
Macromolecules Containing Metal and Metal-Like Elements

Volume 5

Metal-Coordination Polymers

Edited by

Alaa S. Abd-El-Aziz

*Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba,
Canada*

Charles E. Carraher Jr.

*Department of Chemistry and Biochemistry, Florida Atlantic University,
Boca Raton, Florida*

Charles U. Pittman Jr.

*Department of Chemistry, Mississippi State University, Mississippi State,
Mississippi*

Martel Zeldin

*Department of Chemistry, Hobart and William Smith Colleges, Geneva,
New York*

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Contributors

Alaa S. Abd-El-Aziz, Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba R3B 2E9, Canada (a.abdelaziz@uwinnipeg.ca)

Ronald D. Archer, Department of Chemistry, University of Massachusetts, Amherst, MA 01003-9336 (archer@chem.umass.edu)

Charles E. Carraher Jr., Florida Atlantic University, Boca Raton, FL 33431 and Florida Center for Environmental Studies, Palm Beach Gardens, FL 33410 (carraher@fau.edu)

Wai Kin Chan, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China (waichan@hku.hk)

Hiroki Fukumoto, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Issifu I. Harruna, Department of Chemistry, Clark Atlanta University, Atlanta, GA 30311 (iharruna@cau.edu)

Pierre D. Harvey, Département de Chimie, Université de Sherbrooke, 2500 Boul. Université, Sherbrooke, Québec J1K 2R1, Canada (Pierre.Harvey@USherbrooke.ca)

Masayoshi Higuchi, Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

Harald Hofmeier, Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Toshikazu Hirao, Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada oka, Suita, Osaka 565-0871, Japan (hirao@chem.eng.osaka-u.ac.jp)

Julie Lefebvre, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

Daniel B. Leznoff, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada (dleznoff@sfu.ca)

Piero Mastrorilli, Department of Water Engineering and Chemistry, The Polytechnic of Bari, Italy

Amanda Taylor Murphy, Florida Atlantic University, Boca Raton, FL 33431

Cosimo Francesco Nobile, Department of Water Engineering and Chemistry, The Polytechnic of Bari, Italy

Moonhyun Oh, Department of Chemistry, Northwestern University, Evanston, IL 60208 (m-oh@northwestern.edu)

Odessa N. Petzold, Corning Inc., Corning, NY 14831 (petzoldon@corning.com)

Charles U. Pittman Jr., Department of Chemistry, Mississippi State University, Mississippi State, MS 39762 (cpittman@ra.msstate.edu)

Jeffrey A. Reingold, Department of Chemistry, Brown University, Providence, RI 02912

Stefan Schmatloch, Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Ulrich S. Schubert, Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands (u.s.schubert@tue.nl)

Dwight A. Sweigart, Department of Chemistry, Brown University, Providence, RI 02912 (Dwight_Sweigart@Brown.edu)

Kimihisa Yamamoto, Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan (yamamoto@chem.keio.ac.jp)

Takakazu Yamamoto, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Preface

Naturally occurring coordination polymers are integral to plant and animal life and allow specificity of structural agglomeration and biological function. Hemoglobin and myoglobin contain chelated iron at their center whereas coordinated magnesium is at the center of the chlorophylls that trap light, converting it to chemical energy. This leads to the synthesis of simple and complex carbohydrates. Coordinated metals also serve as the critical sites for metalloproteins. Synthetic coordination polymers were the first metal-containing polymers investigated in a widespread in-depth study in the 1950s, as part of the Air Force Advanced Materials Program. The purpose of this program was to search for materials with outstanding thermal stability.

The wide number of metals, variability of oxidation states, and variety of coordinating ligands provide the synthetic chemist with a multitude of tools for creation of materials for the twenty-first century.

This volume begins with an introductory chapter that lays the foundation for coordination chemistry aimed at those not already familiar with the area. It is followed by a variety of chapters that illustrate the breadth of materials available and their potential applications, from harvesting light for solar energy conversion to electronic applications. Structural variations from dendrimers and supramolecular structures to linear materials are covered. The history of coordination polymers is the subject of Volume 1 of this series. The most important coordination polymers for biomedical applications are covered in Volume 3 of this series, where platinum-containing macromolecules and dental materials are presented.

Alaa S. Abd-El-Aziz
Charles E. Carraher Jr.
Charles U. Pittman Jr.
Martel Zeldin

Series Preface

Most traditional macromolecules are composed of less than 10 elements (mainly C, H, N, O, S, P, Cl, F), whereas metal and semi-metal-containing polymers allow properties that can be gained through the inclusion of nearly 100 additional elements. Macromolecules containing metal and metal-like elements are widespread in nature with metalloenzymes supplying a number of essential physiological functions including respiration, photosynthesis, energy transfer, and metal ion storage.

Polysiloxanes (silicones) are one of the most studied classes of polymers. They exhibit a variety of useful properties not common to non-metal-containing macromolecules. They are characterized by combinations of chemical, mechanical, electrical, and other properties that, when taken together, are not found in any other commercially available class of materials. The initial footprints on the moon were made by polysiloxanes. Polysiloxanes are currently sold as high-performance caulks, lubricants, antifoaming agents, window gaskets, O-rings, contact lens, and numerous and variable human biological implants and prosthetics, to mention just a few of their applications.

