
INORGANIC AND ORGANOMETALLIC POLYMERS

RONALD D. ARCHER

Professor Emeritus

University of Massachusetts, Amherst

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SPECIAL TOPICS IN INORGANIC CHEMISTRY

This text represents the second in a series of one-volume introductions to major areas of inorganic chemistry written by leaders in the field. Inorganic chemistry covers a variety of diverse substances including molecular, coordination, organometallic, and nonmolecular compounds as well as special materials such as metallobiomolecules, semiconductors, ceramics, and minerals. The great structural diversity of inorganic compounds makes them vitally important as industrial feedstocks, fine chemicals, catalysts, and advanced materials. Inorganic compounds such as metalloenzymes also play a key role in life processes. This series will provide valuable, concise graduate texts for use in survey courses covering diverse areas of inorganic chemistry.

R. Bruce King, Series Editor
Department of Chemistry
University of Georgia
Athens, Georgia USA

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PREFACE

If I were to have a special dedication, it would be to the late John C. Bailar, Jr., my Ph.D. mentor. John piqued my interest in the stereochemistry of monomeric coordination compounds initially, and his statement regarding the apparent impossibility of preparing soluble metal coordination polymers of high molecular mass became a challenge that twenty years later put me on the quest for the soluble eight-coordinate polymers. You will find the successful results sprinkled throughout this book.

A number of books and textbooks on inorganic materials chemistry exist. The only recent textbook on inorganic polymers is very heavily weighted toward main group polymers. Recent advances in metal-containing polymers led me to develop a special-topics graduate course on inorganic polymers. The success of this course led Prof. R. Bruce King, the series editor, to suggest that I write “an inorganic polymer book suitable for graduate students.” It has been a joy to write the book because so much is happening in the field and I have learned so much more myself.

I thank profusely the research students, postdoctoral associates, visiting scientists, and co-investigators with whom I worked on inorganic polymers and who provided the incentive for producing this text. This includes several short-term undergraduate exchange students from Germany and Britain who made significant research contributions, too. Also, special thanks to the graduate students who took the special-topics graduate course on inorganic polymers and provided valuable input to the manuscript. Thanks also to the University of Massachusetts Polymer Science and Engineering Department and Department of Chemistry colleagues who have aided my knowledge in polymer science and have allowed my group to use their equipment.

Prepublication materials from Leonard Interrante and Charles Carraher are most graciously appreciated. I wish to acknowledge the help received from

the extensive reviews by Harry Allcock, (especially his and F. W. Lampe's *Contemporary Polymer Chemistry* textbook published by Prentice-Hall in 1981 and 1990), Charles Carraher, Ian Manners, Charles Pittman, Jan Rehahn, and many others you will find referenced in the text.

The staff at John Wiley have been most helpful, and I especially want to thank Darla Henderson, Danielle Lacourciere, and Amy Romano, all of whom have shown me an extraordinary amount of patience.

Finally, ardent thanks and appreciation to Joyce, my devoted wife since 1954, for all of the sacrifices she has endured to make my career and this book a reality. Without her support, this book could not have been completed.

Ronald D. Archer
Amherst, Massachusetts

CHAPTER 1

INORGANIC POLYMERS AND CLASSIFICATION SCHEMES

1.1 INTRODUCTION

This is an exciting time to be involved in the field of inorganic polymers. The advances being made in the core areas of inorganic polymer chemistry are truly remarkable and outstanding, using any logical definition. Recent synthetic breakthroughs are very impressive. Just a few years ago, no one envisioned the synthesis of polyphosphazenes at room temperature or the ready synthesis of organometallic polymers through ring-opening polymerizations. Both are realities at the present time. These and other examples of both main group and metal-containing polymers are discussed in Chapter 2.

Uses for inorganic polymers abound, with advances being made continually. Polysiloxane and polyphosphazene elastomers, siloxane and metal-containing coupling agents, inorganic dental polymers, inorganic biomedical polymers, high temperature lubricants, and preceramic polymers are examples of major applications for inorganic polymers. Conducting and superconducting inorganic polymers have been investigated as have polymers for solar energy conversion, nonlinear optics, and paramagnets. These uses are detailed in Chapter 4. If we were to include inorganic coordination and organometallic species anchored to organic polymers and zeolites, catalysis would also be a major use.

