

8 Reaction and Physical Properties

Organic synthesis using complexes and organometallic compounds, homogeneous catalysis, bioinorganic chemistry to elucidate biological reactions in which metals participate, and studying solid state properties such as solid state catalysis, conductivity, magnetism, optical properties are all important fields of applied inorganic chemistry. Basic inorganic chemistry, although previously less developed compared with organic chemistry, is now making fast progress and covers all elements. Construction of general theories of bonding, structure, and reaction covering molecules and solids is a major problem for the near future.

8.1 Catalytic reactions

Catalysts reduce the activation energy of reactions and enhance the rate of specific reactions. Therefore they are crucially important in chemical industry, exhaust gas treatment and other chemical reactions. While the chemical essence of **catalysis** is obscure, practical catalysts have been developed based on the accumulation of empirical knowledge. However, while gradually we have come to understand the mechanisms of homogeneous catalysis through the development of inorganic chemistry, our understanding of surface reactions in solid catalysts is also deepening.

(a) Homogeneous catalysis

The chemistry of catalysts that are soluble in solvents has developed remarkably since the epoch-making discovery (1965) of the **Wilkinson catalyst**, $[\text{RhCl}(\text{PPh}_3)_3]$. This complex is a purplish red compound which forms by heating $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PPh_3 under reflux in ethanol. When dissolved in an organic solvent, this complex is an excellent catalyst for **hydrogenation** of unsaturated hydrocarbons by H_2 at ambient temperatures and pressures to form saturated hydrocarbons, and **hydroformylation** reactions of olefins with H_2 and CO to form aldehydes.

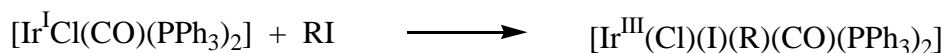
In the past, the mechanism of catalytic reactions were generally not very clear. Before the Wilkinson catalyst, the **Reppé process**, which oligomerize acetylenes or the **Ziegler-Natta catalysts** that polymerize olefins and dienes, had been discovered and detailed studies on **homogeneous catalysis** had been conducted from the viewpoint of the chemistry of complexes. Consequently, catalytic reactions are now established as a cycle

of a combination of a few elementary steps that occur on the metals of catalyst complexes.

Coordination and dissociation There must be a process in which reactants such as olefins are activated and react with other reactants after being coordinated to the central metal of a complex, and they dissociate from the metal as products.

Oxidative addition Oxidative addition is one among a few key elementary reactions of metal complexes. This is a reaction of such compounds as alkali metal halides, RX, acids, HX or dihydrogen, H₂, to the metal in a complex which then dissociate into R and X, H and X, or H and H, which are bonded to the metal as two fragment anions. If other ligands on the start complex are not removed, the coordination number increases by two. As alkyl, halogen, and hydride ligands are more electronegative than the central metal, they are regarded as formally anionic ligands after coordination. Therefore, the oxidation number of the central metal increases after an addition reaction. As it is an addition reaction accompanied by oxidation of the central metal, it is called oxidative addition.

For example, in the addition reaction of an alkyl halide to a tetra-coordinate iridium(I) complex [IrCl(CO)(PPh₃)₂],



iridium becomes hexa-coordinate and undergoes two-electron oxidation from +1 to +3. Since a neutral RI molecule is added, there must be no change in the charge of the whole complex, and if an alkyl and iodine are anions, the oxidation number of the central metal should increase by 2. Similar change occur when two hydride ligands are formed as the result of the addition of dihydrogen.

The reverse reaction is called **reductive elimination**. Both oxidative and reductive reactions are very important as elementary steps in the mechanism of homogeneous catalysis involving hydrocarbons and dihydrogen.

Exercise 8.1 How does the oxidation number of rhodium change with reductive elimination of dihydrogen from [RhCl(H)₂(PPh₃)₂ (Sol)]?

“Answer” It changes to Rh(I) from Rh(III).

Insertion reaction In the reaction of an alkyl or hydride ligand to shift to a carbonyl or olefin ligand coexisting on the central metal, the resultant complex appears as

if a carbonyl or an olefin has inserted between the M-R or M-H bond. This is called an insertion reaction.

Reaction of a coordinated ligand This is the process in which a coordinated reactant reacts to form a product. By coordinating to a metal, the reactants take geometrically and electronically suitable conformations. It is the basis of catalyst design to control these reaction conditions.

Since a reaction is repeated while the complex used as a catalyst remains unchanged by forming a cycle of reactions, the reactants/complex ratio is very small, co-inciding with the definition of a catalyst. The catalytic cycle in hydrogenation of ethylene is illustrated in Fig. 8.1.