The variety of macromolecules containing metal and metal-like elements is extremely large, not only because of the large number of metallic and metalloid elements, but also because of the diversity of available oxidation states, the use of combinations of different metals, the ability to include a plethora of organic moieties, and so on. The appearance of new macromolecules containing metal and metal-like elements has been enormous since the early 1950s, with the number increasing explosively since the early 1990s. These new macromolecules represent marriages among many disciplines, including chemistry, biochemistry, materials science, engineering, biomedical science, and physics. These materials also form bridges between ceramics, organic, inorganic, natural and synthetic, alloys, and metallic materials. As a result, new materials with specially designated properties have been made as composites, single- and multiple-site catalysts, biologically active/inert materials, smart materials, nanomaterials, and materials with superior conducting, nonlinear optical, tensile strength, flame retardant, chemical inertness, superior solvent resistance, thermal stability, solvent resistant, and other properties.

There also exist a variety of syntheses, stabilities, and characteristics, which are unique to each particular material. Further, macromolecules containing metal and metal-like elements can be produced in a variety of geometries, including linear, two-dimensional, three-dimensional, dendritic, and star arrays.

In this book series, macromolecules containing metal and metal-like elements will be defined as large structures where the metal and metalloid atoms are (largely) covalently bonded into the macromolecular network within or pendant to the polymer

backbone. This includes various coordination polymers where combinations of ionic, sigma-, and pi-bonding interactions are present. Organometallic macromolecules are materials that contain both organic and metal components. For the purposes of this series, we will define metal-like elements to include both the metalloids as well as materials that are metal-like in at least one important physical characteristic such as electrical conductance. Thus the term includes macromolecules containing boron, silicon, germanium, arsenic, and antimony as well as materials such as poly(sulfur nitride), conducting carbon nanotubes, polyphosphazenes, and polyacetylenes.

The metal and metalloid-containing macromolecules that are covered in this series will be essential materials for the twenty-first century. The first volume is an overview of the discovery and development of these substances. Succeeding volumes will focus on thematic reviews of areas included within the scope of metallic and metalloid-containing macromolecules.

Alaa S. Abd-El-Aziz
Charles E. Carraher Jr.
Charles U. Pittman Jr.
Martel Zeldin

CHAPTER 1

Introduction to Metal-Coordination Polymers

Charles E. Carraher Jr.

Department of Chemistry and Biochemistry, Florida Atlantic University, Boca Raton, Florida

Charles U. Pittman Jr.

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi

Alaa S. Abd-El-Aziz

Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba, Canada

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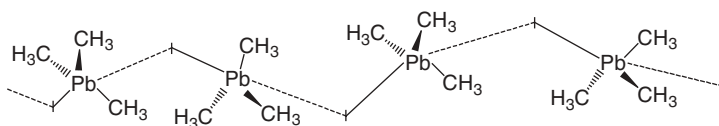
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I. INTRODUCTION

In this volume, a coordination polymer is defined as a polymer that contains a metal, which coordinates to Lewis base-like ligands, and these coordination complexes are part of the overall polymer. Many biologically important metal-containing polymers are coordination polymers, which includes metal-containing macromolecules in the human body such as transferrin and hemoglobin (iron), xanthine oxidase (molybdenum), hemovanadin (vanadium), carbonic anhydrase (zinc), and heparocuprein (copper). Coordination polymers also play an essential role in plants where photosynthesis, via chlorophyll, lies at the heart of energy use to build biomass.

There are a variety of ways of defining coordination compounds. This chapter will be somewhat restrictive, requiring a material to exist in polymeric form in solution to be considered a coordination polymer. Thus, compounds such as lead chloride that are polymeric as solids from X-ray studies, will not be considered as coordination polymers since in solution they are monomeric or they exist as distinct monomers. Thus, a number of organolead halides exist in the solid as collections of supramolecular assemblies, but in solution exist as monomeric compounds. One such structure is trimethyllead(IV) iodide, **1**, which exists as a zigzag chain conformation in the solid phase.¹



The term “classical complexes” is employed to describe the materials covered in this volume.² Classical complexes include ligands with a discrete electron population bound to a metal with a well-defined oxidation number. This eliminates complexes where the metal–ligand bonding is highly covalent and/or multiple bonding. Thus, metallocenes such as ferrocene are not covered in this chapter. Further, using this logic, organometallic compounds, such as dibutyltin dichloride, are eliminated from consideration in this chapter.

Coordination polymers hold a special place among metal-containing polymers. These materials were first emphasized in the late 1940s–1960s, when they were the subjects of widespread research activity. Much of this effort was supported by the U.S. government through activity headquartered at Wright-Patterson Air Force Base, just outside of Dayton, OH. The effort was largely aimed at the production of materials with outstanding thermal stabilities for use in the emerging space program. This activity stemmed from the observation that some organometallic coordination complexes were thermally stable from 200 to 400°C and the hope that the thermal stability of coordination polymers would greatly exceed this stability. Unfortunately, polymeric analogues did not generally give more thermally stable materials. Often the polymeric versions underwent thermally induced degradation at lower temperatures. Many outstanding polymer and inorganic chemists were involved in this effort including Marvel and Bailor.