1.1.1 What Is an Inorganic Polymer?

Inorganic by its name implies nonorganic or nonhydrocarbon, and polymer implies many *mers*, monomers or repeating units. Organic polymers are characteristically hydrocarbon chains that by their extreme length provide entangled materials with unique properties. The most obvious definition for an inorganic polymer is a polymer that has inorganic repeating units in the backbone. The intermediate situation in which the backbone alternates between a metallic element and organic linkages is an area where differences in opinion occur. We will include them in our discussions of inorganic polymers, although, as noted below, such polymers are sometimes separated out as inorganic/organic polymers or organometallic polymers or are excluded altogether.

Various scientists have provided widely differing definitions of inorganic polymers. For example, Currell and Frazer (1) define an inorganic polymer as a macromolecule that does not have a backbone of carbon atoms. In fact, several other reviews define inorganic polymers as polymers that have no carbon atoms in the backbone (2–4). Such definitions leave out almost all coordination and organometallic polymers, even though a sizable number of such polymers have backbone metal atoms that are essential to the stability of the polymer chains.

Some edited books (3), annual reviews (5), and the present work include metal-containing polymers in the definition by using titles like inorganic and organometallic polymers. One text includes these polymers but only gives them a few percent of the total polymer coverage (6). Research papers sometimes use the term inorganic/organic polymers, inorganic/organic hybrid polymers, organometallic polymers, or metal-containing polymers for polymers that have both metal ions and organic groups in the backbone. MacCallum (7) restricts inorganic polymers to linear polymers having at least two different elements in the backbone of the repeat unit. This definition includes the coordination and organometallic polymers noted above, but it classifies polyesters and polyamides as inorganic polymers while leaving out polysilanes and elemental sulfur!

Holliday (8) is also very inclusive by including diamond, graphite, silica, other inorganic glasses, and even concrete. Thus it seems that ceramics and ionic salts would also fall under his definition. Anderson (9) apparently uses a similar definition; however, Ray (10) suggests that the term inorganic polymers should be restricted to species that retain their properties after a physical change such as melting or dissolution. Although this would retain silica and other oxide glasses, inorganic salts would definitely be ruled out. Whereas other definitions could undoubtedly be found, the lack of agreement on the definition of inorganic polymers allows for either inclusiveness or selectivity.

This book will explore the classifications of polymers that are included in the more inclusive definitions and will then take a more restrictive point of view in terms of developing the details of inorganic (including metal-containing organometallic) polymer synthesis, characterization, and properties. The synthesis and characterization chapters will emphasize linear polymers that have either at least one metal or one metalloid element as a regular essential part of the backbone and others that have mainly noncarbon main group atoms in the

backbone. Inorganic species that retain their polymeric nature on dissolution will be emphasized rather than species that happen to be polymeric in the solid state by lattice energy considerations alone.

For the main group elements, linear chain polymers containing boron, silicon, phosphorus, and the elements below them in the periodic table will be emphasized provided they have sufficient stability to exist on a change of state or dissolution. For transition and inner transition elements, linear polymers in which the metal atom is an essential part of the backbone will be emphasized, with the same restriction noted for the main group elements.

To categorize inorganic polymers further, we must distinguish between oligomers and polymers on the basis of degrees of polymerization. Too often in the literature, a new species is claimed to be polymeric when only three or four repeating units exist per polymer chain on dissolution. For our purposes, we will use an arbitrary cut-off of at least 10 repeating units as a minimum for consideration as a polymer. Anything shorter will be classed as an oligomer.

Note: In step-growth and condensation polymers of the AA + BB type, where the repeating unit is AABB, 10 repeating units, (AABB)₁₀, corresponds to a degree of polymerization of 19. That is, $2n - 1$ reaction steps are necessary to assemble the 20 reacting segments that make up the polymer. The reader can verify this relationship with a simple paper-and-pencil exercise. One of the greatest challenges in transition metal polymer chemistry has been to modify synthetic procedures such that polymers rather than oligomers are formed before precipitation (cf. Exercise 1.1).

1.2 CLASSIFICATIONS BY CONNECTIVITIES

N. H. Ray, in his book on inorganic polymers (10), uses *connectivity* as a method of classifying inorganic polymers. Ray defines connectivity as the number of atoms attached to a defined atom that are a part of the polymer chain or matrix. This polymer connectivity can range from 1 for a side group atom or functional group to at least 8 or 10 in some metal-coordination and metal-cyclopentadienyl polymers, respectively. Multihapticity is designated with a superscript following the η for example, the cyclopentadienyl ligand in Figure 1.2b is η^5 .

An alternate designation of connectivity of the cyclopentadienyl ring is based on the number of electron pairs donated to the metal ion. Thus a metal species with a bis(cyclopentadienyl) bridge has a connectivity of 6 using this alternate designation. This is more in keeping with its bonding.

