IRON COMPOUNDS

1. Introduction

Iron (qv) has a high relative abundance in the universe because nuclei of the element's isotopes lie at the maximum of the nuclear binding energy curve. It is thought to be the major component of the earth's core. After oxygen, silicon, and aluminum, iron is the fourth most abundant element in the earth's crust and is more abundant than any other transition metal element. Iron and its compounds are of fundamental importance in biology and in the development of human industry and society.

Iron is the lightest element of Group 8 (VIIIB) of the Periodic Table and is the first metallic element in the Table that fails to attain an oxidation state equal to the number of electrons in the valence shell, i.e., no Fe(VIII) is known. Compounds of iron are known in which the oxidation state of iron ranges from −II ($3d^{10}$) to VI ($3d^2$); but aqueous chemistry of iron is dominated by the ferrous (d^6) and ferric (d^5) states, which are designated iron(II) and iron(III), respectively, in the preferred nomenclature. Higher oxidation states of iron generally occur in compounds that contain terminal oxo ligands. Examples include iron(VI) in $[FeO_4]^{2-}$, iron(V) in $[FeO_4]^{3-}$, and iron(IV) in compound I of cytochrome P450 and in the $[Fe(O)$(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)-$(NCCH_3)]^{2+}$ cation (1). All of these are potent oxidizing agents. Lower oxidation states of iron occur in compounds that contain π-acceptor ligands such as phosphines, olefins, and carbon monoxide. Examples include iron(−II) in $Na_2[Fe(CO)_4]$ [14878-31-0] and iron(0) in $Fe(CO)_5$ [13463-40-6] and in [Fe(1,5-cyclooctadiene)$_2$] [55823-33-1]. Many low valent iron compounds are pyrophoric in air (see METAL CARBONYL; COORDINATION COMPOUNDS).

The standard aqueous reduction potentials of the Fe(II)/Fe(0) couple is −0.44 V and that of the Fe(III)/Fe(II) couple is + 0.77 V. Consequently, iron metal reacts readily with most nonmetals and dissolves in dilute acids to afford the iron(II) cation. Dissolution does not occur in chromic acid, concentrated nitric acids, or hydrogen peroxide (qv), H_2O_2, because the metal is protected by formation of a passivating oxide film, which can be removed mechanically or by acids of coordinating anions such as HCl. Iron(II) is unstable with respect to oxidation to iron(III) in the presence of air and many other oxidizing agents. The rate of air oxidation is slow in acidic solution. Both the thermodynamic and kinetic stability of iron(II) decrease in basic solution. A consequence of the facile formation of iron(III) is that many iron(II) compounds are unstable and/or nonstoichiometric. Deficiency of iron results from the substitution of iron(III) for iron(II). The ligands coordinated to iron can change the standard potentials over a substantial range of E° values. The facile interconversion of iron(II) and iron(III) and the ability of the coordination environment to fine tune the redox potential of the couple is reflected in the large variety of functions that iron performs in biological systems.

Iron(II) forms complexes with a wide variety of both hard and soft ligands, a behavior that contrasts with that of iron(III). Salts of iron(II) are known for almost all of the common anions. The exceptions, including NO_2^-, result from redox incompatibilities. Many of the salts are hydrates and are subject to either efflorescence or hydration. Aqueous solutions of the salts contain the pale green hexaaquairon(II) ion [15365-81-8], $[Fe(H_2O)_6]^{2+}$, if the anion is noncomplexing.

Hydrolysis of the hexaaquairon(II) ion is insignificant. Most iron(II) complexes are octahedral, but other coordination numbers and geometries are not unusual. Common geometries include tetrahedral in $[FeCl_4]^{2-}$ and $[Fe(SR)_4]^{2-}$; square planar in porphyrin, phthalocyanine, and tetraazamacrocycle compounds; and square pyramidal and trigonal bipyramidal in five-coordinate complexes. Seven- and eight-coordinate complexes are less common. Two- and three-coordinate complexes are comparatively rare. Interest in these low-coordinate complexes, which are accessible with bulky alkyl, silylamide, β-diketimine, or thiolate ligands, has grown both as a consequence of an initial, incorrect report that six of the iron sites in the iron—molybdenum cofactor of the enzyme nitrogenase have trigonal sulfido coordination (see IRON COMPOUNDS, below) and as a result of the unusual reactivity of the complexes (2,3).

The iron(II) ^5D free-ion ground state is split by octahedral fields or tetrahedral fields into $^5T_2$ and ^5E states. Tetrahedral and high spin octahedral complexes have magnetic moments of about $4.6–4.8 \times 10^{-23}$ J/T (5.0–5.2 Bohr magnetons). The octahedral complexes exhibit a single weak $d–d$ transition, which falls in the visible/near ir region of the spectrum and is broadened by the Jahn-Teller effect. Strong field ligands can cause spin pairing to afford diamagnetic low spin octahedral complexes that have a $^1A_{1g}$ ground state. These may be intensely purple or red in color, owing to metal-to-ligand charge-transfer bands. Low spin octahedral iron(II) complexes are kinetically inert, as are the isoelectronic low spin cobalt(III) complexes. Examples of high, low, and intermediate spin ($S = 1$) complexes are known for square planar complexes.

The high charge density of the Fe^{3+} ion results in a strong preference for class A or hard donors such as F^- and oxygen donors. Stable compounds of amines, phosphines, and sulfur donors are relatively few in number. As in the case of iron(II), compounds of iron(III) are most typically high spin octahedral, but other spin states, coordination numbers, and geometries are well represented. The high charge density of iron(III) is also responsible for its marked tendency to hydrolyze in aqueous solution (4). The undissociated hexaaquairon(III) ion [15377-81-8], predominates only below pH ~2. $[Fe(H_2O)_5(OH)]^{2+}$ forms at slightly higher pH and is then converted to the hydroxo-bridged dinuclear species $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4]^{4+}$. Further increase in the pH results in formation of additional polynuclear species, colloidal gels, and finally a precipitate of red-brown hydrated ferric oxide.

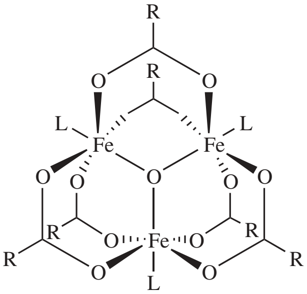
High spin octahedral iron(III) compounds are d^5 and have a $^6A_1$ ground state. All excited states have a different spin multiplicity. Consequently, $d–d$ transitions are spin and parity forbidden and many simple salts and complexes have little or no color. These bands are often obscured by the low energy tails into the visible of ligand-to-metal charge-transfer absorptions in the near-uv region. When strong color occurs, charge-transfer absorptions are usually responsible. The magnetic moments of high spin complexes are all very close to the spin-only value of 5.47×10^{-23} J/T ($5.9\ \mu_B$) because of the absence of an orbital angular momentum contribution or coupling to excited states. Deviations from this value are often the result of antiferromagnetic interactions between two or more iron centers. Low spin complexes typically have magnetic moments of 2.04×10^{-23} J/T ($2.2\ \mu_B$). In lower symmetry ligand fields such as square pyramidal, intermediate spin states with moments of 3.71×10^{-23} J/T ($4.0\ \mu_B$) are possible.

2. Salts and Simple Coordination Compounds

2.1. Acetates. Anhydrous iron(II) acetate [3094-87-9], $Fe(C_2H_3O_2)_2$, can be prepared by dissolving iron scraps or turnings in anhydrous acetic acid (~2% acetic anhydride) under an inert atmosphere. It is a colorless compound that can be recrystallized from water to afford hydrated species. Iron(II) acetate is used in the preparation of dark shades of inks (qv) and dyes and is used as a mordant in dyeing (see DYES AND DYE INTERMEDIATES). An iron acetate salt [2140-52-5] that is a mixture of indefinite proportions of iron(II) and iron(III) can be obtained by concentration of the black liquors obtained by dissolution of scrap iron in acetic acid. It is used as a catalyst of acetylation and carbonylation reactions.

Iron(III) acetate [1834-30-6], $Fe(C_2H_3O_2)_3$, is prepared industrially by treatment of scrap iron with acetic acid followed by air oxidation. Iron(III) acetate is used as a catalyst in organic oxidation reactions, as a mordant, and as a starting material for the preparation of other iron-containing compounds.

Basic iron(III) acetate [10450-55-2] is a brown-red material which precipitates from boiling solutions of anhydrous iron(II) or iron(III) acetate or most any soluble iron(III) salt in the presence of acetate. It is soluble in alcohols and acids but insoluble in water. The chemical formula is often given as $Fe(C_2H_3O_2)_2(OH)$, but the actual composition is variable and depends on the method and conditions of preparation (5). The structure of the material is related to other basic metal acetates of the general formula $[M_3O(RCO_2)_6L_3]X$ where $L = H_2O$, CH_3OH, pyridine, or other ligand, and X is a monoanion (**1**). It consists of an equilateral triangle of iron atoms with a triply bridging (μ_3) oxygen atom at the center. Two acetate ligands bridge each edge of the triangle and a terminal ligand L coordinates to an iron at each vertex. Similar compounds exist for other carboxylates including amino acids (qv). In addition, related neutral, mixed-valent compounds of the type $[Fe^{II}Fe^{III}{}_2O(RCO_2)_6L_3]$ are known. The Fe_3O triangle is a structural motif in larger oxo-bridged iron clusters, which may model the polyiron core of the iron storage protein ferritin. Basic iron acetate is used as a mordant in dyeing and printing and for the weighting of silk (qv) and felt. It is reported to affect the oxidation of saturated hydrocarbons (qv) in the presence of oxygen, acetic acid, aqueous pyridine, and zinc powder (6).



(**1**)

2.2. Alkoxides. Iron(III) alkoxides are prepared by reaction of anhydrous ferric chloride with sodium alkoxide or magnesium bromide alkoxide, MgBrOR, in the absolute alcohol of the alkoxide. Ferric ethoxide [5058-42-4],

$Fe(C_2H_5O)_3$, and ferric isopropoxide [14972-42-0] are commercially available. Iron(III) alkoxides have been used in the sol-gel synthesis of metal oxides and as catalysts for the polymerization of lactide. The complexes do not appear to be simple monomeric species. Ebullioscopic and cryoscopic data suggest that the alkoxide compounds are dimeric or trimeric species in solution. Moreover, iron oxide-alkoxide clusters can be isolated from these compounds. $Fe_9O_3(OC_2H_5)_{21}\cdot C_2H_5OH$ [331829-84-6] is obtained in good yield from the residue that remains after the solvent is removed from ethanolic solutions of ferric ethoxide (7). Extraction of ferric ethoxide with tetrahydrofuran affords $Fe_5(\mu_5\text{-}O)(OC_2H_5)_{13}$ [326806-28-4], whose structure consists of a square pyrimid of Fe atoms that is bridged in the basal plane by the μ_5-O and between adjacent Fe atoms by eight μ_2-ethoxides (8). Each iron also has one terminal ethoxide. The five-iron cluster appears to form when the nine-iron cluster is dissolved in benzene solution.

2.3. Carbonates. Iron(II) carbonate [563-71-3], $FeCO_3$, precipitates as a white solid when air-free solutions of alkali metal carbonates and iron(II) salts are mixed. The limited tendency of $[Fe(H_2O)_6]^{2+}$ to hydrolyze is illustrated by the lack of carbon dioxide evolution in this reaction. The solid rapidly darkens when exposed to air or begins to decompose when heated to 200°C. Ferrous carbonate occurs naturally as siderite [14476-16-5] or spathic iron ore. The compound is used as a flame retardant and as an iron supplement in animal feed (see FEEDS AND FEED ADDITIVES, NONRUMINANT FEEDS; FLAME RETARDANTS: AN OVERVIEW). Ferrous carbonate redissolves in water in the presence of carbon dioxide to yield iron(II) hydrogen carbonate [6013-77-0], $Fe(HCO_3)_2$, which also can be formed from iron and carbon dioxide saturated water in the absence of oxygen. It undergoes air oxidation which evolves carbon dioxide and a precipitate of hydrated iron(III) oxide. This reaction accounts for the precipitation of iron from the water of many springs on exposure to air.