The bonding between the ligand and the metal ion is generally formed by a typical Lewis acid–base reaction where the Lewis acid, A (acceptor atom), and base, :B (donor atom), form a coordinate bond, A:B. An example coordination compound made from ethylenediamine (en) and nickel in sulfate solution is $\text{Ni(en)}_2\text{SO}_4$. Here, the “en” is a multidentate or a chelate ligand. The nickel complex is a chelate compound, and the cation is a chelate ion. Further, the number of binding sites used by the chelating ligand can be two, bidentate; three, tridentate; four, quadridentate; five, quinqueidentate; and six, sexadentate.

The reason metals are included into coordination polymers is to take advantage of the chemical and/or physical properties, which the metal may add to the polymer. Further, introduction and greater in-depth coverage of coordination compounds is given in general and specific texts.^{2–9}

II. POLYMER SOLUBILITY

A general problem with coordination polymers is their lack of ready solubility limiting both the use and characterization of the products. Even when solubilized, solubility is often accompanied by polymer degradation, rearrangement, solvation, and so on. Further, because of the difficulty of obtaining single crystals of coordination polymers, few X-ray studies have been carried out so structural characterization of coordination polymers is often difficult and incomplete.

The following is a brief review of comments related to coordination polymers as described by Bailor.¹⁰ These principles are generally applicable.

- Little flexibility is imparted by the metal ion and within its immediate environment.
- Metal ions only stabilize those ligands in the immediate vicinity, thus the chelates should be stable and close to the metal atom.
- Polymers must be designed specifically for the properties desired, such as solubility.
- Metal–ligand bonds have enough ionic character to permit them to rearrange more readily than typical “organic bonds”.

- Flexibility often increases as the covalent nature of the metal–ligand bond increases.
- The coordination number and stereochemistry of the metal ion or oxide dictate polymer structure.
- Solvents that are employed to solubilize coordination polymers should not form strong complexes with the metal atom or chelating agent. They could be incorporated into the polymer structure or prevent desired subsequent reactions from occurring.

Archer¹¹ and Carraher et al.¹² described attempts to increase the solubility of metal-containing polymers including coordination polymers. Archer lists the following as approaches to overcoming solubility problems.

1. The presence of bulky ligands minimizes stacking interactions providing soluble planar divalent d^8 polymers.
2. Eight-coordinate centers that tend to be nonrigid have been used for synthesizing soluble polymers.
3. Octahedral coordination centers with a metal ion surrounded by three bidentate ligands can be made to produce soluble polymers.
4. Strong solvent interactions with metal coordination centers assist in the solubility of metal-containing polymers.
5. Small tetrahedral centers allow for the production of soluble polymers.

With respect to the use of strong solvent interactions, item 4, Archer,¹¹ our group,^{12–19} and others have found that the solvent molecules may actually act as a ligand complexing the metal site as solution occurs. This additional complexing can occur through substitution of an existing ligand or through expansion of the coordination number.

Other items that have aided solubility include

- Use of nonsymmetrical ligands and metal sites.^{11–19}
- Use of flexible units in the polymer backbone including dimethylsiloxane, methylene oxide, ethylene oxide, and methylene units.¹⁸
- Use of strongly polar–dipolar aprotic liquids that also can coordinate to metal centers. Examples include dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), dimethylformamide (DMF), hexamethylphosphoramide (HMPA), and NMP (*N*-methylpyrrolidone).^{11–19}
- Use of flexibilizing units as side chains to both increase the flexibility of the polymers and to discourage orderly packing and crystalline formation.
- Polymer isolation from rapidly stirred systems before the polymer becomes a solid. The precompletely solidified polymer still retains some reaction solvent molecules.¹⁹
- Addition of a plasticizing agent as polymer formation occurs.
- Use of bulky and extended groups that tend to inhibit crystal formation.
- Through heating.

The presence of alkyl groups tends to increase solubility in organic solvents while phenyl and rigid groups reduce polymer solubility. Solubility in polar solvents often is

enhanced by polar units in the polymers while the absence of polar units enhances the solubility in nonpolar liquids.

III. POLYMER FORMATION

John Bailor was kind enough to write a review for us on coordination polymers in 1978. Readers are referred to this book for Bailor's review of older material.¹⁹

Coordination polymers were reviewed in Volume 1, Chapter 5 of this series.²¹ Related topics will be briefly covered.²⁰

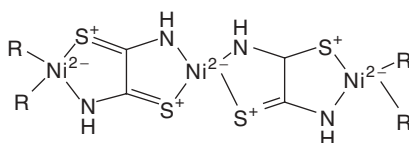
There are three main approaches to metal-containing coordination polymer synthesis.^{19,21} They are coordination polymer formation through:

1. Complexation with ligands that produce a polymer backbone containing the ligand and metal in the backbone.
2. Chelation of metals to an already formed polymer that contains complexing ligand moieties.
3. Polymerization of ligand groupings that already complex the metal.