Also note that double-ended bridging ligands in linear coordination polymers are classed as bis(monodentate), bis(bidentate), bis(tridentate), bis(tetradentate), etc. and provide connectivities of 2, 4, 6, or 8, respectively.

1.2.1 Connectivities of 1

Anchored metal-containing polymers used for catalysis can have connectivity values as low as 1 with respect to the polymer chain as shown in Figure 1.1.

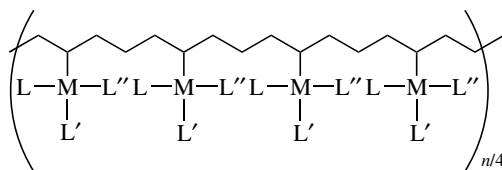


Figure 1.1 Schematic of anchored metal-containing polymer with a connectivity of 1, where M might be palladium or platinum with three other ligands. For catalytic activity, at least one of the three must be easily removed by a substrate.

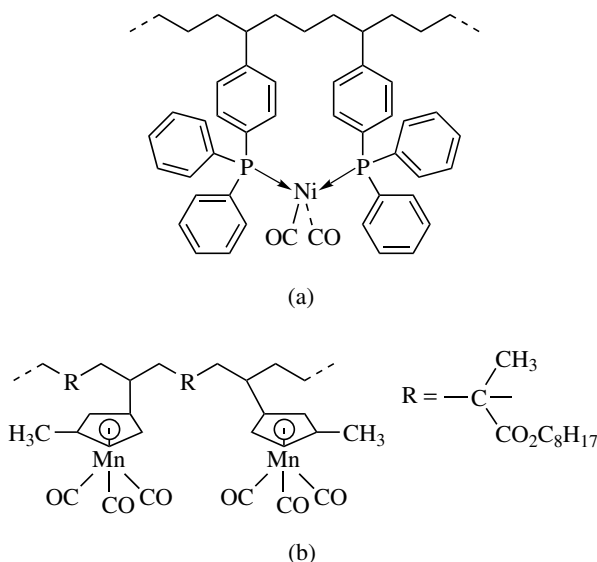


Figure 1.2 Higher connectivities for metal-anchored polymers: (a). Schematic representation of an anchored polymer that can convert dienes to cyclohexene aldehydes under the right conditions. (b). Schematic representation of an anchored polymer that can photolytically transport N_2 across membranes. The analogous manganese cyclopentadienyl tricarbonyl monomer decomposes under comparable conditions.

TABLE 1.1 Dentate Number (Denticity) Designation of Metal Chelates.

Donor Atoms on Metal	Designation in This Text ^a	Alternate Designation
one	monodentate [Fig. 1.3d]	unidentate
two	bidentate ^b [Fig. 1.8b,c]	didentate
three	tridentate [Fig. 1.10a]	terdentate
four	tetradentate [Fig. 1.12]	quadridentate
five	pentadentate	ququidentate
six	hexadentate	sexadentate

^a1990 IUPAC nomenclature except when noted otherwise [text examples in brackets]

^b1970 IUPAC nomenclature

Note that the metal can have other ligands (groups coordinated to the metal) as well, but inasmuch as they do not affect the polymer connectivity, the metal is defined as having a connectivity of 1. Important connectivities of 1 are fairly rare because the inertness of a single metal connection to a polymer is appreciably less than cases in which multidentate chelation (2 or more ligating atoms from a single ligand are coordinated to the same metal atom; cf. Table 1.1) or multihapticity (2 or more atoms from the same molecule interacting with the same metal atom in an organometallic species; cf. Fig. 1.2) occurs.

1.2.2 Connectivities of 2

Sulfur and selenium in their chain polymer allotropes undoubtedly possess a connectivity of 2. They also have a connectivity of 2 in their ring structures, for example, the crown S_8 structure. Linear polyphosphates, polyphosphazenes, poly(sulfur nitride), polycarboranes, pyroxenes (single-chain silicates), silicones