2.4. Citrates. Iron citrate [2338-05-8] is a compound that contains citric acid and iron(II) and iron(III) in indefinite ratios. Iron(II) citrate [23383-11-1] and iron(III) citrate [28633-45-6] are also of indefinite stoichiometry, although iron(III) citrate which contains Fe and citric acid in a 1:1 ratio [3522-50-7] is known. These compounds dissolve slowly in water and are more readily soluble in hot water. The solution chemistry of these compounds is complicated by formation of a number of monomeric and oligomeric species. All of the iron citrate compounds are used as supplements to soils and animal diets.

Iron(III) ammonium citrate [1185-57-5] is of indefinite stoichiometry. A brown hydrated compound [1332-98-5] of iron(III) ammonium citrate contains 16.5–18.5% iron, ~9% ammonia, and 65% citric acid. A green hydrated compound [1333-00-2] contains 14.5–16% iron, ~7 ammonia, and 75% citric acid. Iron ammonium citrates are water soluble but are insoluble in alcohol. The compounds are used to fortify bread, milk, and other foods (see FOOD ADDITIVES; MINERAL NUTRIENTS).

2.5. Cyanides. As a monodentate ligand, the cyanide ion coordinates to metal ions almost exclusively through the carbon atom. In this mode, it is very high in the spectrochemical series, thus most cyanide complexes are low spin (9). As a bidentate ligand the cyanide ion can bridge two metal ions by coordinating to metal ions through either the carbon or nitrogen atoms. Bonding to iron by cyanide involves synergistic σ-donation and π-acceptance by the ligand. Owing to the negative charge, the cyanide anion is a somewhat stronger donor and weaker acceptor than isoelectronic, neutral carbon monoxide (qv) (see CYANIDES).

Hexacyano Complexes. Ferrocyanide [13408-63-4] (hexakiscyanoferrate-(4−)), $(Fe(CN)_6)^{4-}$, is formed by reaction of iron(II) salts with excess aqueous cyanide. The reaction results in the release of 360 kJ/mol (86 kcal/mol) of heat. The thermodynamic stability of the anion accounts for the success of the original method of synthesis, fusing nitrogenous animal residues (blood, horn, hides, etc) with iron and potassium carbonate. Chemical or electrolytic oxidation of the complex ion affords ferricyanide [13408-62-3] (hexakiscyanoferrate(3−)), $[Fe(CN)_6]^{3-}$, which has a formation constant that is larger by a factor of 10^7. However, hexakiscyanoferrate (3−) cannot be prepared by direct reaction of iron(III) and cyanide because significant amounts of iron(III) hydroxide also form. Hexacyanoferrate(4−) is quite inert and its salts are nontoxic and do not react like simple iron salts in analytical tests for iron. In contrast, hexacyanoferrate(3−) is toxic because it is more labile and cyanide dissociates readily. Both complexes liberate some HCN upon addition of acids.

Alkali or alkaline-earth salts of both complexes are soluble in water (except for $Ba_2[Fe(CN)_6]$) but are insoluble in alcohol. The salts of hexakiscyanoferrate(4−) are yellow and those of hexakiscyanoferrate(3−) are ruby red. A large variety of complexes arise when one or more cations of the alkali or alkaline-earth salts is replaced by a complex cation, a representative metal, or a transition metal. Many salts have commercial applications, although the majority of industrial production of iron cyanide complexes is of iron blues such as Prussian Blue, used as pigments (see PIGMENTS, INORGANIC). Many transition-metal salts of $[Fe(CN)_6]^{4-}$ have characteristic colors. Addition of $[Fe(CN)_6]^{4-}$ to an unknown metal salt solution has been used as a qualitative test for those transition metals.

Tetrapotassium hexakiscyanoferrate trihydrate [14459-95-1], $K_4[Fe(CN)_6] \cdot 3H_2O$, is an efflorescent lemon yellow compound known as yellow prussiate of potash. The anhydrous material [13943-58-3] is obtained at 70°C. The compound is soluble in water and acetone, but insoluble in alcohol, ether, and ammonia. It is oxidized to hexakiscyanoferrate (3−) by oxygen in acidic solution, or by oxidants such as ozone, Cl_2, Br_2, H_2O_2, or $MnO_4{}^-$. A large number of insoluble or slightly soluble mixed salts of the general formula $K_2M^{II}[Fe(CN)_6]$ and $KM^{III}[Fe(CN)_6]$ are known, eg, M^{II} = cobalt(II) [13821-10-8], copper(II) [14481-39-1], manganese(II) [15631-19-3], and nickel(II) [13601-16-6]. These have polymeric structures that contain bridging Fe−CN−M units. Many of the $K_2M^{II}[Fe(CN)_6]$ compounds are useful ion-exchange (qv) materials. $K_2Co[Fe(CN)_6]$ absorbs silver(I) ions from wastewater. $K_2Cu[Fe(CN)_6]$ forms a semipermeable membrane which was used by van't Hoff in the measurements on which the theory of osmotic pressure was based (9).

$K_4[Fe(CN)_6] \cdot 3H_2O$ [14459-95-1] is prepared from calcium cyanide and iron(II) sulfate above 100°C. The soluble $Ca_2H\ [Fe(CN)_6]$ [13821-08-4] which forms is separated from insoluble calcium sulfate. Addition of KCl precipitates $CaK_2[Fe(CN)_6]$ [20219-00-5], which is redissolved as the potassium salt by addition of potassium carbonate. Calcium carbonate is removed by filtration and $K_4[Fe(CN)_6] \cdot 3H_2O$ is crystallized by rapid cooling. $K_4[Fe(CN)_6] \cdot 3H_2O$ is used in the synthesis of other hexakiscyanoferrates (4−), in metal coatings (see METALLIC COATINGS, SURVEY), electroplating (qv), dyeing and printing of textiles (qv), engraving and lithography, and in the quantitative titrations of other metal salts.

Tetrasodium hexakiscyanoferrate decahydrate [14434-22-1], Na_4-$[Fe(CN)_6] \cdot 10H_2O$, or yellow prussiate of soda, forms yellow monoclinic crystals that are soluble in water but insoluble in alcohol. It is slightly efflorescent at room temperature, but the anhydrous material, tetrasodium hexakiscyanoferrate [13601-19-9], $Na_4[Fe(CN)_6]$, is obtained at 100°C. The decahydrate is produced from calcium cyanide, iron(II) sulfate, and sodium carbonate in a process similar to that for the production of $K_4[Fe(CN)_6] \cdot 3H_2O$. It is used in the manufacture of trisodium hexakiscyanoferrate, black and blue dyes, as a metal surface coating, and in photographic processing.

Tetraammonium hexakiscyanoferrate [14481-29-9], $(NH_4)_4[Fe(CN)_6]$, is obtained by the addition of ammonia to $[Fe(CN)_6]^{4-}$ or by the addition of ammonium sulfate to an aqueous solution of the barium or calcium salt of $[Fe(CN)_6]^{4-}$. It is soluble in water, insoluble in alcohol, and subject to air oxidation. Diammonium barium hexakiscyanoferrate [60700-20-1], $(NH_4)_2Ba[Fe(CN)_6]$, and diammonium calcium hexakiscyanoferrate [60674-40-0], $(NH_4)_2Ca[Fe(CN)_6]$, salts are also known.

Dibarium hexakiscyanoferrate [13821-06-2], $Ba_2[Fe(CN)_6]$, is a sparingly water-soluble compound prepared by addition of a solution of $Na_4[Fe(CN)_6]$ to a concentrated solution of an appropriate barium salt. It is useful in the preparation of other $[Fe(CN)_6]^{4-}$ salts because of the insolubility of barium sulfate.

Dicalcium hexakiscyanoferrate [13821-08-4], $Ca_2[Fe(CN)_6]$, is formed as yellow crystals by reaction of liquid or gaseous HCN with iron(II) chloride in water containing $Ca(OH)_2$ or $CaCO_3$ and having $pH > 8$. It is used to prevent caking of other substance and serves as a useful starting material in the preparation of other $[Fe(CN)_6]^{4-}$ salts. Examples of mixed salts include calcium dicesium hexakiscyanoferrate [15415-35-7], $CaCs_2[Fe(CN)_6]$, and calcium dipotassium hexakiscyanoferrate [20219-00-5], $CaK_2[Fe(CN)_6]$.

Dilead hexacyanokisferrate [14402-61-0], $Pb_2[Fe(CN)_6]$, is a white precipitate that forms when lead acetate is added to $Ca_2[Fe(CN)_6]$. It is insoluble in water or dilute acids but is soluble in hot ammonium chloride or ammonium succinate solutions. It has been used as a qualitative analytical reagent in tests for cadmium and chromate.

Tripotassium hexakiscyanoferrate [13746-66-2], $K_3[Fe(CN)_6]$, forms anhydrous red crystals. The crystalline material is dimorphic; both orthorhombic and monoclinic forms are known. The compound is obtained by chemical or electrolytic oxidation of hexacyanoferrate(4−). $K_3[Fe(CN)_6]$ is soluble in water and acetone, but insoluble in alcohol. It is used in the manufacture of pigments, photographic papers, leather (qv), and textiles and is used as a catalyst in oxidation and polymerization reactions.

Trisodium hexakiscyanoferrate [14217-21-1], $Na_3[Fe(CN)_6]$, forms red hygroscopic crystals that are soluble in water. A monohydrate [13755-37-8] and a dihydrate [36249-31-7] are also known. The sodium salt is used for many of the same purposes as the potassium salt.

Several simple salts and double salts of hexakiscyanoferrate (3−) are known. The simple salts include the ammonium [14221-48-4], $(NH_4)_3[Fe(CN)_6]$, and barium [21729-04-4], $Ba_3[Fe(CN)_6]_2$, salts. Mixed salts include $(NH_4)Ag_2[Fe(CN)_6]$, [58675-53-9]; $KCo[Fe(CN)_6]$, [14874-73-8]; $KNi[Fe(CN)_6]$, [53295-14-0]; $KCu[Fe(CN)_6]$, [53295-15-1]; and $K_2Na[Fe(CN)_6]$, [31940-93-9].

All of the $[Fe(CN)_6]^{4-}$ salts may be considered salts of ferrocyanic acid or tetrahydrogen hexakiscyanoferrate [17126-47-5], $H_4[Fe(CN)_6]$, a strongly acidic, air-sensitive compound. It is soluble in water and alcohol but is insoluble in ether. It can be prepared by precipitation of an etherate by adding ether to a solution of $[Fe(CN)_6]^{4-}$ that was acidified with concentrated sulfuric acid. Removal of the ether of solvation affords a white powder which is stable when dry but slowly turns blue in moist air because of Prussian Blue formation.

The parent acid of the hexakiscyanoferrate(3−) salts is ferricyanic acid [17126-46-4] (trihydrogen hexakiscyanoferrate). Red-brown needles are obtained by evaporation of solutions prepared by adding sulfuric acid to tribarium bis(hexakiscyanoferrate). The acid is used to prevent metal surface corrosion.