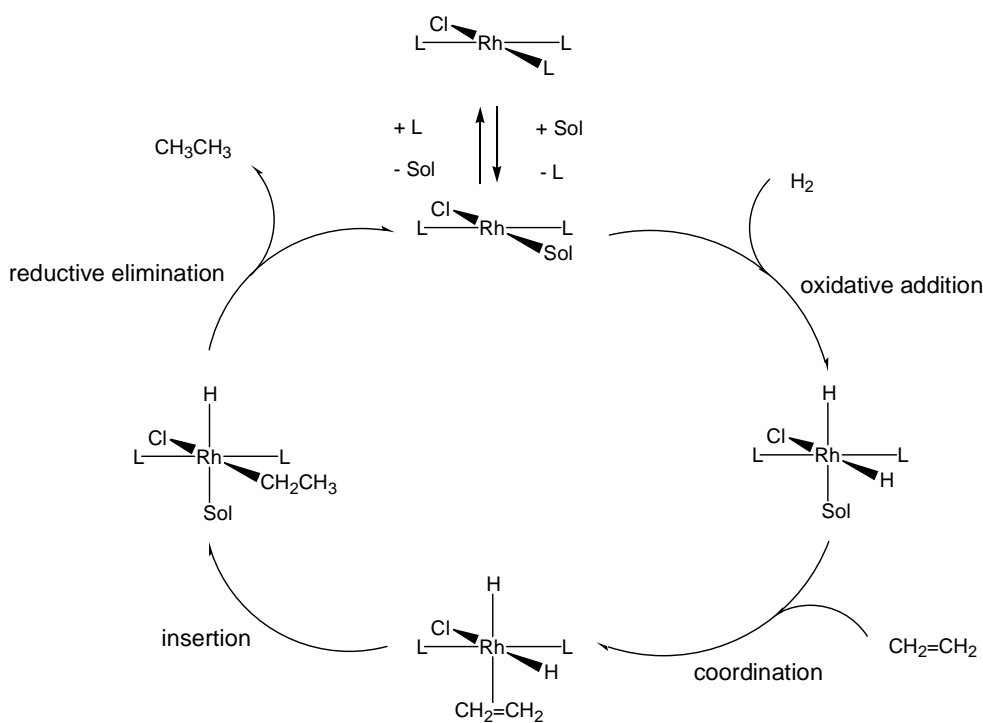


Figure 8.1 Catalytic cycle of ethylene hydrogenation by the Wilkinson catalyst. L is a ligand and Sol is a solvent molecule.

If the triphenylphosphine ligand $\text{P}(\text{C}_6\text{H}_5)_3$ in the Wilkinson catalyst is replaced by an optical active phosphine, **asymmetric hydrogenation** is realized. Asymmetrical catalysis equivalent to enzyme reactions have been developed by skillful design of asymmetrical ligands. In particular, the asymmetric induction of binaphtyldiphosphine (BINAP) has attracted attention.

(b) Solid state catalysis

A solid catalyst is also called a **heterogeneous catalyst**, and promotes the reaction of reactants in gaseous or liquid phases in contact with a solid material. Since adsorption of reactants on the catalyst surface is the initial step, a large surface area is required for good efficiency of catalysis. Polyphase systems, which carry active catalysts on materials such as zeolites with small pores of molecular sizes, and gamma alumina and silica gel with large surface area, are often used.

Previously, solid state catalysis was explained as arising from a mysterious activation of reactants due to adsorption, but it has become increasingly clear that catalysis is ascribable to surface chemical reactions. Namely, the action of solid state catalysts depends on activation of reactants by surface acids or bases, and by coordination to the metal surface. It is possible to observe these interactions using various spectroscopies (infrared spectroscopy, EXAFS (extended X-ray absorption fine structure), electronic spectra), electron microscopy, or STM (scanning tunnelling microscopy).

Since mechanisms of homogeneous catalysis have been clarified considerably, solid surface reactions can also be analyzed by introducing concepts such as “surface complexes” or “surface organometallic compounds”. However, unlike homogeneous catalysis, in which only one or a few metal centers participate, many active sites are involved in solid state catalysis. Since surface homogeneity and reproducibility are difficult to maintain, major parts of reaction mechanisms are obscure even for such simple reactions as ammonia synthesis.

During the direct production of ammonia from dinitrogen and dihydrogen, reactions occur using iron catalysts containing alkali metal or alkaline earth metal oxides as activators at high temperatures (about 450 °C) and under high pressures (about 270 atm). Prior to the epoch-making discovery of this process by F. Haber (1909), all nitrogen compounds came from natural resources. The realization of this discovery has had an immeasurable influence upon chemical industries, as ammonia is indispensable to the manufacture of fertilizers, gunpowder and other inorganic compounds containing nitrogen. In recognition of this, a Nobel Prize was awarded to F. Haber for this invention (1918). A huge volume of research on the elucidation of the reaction mechanism of ammonia synthesis has been performed up until the present, because the reaction of dinitrogen and dihydrogen on iron catalysts is a good model of solid state catalysis.