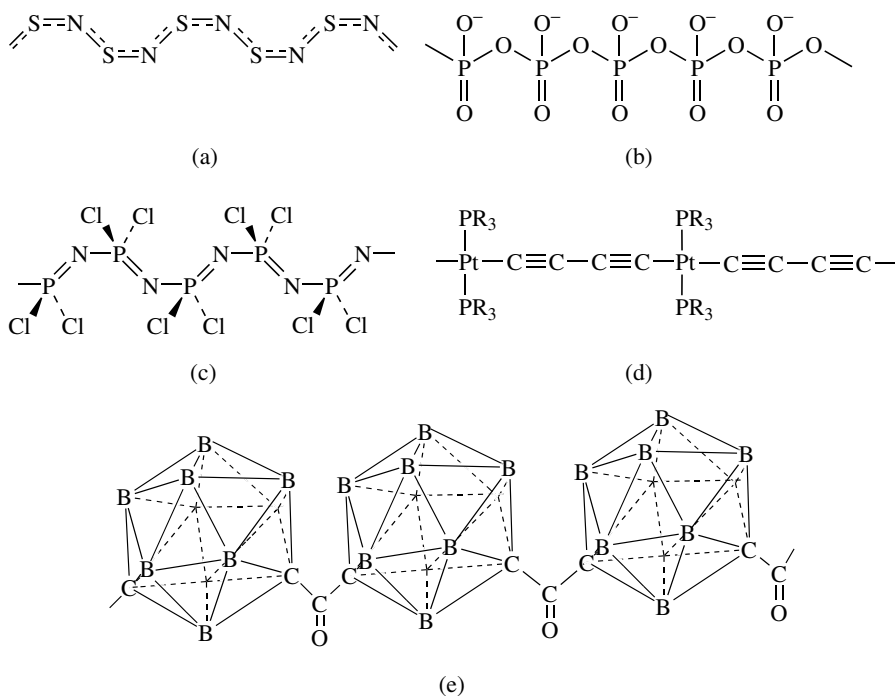


Figure 1.3 Examples of inorganic polymeric species with connectivity of 2: (a) poly(sulfur nitride); (b) linear polyphosphate; (c) poly(dichlorophosphazene); (d) poly[bis-(R_3 phosphine)- μ_2 -diacetylenato- C_1 , $C_4(2-)$ platinum(II)], where R is a large organic group; (e) carborane oligomer with *meta*- $B_{10}H_{10}C_2$ polyhedra linked by CO (although the hydrogens on the boron atoms and the BH groups in the back of the $B_{10}H_{10}C_2$ polyhedra are not shown). Carborane polymers with $-\text{SiR}_2(\text{OSiR}_2)_n-$ linkages also exist and have been shown to have practical applications (cf. Chapter 4).

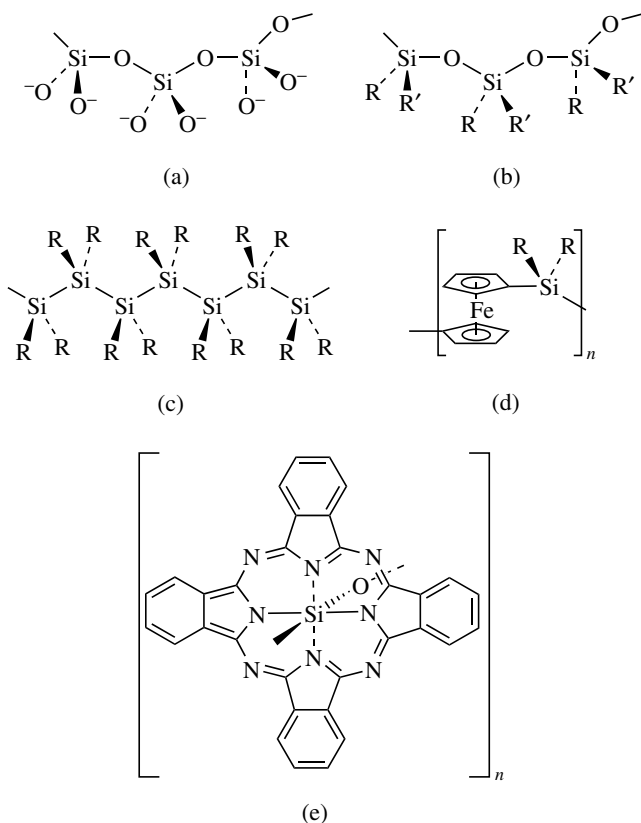


Figure 1.4 Examples of silicon polymers with silicon connectivities of 2: (a) a portion of a pyroxene silicate chain; (b) a portion of a silicone chain where R is typically an alkyl organic group; (c) a portion of a polysilane chain where again R is typically an alkyl organic group; (d) the repeating unit of a high-molecular-weight ferrocene/dialkylsilicon polymer; and (e) the repeating unit of the six-coordinate silicon in poly[oxophthalocyaninosilicon(IV)] (cf. Figure 1.14c).