Each of these avenues to metal-coordination polymers is covered in greater depth in various locations throughout this volume.

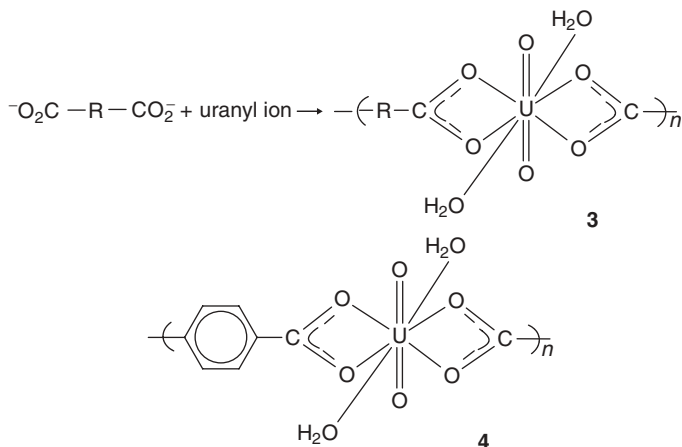
There are numerous coordination complexes that can be defined in the solid state as polymeric materials. X-ray diffraction studies show that various components of the structure are sufficiently close enough to one another to be called polymers or supramolecular. One such example is Prussian Blue, a mixed-Fe(II) and -Fe(III) three-dimensional (3D) solid structure, where each iron is octahedrally coordinated by six cyano ligands. Upon dissolution, a polymeric, high molecular weight species no longer exists. As noted before, this class of complexes will not be emphasized in this chapter.

1. **Complexation with ligands that produce a polymer backbone containing the ligand and metal in the backbone.** Here ligands simultaneously attach themselves to two or more metals. There is a vast array of structures that have been formed through ligand attachment to a metal. If the complexing groups are somewhat removed from one another, then there is opportunity for larger structures to be formed including macromolecular structures. These ligands can be chelating with several complexing sites acting in concert as in the rubeanate bis-chelating agents during the formation of structure **2**.²²



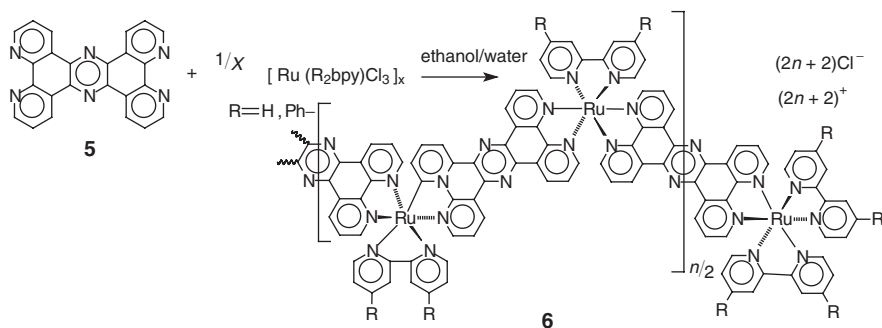
2

The ligand can be composed of two “widely” spaced mono or chelating complexing groups as was used to complex the uranyl ion^{22–25} forming general structures such as **3**. Reaction with disodium terephthalate gives polymer **4**.



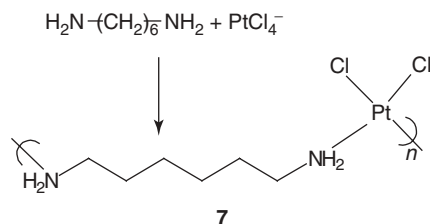
Product of the uranyl ion and the salt of terephthalic acid

The synthesis²⁷ of the soluble, ruthenium-containing octahedral polymer **6** from the bis-chelating rigid ligand **5** is a typical example of coordination polymerization where a ligand binds to two different metals. Ruthenium is an integral and necessary part of the polymer backbone in **7**.²⁶

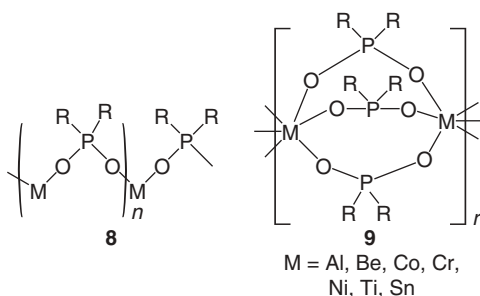


Where bpy = 2, 2' - or 4, 4' - bipyridine

Polymers are formed from single attachments by at least two coordination sites on the same ligand molecule to two metal atoms. Thus, coordination polymers are envisioned to be important alternatives to small coordination complexes such as cis-platin in the treatment of cancer.^{27–34} The product polymer, **7**, from tetrachloroplatinate and 1,6-hexamethylenediamine is shown below. These products were reviewed in Volume 3 of this series.