Pentacyano Complexes. Iron cyanide complexes that contain only five cyanide ligands are known as the prusside compounds. The best known of these complexes is sodium nitroprusside (sodium pentacyanonitrosylferrate(2−)), formed by the action of nitric acid or sodium nitrite on hexacyanoferrate(4−). The compound forms red, air-stable, rhombic crystals of the dihydrate [13755-38-9], $Na_2[Fe(CN)_5NO] \cdot 2\,H_2O$. It is readily soluble in water and alcohol, but the solutions are not stable. The dihydrate may be dehydrated *in vacuo* to afford an anhydrous material [14402-89-2]. Sodium nitroprusside is used as an analytical reagent for aldehydes (qv), acetone (qv), active methylene and sulfur compounds, giving an intense violet color with HS^- or S^{2-} and a red color with SO_3^{2-}. It is also a useful starting material for the preparation of other prusside complexes of general formula $[Fe(CN)_5L]^{3-}$, including $L = H_2O$, NH_3, NO_2^-, and CO. The compound is known by the trade names Nipride, Nipruss, and Nitropress and is used medically as a hypotensive (see CARDIOVASCULAR AGENTS). Blood pressure is lowered within seconds of infusion and continues only as long as administered.

Prussian Blue. Reaction of $[Fe(CN)_6]^{4-}$ with an excess of aqueous iron(III) produces the finely divided, intensely blue precipitate Prussian Blue [14038-43-8] (tetrairon(III) tris(hexakiscyanoferrate)), $Fe_4[Fe(CN)_6]_3$, also known as Berliner Blau. The complex was discovered accidentally by the color maker Diesbach and the alchemist Dippel in 1704 and is among the first isolated coordination complexes. Prussian Blue is identical to Turnbull's Blue, the name which originally was given to the material produced by reaction of $[Fe(CN)_6]^{3-}$ with excess aqueous iron(II). The solid contains or has absorbed on its surface a large and variable number of water molecules, potassium ions (if present in the reaction), and iron(III) oxide. The iron(II) centers are low spin and diamagnetic; iron(III) centers are high spin. Variations of composition and properties result from variations in reaction conditions. Rapid precipitation in the presence of potassium ion affords a colloidal suspension of Prussian Blue [25869-98-1] which has the approximate composition $KFe[Fe(CN)_6]$. Prussian Blue compounds are used as pigments in inks and paints and its formation on sensitized paper is utilized in the production of blueprints.

The structure of Prussian Blue and its analogues consists of a three-dimensional polymeric network of Fe^{II}–CN—Fe^{III} linkages. Single-crystal x-ray and neutron diffraction studies of insoluble Prussian Blue establish that the structure is based on a rock salt-like face-centered cubic (fcc) arrangement with Fe^{III} centers occupying one type of site and $[Fe(CN)_6]^{4-}$ units randomly occupying three-quarters of the complementary sites (10). The cyanides bridge the two types of sites. The vacant $[Fe(CN)_6]^{4-}$ sites are occupied by some of the water molecules. Other waters are zeolitic, ie, interstitial, and occupy the centers of octants of the unit cell. The structure contains three different iron coordination environments, $Fe^{II}C_6$, $Fe^{III}N_6$, and $Fe^{III}N_4(H_2O)$, in a 3:1:3 ratio.

The intense blue color of Prussian Blue is attributed to electron transfer between the $[Fe(CN)_6]^{4-}$ and Fe(III) ions. A related pigment called Berlin Green is obtained by oxidation of Prussian Blue. It is thought that the intense color of this other compound results only if oxidation of the $[Fe(CN)_6]$ units is incomplete and some remain as hexakiscyanoferrate(4–). The compound in which only iron(III) is present, $Fe[Fe(CN)_6]$ [14433-93-3], is brown and is subject to autoreduction processes.

A variety of Prussian Blue analogues of general formula $(M^A)_k$-$[Fe(CN)_6]_{l\cdot x}H_2O$ are known which have structures based on that of Prussian Blue. The occupancy of the $Fe^{II}C_6$ site and the average structure of the M^A site vary with the stoichiometry of the material. There are also analogues in which iron is replaced at both sites. If M^A is a divalent metal, as in $M^A =$ cobalt(II) [15415-49-3], copper(II) [13601-13-3], iron(II) [14460-02-7], or manganese(II) [14402-63-3], $k = 2$, $l = 1$, and the $Fe^{II}C_6$ site is half occupied. The copper(II) salt is red-brown, the iron(II) salt is white when pure but is very susceptible to air oxidation to Prussian Blue, and the manganese(II) salt is green-white. For $M^A =$ silver(I) [14308-75-6], $k = 4$ and $l = 1$. The analogues are usually insoluble in water and can be used as ion exchangers and pigments.

2.6. Formates. Iron(II) formate dihydrate [13266-73-4], $Fe(HCO_2)_2 \cdot 2H_2O$, is a green salt which can be prepared from iron(II) sulfate and sodium formate in an inert atmosphere. The compound is slightly soluble in water and fairly resistant to air oxidation. The anhydrous salt [3047-59-4] is known.

Iron(III) formate [555-76-0], $Fe(HCO_2)_3$, can be obtained from iron(III) nitrate [14104-77-9] and formic acid in alcohol solution. The red compound is soluble in water but only slightly soluble in alcohol. Up to two waters of hydration may be included, in which event the color of the compound is more yellow. Aqueous solutions hydrolyze to afford basic iron(III) formates (analogous to basic acetates) and eventually a precipitate of iron hydroxide and free formate.

2.7. Fumarates. Iron(II) fumarate [141-01-5], $Fe(C_4H_2O_4)$, is prepared by mixing hot aqueous solutions of sodium fumarate and iron(II) sulfate followed by filtration of the resulting slurry. It has limited solubility in water but is more soluble in acid solution. The compound is red-orange to red-brown and finds uses as a hematinic. A nonstoichiometric compound [7705-12-6] and iron(III) fumarate [52118-11-3], $Fe_2(C_4H_2O_4)_3$, are also available.

2.8. Halides. All of the anhydrous and hydrated binary halides of iron(II) and iron(III) are known with the exception of the hydrated iodide of iron(III). A large number of complex iron halides have been prepared and characterized (11).

Iron(II) fluoride [7798-28-8], FeF_2, can be prepared by the reaction of iron metal and anhydrous HF at elevated temperatures, reaction of anhydrous $FeCl_2$

and HF in a flow system at ca 500°C, reduction of FeF_3, or dehydration of the tetrahydrate. The solid can be sublimed and is monomeric in the gas phase above 690°C. Pure FeF_2 is a white crystalline compound and has a rutile structure in which the FeF_6 octahedra are tetragonally distorted by compression along one axis. It is sparingly soluble in water, slightly soluble in dilute HF, and insoluble in alcohol, ether, and benzene. Above 100 K, it has a magnetic moment of 5.56 BM. Iron(II) fluoride is used as a catalyst in organic fluorinations.

Iron(II) fluoride tetrahydrate [13940-89-1], $FeF_2 \cdot 4H_2O$, is prepared by dissolving iron metal in warm hydrofluoric acid and precipitating with ethanol. The structure of the solid consists of discrete $[FeF_2(H_2O)_4]$ octahedra in which F^- and H_2O are randomly distributed over the possible sites. The white solid turns brown in air and decomposes at 100°C. It is slightly soluble in water, alcohol, and ether and is soluble in dilute acid.

Iron(III) fluoride [7783-50-8], FeF_3, is prepared from $FeCl_3$ and anhydrous HF or other fluorinating agents in a flow system at elevated temperature. The green hexagonal crystals sublime above 1000°C. Iron(III) fluoride is slightly soluble in water, freely soluble in dilute HF, and nearly insoluble in alcohol, ether, and benzene. It is used as a catalyst in organic reactions. The most important use for iron(III) fluoride is in the manufacture of Fe—Co–Nd magnets.

Iron(III) fluoride trihydrate [15469-38-2], $FeF_3 \cdot 3H_2O$, crystallizes from 40% HF solution in two possible crystalline forms. At low temperature the α-form, which is isostructural with α-$AlF_3 \cdot 3H_2O$, is favored. High temperatures favor β-$FeF_3 \cdot 3H_2O$, the structure of which consists of fluoride -bridged octahedra with one water of hydration per unit cell.

Iron(II) chloride [7758-94-3], $FeCl_2$, is prepared by reaction of iron and HCl at red heat, iron and a mixture of HCl and Cl_2 at 700°C in a flow system, iron and CCl_4, or by decomposition of $FeCl_3$ at 300°C *in vacuo*. Several methods employ reduction of $FeCl_3$. The compound occurs naturally as the mineral lawrencite. White, very hygroscopic crystals can be obtained by sublimation at 700°C in a stream of HCl. The compound decomposes to $FeCl_3$ and Fe_2O_3 on heating in air. Under normal conditions, the crystalline solid has the $CdCl_2$ structure. The room temperature magnetic moment is 5.44×10^{-23} J/T ($5.87\mu_B$). The compound is soluble in water, alcohol, and acetone; slightly soluble in benzene; and insoluble in ether. It reacts with numerous ligands to form complexes. Iron(II) chloride is used as a reducing agent, as a mordant in dyeing, and in pharmaceuticals (qv) and metallurgy (qv).

Iron(II) chloride tetrahydrate [13478-10-9], $FeCl_2 \cdot 4H_2O$, is obtained by dissolving iron metal in aqueous HCl and allowing the product to crystallize at room temperature. The solid consists of monomeric *trans*-$FeCl_2(H_2O)_4$ octahedra which hydrogen bond extensively with each other. Iron(II) chloride dihydrate [16399-77-2], $FeCl_2 \cdot 2H_2O$, is obtained by crystallization at 75°C or by careful dehydration of the tetrahydrate at 105–115°C. The dihydrate consists of chains of *trans*-$FeCl_4(H_2O)_2$ octahedra linked by two bridging chlorides. At 150–160°C the dihydrate loses water to yield iron(II) chloride monohydrate, $FeCl_2 \cdot H_2O$, which at 220°C loses the remaining water of hydration.

Iron(III) chloride [7705-08-0], $FeCl_3$, can be prepared from iron in a stream of Cl_2 at 350°C. Pure material sublimes in the stream of Cl_2 and is obtained as hexagonal crystals which appear green to reflected light but red to transmitted light. The crystals are very hydroscopic and in moist air form a dark brown liquid which contains the hexahydrate. Iron(III) chloride is very soluble in water, alcohol, ether, and acetone, but only slightly soluble in carbon disulfide and essentially insoluble in ethyl acetate. Dissolution in water is exothermic. Iron(III) chloride melts and volatilizes at ca 300°C and boils at ca 316°C. Below 400°C, the vapor contains dimeric Fe_2Cl_6, which consists of two edge-sharing tetrahedra. At higher temperatures the vapor becomes monomeric and eventually decomposes to $FeCl_2$ and Cl_2. Iron(III) chloride is a convenient starting material in the syntheses of other iron(III) compounds and salts. Many adducts and substitution products are known. It is used as a chlorinating and oxidizing agent and is used in the manufacture of dyes, inks, and pigments. Iron(III) chloride's main use is in water treatment. Miscellaneous uses include electronic and photographic etchants metal surface treatments, iron compounds, catalysts, and as a chlorinating and oxidizing agents (12).

Iron(III) chloride hexahydrate [10025-77-1], $FeCl_3 \cdot 6H_2O$, is a brown-yellow to orange material that crystallizes from a solution of iron or iron salt dissolved in hydrochloric acid that contains an oxidant such as Cl_2 or nitric acid. The monoclinic crystals contain the complex salt *trans*-$[FeCl_2(H_2O)_4]Cl \cdot 2H_2O$. The crystals are very hygroscopic and dissolve readily in water, alcohol, acetone, and ether. In aqueous solutions, hydrolysis is extensive and iron hydroxide precipitates. A series of compounds with varying hydration can be formed by drying $FeCl_3 \cdot 6H_2O$.