(–Si–O– backbones), polysilanes (–Si–Si– backbones), and simple linear coordination and organometallic polymers that are joined by monodentate ligands also have a connectivity of 2. Examples are shown in Figures 1.3 and 1.4. Such polymers will be a primary emphasis of this book.

1.2.3 Connectivities of 3 (Fig. 1.5)

Boron in boric oxide has a connectivity of 3, as do the pnictides (N, P, As, Sb, Bi) in some of their binary chalcogenides (e.g., As has a connectivity of 3 in As_2S_3), silicon in silicates such as mica, talc, and pyrophyllite, and carbon in graphite. Such connectivities of 3 provide two-dimensional polymers that

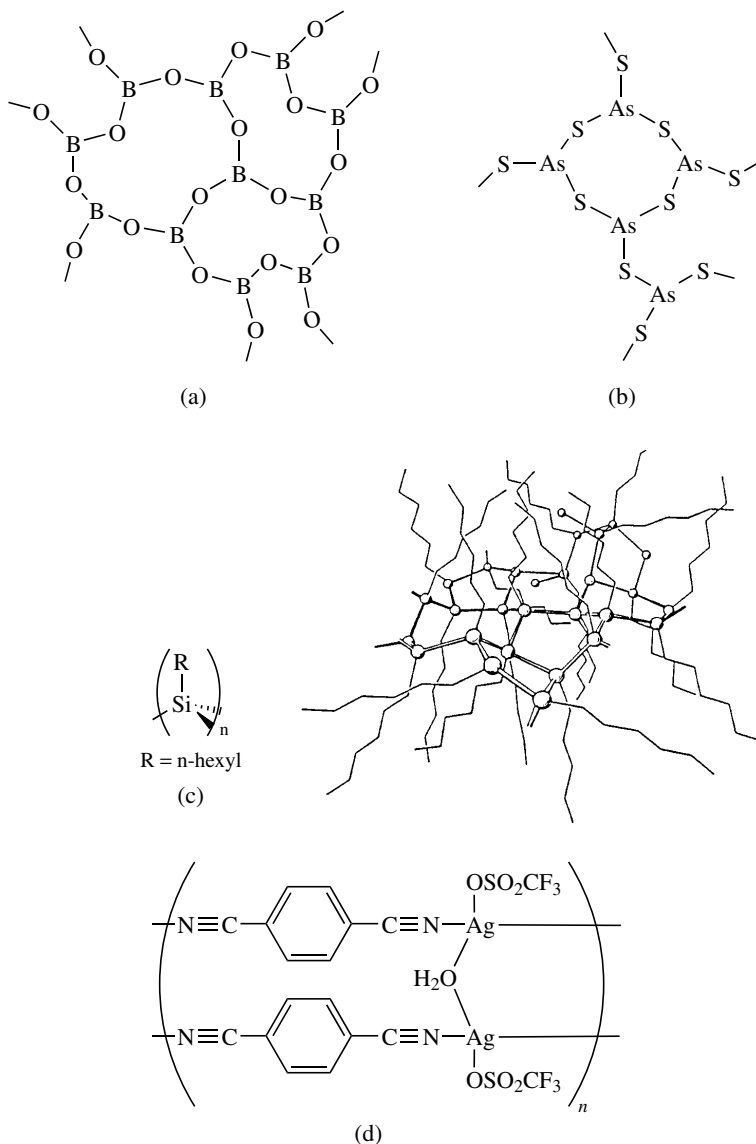


Figure 1.5 Examples of connectivity of 3: (a) boric acid, (b) arsenic(III) sulfide, (c) a synthetic polysilylene (Reprinted with permission from Bianconi et al., *Macromolecules*, 1989, **22**, 1697; © 1989 American Chemical Society); and (d) a synthetic silver polymer (Venkataraman et al., *Acta Cryst.* 1996, **C52**, 2416).

are good lubricants and film- and sheet-forming materials. Polysilynes of the type $[\text{RSi}]_n$ and metals [e.g., silver(I)] surrounded with three donors provide synthetic examples of connectivities of 3, although the latter example would not be expected to keep this connectivity in solution.

