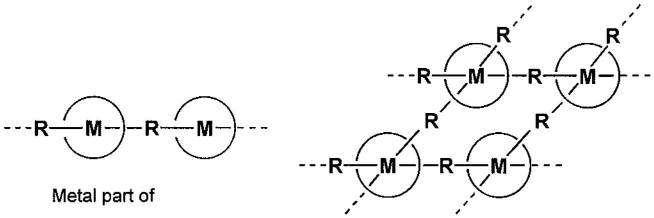


Ligand part of
a linear chain

Ligand part of
a network

Fig. 3. Type II: Ligand of a metal complex as part of a macromolecule.

Type III: Several examples of compounds exist in which the metal of a metal complex or another metal derivative is directly part of a macromolecular chain or network (Figure 4). In type III the macromolecular chain can consist only of metal atoms. But in most cases the metal is connected with another element such C, N, O, S via a covalent, a coordinative, an ionic or a π–bond.

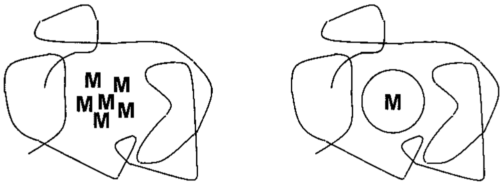


Metal part of
a linear chain

Metal part of
a network

Fig. 4. Type III: Metal as part of a macromolecule.

Type IV: The physical incorporation of metal (and also semiconductor) clusters or metal complexes in macromolecules has become an important field (Figure 5). By stabilization of metal clusters in a macromolecular environment new composite materials have been synthesized. In dependence on the envisaged properties the monomolecular or aggregated distribution of metal complexes in macromolecules had been synthesized.



Physical incorporation
of metal nano-particles

Physical incorporation
of metal complexes

Fig. 5. Type IV: Physical incorporation of a metal or metal complex.

The formation of a macromolecular metal complex is in general thermodynamically favored by a negative free energy. An additional contribution to the free energy in comparison to the known "chelate effect" for the formation or stabilization of a low molecular weight metal complex/metal is given by the so-called "polymer chelate effect": change of the free energy due to the addition of a metal derivative to a macromolecular ligand for polymer binding, the reaction of a metal with a bi/higher-functional precursor for the formation of a macromolecular chain/network or the stabilizing macromolecular environment for a metal complex/metal. Compared to low molecular weight metal complexes, the situation for macromolecular analogues is more complicated due to the local, molecular and supramolecular organization of different kinds of macromolecules. This influences kinetic parameters, formation constants, cooperative effects, reorganization of structured arrangements and other transformations. For all these aspects it is important to consider the formation and stereochemistry of low molecular weight coordination compounds, the chemical and physical behavior of macromolecules and aspects of physical and theoretical chemistry.

Properties and Potential Applications of Metal Complexes and Metals in Macromolecules

The combination of a specific metal with a definite macromolecule (organic or inorganic, either linear or cross-linked) gives rise to both active and selective properties, with high performance and stability. Therefore the first step must be the planning and carrying out of a successful synthesis. The necessary second step is a detailed analysis by different instrumental analytical techniques. The complex molecular arrangements on different levels must consider:

- primary structure → composition of the metal-containing macromolecule,
- secondary structure → steric orientation of a metal-containing macromolecular unit,
- tertiary structure → orientation of a whole metal-containing macromolecule,
- quarternary structure → interaction of different metal-containing macromolecules.

Nature shows how complicated it is to construct metal-containing macromolecules that are active but also selective with respect to a specific property. Natural systems do not need to exhibit a high stability towards storage and heat because the active materials are readily replaced. On the other hand, artificial systems must be more stable over time and towards heat. Therefore extreme demands are placed upon artificial metal-containing macromolecules. It is important to point out that the fundamental behaviors of low molecular weight metal complexes will be shown also in macromolecular analogues. But these behaviors, and thus the properties, are strongly influenced by the kind of macromolecular environment or the kind of incorporation into a macromolecule.