Iron(II) bromide [7789-46-0], $FeBr_2$, can be prepared by reaction of iron and bromine in a flow system at 200°C and purified by sublimation in nitrogen or under vacuum. Other preparative routes include the reaction of Fe_2O_3 with HBr in a flow system at 200–350°C, reaction of iron with HBr in methanol, and dehydration of hydrated forms. $FeBr_2$ crystallizes in a layered lattice of the CdI_2 type and has a magnetic moment of 5.30×10^{-23} J/T ($5.71\,\mu_B$) at room temperature. It is air stable at 25°C, but is slowly converted to Fe_2O_3 and bromine at 310°C. The light yellow to brown hydroscopic solid is soluble in water, alcohol, ether, and acetonitrile. Iron(II) bromide forms adducts with a wide range of donor molecules. Pale green nona-, hexa-, tetra-, and dihydrate species can be crystallized from aqueous solutions at different temperatures. A hydrate of variable water content, $FeBr_2 \cdot xH_2O$ [13463-12-2], is commercially available. Anhydrous iron(II) bromide is used as a catalyst in organic brominations and polymerization reactions.

Iron(III) bromide [10031-26-2], $FeBr_3$, is obtained by reaction of iron or iron(II) bromide with bromine at 170–200°C. The material is purified by sublimation in a bromine atmosphere. The structure of iron(III) bromide is analogous to that of iron(III) chloride. $FeBr_3$ is less stable thermally than $FeCl_3$, as would be expected from the observation that Br^- is a stronger reductant than Cl^-. Dissociation to iron(II) bromide and bromine is complete at ca 200°C. The hygroscopic, dark red, rhombic crystals of iron(III) bromide are readily soluble in water, alcohol, ether, and acetic acid and are slightly soluble in liquid ammonia. Several hydrated species and a large number of adducts are known. Solutions of iron(III) bromide decompose to iron(II) bromide and bromine on boiling. Iron(III) bromide is used as a catalyst for the bromination of aromatic compounds.

Iron(II) iodide [7783-86-0], FeI_2, is easily prepared by direct reaction of the elements. It has a CdI_2-type structure and a magnetic moment of 5.33×10^{-23} J/T ($5.75\ \mu_B$) at room temperature. The hydroscopic, red-black crystals are very soluble in water, alcohol, and ether. Aqueous solutions are readily oxidized by air. The green tetrahydrate [13492-45-0], $FeI_2 \cdot H_2O$, can be obtained by evaporation at room temperature; a yellow hexahydrate can be obtained at lower temperature. The hydrated salts and their solutions turn black when heated to 50°C, but regain their original color on cooling. FeI_2 forms many adducts with donor ligands. It is used as a catalyst in organic reactions and as a source of both iron and iodine in veterinary medicine (see VETERINARY DRUGS).

Iron(III) iodide [15600-49-4], FeI_3, is prepared by the oxidative photodecarbonylation of diiodotetracarbonyliron(II) [14878-30-9] in the presence of diiodine (13). The metastable black solid obtained is extremely hygroscopic, sparingly soluble only in dichloromethane, and decomposes to iron(II) iodide and diiodine when exposed to donor solvents such as tetrahydrofuran, acetonitrile, water, or pyridine. It also decomposes when exposed to light. The compound is an effective catalyst for the replacement by iodide of other halides in alkyl halides.

Iron halides react with halide salts to afford anionic halide complexes. Because iron(III) is a hard acid, the complexes that it forms are most stable with F^- and decrease in both coordination number and stability with heavier halides. $[FeF_5(H_2O)]^{2-}$ is the predominant iron fluoride species in aqueous solution. The $[FeF_6]^{3-}$ ion can be prepared in fused salts. Whereas six-coordinate $[FeCl_6]^{3-}$ is known, four-coordinate complexes are favored for chloride and the heavier halides. Salts of tetrahedral $[FeCl_4]^-$ can be isolated if large cations such as tetraphenylarsonium or tetraalkylammonium are used. $[FeBr_4]^-$ is known but is thermally unstable in aqueous solution and disproportionates to iron(II) and bromine. Greater stability is observed in nonaqueous solution and the solid state. The extremely air and moisture sensitive salts $M[FeI_4]$, $M = K$, Rb, and Cs, are obtained from metallic iron, I_2, and the alkali metal halide at 300°C (14). Attempts to prepare the Li or Na analogues afford mixtures of MI and FeI_2. Tetraalkylammonium salts of $[FeI_4]^-$ can be prepared in tetrohydrofuran or nitromethane solution. Several, including tetraethylammonium tetraiodoferrate [25478-69-7], $[(C_2H_5)_4N][FeI_4]$ are sufficiently stable to have been characterized by X-ray diffraction. Complex anions of iron(II) halides are less common. $[FeCl_4]^{2-}$ has been obtained from $FeCl_2$ by reaction with alkali metal chlorides in the melt or with tetraethylammonium chloride in deoxygenated ethanol.

Several complex anions are known in which one or more halide ligands are replaced by other ligands. One important example is the μ-oxo-bridged binuclear anion $[Fe_2OCl_6]^{2-}$, which consists of two $FeOCl_3$ tetrahedra sharing the oxygen vertex. The two iron centers are strongly antiferromagnetically coupled. The anion is the first example of a μ-oxo-bridged binuclear iron(III) complex that has tetrahedral coordination and monodentate supporting ligands. The anion is finding use as a starting material for the synthesis of larger oxo-bridged iron clusters (15).

2.9. Gluconates. Iron(II) gluconate dihydrate [6047-12-7], $Fe[HOCH_2(CHOH)_4CO_2]_2 \cdot 2H_2O$, is prepared from barium or calcium gluconate and iron(II) sulfate. It is a yellow-green powder and has a slight odor of caramel.

The compound is quite soluble in water but is nearly insoluble in alcohol. It is used as a hematinic, in the treatment of anemia, and to color, fortify, and flavor foods (see FLAVORS). Isotonic solutions are available. An anhydrous salt [299-29-6] is also known. Iron(III) gluconate [38658-53-6], $Fe[HOCH_2(CHOH)_4CO_2]_3$, has been examined as a nutritional supplement.

2.10. Nitrates. Iron(II) nitrate hexahydrate [14013-86-6], $Fe(NO_3)_2 \cdot 6H_2O$, is a green crystalline material prepared by dissolving iron in cold nitric acid that has a specific gravity of less than 1.034 g/cm^3. Use of denser, more concentrated acid leads to oxidation to iron(III). An alternative method of preparation is the reaction of iron(II) sulfate and barium or lead nitrate. The compound is very soluble in water. Crystallization at temperatures below $-12°C$ affords an nonahydrate. Iron(II) nitrate is a useful reagent for the synthesis of other iron-containing compounds and is used as a catalyst for reduction reactions.

Iron(III) nitrate nonahydrate [7782-61-8], $Fe(NO_3)_3 \cdot 9H_2O$), is prepared by dissolving iron in nitric acid that has a specific gravity of at least 1.115 g/cm^3. Acid of too high concentration passivates the iron, however. The hygroscopic, monoclinic, colorless-to-pale violet crystals are very soluble in water and soluble in alcohol and acetone. Iron(III) nitrate hexahydrate [13476-08-9], $Fe(NO_3)_3 \cdot 6\,H_2O$, forms colorless, cubic crystals. It is also very soluble in water. Iron(III) nitrate is used as a mordant in dyeing, weighting silks, leather tanning, as a catalyst for oxidation reactions, and as a reagent for the synthesis of other iron-containing compounds.

2.11. Oxides and Hydroxides. Iron(II) oxide [1345-25-1], FeO, is a black solid that can be obtained by heating iron in a low partial pressure of oxygen, or by heating iron(II) oxalate in a vacuum. This affords a fine, pyrophoric powder that can decompose water. Strong heating of the freshly prepared powder decreases its state of division and its reactivity. Below ca 575°C, FeO is unstable with respect to disproportionation into Fe and Fe_3O_4, but a metastable phase can be obtained by rapidly cooling the hot product. FeO occurs naturally as the mineral wüstite [17125-56-3]. Crystalline FeO has a cubic, rock salt structure, but is always deficient in iron because of the presence of some iron(III). The solid is easily oxidized in air, is a strong base, and absorbs carbon dioxide. It is insoluble in water, alcohol, or alkali, but is readily soluble in acids. Iron(II) oxide is used in the manufacture of green, heat-absorbing glass, in ceramic mixtures, and in a variety of catalyst preparations, notably those used in ammonia synthesis and methanation.

Iron(III) oxide [1309-37-1], Fe_2O_3, exists in two different crystalline forms. The α-form occurs naturally as the mineral hematite [1309-37-1], which is the principal ore of iron. It can be prepared synthetically by heating brown hydrous iron hydroxide oxide [20344-49-4], Fe(OH)O, at 200°C. α-Fe_2O_3 has the corundum structure in which the oxide ions form hexagonal close-packed layers and the iron(III) ions occupy two-thirds of the octahedral sites. The γ-form occurs naturally as the mineral maghemite, and can be prepared synthetically by careful oxidation of Fe_3O_4. γ-Fe_2O_3 has a spinel structure in which the oxide ions form cubic close-packed layers and the iron(III) ions are randomly distributed over the tetrahedral and octahedral holes. Unlike the α-form, which is paramagnetic, the γ-form is ferrimagnetic and is used as a magnetic material in the production of magnetic recording media (see MAGNETIC MATERIALS, BULK). Iron(III) oxide is insoluble in water but dissolves in hydrochloric or sulfuric acids. The color and appearance of iron(III) oxide depend on the size and shape of the particles, and the identity and amount of impurities and water present. Yellow, orange, or red pigments are known. It is used in large quantities as a red pigment for paint, rubber, ceramics (qv), and paper (qv), and in coatings for steel and other metals. Iron(III) oxide also finds use in the preparation of rare-earth/iron garnets and other ferrites; as a polish agent for glass, diamonds, and precious metals (jeweler's rouge); and as a catalyst for oxidation reactions.

Triiron tetroxide [1317-61-9] (iron(II, III) oxide), Fe_3O_4, is a mixed Fe^{II}/Fe^{III} oxide which occurs naturally as the mineral magnetite (lodestone). It is an important ore of iron. It can be prepared by the partial oxidation of FeO or by heating Fe_2O_3 above ca 1400°C. The black, cubic crystals have an inverse spinel structure in which the oxide ions form cubic close-packed layers, all iron(II) ions occupy octahedral interstitial sites, half of the iron(III) ions occupy octahedral sites, and the other half of the iron(III) ions occupy tetrahedral sites. The compound is strongly ferrimagnetic and has a Curie point of 860 K, at which temperature the effective magnetic moment is 3.9×10^{-23} J/T ($4.2\,\mu_B$). Iron(II,III) oxide is insoluble in water, alcohol, ether, and dilute acids but dissolves in concentrated acids. It is a fairly good conductor of electricity, owing to electron transfer between iron(II) and iron(III). Blue steel has a surface coating of iron(II,III) oxide as a corrosion-resistant film. The compound is used as a pigment for glass (qv), ceramics, and paint; in magnetic recording media; as a polishing compound; and in many catalytic preparations. Ferrofluids contain nanoparticles (~10 nm diameter) of Fe_3O_4 suspended in a liquid medium. These materials, which have the fluid properties of a liquid and the magnetic properties of a solid, are used in rotating shaft seals in computer hard disk drives, in voice coil gaps of loudspeakers to damp undesired vibrations and for cooling, and to separate metals from ores.

Iron(II) hydroxide [18624-44-7], $Fe(OH)_2$, is prepared by precipitation of an iron(II) salt solution by strong base in the absence of air. It occurs as pale green, hexagonal crystals or a white amorphous powder. It is practically insoluble in water, fairly soluble in ammonium salt solutions, and soluble in acids and in concentrated NaOH solution. It is slowly oxidized by air. Conversion to $Fe_2O_3 \cdot xH_2O$ is eventually complete.