8.2 Bioinorganic chemistry

Many biological reactions are known to involve metal ions. There are also metals recognized as essential elements, although their roles in living organisms are not clear. Bioinorganic chemistry, the study of the functions of metals in biological systems using the knowledge and methods of inorganic chemistry, has progressed remarkably in recent years.

The following list shows typical bioactive substances containing metals.

- (1) Electron carriers. Fe : cytochrome, iron-sulfur protein. Cu : blue copper protein.
- (2) Metal storage compound. Fe : ferritin, transferrin. Zn : metallothionein.
- (3) Oxygen transportation agent. Fe: hemoglobin, myoglobin. Cu: hemocyanin.
- (4) Photosynthesis. Mg: chlorophyll.
- (5) Hydrolase. Zn: carboxypeptidase. Mg: aminopeptidase.
- (6) Oxidoreductase. Fe: oxygenase, hydrogenase. Fe, Mo: nitrogenase.
- (7) Isomerase. Fe: aconitase. Co: vitamin B₁₂ coenzyme.

The basis of chemical reactions of metalloenzymes are

- (1) Coordinative activation (coordination form, electronic donating, steric effect),
- (2) Redox (metal oxidation state),
- (3) Information communication,

and, in many cases, reaction environments are regulated by biopolymers such as proteins, and selective reactions are performed.

Examples of actions of metals other than by metalloenzymes include

- (1) Mg: MgATP energy transfer,
- (2) Na/K ion pumping,
- (3) Ca : transfer of hormone functions, muscle contraction, nerve transfer, blood coagulation, are some of the important roles of metals.

(a) Oxidation

Oxidation reactions in living systems are fundamental to life, and many studies of these systems have been performed. In particular, the mechanisms of oxygen gas transportation by hemoglobin and mono-oxygen oxidation by the iron porphyrin compounds named P-450 have been studied at length. Oxygen gas transportation, which has been studied for many years, is described below. Iron porphyrins hemoglobin and myoglobin and the copper compound hemocyanin are involved in the transportation of oxygen gas in air to cells in living organisms. The basis of this function is reversible bonding and dissociation of dioxygen to iron or copper ions. In order to perform these functions, metals must be in oxidation states and coordination environments suitable for

the reversible coordination of dioxygen. The iron porphyrin compound hemoglobin is found in red bloods of human beings and other animals.

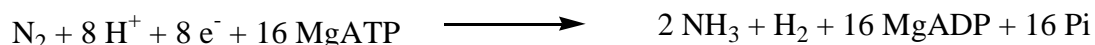
Hemoglobin has the structure of heme iron with four iron porphyrin units combined with a globin protein. Dioxygen is transported in blood by being coordinated to ferrous ions in the heme iron unit. The Fe (II) ion is penta-coordinate with four nitrogen atoms of porphyrin and a nitrogen atom of the polypeptide histidine, and becomes hexa-coordinate when a dioxygen coordinates to it. The spin state of Fe (II) changes from high spin to low spin upon the coordination of dioxygen. The high spin Fe(II) is above the plane of porphyrin because it is too large to fit in the available space. When the Fe(II) ion becomes low spin upon dioxygen coordination, the size of the iron ion decreases and it just fits into the hole of the porphyrin molecule.

This molecular-level movement has attracted interest as an **allosteric effect** because it affects the whole protein through the histidine coordinate bond and governs the specific bond of a dioxygen molecule. Oxidation of the Fe(II) ion of a heme molecule is prevented by a macromolecular protein, and if the heme iron is taken out of the protein, Fe(II) ion is oxidized to Fe(III), and two porphyrin rings are bridged by a peroxide $\mu\text{-O}_2^{2-}$, which finally changes to a bridging $\mu\text{-O}_2$ -structure.

When the heme is in this state, it loses the ability to coordinate to the dioxygen molecule. Based on this phenomenon, a synthetic porphyrin that is able reversibly to coordinate to a dioxygen by suppressing dimerization of the iron porphyrin has been developed, and was named the **picket fence porphyrin** after its three dimensional form.

(b) Nitrogen fixation

The reaction which converts the nitrogen in air into ammonia is basic to all life. **Nitrogen fixation**, the reaction to fix atmospheric nitrogen to form ammonia, is carried out by *Rhizobium* in the roots of legumes or by bacteria in algae in an anaerobic atmosphere. All animals and plants, including mankind, were depended on biological nitrogen fixation as a source of nitrogen for protein and other compounds containing nitrogen before the invention of the Harber-Bosch process.