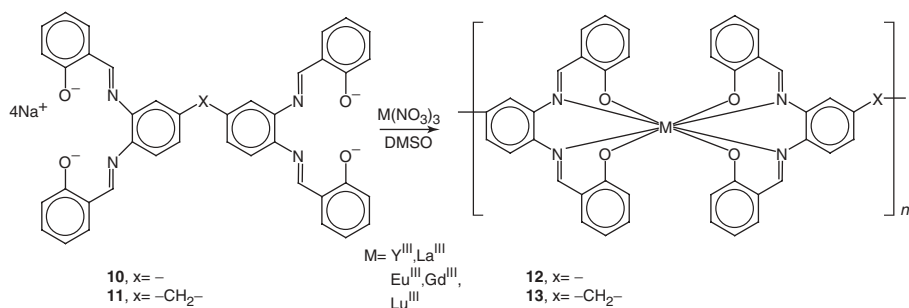


In some cases, when the ligands can bind to a metal, single and multiple bridges are formed leading to polymers. Block et al. prepared many products of this kind where the metal ions are linked together by substituted phosphinous anions.³⁵ Structures **8** and **9** are examples. High molecular weight polymers were achieved and these were among the worst coordination polymers to exhibit good solubilities. The metals Al, Be, Co, Cr, Ni, Ti, and Sn were used. Commercial film products with high thermal stabilities (to 450°C) were made. The chromium(III) polyphosphinates were used in high-pressure silicone greases.

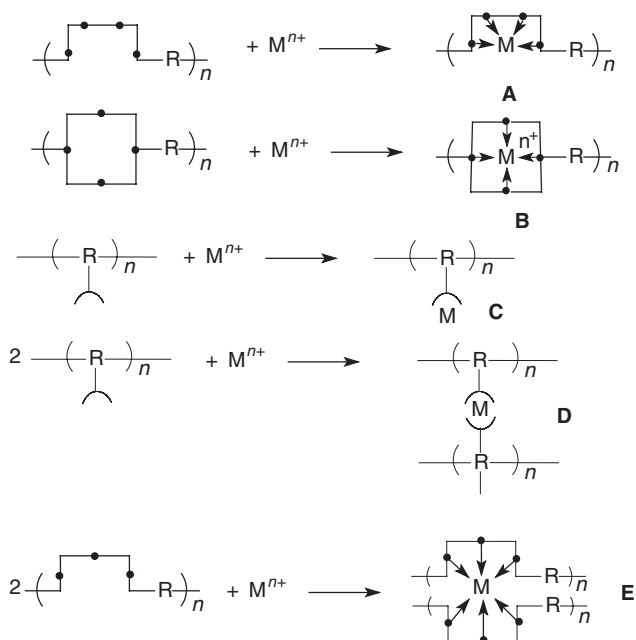


Some of these coordination polymers are linear (e.g., **8**) with $(-\text{M}-\text{O}-\text{P}-\text{O}-)$ repeat units while others exhibit the bridging shown above in **9**.

An excellent example of polymer formation by reacting a bis-chelating ligand with metal ions was provided by Chen and Archer.^{36,37} Trivalent lanthanide nitrates were reacted with the sodium salts of bridging tetradentate Schiff-based ligands **10** and **11** to generate polymers **12** and **13** in DMSO. Dimethyl sulfoxide was able to solubilize both the lanthanide nitrates and the ligand salts. Importantly, DMSO is able to dissolve the polymers produced, which allows the formation of soluble, high molecular weight products. The lanthanide ions used (Y^{III} , La^{III} , Eu^{III} , Gd^{III} , and Lu^{III}) are expected to be very labile. However, these polymers are stable in solution and do not break down into low molecular weight species. The key to this stability is the tetradentate nature of the binding, which holds each ligand to the metal ion. In order to fragment a chain, all four binding sites between the ligand and metal must be simultaneously broken. Each metal ion is eight coordinate. These eight-coordinate centers are conformationally nonrigid and conformational fluctuations enhance the solubility and decrease the tendency for regular packing of the polymer chains during solidification. Molecular weights of 21,600 and 18,500 were obtained using nuclear magnetic resonance (NMR) methods for $\text{M} = \text{Y}$ and Eu , respectively.



2. Chelation to an already formed polymer that contains complexing ligand moieties. Polymers, which have chelating ligands, either in the backbone or pendent to the backbone, can capture metal ions leading to coordination polymers. Rehahn³⁸ divided this class of polymers into three subclasses, **A–C** shown below. One can imagine a large number of possibilities for each of these classifications. For example, the ligand in each case could have a variety of types of binding sites. It could have mono-, di-, tri-, tetra-, or other polydentate sites. Furthermore, type **A** and **C** subclasses could actually form so as to cross-link different chains together, giving network polymers of the types **D** or **E**. In **A**, a metal ion has been chelated to ligand sites all lying along the backbone. In **B**, a cyclic chelating agent such as a porphyrin is in the main chain and chelates a metal. A pendent ligand along a polymer chain can capture a metal ion as shown in **C**. If two pendent chelating ligands are required, cross-linking can give **D** and **E** is formed if the chelating sites are along the main chains of two polymer molecules.