Iron(III) hydroxide [1309-33-7], $FeHO_2$, is a red-brown amorphous material that forms when a strong base is added to a solution of an iron(III) salt. It is also known as hydrated iron(III) oxide. The fully hydrated $Fe(OH)_3$ has not been isolated. The density of the material varies between 3.4–3.9 g/cm^3, depending on its extent of hydration. It is insoluble in water and alcohol, but redissolves in acid. Iron(III) hydroxide loses water to form Fe_2O_3. Iron(III) hydroxide is used as an absorbent in chemical processes, as a pigment, and in abrasives. Salt-free iron(III) hydroxide can be obtained by hydrolysis of iron(III) alkoxides. Iron(III) hydroxide is the highly colored precipitate known as yellow boy that deposits in streams affected by acid mine drainage.

2.12. Ferrites, Garnets, and Ferrates.

Iron in oxidation states +3 and higher forms numerous oxide compounds that formally appear to contain oxo ligands (O^{2-}). Many of these have interesting magnetic and chemical properties. The ferrites (FeO_2^-) and garnets are really mixed metal oxides. Ferrites (qv) of the alkali metals can be obtained by fusing iron(III) oxide with the alkali metal chloride, carbonate, or hydroxide, or by decomposing the alkali iron(VI) oxo compound in boiling water. Sodium ferrite [12062-85-0], $NaFeO_2$, occurs as brown hexagonal plates or needles which are soluble in dilute HCl. Lithium ferrite [12022-46-7] is also known. Ferrites of divalent metals are prepared by heating iron(III) oxide with the carbonate of the desired metal, or by addition of strong base to a solution of the M(II) and iron(III) salts. Examples include magnesium ferrite [12068-86-9], calcium ferrite [12013-33-1], barium ferrite [12009-00-6], and zinc ferrite [1317-55-1] which occurs naturally as the mineral franklinite. Ferrite compounds are spinels and have the general formula $M^{2+}Fe^{III}{}_2O_2$. Some adopt normal spinel structures, in which the M(II) ions occupy tetrahedral sites in the cubic oxide lattice and the Fe(III) ions occupy octahedral sites. Others have the inverse spinel structure in which one half of the Fe(III) ions occupy tetrahedral sites and the other half occupies octahedra sites. Inverse spinels are ferrimagnetic. One such material is iron(II,III) oxide. The inverse spinel ferrites are used in magnetic recording media, as cores in high frequency transformers, and in computer memory systems. Hexagonal ferrites, such as $BaFe_{12}O_{19}$, are used to construct permanent magnets. Garnets have the general formula $M_3Fe_5O_{12}$, where M is trivalent, and are useful in microwave applications (see MICROWAVE TECHNOLOGY).

Mixed oxides of Fe(IV) can be prepared by heating iron(III) oxide with a metal oxide or hydroxide in oxygen at elevated temperatures. These black compounds have general formulas M_4FeO_4, M monovalent, or M_2FeO_4, M divalent, but do not contain discrete $[FeO_4]^{4-}$ ions. They are readily decomposed by mineral acids to iron(III) and oxygen.

Compounds of iron(V) are extremely rare. K_3FeO_4 has been prepared by heating K_2FeO_4 with KOH in oxygen at 700–800°C. It appears to contain tetrahedral $[FeO_4]^{3-}$ anions. An impure sodium salt has also been prepared. The best known oxoanion of iron is the ferrate(VI) prepared by oxidizing a suspension of hydrous iron(III) oxide in concentrated alkali with potassium hypochlorite or by anodic oxidation of iron in concentrated alkali. Crystals of potassium ferrate [13718-66-6], K_2FeO_4, are deep purple, orthorhombic, and contain discrete tetrahedral $[FeO_4]^{2-}$ anions. Barium ferrate [13773-23-4] can be precipitated from solutions of soluble ferrate salts. Other ferrate salts include calcium ferrate [35764-67-1], and sodium ferrate [13773-03-0]. The magnetic moments of these materials are 2.63×10^{-23} J/T (2.8–3.2 μ_B), which is consistent with the expectation of two unpaired electrons. The $[FeO_4]^{2-}$ ion is an extremely strong oxidizing agent, oxidizing NH_3 to N_2 at room temperature, and in neutral or acidic solutions rapidly oxidizing water to oxygen. The $[FeO_4]^{2-}$ is a stronger oxidant than permanganate and has found use in the oxidation of organic compounds.

2.13. Perchlorates. Iron(II) perchlorate hexahydrate [13922-23-8], $Fe(ClO_4)_2 \cdot 6H_2O$, is prepared by dissolving iron in cold, dilute perchloric acid or by dissolving FeS in perchloric acid. It crystallizes in hygroscopic, light green hexagonal prisms which are stable in dry air and extremely soluble (0.978 g/mL H_2O at 0°C) in water and alcohol. It is susceptible to air oxidation in aqueous solution and decomposes above 100°C. Yellow iron(III) perchlorate hexahydrate [13537-24-2], $Fe(ClO_4)_3 \cdot 6H_2O$, is also extremely soluble in water (1.198g/mL H_2O at 0°C).

2.14. Sulfates. Iron(II) sulfate heptahydrate [7782-63-0], $FeSO_4 \cdot 7H_2O$, forms blue-green monoclinic crystals that are very soluble in water and somewhat soluble in alcohols. It is known by many other names including cupperas, green vitriol, and iron vitriol. The compound is efflorescent in dry air. In moist air, the compound oxidizes to yellow-brown basic iron(III) sulfate. Aqueous solutions tend to oxidize. The rate of oxidation increases with an increase in pH, temperature, and light. The compound loses three waters of hydration to form iron(II) sulfate tetrahydrate [20908-72-0], $FeSO_4 \cdot 4H_2O$, at 56°C. Further warming to 65°C forms white iron sulfate monohydrate [17375-41-6], $FeSO_4 \cdot H_2O$, which is stable to 300°C. Strong heating results in decomposition with loss of sulfur dioxide. Solutions of iron(II) sulfate reduce nitrate and nitrite to nitric oxide, whereupon the highly colored $[Fe(H_2O)_5(NO)]^{2+}$ ion is formed. This reaction is the basis of the brown ring text for the qualitative determination of nitrate or nitrite.

Iron(II) sulfate forms double salts of formula $M_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ with alkali sulfates. Iron(II) ammonium sulfate [7783-85-9] (Mohr's salt), $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, is used as a primary standard for iron. It is soluble in water but insoluble in alcohols. Both the solid and its solution are more stable to oxidation than iron(II) sulfate.

Most iron(II) sulfate is a by-product of the steel (qv) industry. Prior to tinning, galvanizing, electroplating, or enameling, steel surfaces are dipped in sulfuric acid for cleaning (pickling) (see METAL SURFACE TREATMENTS, CASE HARDENING). The resulting pickle liquor contains ca 15% iron(II) sulfate and 2–7% acid. Scrap iron is added to reduce the acid concentration to ca 0.03%. The solution is filtered, concentrated at 70°C to a specific gravity of 1.4, and is allowed to cool to room temperature which results in crystallization of the heptahydrate. Industry produces on the order of 10^6 t/yr of the heptahydrate. Because supply exceeds demand, the pickling liquor presents a serious waste disposal problem. Iron(II) sulfate, along with iron(III) sulfate, and sulfuric acid can also be produced by leaching or weathering of FeS and pyrites, which is a source of acid mine drainage. Iron(II) sulfate has a large variety of uses including production of iron oxide pigments and salts, in fertilizer, as food and feed supplements, in inks (qv) and dyes, as a reducing agent, a polymerization catalyst, and in water and waste treatment (16).

Iron(III) sulfate [10028-22-5], $Fe_2(SO_4)_3$, is a gray-white material that forms hygroscopic rhombic or rhombohedral crystals. It is slightly soluble and dissolves slowly in cold water and decomposes in hot water. Several hydrates are known including the monohydrate [43059-01-4], the hexahydrate [13761-89-2], the heptahydrate [35139-28-7], and the nonahydrate [13520-56-4]. These can be difficult to obtain pure. The commercially available hydrate [15244-10-7] contains about 20% water by weight and is yellowish in color. Alum compounds of the general formula $MFe(SO_4)_2 \cdot 12H_2O$, M monovalent, are known. Iron(III) ammonium alum dodecahydrate [7783-83-7], $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$, and iron(III) potassium alum dodecahydrate [13464-29-1], $KFe(SO_4)_2 \cdot 12H_2O$, are important as mordants in dyeing. Iron(III) sulfate is obtained by oxidation of iron(II) sulfate using nitric acid or by treating iron(II) oxide with sulfuric acid. It is used in pigments, as a coagulant in water and sewage treatment, and as a mordant.

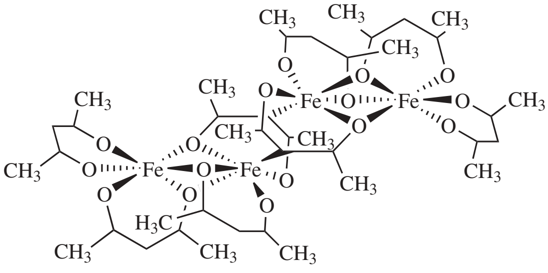
2.15. Sulfides. Three sulfides of iron are known. Iron(II) sulfide [1317-37-9], FeS, is a gray nonstoichiometric material obtained by direct reaction of iron and sulfur. The actual stoichiometry is typically $Fe_{0.9}S$. It can also be prepared by treating iron(II) solutions with alkali metal sulfide. It is found in nature as the mineral pyrrhotite [1310-50-5], which also usually contains nickel as well. FeS has a NiAs structure. It is almost insoluble in water, oxidizes readily in air, and dissolves in aqueous acids with the evolution of H_2S. The above reactions represent a reasonable route for the synthesis of H_2S gas. Iron disulfide [12068-85-8], FeS_2, can be prepared by heating Fe_2O_3 in H_2S. FeS_2 is found in nature as the minerals pyrite [1309-36-0] (fool's gold) and marcasite [1317-66-4], both of which have a brassy yellow color and a metallic luster. Pyrite is frequently found in large, well-formed crystals and is composed of iron(II) and S_2^{2-} ions in a distorted rock salt structure. Heating solid pyrite affords Fe_2O_3 and SO_2 in air or FeS and sulfur in a vacuum. Roasting of pyrites has been used in the past to produce SO_2 for sulfuric acid production and iron(III) oxide for use as an iron ore (see SULFURIC ACID AND SULFUR TRIOXIDE). Marcasite is less stable than pyrite and therefore is more reactive. Fe_2S_3 [12063-27-3] is an unstable black precipitate produced when aqueous iron(III) solutions are treated with S^{2-}. It is rapidly decomposed in moist air to Fe_2O_3 and sulfur. A purer material can be obtained by reaction of anhydrous $FeCl_3$ with bistrimethylsilylsulfide. Iron(III) sulfide occurs in nature in the form of the double sulfide minerals chalcopyrite [1308-56-1], $CuFeS_2$, and bornite [1308-82-3], Cu_3FeS_3, which can be represented as $Cu_2S \cdot Fe_2S_3$ and $3Cu_2S \cdot Fe_2S_3$, respectively. Iron(III) sulfide finds applications in cathodes in secondary Li batteries (qv), coal liquefaction, and desulfurization (see COAL CONVERSION PROCESSES, CARBONIZATION).