(where Pi is an inorganic phosphate)

An enzyme named **nitrogenase** catalyzes this reaction. Nitrogenase contains iron-sulfur and iron-molybdenum sulfur proteins, and reduces dinitrogen by coordination

and cooperative proton and electron transfers, while using MgATP as an energy source. Because of the importance of this reaction, attempts to clarify the structure of nitrogenase and to develop artificial catalysts for nitrogen fixation have continued for many years. Recently, the structure of an active center in nitrogenase called iron-molybdenum cofactor was clarified by single crystal X-ray analysis (Fig. 8.2). According to this analysis, its structure has Fe_3MoS_4 and Fe_4S_4 clusters connected through S.

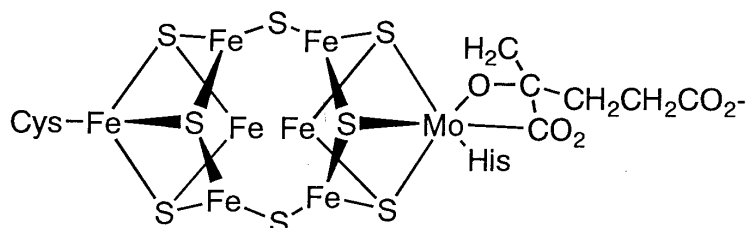


Figure 8.2 Structure of Fe-Mo cofactor in nitrogenase.

It is believed that dinitrogen is activated by coordination between the two clusters. On the other hand, the portion called P cluster consists of two Fe_4S_4 clusters. The roles and reaction mechanism of both parts are not yet clear.

(c) Photosynthesis

The formation of glucose and dioxygen by the reaction of carbon dioxide and water is a skillful reaction using photoenergy and in which chlorophyll (Fig. 8.3), which is a magnesium porphyrin and a manganese cluster complex, plays the central role. A chloroplast contains photosystem I (PSI) and photosystem II (PSII), which use light energy to reduce carbon dioxide and to oxidize water.

Chlorophyll is a fundamental component of PSI. Chlorophyll is a porphyrin complex of magnesium and is responsible for the green colors of leaves. It plays an important role in receiving light energy and transferring it to redox reaction systems. Chlorophyll is excited from the singlet ground state to the singlet excited state by light, the energy of the excited state is transferred to an acceptor within 10 ps, and the resultant energy reduces an iron-sulfur complex and is finally used for reduction of carbon dioxide in subsequent dark reactions. Since charge separation by photochemical excitation is the most important first stage, studies on photoinduced electron transfer have been actively performed using various kinds of porphyrin compounds as models of chlorophylls. PSI, which obtains oxidizing energy by electron transfer, converts ADP to ATP.

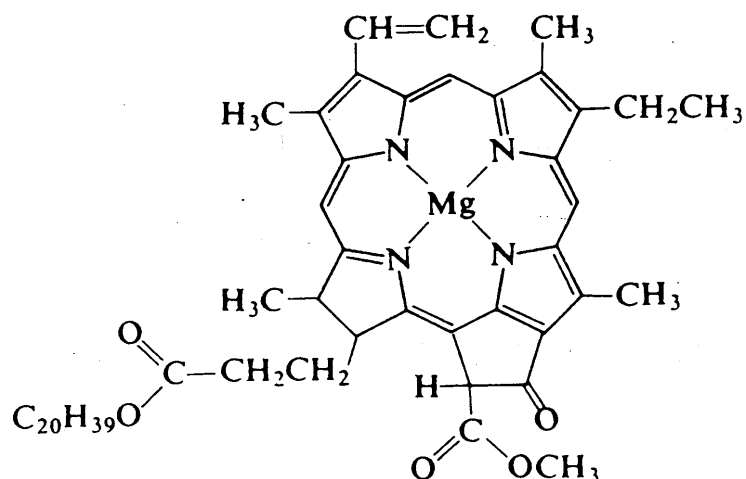


Figure 8.3 Chlorophyll *a*.

On the other hand, the oxidized form of PSII oxidizes water through a chain of redox reactions of oxo cluster complexes of manganese, and generates oxygen. Since four electrons shift in the reduction of Mn(IV) to Mn (II) in this reaction, at least two manganese species are involved. Probably, a cluster complex which contains two Mn(II) and two Mn(IV) species mediates the electron transfer via four step reactions. However, the details of this reaction are as yet unclear because it is very difficult to isolate this cluster and to analyze its structure. The electron transfer stage is being studied at present by using various manganese complexes as model systems.

Photosynthesis is a very interesting research theme in bioinorganic chemistry as it involves a few metal ions, a porphyrin, sulfide and oxide clusters that constitute a cycle of subtle electron transfer and redox reactions, and generate oxygen gas by photolysis of water and produce carbohydrates from carbon dioxide by reductive dark reactions,. Recently, the reaction center of a photosynthetic bacteria was crystallized and J. Deisenhofer and his colleagues won a Nobel prize for its structural analysis (1988).

Exercise 8.2 Give examples of small molecules that are fundamentally important for living things.

“Answer” H₂O, O₂, N₂, CO₂.