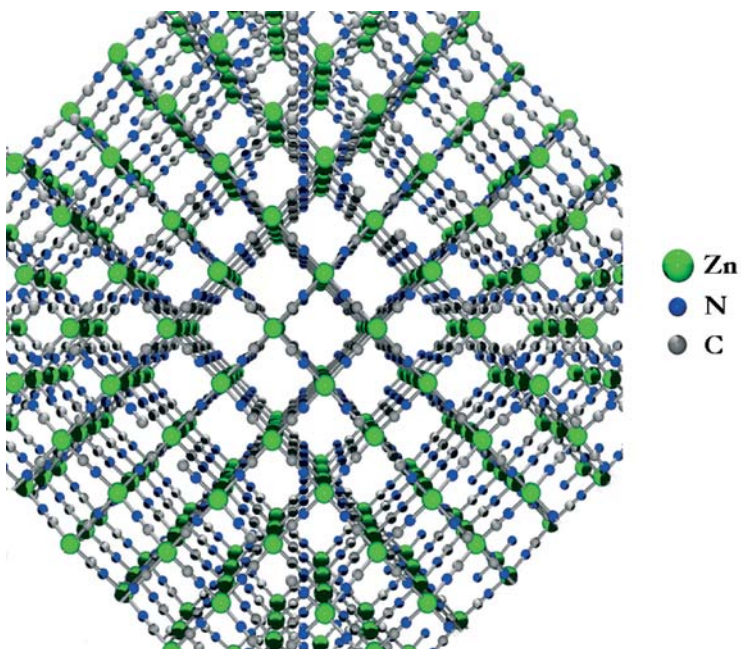


Figure 14 One of the two interpenetrated diamond-like networks of $\text{Zn}[\text{Zn}(\text{CN})_4]$. [Adapted from (137).]

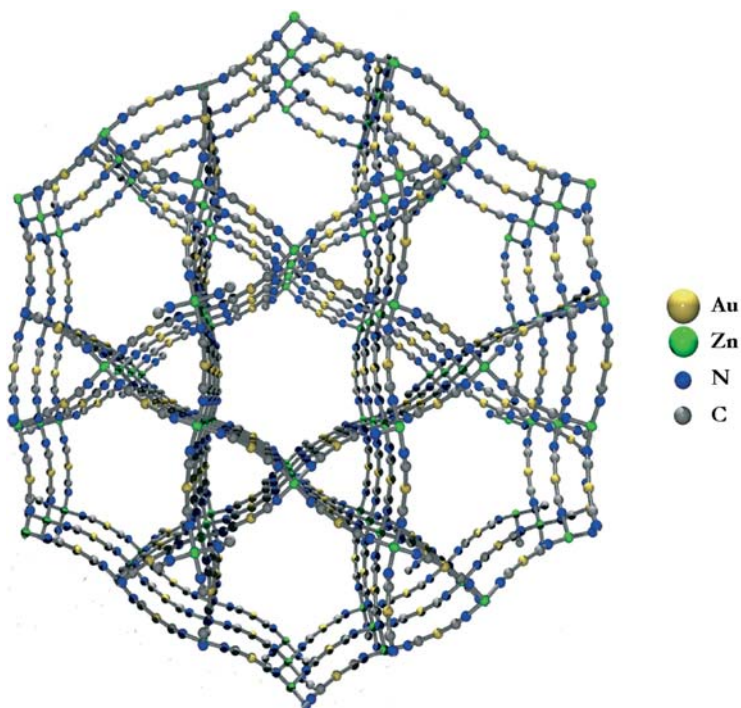


Figure 15 Quartz-like structure of $\text{Zn}[\text{Au}(\text{CN})_2]_2$, showing only one of the six interpenetrated nets. [Adapted from (138).]