2.16. Chelate Compounds. A chelate is a multidentate ligand which binds to a metal atom at more then one coordination site resulting in a complex having a closed-ring structure (see COORDINATION COMPOUNDS). Chelate complexes are more stable, ie, have greater formation constants, than analogous complexes of unidentate ligands, wherein no rings are formed. The enhanced stability is called the chelate effect and is thought to result predominantly from favorable entropic effects. In general, chelates that contain five-membered rings are more stable than chelates that contain six-membered rings.

Diketones. The protons on the carbon between the two carbonyl groups of 2,4-pentanedione, also called acetylacetone (acacH), and other β-diketone compounds are relatively acidic because the negative charge of the conjugate base anion is delocalized through resonance onto the two carbonyl oxygen atoms. The anion can coordinate to a metal ion by means of the two negatively charged oxygen atoms. This results in formation of a six-membered chelate ring.

In the presence of piperidine, iron(II) sulfate or chloride reacts with 2,4-pentanedione in degassed water under nitrogen to form hydrated bis(2,4-pentanedionato)iron(II). Drying under high vacuum affords the anhydrous compound bis(2,4-pentanedionato)iron(II) [14024-17-0], $Fe(C_5H_7O_2)_2$ or $Fe(acac)_2$ (**2**). Although the stoichiometry suggests the compound is simple, it is coordinatively unsaturated and has an unusual tetrameric structure which consists of two asymmetric Fe_2 linked by long Fe—C bonds. The acac-ligand which contains the methylene carbon bound to iron in the second asymmetric unit also has an oxygen atom that bridges the two iron atoms of the first asymmetric unit.

$Fe(acac)_2$ reacts with numerous bases to form six-coordinate adducts. All of the iron(II) acac complexes are air sensitive. $Fe(acac)_2$ is used as a catalyst in several types of reactions.



(**2**)

Tris(2,4-pentanedionato)iron(III) [14024-18-1], $Fe(C_5H_7O_2)_3$ or $Fe(acac)_3$, forms ruby red rhombic crystals that melt at 184°C. This high spin complex is obtained by reaction of iron(III) hydroxide and excess ligand. It is only slightly soluble in water, but is soluble in alcohol, acetone, chloroform, or benzene. The structure has a near-octahedral arrangement of the six oxygen atoms. Related complexes can be formed with other β-diketones by either direct synthesis or exchange of the diketone into $Fe(acac)_3$. The complex is used as a catalyst in oxidation and polymerization reactions.

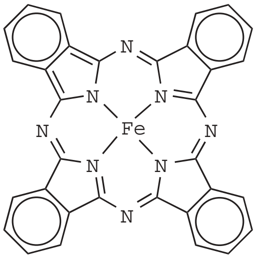
Ethylenediaminetetraacetic Acid. Ethylenediaminetetraacetic acid ($EDTAH_4$) has six potential donor groups: two nitrogen atoms and four carboxylate groups. If $EDTA^{4-}$ acts as a hexadentate ligand to a metal, the resulting complex contains five five-membered chelate rings and has a charge that is four less than that of the metal ion.

Iron(II) ethylenediaminetetraacetic acid [15651-72-6], $Fe(EDTA)^{2-}$ or *N*,*N*′-1,2-ethanediylbis[*N*-(carboxymethyl)glycinato]ferrate(2−), is a colorless, air-sensitive anion. It is a good reducing agent, having $E^\circ = -0.117V$, and has been used as a probe of outer sphere electron-transfer mechanisms. It can be prepared by addition of an equivalent amount of the disodium salt, Na_2H_2EDTA, to a solution of iron(II) in hydrochloric acid. Diammonium [56174-59-5] and disodium [14729-89-6] salts of $Fe(EDTA)^{2-}$ are known.

Iron(III) ethylenediaminetetraacetic acid [15275-07-7], $Fe(EDTA)^{1-}$ or *N*,*N*′-1,2-ethanediylbis[*N*-(carboxymethyl)glycinato]ferrate(1−), is a pale yellow, high spin complex in which EDTA serves as a hexadentate ligand. A coordinated water molecule is also present, making the iron atom seven-coordinate with a pentagonal bipyramidal structure. The stability constant for the formation of the complex is 10^{25}. At low pH, a six-coordinate complex is obtained as a result of protonation and decoordination of one carboxylate of the $EDTA^{4-}$ ligand. At high pH, μ-oxo species form and eventually precipitate. The ammonium [21265-50-9] and sodium [15708-41-5] salts of $Fe(EDTA)^{-}$ have been prepared and are used as oxidizing agents, especially in photographic bleaching and fixing preparations. The complexes also find use as oxidation catalysts and as a therapeutic source of iron.

Macrocycles. The complexes of cyclic, *n*-dentate ligands exhibit enhanced stability over the complexes of open-chain, *n*-dentate ligands with the same donor set. This phenomenon is termed the macrocyclic effect and results at least in part from favorable entropic factors. Iron forms complexes with a wide variety of macrocyclic ligands. The majority of these involve macrocycles having four nitrogens as the donor groups, but macrocycles containing other numbers of donors and having oxygen, sulfur, and mixed donor atoms are also known. The chemistry of the macrocyclic complexes of iron is too extensive for the scope of this article. Discussion here is limited to phthalocyanine and porphyrin complexes, below.

Iron(II) phthalocyanine [132-16-1] (**3**), a green compound, was first prepared by accidentally during the manufacture of phthalimide. Phthalocyanines are an important group of blue/green pigments that have excellent color intensity, photochemical and thermal stability, and chemical inertness (see PHTHALOCYANINE COMPOUNDS). They find use in dyes, inks, paints, toners, and optical recording media. Iron(II) phthalocyanine is prepared by reductive cyclization of phthalonitrile with finely divided iron in a high boiling solvent such as 1-chloronaphthalene and is purified by sublimation at 450°C under partial vacuum. The iron in the complex has a square planar coordination geometry and an intermediate spin, $S = 1$, ground state. The complex is insoluble in most noncoordinating organic solvents, but dissolves in very strong acids such as sulfuric and chlorosulfonic acids owing to protonation of the basic bridging aza groups. The compound does not dissolve in hot hydrochloric acid, but instead reacts with it to form a material called chloroferric phthalocyanine [14285-56-4] the nature of which is not fully resolved. Iron(II) phthalocyanine forms adducts in coordinating solvents or in the presence of bases, for example phthalocyaninatobis(pyridine)iron [20219-84-5], which can be low spin. Water-soluble iron phthalocyanine complexes are obtained by sulfonating the phenyl residues to obtain tetrasodium phthalocyaninetetrasulfonatoferrate [41867-66-7]. Purer materials may be obtained, however, by cyclization of sulfonated phthalic acid or nitrile monomers. Iron(II) phthalocyanine may be reduced by up to four electrons. The complex finds use as a catalyst for a variety of chemical and electrochemical redox reactions.



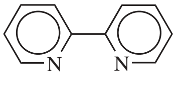
(3)

Oxalates. Iron(II) oxalate dihydrate [6047-25-2], $FeC_2O_4 \cdot 2H_2O$, forms by reaction of oxalic acid and aqueous iron(II) solutions. The pale yellow compound is slightly soluble in water, soluble in dilute mineral acids, and decomposes to iron(II) oxide above 190°C. It is used as a photographic developer, to impart greenish brown tints to glass, and as a pigment for plastics, paints, and lacquers.

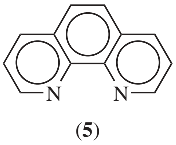
Complex oxalatoferrate(2−) salts of general formula $M_2[Fe(C_2O_4)_2] \cdot xH_2O$, M monovalent, where x depends on M, can be precipitated from solutions which contain alkali oxalates. Tris(ethanedioato)ferrate(4−) [30948-48-2], $[Fe(C_2O_4)_3]^{4-}$, is known but has been studied primarily in solution as an electron-transfer agent.

Tris(ethanedioato)ferrate(3−) [15321-61-6], $[Fe(C_2O_4)_3]^{3-}$, can be prepared by addition of an excess of oxalate to a solution of almost any soluble ferric salt. The anion forms isolable salts with many cations including iron(III). Iron(III) oxalate hexahydrate [19469-07-9], $Fe_2(C_2O_4)_3 \cdot 6H_2O$, is a yellow powder which is very soluble in water and acid. The green crystalline tripotassium tris(oxalato)ferrate trihydrate [5936-11-8] and triammonium tris(oxalato)ferrate trihydrate [14221-47-7] are among the other known salts. The potassium salt contains high spin iron ions in discrete trisoxalato units. The FeO_6 coordination sphere has some trigonal distortion from octahedral symmetry. The trihydrate yields the anhydrous tripotassium tris(oxalato)ferrate [14883-34-2] at ca 120°C and decomposes at 230°C. Although tris(oxalato)ferrate(3−) is stable toward dissociation of oxalate, its solutions and salts are photosensitive. The oxalate ligand is oxidized to CO_2 and iron(III) is concurrently reduced to iron(II). This reaction provides the basis for the first step in the blueprint process. The complex anion is used in other photochemical processes as well as in a variety of redox processes.

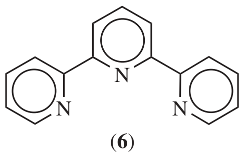
Polypyridyl Ligands. Three important polypyridyl ligands are 2,2′-bipyridine [366-18-7] (bipy) (**4**), 1,10-phenanthroline [66-71-7] (phen) (**5**), and 2,2′:6′,2″-terpyridine [1148-79-4] (terpy) (**6**). The good σ-donor and π-acceptor properties of these α,α′-diimine chelate ligands make them high field donors of comparable strength to the cyanide ion. As a consequence, the tris chelate complexes of the first two of these ligands and the bis chelate complex of terpy with both iron(II) and iron(III) are low spin. Iron(II) has a very high affinity for these ligands and their substituted derivatives. The complexes are substitution inert and have overall formation constants as high as 10^{23}. The complexes form readily even in dilute solutions. This and the intense red color of the tris iron(II) or ferroin complexes, where the molar extinction coefficient ε_M is ca 10^4 $(M \cdot cm)^{-1}$, are responsible for the extensive use of these ligands for the spectrophotometric determination of iron. The large, cationic iron(II) complexes are also useful in the specific precipitation of anions in gravimetric procedures. The phenanthroline complexes find use as reversible, high potential (∼1.1V) redox indicators. The iron(III) complexes are blue and nearly colorless ($\varepsilon \sim 10^2$) when compared to the iron(II) complexes. In keeping with the preference of iron(III) for hard donors, the α,α′-diimine chelate complexes of iron(III) have much smaller formation constants. These are unstable with respect to reduction and ligand dissociation. Complexes of the type $[Fe(L{-}L)_2X_2]$ and $[Fe(L{-}L)X_4]^{2-}$, where L—L = bipy or phen, are also known.



(**4**)



(**5**)



(**6**)

The tris(2,2′-bipyridine)iron(2+) ion [15025-74-8], $[Fe(bipy)_3]^{2+}$, has an absorption maximum at 522 nm and an absorptivity of 8650 $(M \cdot cm)^{-1}$. The overall formation constant of the low spin complex is 10^{17}. For most common counterions the ion has good solubility in water, but may be extracted into organic solvents. The complex dissociates in strong acids and highly alkaline solution. Complexes having different solubility properties can be prepared from bipy ligands which have one or more substituent groups at different ring positions. The symmetry of the FeN_6 unit is D_3 and the five-membered chelate ring is coplanar with the rest of the bipy ligand. Resolution of the enantiomers has been achieved and racemization is slow. The reduction potential of the complex is 1.02 V. Many stable salts have been isolated including the dibromide [15388-40-6], the dichloride [14751-83-8], and the diperchlorate [15388-48-4].