8.3 Physical properties

It is barely imaginable that materials based on the physical properties of solid inorganic compounds have played such decisive roles in present-day technology and industry. One may think that this field belongs more to material physics. However, apart

from the theories of physical properties, the contribution of chemistry and chemists to the preparation of materials and their structural analysis has been greater than that of other branches of science. Material science is the application of the fundamental physical properties of materials such that basic theories and their applications converge. Therefore, by surveying the applications in such fields, the outlines of research themes and their purposes can be understood.

Important inorganic materials are surveyed from the chemical point of view by focusing on the relationship between preparation and isolation, and structure and physical properties.

(a) Electric properties

A semiconductor is an electrical conductor with electrical resistance in the range of about 10^4 to 10^8 ohms. A typical semiconductor is a super-high grade silicon that is manufactured on a large scale and is widely used for information processing devices such as computers and energy conversion devices such as solar cells. VLSI (very large-scale integrated circuits) are printed on wafers made from almost defectless silicon single crystals with diameters of no less than 20 cm, prepared from polycrystalline silicon by the Czochralski method. Memory chips with a very high degree of integration as well as highly efficient computer chips have recently been realized.

In a short periodic table, silicon is a group IV element and has four valence-electrons. Although silicon semiconductors currently represent 90% or more of all semiconductors, isoelectronic 1:1 compounds of II-VI or III-V groups form compound semiconductors and are also used for optical or ultra high-speed electronic devices. For example, ZnS, CdS, GaAs, InP, *etc.* are typical compound semiconductors and the development of technologies to grow single crystals of these materials is remarkable. Light emitting diodes (LED) or semiconductor lasers are important applications of compound semiconductors.

As thin films of compound semiconductors are made by MBE (molecular beam epitaxy) or MOCVD (metallorganic chemical vapor deposition), special organometallic compounds, such as trimethyl gallium $\text{Ga}(\text{CH}_3)_3$ and trimethylarsenic $\text{As}(\text{CH}_3)_3$, which previously found little application, are now used industrially.

Exercise 8.3 What compounds other than the examples given are suitable as semiconductors?

“Answer” ZnO, CdS, PbS, GaP, and InSb

Superconductivity is a phenomenon of zero electrical resistance below a critical

temperature, T_c , and was discovered in 1911 by Kamerlingh Onnes (1913 Nobel Prize for physics), who succeeded in liquefying helium during his experiments to measure the electrical resistance of mercury at ultra low temperatures. About 1/4 of the elements, such as Nb ($T_c = 9.25$ K), In, Sn, and Pb behave as superconductors and more than 1000 alloys and intermetallic compounds are also superconductors, but only Nb-Ti alloy ($T_c = 9.5$ K) and Nb₃Sn ($T_c = 18$ K) find application. Nb₃Sn, Nb₃Ge, V₃Ga, *etc.*, are cubic A-15 type compounds, in which transition metal atoms are aligned in chains, and interatomic distances are shorter than those in the crystalline bulk metal, raising the density of states of the conduction band and the critical temperature, T_c , of the compound.

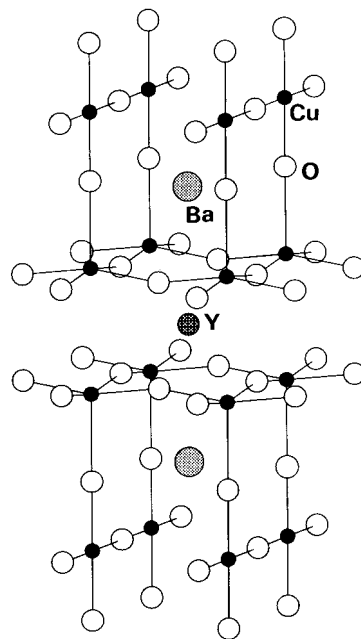


Figure 8.4 Structure of YBa₂Cu₃O_{7-x}.

Among inorganic compound superconductors, chalcogenide compounds M_xMo₆X₈ (X = S, Se, Te, and M = Pb, Sn, *etc.*) of molybdenum called **Chevrel phases** and high-temperature superconductors of copper oxide derivatives, which J. G. Bednorz and K. A. Müller discovered in 1986 (1987 Nobel Prize for physics), have attracted attention. Chevrel phases have structures (refer to Section 4.4) in which hexanuclear cluster units of molybdenum are joined and the highest T_c is only 15 K of PbMo₆S₈, but the superconductive state is not broken even in strong magnetic fields. In the copper oxide system, more than 100 similar compounds have been prepared since the first discovery and the highest T_c so far discovered is 134 K. A typical compound, YBa₂Cu₃O_{7-x}, has a structure (Fig. 8.4) in which CuO₅ square pyramids and CuO₄ planes are connected by

corner-sharing, Ba and Y are inserted between them, and the oxygen content is non-stoichiometric.