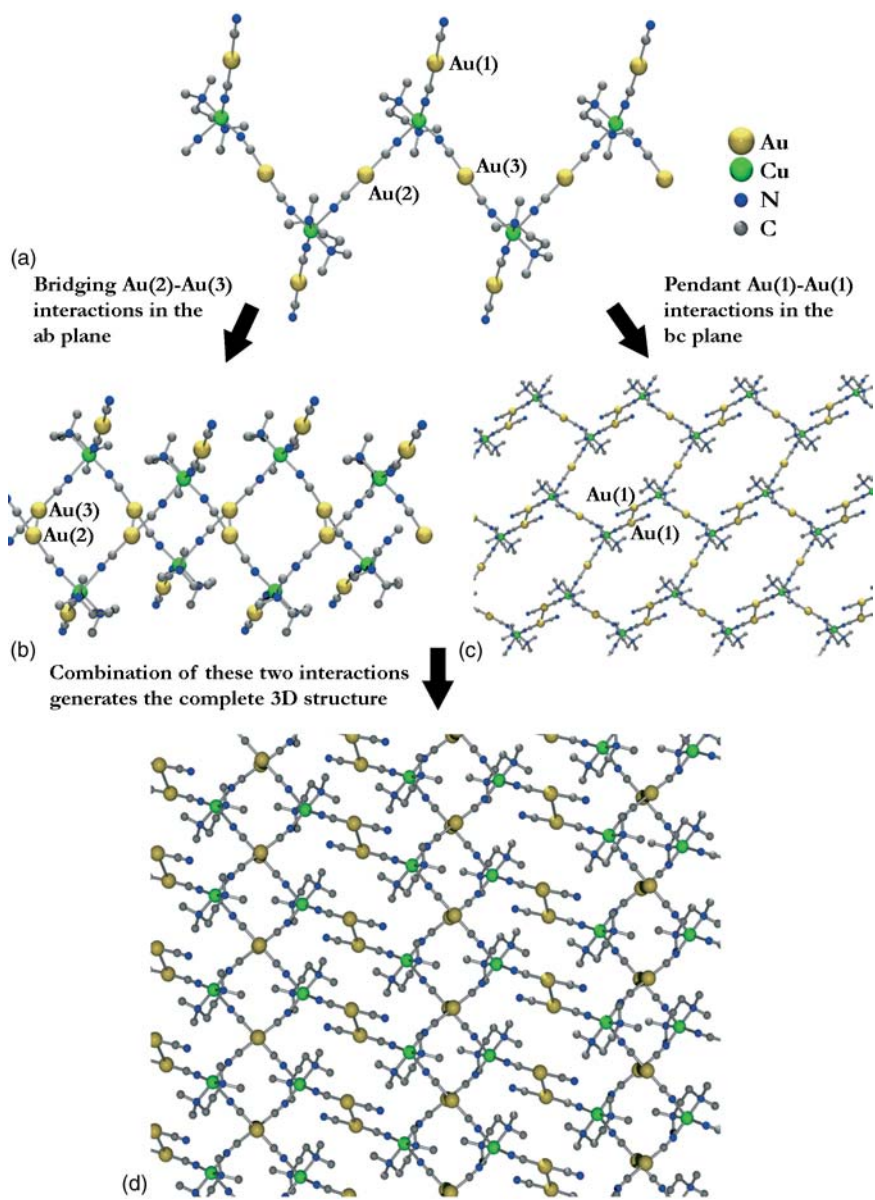


Figure 17 Construction of the 3D structure of $\text{Cu}(\text{tmeda})[\text{Au}(\text{CN})_2]_2$ via aurophilic interactions.¹⁴²

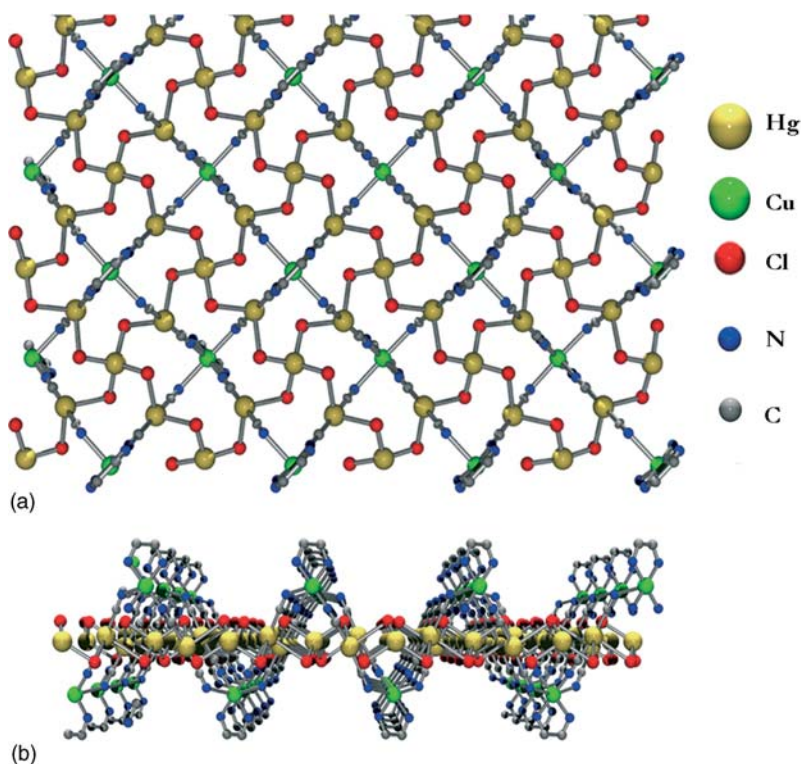


Figure 19 2D layered structure of $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ viewed from above (a) and the side (b) [Adapted from (160).]