The pale blue tris(2,2′-bipyridine)iron(3+) ion [18661-69-3], $[Fe(bipy)_3]^{3+}$, can be obtained by oxidation of $[Fe(bipy)_3]^{2+}$. It cannot be prepared directly from iron(III) salts. Addition of 2,2′-bipyridine to aqueous iron(III) chloride solutions precipitates the doubly hydroxy-bridged species $[(bipy)_2Fe(\mu\text{-}OH)_2Fe(bipy)_2]Cl_4$ [74930-87-3]. $[Fe(bipy)_3]^{3+}$ has an absorption maximum at 610 nm, an absorptivity of 330 $(M \cdot cm)^{-1}$, and a formation constant of 10^{12}. In mildly acidic to alkaline aqueous solutions the ion is reduced to the iron(II) complex. $[Fe(bipy)_3]^{3+}$ is frequently used in studies of electron-transfer mechanisms. The triperchlorate salt [15388-50-8] is isolated most commonly.

The orange-red tris(1,10-phenanthroline)iron(2+) ion [14708-99-7], $[Fe(phen)_3]^{2+}$, has an absorption maximum at 510 nm, an absorptivity of $1.10 \times 10^4 (M \cdot cm)^{-1}$, and a formation constant of 10^{21}. The reduction potential is 1.06 V. The complex is stable in the pH range of 2 to 9, but also persists at higher pH if a reducing agent is present. It has good solubility in water, but may be extracted into organic solvents. The solubility of analogous complex ions in organic solvents increases with the number and size of organic ring substituents. An example is the tris(4,7-diphenyl-1,10-phenanthroline)iron(2+) ion [21412-03-3], which is sometimes used to determine iron concentrations because its higher absorptivity (2.24×10^4 $(M \cdot cm)^{-1}$ at 533 nm) leads to greater sensitivity. $[Fe(phen)_3]^{2+}$ serves as an electron-transfer mediator, is an excellent indicator in redox titrations, and a constituent of many oscillating reaction systems. Well-known salts of $[Fe(phen)_3]^{2+}$ include the dichloride [14978-15-5], the diiodide [15553-89-6], and the diperchlorate [14586-54-0].

In analogy to the situation for bipyridine, the blue tris(1,10-phenanthroline)iron(3+) ion [13479-49-7], $[Fe(phen)_3]^{3+}$, must be obtained by oxidation of the corresponding iron(II) ion. $[Fe(phen)_3]^{3+}$ has an absorption maximum at 590 nm, an absorptivity of 600 $(M \cdot cm)^{-1}$, and a formation constant of 10^{14}. In solutions of $pH > 4$, this species is reduced to the iron(II) complex. The reduction is instantaneous in alkaline solution. At $pH < 2$, protons compete with iron(III) for the phenanthroline nitrogens and coordination is incomplete. $[Fe(phen)_3]^{3+}$ is used most often in solution as an oxidant, but the trichloride [40273-22-1] and the triperchlorate monohydrate [20774-81-6] salts have been prepared.

The intensely purple bis(2,2′:6′,2″-terpyridine)iron(2+) ion [17455-70-8], $[Fe(terpy)_2]^{2+}$, has an absorption maximum at 552 nm, an absorptivity of $1.15 \times 10^4 (M \cdot cm)^{-1}$, and a formation constant of 10^{19}. The reduction potential is 1.13 V. The fit of the ligand is not ideal for an octahedral FeN_6 unit. The N—Fe—N angles are less than 90°. The diperchlorate salt [22079-98-7] precipitates upon addition of perchloric acid to solutions of the ion.

The unstable pale blue-green bis(2,2′:6′,2″-terpyridine)iron(3+) ion [47779-99-7], $[Fe(terpy)_2]^{3+}$, has been obtained by oxidation of $[Fe(terpy)_2]^{2+}$. It is very unstable with respect to reduction by solvent and ligand dissociation. The perchlorate salt [21536-42-5] has been reported.

3. Organometallic Compounds

The discussion herein is limited to several simple compounds that are stable, readily available, and used as starting materials for many other organoiron compounds.

3.1. Carbonyls. Iron pentacarbonyl [13463-40-6], $Fe(CO)_5$, is a toxic, yellow-orange, oily liquid which does not react with air at room temperature. It has a musty odor, a relatively high vapor pressure (Pa-21 torr at 20°C), and boils at 103°C. It is readily soluble in benzene, hydrocarbons, and ether, but is insoluble in water. Iron pentacarbonyl is prepared by direct reaction of carbon monoxide with finely divided iron metal at somewhat elevated temperature and pressure. It may be prepared at room temperature and pressure if very highly activated iron metal is used. As a consequence of its method of preparation, iron pentacarbonyl can be a contaminant in coal gas and in carbon monoxide which has been stored at high pressure in steel cylinders. The compound has a trigonal bipyramical structure but is stereochemically nonrigid. Iron pentacarbonyl is slowly converted to iron nonacarbonyl by light. At temperatures above ca 100°C and in the absence of a high CO pressure, iron pentacarbonyl decomposes and produces pure metallic iron. Iron pentacarbonyl has been used as an antiknock agent in gasoline. It burns in air to yield finely divided iron(III) oxide which is suitable for use in pigments and polishing compounds. It also finds use in organic synthesis (17,18).

The reaction chemistry of iron pentacarbonyl is extensive. Soft ligands including phosphines and arsines react with the compound thermally and photochemically to afford CO substitution products of the types $Fe(CO)_4L$ and $Fe(CO)_3L_2$. Alkynes, alkenes, and dienes form compounds in which the unsaturated hydrocarbon is coordinated to $Fe(CO)_4$ or $Fe(CO)_3$ groups. Hard ligands such as hydroxide and amines tend to induce redox disproportionations and afford iron carbonyl anions, iron carbonyl hydrides, and iron carbonyl clusters. Halogens and pseudohalogens oxidatively add to $Fe(CO)_5$ to produce *cis*-$Fe(CO)_4X_2$ compounds. Reduction of $Fe(CO)_5$ using sodium amalgam or sodium benzophenone ketyl in refluxing dioxane affords the pyrophoric compound disodium tetracarbonylferrate [59733-73-2], $Na_2[Fe(CO)_4]$, which is useful in several organic transformations as an acyl anion equivalent (18,19).

Diiron nonacarbonyl [15321-51-4], $Fe_2(CO)_9$, forms as an impurity in iron pentacarbonyl exposed to light. It is prepared more conveniently by photolysis of solutions of $Fe(CO)_5$ in cooled acetic acid. The material forms as shiny yellow-gold hexagonal platelets. The compound is sensitive and is best stored at reduced temperature under CO or an inert atmosphere. The crystals darken slowly at low temperature. The decomposition products include $Fe_3(CO)_{12}$ and finely divided iron, which can make the material pyrophoric. $Fe_2(CO)_9$ is insoluble in water, ether, and benzene and only slightly soluble in alcohols and acetone. The only solvent in which it has appreciable solubility without reaction is $Fe(CO)_5$. Diiron nonacarbonyl has a structure of approximately D_{3h} symmetry that consists of two face-sharing octahedra (ie, bridging carbonyl ligands at the three shared vertices) with the iron atoms further linked by an Fe–Fe bond. The reactivity of $Fe_2(CO)_9$ toward ligands is higher than that of $Fe(CO)_5$. The reactions of the compound give a variety of products, which frequently can also be obtained from $Fe(CO)_5$ or $Fe_3(CO)_{12}$.

Triiron dodecacarbonyl [12088-65-2], $Fe_3(CO)_{12}$, is prepared by heating $Fe_2(CO)_9$ to 60°C in a variety of inert organic solvents or by treatment of $Fe(CO)_5$ with alkali followed by MnO_2, a mild oxidizing agent. The compound forms very dark green monoclinic prismatic crystals, which are soluble in a wide variety of solvents. The pure compound oxidizes slowly in air and is somewhat thermally unstable at room temperature. The structure of triiron dodecacarbonyl consists of a triangle of $Fe(CO)_4$ units connected by Fe–Fe single bonds, one of which is supported by two CO bridges. Triiron dodecacarbonyl is a useful compound for synthesis of iron carbonyl derivatives because it is more reactive than $Fe(CO)_5$ and more soluble and stable than $Fe_2(CO)_9$.

3.2. Metallocenes.

Bis(cyclopentadienyl)iron or ferrocene [102-54-5], $Fe(C_5H_5)_2$, is an air and thermally stable orange solid that sublimes above 100°C and melts at 173°C. It is insoluble in water but dissolves in alcohols, ether, and benzene. Ferrocene can be prepared by numerous methods, including the reaction of cyclopentadienyl anion, $C_5H_5^-$, with anhydrous $FeCl_2$. Its extensive reaction chemistry is notable for the aromaticity of the cyclopentadienyl rings, which readily undergo Friedel-Crafts acylation, alkylation, and metallation. It does not undergo reactions typical of conjugated dienes and resists catalytic hydrogenation. Attempts at direct nitration or halogenation result in oxidation to afford the red-blue dichroic ferricinium ion. The reversibility of the ferrocene/ferricinium couple leads to its use as an internal standard in electrochemistry.

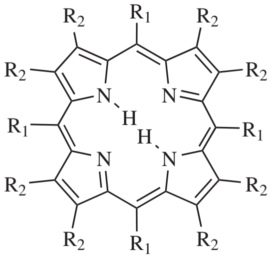
Bis(cyclopentadienyldicarbonyliron) [12154-95-9], $[Fe(CO)_2(C_5H_5)]_2$, is a purple-red, air-sensitive solid. It is frequently designated Fp_2 where Fp is an abbreviation for $(C_5H_5)Fe(CO)_2$. The compound is prepared by reacting $Fe(CO)_5$ and dicyclopentadiene at 135°C in an autoclave. Strong reducing agents cleave Fp_2 to Fp^- in polar aprotic solvents. The anion can be alkylated to afford $(C_5H_5)Fe(CO)_2R$ complexes, which in turn react with hydride abstracting reagents to afford cationic $(C_5H_5)Fe(CO)_2$(olefin) complexes. Both of these mononuclear compounds have considerable utility in organic syntheses (18,20).

4. Compounds of Biochemical Relevance

Iron is perhaps the most important of the transition elements that play a role in biochemistry. It is an essential element for all organisms. The functions of iron-containing metalloproteins include electron transfer, dioxygen transport and storage, activation of dioxygen and hydrogen peroxide with concurrent oxidation of substrates, dismutation of superoxide and peroxide, activation and production of dihydrogen, reduction and rearrangement of substrates, and phosphate hydrolysis, among others. Because of the near total insolubility of iron under physiological conditions, iron metalloproteins and chelate compounds function in the solubilization, uptake, transport, and storage of iron.

Iron-containing proteins are classified as either heme proteins or nonheme iron proteins. The former contain iron that is coordinated to a porphyrin ligand.

4.1. Iron Porphyrins. Porphyrins (21,22) are aromatic cyclic compounds that consist of four pyrrole units linked at the α-positions by methine carbons. The extended π-systems of these compounds give rise to intense absorption bands in the uv/vis region of the spectrum. The most intense absorption, which is called the Soret band, falls near 400 nm and has $\varepsilon_M \sim 10^5$. The π-system is also responsible for the notable ring current effect observed in ^{1}H-nmr spectra, the preference for planar conformations, the prevalence of electrophilic substitution reactions, and the redox chemistry of these compounds. Porphyrins obtained from natural sources have a variety of peripheral substituents and substitution patterns. Two important types of synthetic porphyrins are the meso-tetraaryl porphyrins, such as 5,10,15,20-tetraphenylporphine [917-23-7] (H_2(TPP)) (**7**) and β-octaalkylporphyrins, such as 2,3,7,8,12,13,17,18-octaethylporphine [2683-82-1] (H_2(OEP)) (**8**). Both types can be prepared by condensation of pyrroles and aldehydes (qv).