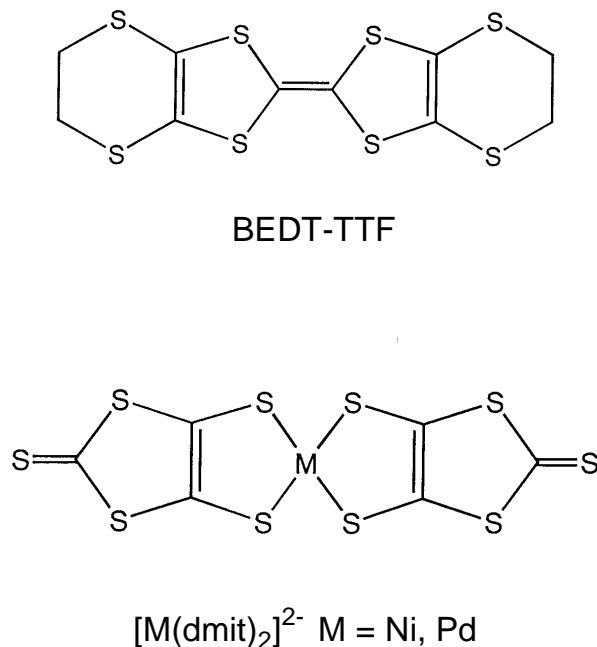


Figure 8.5 An electron donor and acceptor in a complex superconductor.

On the other hand, molecular superconductors have also been studied. Representative donor-acceptor complexes are composed of TTF and BEDT-TTF (Fig. 8.5) as electron donors, and ClO_4^- or $[\text{Ni}(\text{dmit})_2]^{2-}$ as electron acceptors. The first example of this kind of superconductor was discovered in 1980, and of the about 50 complexes known at present, the highest T_c is 13K. Recently (1991) fullerene C_{60} doped with alkali metals showed a T_c of about 30K.

Although thousands of superconductors are known, only a few of them find application. Because compound superconductors are very brittle; either it is difficult to make them into wires or only small single crystals are obtained. It will take considerable time before some of them find practical use. Therefore, mainly Nb-Ti wires are used as the superconducting magnets of analytical NMR, medical MRI (magnetic resonance imaging instrument) or maglev trains, *etc.* Efforts are concentrated on discovering materials that have suitable mechanical and other properties by cooperation between inorganic chemistry and solid-state physics.

Various metal oxides are used as thermistors (temperature sensitive resistance

device), varistors (nonlinear resistance device), capacitors, *etc.* For example, BaTiO₃, with a perovskite structure, and SrTiO₃, *etc.* can be used for any of the above-mentioned purposes. Ionic conduction materials are also called solid electrolytes and α -AgI, β -Al₂O₃, stabilized zirconia (a part of Zr in ZrO₂ is replaced by Ca or Y), *etc.* are used in solid state batteries or fuel cells.

(b) Magnetism

Magnetic materials are divided into hard (permanent magnets) and soft magnetic materials. Permanent magnets are indispensable to machines using motors and MRI, which requires a high magnetic field. Japan has a strong tradition in the development of magnets, and has made many epoch-making magnetic materials for practical use. Alnico magnets with Fe, Ni, and Al as their main constituents, ferrite magnets composed of solid solutions of CoFe₂O₄ and Fe₃O₄, cobalt-rare earth magnets such as SmCo₅, and Nb-Fe-B magnets were especially significant achievements. Since soft magnetic materials are strongly magnetized in weak magnetic fields, they are most suitable for use as core materials in transformers. Hard magnetic properties are necessary for the stable maintenance of information whereas soft magnetic properties are required for recording and over-writing information in magnetic recording materials such as magnetic tapes, floppy disks, and hard disks. Although γ -Fe₂O₃ is a typical magnetic powder used for these purposes, Co⁺ or crystalline CrO₂ is added to it to improve its magnetic properties. Recording materials as well as semiconductor devices are indispensable to our modern information-oriented society, and the role played by inorganic chemistry in the improvement of the performance of these materials is significant. Recently, ferromagnetism of organic compounds or metal complexes has been discovered, in which unpaired spins are aligned parallel in a molecule and coupled ferromagnetically. The study of molecular magnets has the subject of intensive investigation. Molecular design to couple paramagnetic metal complexes and to make spins parallel is an interesting subject in coordination chemistry.

(c) Optical properties

Mainly inorganic substances are used as materials for optical applications. The optical fiber in particular has been used for optical communications on a large scale, and has had a major social influence in information communication. A necessary property of good optical glass materials is the transmission of information to distant places with little optical loss. Silica fibers are manufactured by lengthening silica glass rods produced from silica grains. The silica is made from ultra pure SiCl₄, which is oxidized in the vapor phase by an oxyhydrogen flame. As the optical loss along fibers obtained by this method

has already reached its theoretical limit, fluoride glasses are being used in the search for materials with lower levels of loss.