Type I describes the binding of a metal compound at a macromolecule. In linear organic polymers the secondary binding forces of a bound metal to other parts of the chain are weak (coordination bonds, hydrogen bonds, charge-transfer interactions, hydrophobic interactions). But because they are multiple, these binding forces cooperatively play an important role. These dynamic and multiple weak secondary forces are often affected by dynamic conformational changes of the macromolecular molecular environment. Electronic interactions and transfer processes to guest molecules can occur which can lead also to molecular conversions (Figure 6). Binding of metal compounds at rigid cross-linked organic polymers (e.g. cross-linked polystyrene), at the surface of organic polymers (e.g. polyethylene) or at the external and, in the case of porous materials, at the internal surface of inorganic macromolecules (e.g. silica, zeolites) results in more “free” metal compounds, not firmly bound to the matrix by strong interactions. Thus, the properties of such compounds are more comparable with those of analogous low molecular weight metal complexes. Characteristic properties and uses of type I metal-containing macromolecules, which may or may not involve photoexcitation interactions with each other or guest molecules, include:

- Binding of small molecules (gas transport, gas separation, sensor).
- Catalysis, photocatalysis.
- Photoinduced electron or energy transport.
- Electrocatalysis, photoelectrocatalysis.
- Biosensors and biochips.
- Smart materials.
- Polymer electrolytes.
- Ion-exchange resins.
- Polymer coatings.

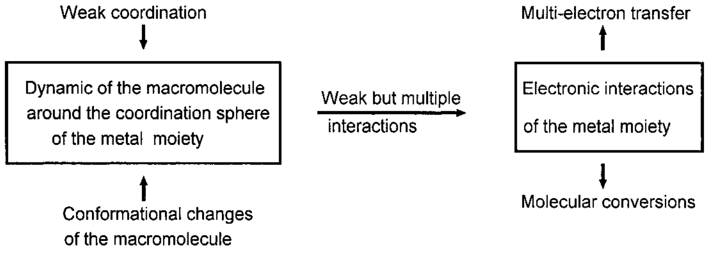


Fig. 6. Dynamic and fixed situations in type I metal-containing macromolecules.

An important use of polymer ligands is the extraction of trace amounts of metals, e.g. gold, uranium, from seawater. For example, an industrial extraction of uranium from seawater has been developed using polymers with amidoxime groups. Also the role of macromolecular metal complexes in Green chemistry is very significant, for example their efficient use in the neutralization of effluents from chemical companies.

Type I macromolecules have become more and more important as drugs in medicine:

- They can supply iron for iron deficiency anemia.[32]
- They can remove toxic metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}).[33]
- Mn^{2+}, Ce^{4+} radioactive isotopes as well as molybdate ions bound to polyoxiranes can be used for treatment of pulmonary disease.[34].
- Products of the reaction of K_2PtCl_4 with polymers are used similarly as the antineoplastic drug *cis*-dichlorodiamminoplatinum, for example for treatment of leukemia.[35]

In **type II and III** metal-containing macromolecules the ligand or the metal is part of a cross-linked macromolecule. The solubility of such often rigid macromolecules is enhanced by introducing bulky substituents, which also improve the processibility. The alignment of complex moieties along the macromolecule matrix or within the macromolecule results in a material with integrated electronic processes (Figure 7). Charge interaction/transfer, induced by an electrical field or by photoexcitation, yields materials with the following uses:

- Conductors, photoconductors.
- Photovoltaic cells, light emitting diodes.
- Electrochemical, photoelectrochemical cells.

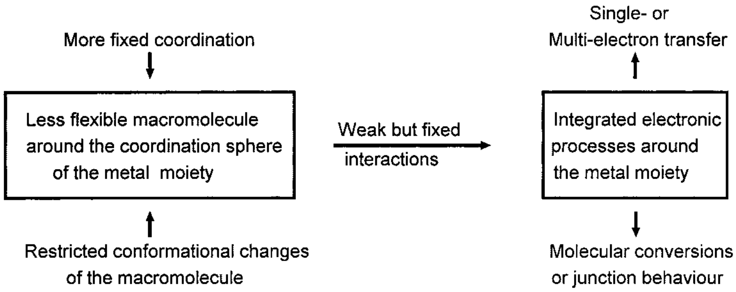


Fig. 7. Electronic interactions in type II or III metal-containing macromolecules.