1.2.4 Mixed Connectivities of 2 and 3

Although both the linear polyphosphoric acids and cyclic metaphosphoric acids have a connectivity of 2 with respect to phosphorus, ultraphosphoric acids exist (Fig. 1.6) that are intermediates in the hydrolysis of P_4O_{10} to simpler phosphoric acids. Note that the connectivity of phosphorus changes from 3 in the oxide through a mixture of 3 and 2 in the ultraphosphoric acids to 2 in the polyphosphoric acids. However, as noted by Ray (10), these are dynamic processes with bond making and bond breaking causing changes in the connectivity of individual phosphorus atoms increasing and decreasing during the hydrolysis process. The phosphate salts possess similar connectivities to the acids.

Amphibole silicates, such as asbestos, have double chains or ladders of silicon and oxygen in which the silicon atoms have connectivities of both 2 and 3. (See Fig. 1.6.) Note that linear polymers with a basic connectivity of 2 typically have mixed connectivities of 2 and 3 when crosslinked because appropriate crosslinking affects only a small portion of the total chain atoms. A number of intractable bis(monodentate) ligand metal coordination species—insoluble, amorphous, uncharacterizable and suspected of being polymers—undoubtedly fall into this class as well.

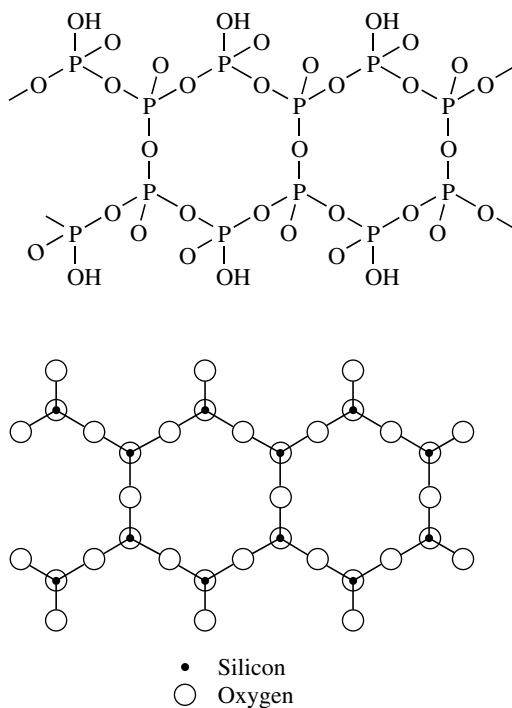


Figure 1.6 Examples of polymeric inorganic species with mixed connectivities of 2 and 3: (a) an ultraphosphoric acid and (b) a portion of an asbestos chain.

1.2.5 Connectivities of 4

Vitreous silica has silicon atoms with a connectivity of 4. Silicate glasses, if counter ions are included (10), also have connectivities of 4. Boron and aluminum phosphates and many other three-dimensional polymers have connectivities of 4 for at least one type of atom in the polymer; cf. Figure 1.7. Another class of inorganic polymers that have connectivities of 4 are metal coordination polymers in which each metal ion in the backbone is coordinated to the polymer chain through two bidentate ligands, where a bidentate ligand is a donor that coordinates to the same metal ion through two donor atoms. Examples are shown in Figure 1.8.

1.2.6 Mixed Connectivities of 3 and 4

A number of polymeric inorganic species have mixed connectivities of 3 and 4, including some borate glasses, where the counter cations provide the counter charges for the four oxide ions connected to at least some of the boron atoms as shown in Figure 1.9. Other examples of mixed connectivity include the silicon atoms in fibrous zeolites and the silicon atoms at the surfaces of silica.

1.2.7 Connectivities of 6

Examples of connectivities of 6 include metal coordination polymers having metal atoms or ions joined with two tridentate ligands. A tridentate ligand is a ligand that has three atoms that are coordinated to the same metal atoms or ion; cf. Figure 1.10.

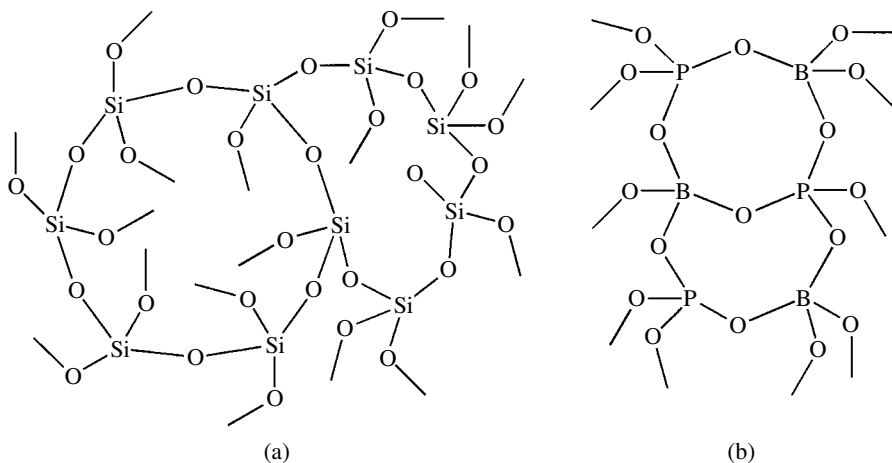


Figure 1.7 Examples of polymeric inorganic species with mixed connectivities of 4: (a) silica with silicon atoms of connectivities of 4 and (b) boron phosphate with both phosphorus and boron atoms with connectivities of 4.