Compound semiconductors such as GaP are widely used as laser light emitting diodes for optical communications, CD players, laser printers, *etc.* A high output YAG laser is made from neodymium-doped yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$, which is a double oxide of Y_2O_3 and Al_2O_3 . Single crystals, such as lithium niobate, LiNbO_3 , are used for changing wavelength of light by means of SHG (second harmonic generation) of nonlinear optics phenomena.

Problem

8.1 Write a catalytic reaction cycle of the hydroformylation reaction which uses $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ as a catalyst.

8.2 Describe differences between ammonia synthesis by the Harber-Bosch process and biological nitrogen fixation reactions.

8.3 A-15 type intermetallic compounds such as Nb_3Sn are cubic crystals with the A_3B composition . Consider how to locate each atom in such a unit cell.

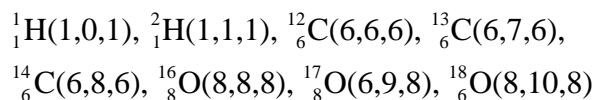
Structure-function correlation

Since all the naturally occurring elements have been discovered, various bonding modes are established and the structures of compounds can be readily determined, studies of the chemical properties of inorganic compounds will give way to studies of reactions and physical properties. The synthesis of new compounds and the elucidation of structure-function correlations will be the foundations of these studies, although the end is distant.

It is considerably difficult quantitatively to explain the thermal stability of a known inorganic compound using our present knowledge of theoretical chemistry and it is almost impossible fully to design compounds by a rational method. Although the selectivity of a catalytic reaction can be explained to some extent, the theoretical calculation of a reaction rate remains difficult. The relation between superconductivity and structure is not understood well, and critical temperatures cannot be predicted. Many of the structures and functions of the metalloenzymes that are the basis of biological activities are unknown. The research problems confronting the next generation of inorganic chemists are extensive, and novel solutions can be anticipated.

Solution of problems

1.1



2.1

$$\Delta = 428 - \sqrt{432 \times 239} \\ = 106.6 \text{ kJ mol}^{-1} = 25.48 \text{ kcal mol}^{-1} \\ \chi_{\text{Cl}} - \chi_{\text{H}} = 0.208 \times \sqrt{25.48}, \chi_{\text{Cl}} = 2.1 + 1.05 = 3.15$$

2.2 In a σ bond, a bonding orbital is a centrosymmetric g orbital, whereas an antibonding orbital is a non-centrosymmetric u orbital.

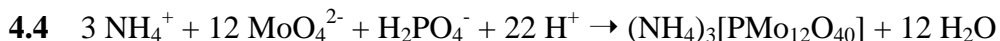
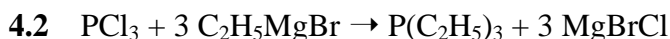
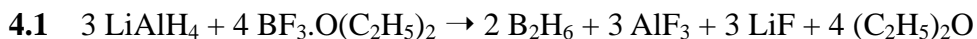
3.1 $\text{O}_2(0), \text{H}_2\text{O}_2(-1), \text{H}_2\text{O}(-2)$.

$$E_0 = \frac{0.70 + 1.76}{2} = 1.23 \text{ V}$$

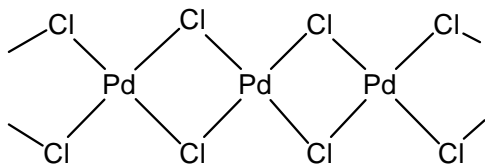
Since the reduction potential is positive, the reaction is spontaneous.

3.2 As the $\text{p}K_{\text{a}}$ of the conjugate acids NH_4^+ is 9.25, and $\text{C}_5\text{H}_5\text{NH}^+$ 5.25, ammonia is more protophilic than pyridine and is a stronger base.

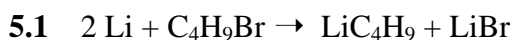
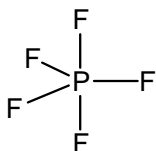
3.3 Electronegativities of halogens are in the order $\text{F} > \text{Cl} > \text{Br}$. A boron trihalide bonded to more electronegative halogens attracts more electrons and the Lewis acidity should become larger. However, opposite tendency is observed and this is considered to be due to π bonding between boron and halogen.



4.5



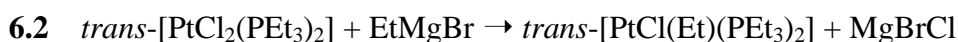
4.7



5.2 Because six ether oxygen atoms of a benzene-soluble crown ether (*e.g.* 18-dibenzo-crown-6) in a cyclic arrangement coordinate to potassium cation K^+ .