In **type II** macromolecules the metal complex moieties can also be connected to each other in a chain via covalent single bonds, which results in a more flexible backbone. In principle, this can give rise to the properties mentioned for type I macromolecules.

Type IV metal-containing macromolecules involve metal nanoparticles or metal complexes physically incorporated in macromolecules. The properties are general influenced greatly by the kind of macromolecular environment:

- Metallo–polymer nanohybrids.
- Polymer–inorganic composites.
- Intercalation metallopolymers.
- Magnetic nanocomposites.
- Bioinorganic nanocomposites.
- Metallized plastics.

Metal complexes can be incorporated in a macromolecule distributed either monomolecularly or in an aggregated state. These materials are characteristically used in thin film devices as:

- Conductors, photoconductors.
- Photoinduced electron or energy transporters.
- Electrocatalysts, photoelectrocatalysts.

Many of the properties described arise from high-order functions of metal complexes and metals in macromolecules, caused by the conjugation of dynamic interactions and electronic processes. The discussed properties and additional advanced functions deriving from molecular-level features are collected in Figure 8.

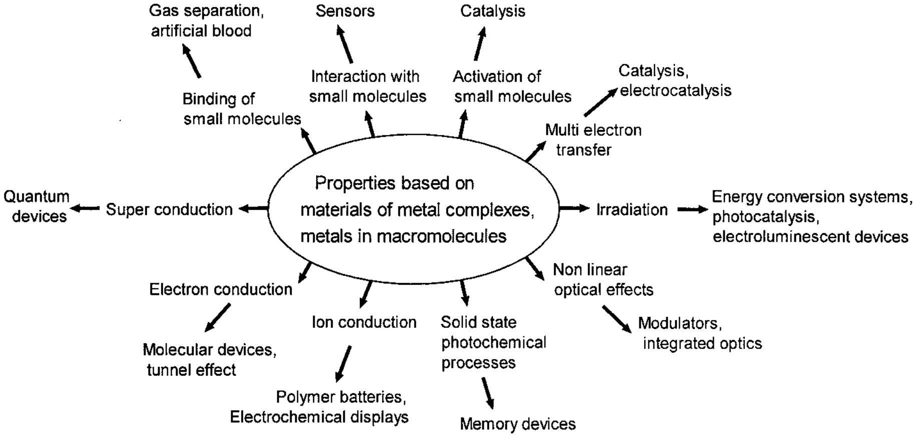


Fig. 8. Properties based on materials containing metal complexes and metals in macromolecules.

Most of the properties of the new materials are under development and promise to have a great impact in related scientific and technological fields.

Conclusion

Systematic studies on artificial combinations of metal ions, metal complexes and metals with macromolecules began only around sixty years ago. Now this field has reached the first advanced state in detailed synthesis, structure investigation and first optimization of structure–property relationships.

The synthesis of macromolecular metal complexes has come close to the level seen in nature. Many examples and routes are available to obtain different and tailor-made structural features. We have therefore attempted to discuss in a recent monograph all the presently available approaches to the preparation of metal complexes and metals in macromolecules from different ligands and metal derivatives, mentioning the related chemical and physical interactions involved and properties obtained.[1]

The extraordinary materials “metal complexes and metals in macromolecules” have reached the scientific standard of an interdisciplinary and natural science. Based on the high level of synthetic procedures and detailed structural characterizations, a more intensive investigation of structure–property relationships is now possible. This will open new areas and contribute efficiently to new processes of fundamental technical importance for synthetic materials. The key for all these developments is the metal complex/metal as the active part in a well-defined macromolecular environment.

Some problems to be solved with high priority are as follows. Until now the specific character (e.g. length, stability) of the metal–polymer ligand bond, and its difference from that of low molecular weight analogues, is not entirely clear. The same is true of the role of the molecular motion of the macromolecular chain on all three levels (local, molecular and permolecular) and to the kinetics and thermodynamics of complexing processes in such systems; there are no quantitative data for comparative analysis. The theory of macromolecular reactions has developed rather slowly. Furthermore, preparation requires a high skill in synthesis and is often a time-consuming and unprofitable process. Therefore, the industrial uses of MMCs, for example, as heterogeneous a d homogeneous catalysts are still at the developmental stage.

Acknowledgement

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