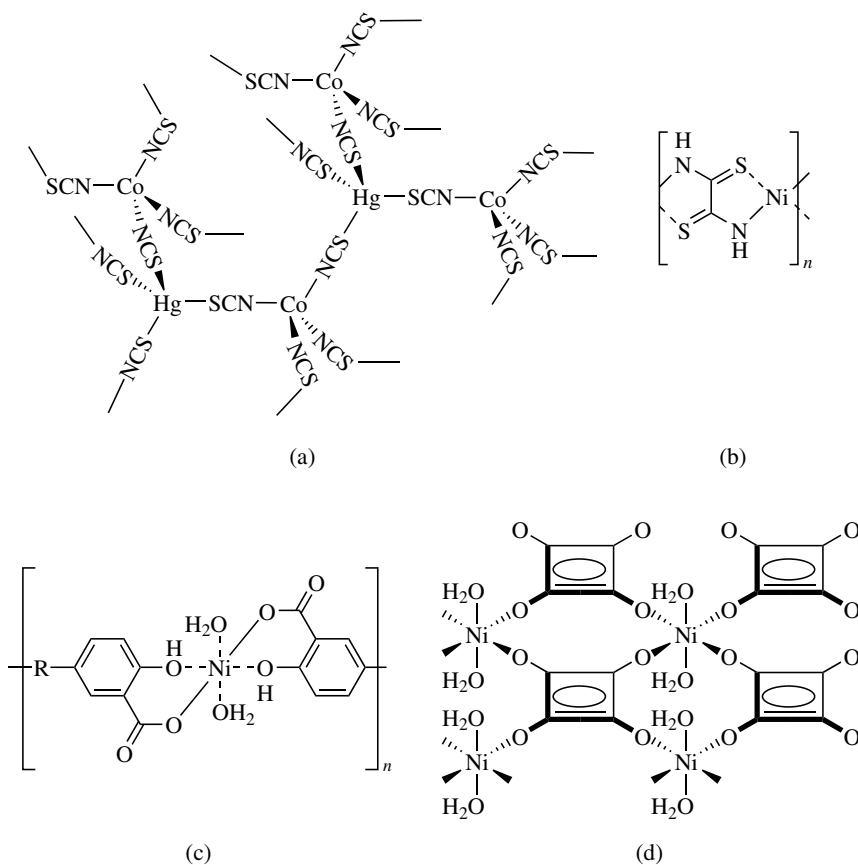


Figure 1.8 Metal coordination polymers with connectivities of 4 for the metal ions: (a) a small portion of the three-dimensional $[\text{CoHg}(\text{SCN})_4]_n$ solid used as a standard for magnetic susceptibility measurements—both Co and Hg are tetrahedrally coordinated; (b) a typical linear polymer for a 4-coordinate metal with a bis-bidentate ligand; (c) a linear polymer for octahedral coordination with two bidentate ligands per metal plus two other ligands not involved in connectivity of the polymer (R can be CH_2 , C_3H_8 , a large diazo link, etc.); (d) coordination analogous to (c) except that each of the four donors of the ligand are bonded to four different metal ions, which gives a two-dimensional sheet.

Ferrocene polymers (Fig. 1.10) can be considered to have iron atoms with connectivities of 6 if each cyclopentadienyl ring is considered a connectivity of 3—consistent with bonding considerations. That is, considering the 18-electron rule, iron(II) can accommodate only six pairs of electrons in addition to the six electrons in its $3d^6$ valence electron levels. Thus, although five carbon atoms of each cyclopentadienyl ring are approximately equidistant from the iron, only the three pairs of pi-symmetry electrons are coordinated or bonded to the iron atom from each ring. However, using the number-of-atoms definition, these polymers have a connectivity of 10.