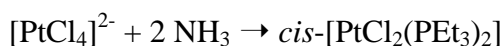
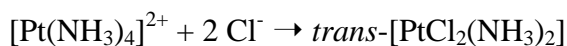
5.3 Two methyl groups in the dimeric $\text{Al}_2(\text{CH}_3)_6$ bridge two aluminum atoms to form formally 8 covalent bonds requiring 16 electrons. The compound is called electron-deficient because only 12 electrons are supplied from two aluminum atoms (6) and six methyl groups (6).

6.1 Oxide ions are weak-field ligands and transition metal ions assume high-spin states. Fe^{3+} ions have d^5 electron configurations and the LFSE is zero either in the octahedral or in tetrahedral coordination. On the other hand, Fe^{2+} ions tend to enter octahedral holes, because the LFSE for the octahedral coordination by six oxide ligands is larger than the one for tetrahedral coordination by four oxide ligands. This is one of the reasons why magnetite Fe_3O_4 has an inverse spinel structure $\text{B}^{3+}[\text{A}^{2+}\text{B}^{3+}]\text{O}_4$.



6.3 $\text{CpV}(\text{CO})_4$, $[\text{CpFe}(\text{CO})_2]_2$

6.4 The trans effect of Cl^- is larger than that of NH_3 . Therefore, it is possible to synthesize geometrical isomers selectively by choosing starting compounds.



6.5 Unless $[\text{Cr}^{36}\text{Cl}(\text{NH}_3)_5]^{2+}$ forms by the addition of an isotope ion ^{36}Cl to the aqueous solution of the reaction



it is concluded that the chloride ion coordinated to cobalt transfers to chromium by the inner-sphere mechanism via a bridged structure $[(\text{NH}_3)_5\text{-Co-Cl-Cr}(\text{OH}_2)_5]^{4+}$.

7.1 Most of lanthanide ions are stable in the 3+ oxidation states but Ce^{4+} and Eu^{2+} are stable ions and solubilities and adsorption ability in the solvent extraction are significantly different from those of other lanthanides which makes the separation easier.

7.2

$$\frac{N}{N_0} = e^{-\lambda \times \frac{\ln 2}{\lambda} \times 10} = e^{-\ln 10} = 2^{-10} = 9.77 \times 10^{-4}$$

8.1 Figure A.1 shows the catalytic cycle.

8.2 The Haber-Bosch process utilizes solid state catalysts containing iron to produce ammonia at high temperatures (440~550 °C) and under high pressures (100~1000 atm). On the other hand, biological nitrogen fixation produces ammonia from air and water under ambient conditions by the action of nitrogenases.

8.3 The unit lattice in the actual structure is shown in Figure A.2.

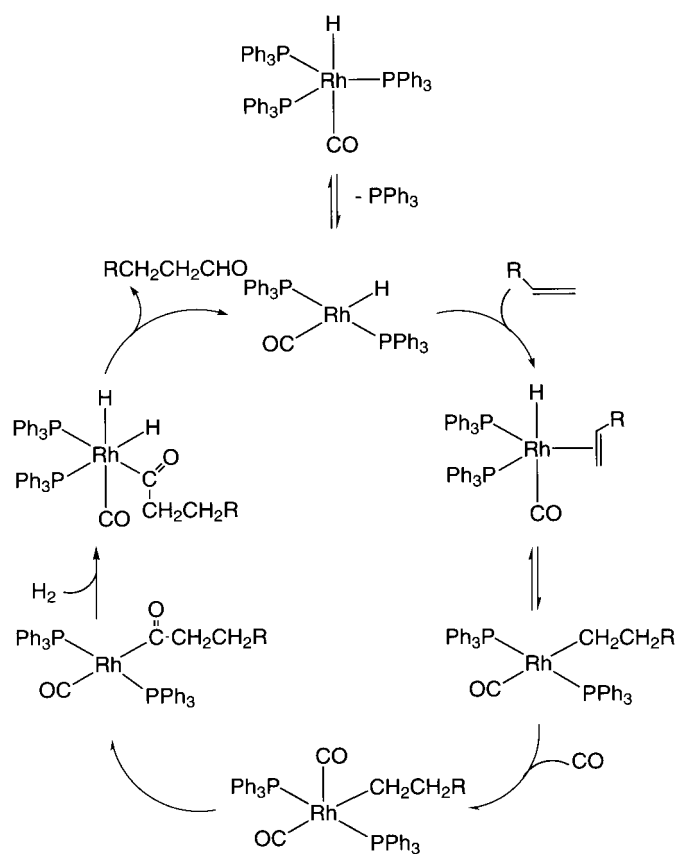


Fig. A.1.

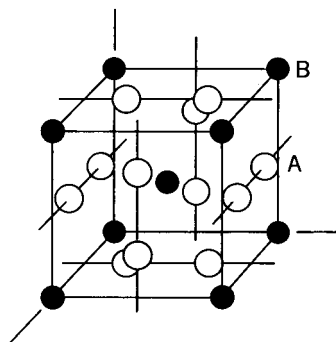


Fig. A.2.