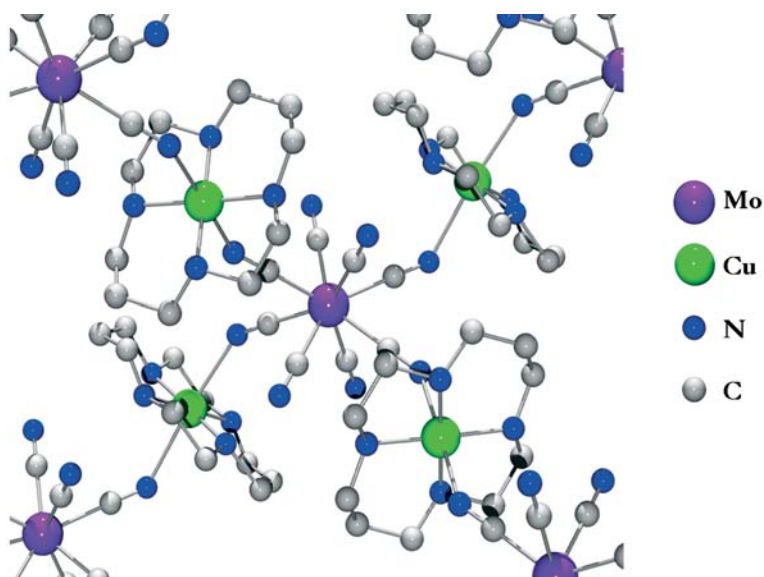


Figure 24 Structure of $[Cu(cyclam)]_2[Mo(CN)_8] \cdot 10.5H_2O$. [Adapted from (177).]

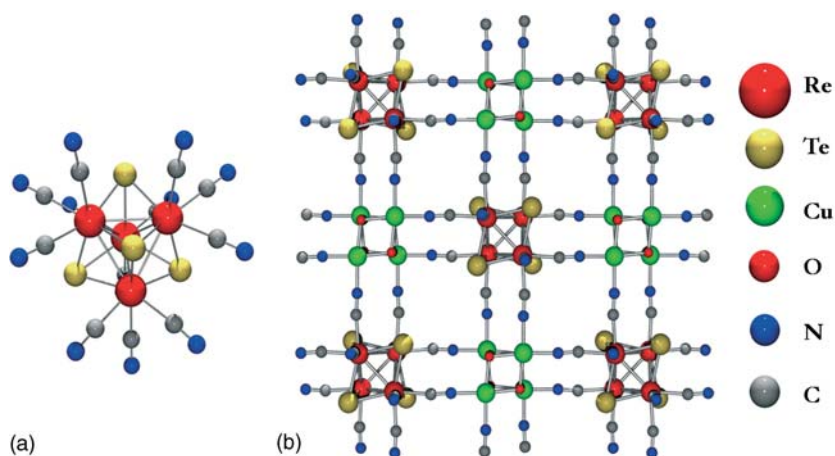


Figure 25 Structure of the anionic chalcocyanide cluster $[\text{Re}_4\text{Te}_4(\text{CN})_{12}]^{4-}$ (a) and of the 2D layered $[\text{Cu}_4(\mu_3\text{-OH})_4][\text{Re}_4\text{Te}_4(\text{CN})_{12}]$ coordination polymer (b). [Adapted from (187).]

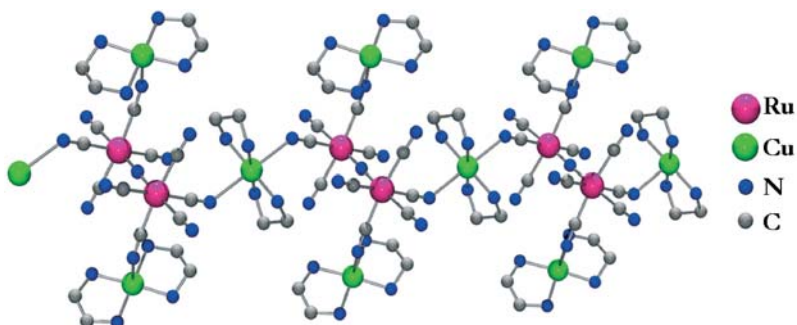


Figure 26 Infinite 1D chain of $\{[\text{Cu}(\text{en})_2]_3[\text{Ru}_2\text{N}(\text{CN})_{10}]\}_n$. [Adapted from (191).]

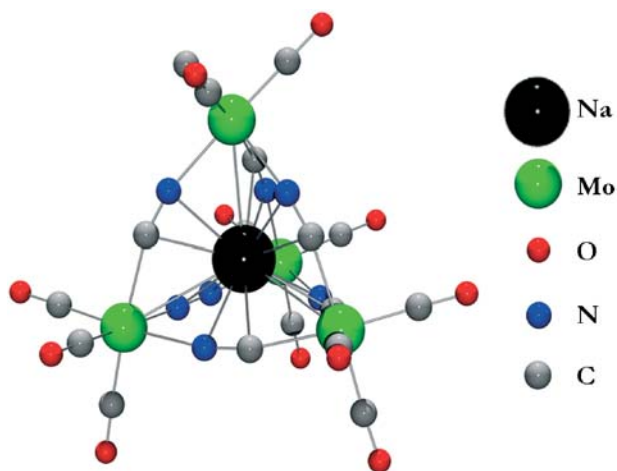


Figure 29 Structure of $[\text{NaC Mo}_4(\text{CN})_6(\text{CO})_{12}]^{5-}$, an alkali metal-templated cyanometalate cage. [Adapted from (216).]