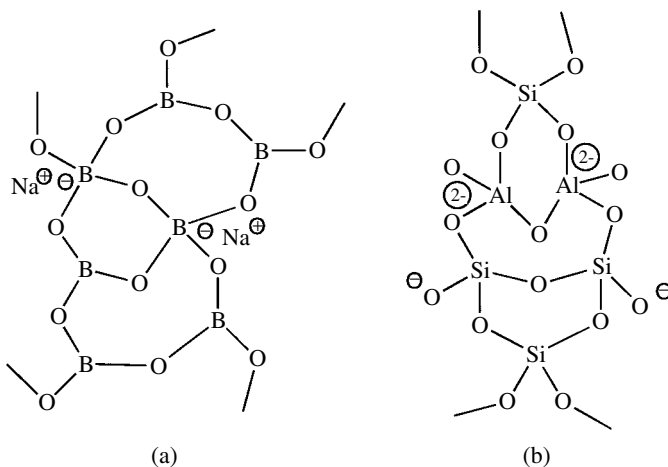


Figure 1.9 An example of mixed connectivities of 3 and 4 for (a) the boron atoms in a typical borate salt and (b) the silicon atoms in a typical fibrous zeolite.

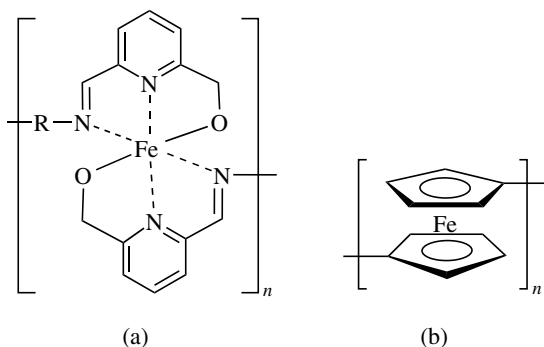


Figure 1.10 Examples of connectivities of 6 (or more) for metal atoms/ions.

Another example of connectivity of 6 can be found in the carborane carbons of the carborane oligomer shown in Figure 1.3e using the atoms-connected definition of connectivity. Naturally, the connectivity would not be more than 4 if the number of electron pairs bonding the carborane carbons to the chain were considered.

1.2.8 Mixed Connectivities of 4 and 6

Orthophosphates and arsenates of titanium, zirconium, tin, cerium, thorium, silicon, and germanium have mixed connectivities of 4 and 6. An example is shown in Figure 1.11.

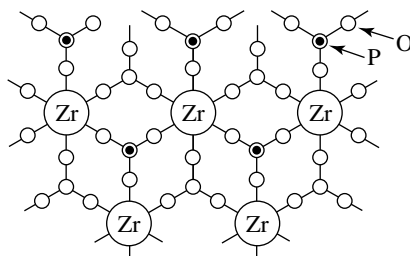


Figure 1.11 An orthophosphate of mixed connectivities of 4 and 6.

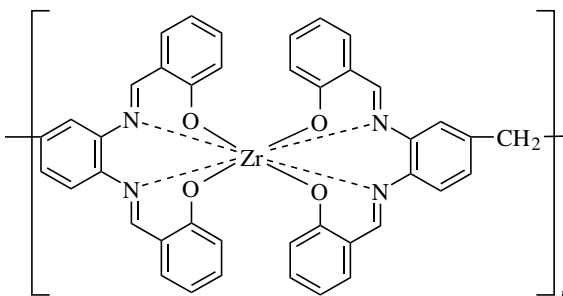


Figure 1.12 A Schiff-base polymer of zirconium with a connectivity of 8.

1.2.9 Connectivities of 8

Metal coordination polymers of zirconium(IV), yttrium(III), and several lanthanide ions [cerium(IV), lanthanum(III), europium(III), gadolinium(III), and lutetium(III)] have been synthesized that possess connectivities of 8 because two tetradentate ligands are coordinated to each metal ion that is part of the polymer chain. An example is shown in Figure 1.12 (cf. Exercises 1.2–1.6).

1.3 CLASSIFICATIONS BY DIMENSIONALITY

Another manner in which polymers can be classed is by dimensionality. Pittman et al. (3) use this classification for polymeric species containing metal atoms in their backbones—one category of metal-containing polymers in the next section. Here we will use the dimensionality for all types of inorganic polymers.

1.3.1 1-D Polymeric Structures

A linear chain polymer is categorized as a one-dimensional (1-D) polymer even though it may have twists and turns in the “linear” chain. Simple polymer chains in which all of the atoms in the chain have a connectivity of 2 are classed as 1-D polymers. However, a linear chain polymer with one or more atoms of each