(7) $R_1 = C_6H_5$, $R_2 = H$
(8) $R_1 = H$, $R_2 = C_2H_5$

Reaction of free-base porphyrin compounds with iron(II) salts in an appropriate solvent results in loss of the two N−H protons and insertion of iron into the tetradentate porphyrin dianion ligand. Five-coordinate iron(III) porphyrin complexes (hemins), which usually have the anion of the iron(II) salt for the fifth or axial ligand, are isolated if the reaction is carried out in the presence of air. Iron(II) porphyrin complexes (hemes) can be isolated if the reaction and workup is conducted under rigorously anaerobic conditions. Typically, however, iron(II) complexes are obtained from iron(III) porphyrin complexes by reduction with dithionite, thiolate, borohydride, chromous ion, or other reducing agents.

Four-coordinate iron(II) porphyrin complexes have the iron atom centered in the plane of the porphyrin, are $S = 1$ intermediate-spin compounds, and can coordinate one or two axial ligands. Five-coordinate iron(II) complexes are square pyramidal where the iron is displaced (up to 50 pm) substantially from the plane. These are high spin, $S = 2$ compounds unless the axial ligand is a strong π-acceptor, in which case the compound has an $S = 0$ spin state. The iron atom moves back toward or into the porphyrin plane in six-coordinate complexes. These remain high spin with weak field axial ligands, but are low spin for stronger field ligands like amines, pyridines, imidazoles, and cyanide. The two stepwise formation constants for coordination of weak field ligands decrease, permitting five-coordinate complexes to be characterized in solution or isolated. Owing to the spin-state change on coordination of a second strong field ligand, the second formation constants for these ligands are usually substantially larger than the first. Thus five-coordinate complexes of strong field ligands are not isolated or observed in solution unless the steric bulk of the ligand precludes formation of a six-coordinate complex.

Iron(II) porphyrins react rapidly with O_2 to afford μ-oxo-bridged complexes $[Fe(III)Por]_2O$ where Por is porphyrin. Antiferromagnetic coupling of the two high spin iron atoms reduces the room temperature magnetic moment to about 1.7×10^{-23} J/T ($1.8\,\mu_B$/Fe). The reaction involves coordination of O_2 to the heme followed by reaction of another a second equivalent of heme to afford a μ-peroxy-bridged $[Fe(III)Por]_2O_2$ intermediate, homolysis to afford two equivalents of an oxo iron(IV) intermediate, and reaction with yet another equivalent of heme to yield the μ-oxo product. In the presence of a reducing agent and a strong field ligand like pyridine or cyanide, both iron(II) and iron(III) porphyrins react with O_2 to afford complexes of oxidized porphyrins, Figure 1. In an initial step, a meso-hydroxy heme (**9**) results from introduction of one oxygen atom from O_2 at a meso position. Subsequent reaction leads to loss of the oxygenated meso carbon as CO and introduction of another oxygen atom at this site to give a verdoheme complex, ie an iron complex of 5-oxaporphyrin (**10**). Verdins (**11**), open chain tetrapyrrole compounds, result from subsequent opening of the verdoheme macrocycle. These transformations are analogous to the oxidative degration of hemes that is carried out by the enzyme heme oxygenase (23).

Reversible binding of dioxygen, O_2, to the heme can occur if steric encumberance of the O_2 binding site prevents the approach of a second heme. This is the basis of the success of synthetic O_2 binding complexes like picket fence porphyrins. Clearly, one function of the protein surrounding the heme site in the biological oxygen carriers myoglobin and hemoglobin is to isolate the oxygen and prevent its irreversible oxidation. A second function in hemoglobin is to mediate cooperative binding of O_2 by the four heme sites in each molecule. The movement of the iron atom with respect to the porphyrin plane upon O_2 binding is thought to play an important role in cooperativity.

All iron(III) porphyrin complexes are five- or six-coordinate. In five-coordinate complexes the fifth ligand can be one of a variety of anions including halides, carboxylates, alkyls, alkoxides, phenoxides, pseudohalides, and mercaptides among others. Most can be prepared from the conjugate acid of the ligand and the μ-oxo complex or by metathesis with the chloride complex. Typically, five-coordinate complexes are high spin ($S = 5/2$) and have iron displaced roughly 50 pm from the porphyrin plane toward the ligand. The displacement of iron in complexes of weak anionic ligands like ClO_4^- decreases to about 25 pm. As a consequence, the $dx^2{-}y^2$ orbital is destabilized and the complex adopts an intermediate-spin state. Organometallic alkyl–iron porphyrin complexes are low spin ($S = 1/2$). Although five-coordinate complexes form adducts with added ligand, the formation constants are relatively small owing to the strong trans-effect of the anionic ligand. Six-coordinate FePorLX complexes can be observed in solution, but generally are not isolable or the sole species in solution. With strong ligands or an excess of ligand, the anionic ligand can be displaced to afford cationic, six-coordinate complexes $[FePorL_2]X$, which may be either high or low spin. The iron atom is centered or nearly centered in the porphyrin plane in both cases.

The reduction potential of the iron(III)/ iron(II) couple is strongly affected by the number and identity of the axial ligands present. Moreover, spin-state and structural changes, ie Fe−N and Fe−L bond lengths and Fe displacement, can occur concurrently with electron transfer, which affects the electron-transfer rate. In this light, the variation of axial ligands to the heme group in cytochrome proteins can be interpreted as a mechanism to vary the potential of the protein. The rapidity of the electron transfer in certain cytochromes such as cytochrome *c* can be attributed to the low spin nature of both members of the redox couple of the protein and the small changes in structure and bond lengths that therefore occur.

The porphyrin ligand can support oxidation states of iron other than II and III. $[Fe(I)Por]^-$ complexes are obtained by electrochemical or chemical reduction of iron(II) or iron(III) porphyrins. The anionic complexes react with alkyl halides to afford alkyl−iron(III) porphyrin complexes. Iron(IV) porphyrins are formally present in the carbene, RR′C−Fe(IV)Por; μ-carbido, PorFe(IV)—C—Fe(IV)Por; nitrene, RN−Fe(IV)Por; and μ-nitrido, PorFe(IV)−N−Fe(IV)Por complexes. Oxo iron(IV) porphyrin cation radical complexes, $[O{-}Fe(IV)Por^{\bullet}]^+$, are important intermediates in oxygen atom transfer reactions. Compound I of the enzymes catalase and peroxidase have this formulation, as does the active intermediate in the catalytic cycle of cytochrome P_{450}. Similar intermediates are invoked in the extensively investigated hydroxylations and epoxidations of hydrocarbon substrates catalyzed by iron porphyrins in the presence of such oxidizing agents as iodosylbenzene, NaOCl, peroxides, and air. An iron porphyrin-like molecule conjugated with an anticancer drug has been reported (24). This complex is said to minimize treatment effects on noncancerous tissue.

4.2. Iron Sulfur Compounds. A large number of compounds are known in which iron is tetrahedrally coordinated by a combination of thiolate and sulfide donors. Figure 2 shows four particularly important classes of iron sulfur compounds that are known to occur in proteins (25). The mononuclear iron site (12) occurs in the one-iron bacterial electron-transfer protein rubredoxin. The [2Fe−2S] (13) and [4Fe−4S] (15) cubane structures are found in the 2-, 4-, and 8-iron ferredoxins, which are also electron-transfer proteins. The [3Fe−4S] voided cubane structure (14) has been found in some ferredoxins and in the inactive form of aconitase, the enzyme which catalyzes the stereospecific hydration−rehydration of citrate to isocitrate in the Krebs cycle. A linear isomer of the [3Fe−4S] is also known. Iron sulfur compounds that contain other metals and types of ligands or are bridged to other metal coordination sites exist in several important enzymes (26). Examples include [4Fe−4S] clusters bridged to a heme group in sulfite reductase, to an $Fe_2(CO)_2(CN)_2$ (μ-X) site in [Fe]-hydrogenase, and to a Ni_2 (peptide) site in [NiFe]-carbon monoxide dehydrogenase; the $(Cys)_2Ni(\mu\text{-}Cys)_2Fe(CO)_3$ site in [NiFe]-hydrogenase; and the (homocitrate)(His)

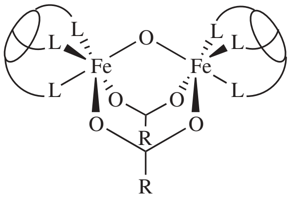
$MoFe_7$ (μ-S)$_3$ (μ_3-S)$_6$ (μ_6-X) core of the Iron-Molybdenum Cofactor of nitrogenase. The μ_6 light atom at the center of the FeMo-cofactor was not detected until higher resolution structer determinations were performed (27). The absence of this light atom in initial reports suggested that the six central iron atoms of the cofactor had trigonal planar coordination and prompted investigations of the chemistry of three coordinate iron (2,3).

Low molecular weight complexes that are synthetic analogues of the protein sites have been prepared and extensively investigated in the cases of structures (**12**), (**13**), and (**15**). The compounds, which are typically isolated as tetraalkylammonium salts, assemble spontaneously from a reaction system that includes an iron salt (usually $FeCl_3$), thiolate, a source of labile S^{2-} (elemental sulfur or HS^-), and a counterion. Individual compounds can be prepared selectively by variation of the ratios of reactants. Both the iron(II) and iron(III) states of the mononuclear cluster are high spin. Strong intramolecular antiferromagnetic coupling occurs in the cluster compounds, which contain bridging sulfides. Several specific oxidation states of the clusters are mixed valence compounds. $[Fe_2S_2(SR)_4]^{3-}$ has a localized iron(II) and a localized iron(III). In contrast, localized iron(II) and iron(III) sites are not observed for the [4Fe−4S] compounds, all of which have mixed valent oxidation states. The redox activity of these compounds parallels the states but not the potentials observed in the proteins. Substitution reactions of the terminal thiolate ligands are also noteworthy.

Several iron sulfide nitrosyl compounds are known. These have structures that in some cases are formally related to the FeS clusters by replacement of thiolate by NO. The compounds include the anions $[Fe_2S_2(NO)_4]^{2-}$ and $[Fe_4S_3(NO)_7]^-$ (Roussin's red and black salts, respectively) and the neutral compounds $[Fe_2S_2(NO)_4]$ and $[Fe_4S_4(NO)_4]$. Roussin's black salt has found use as a NO releasing vasodilator.

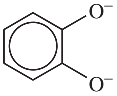
4.3. (μ-Oxo)bis(μ-carboxylato) Diiron Complexes. Several nonheme iron proteins of widely varying function contain a binuclear iron site as a common structural feature. The proteins include hemerythrin, the O_2-transport protein of marine invertebrates; ribonucleotide reductase, an enzyme which catalyzes the deoxygenation of ribonucleoside diphosphates to deoxyribonucleosides; methane monooxygenase, an enzyme which catalyzes the oxidation of methane to methanol; and purple acid phosphatases, which catalyze the dephosphorylation of phosphoproteins and nucleotides. The site contains two antiferromagnetically coupled iron atoms that are coupled by a bridging oxo or hydroxo group and two bridging carboxylate groups and is recognizable as a portion of the basic ferric acetate structure. The enzymes differ in the nature of the terminal ligands to each iron.

The thermodynamic stability of the binuclear site has been demonstrated by the spontaneous assembly of $[Fe_2O(O_2CR)_2L_2]$ (**16**) from ferric salts in the presence of water, an alkyl carboxylate salt, and a tridentate nitrogen donor ligand L that can cap an octahedral face on iron (**14**). Suitable ligands include tris(pyrazolyl)borates and 1,4,7-triazacyclononanes. Structure (**16**) is in essence a portion of the basic ferric acetate structure. The complexes are excellent physical and structural models of the diiron sites and model some aspects of reactivity including redox activity and interconversion of the oxo and hydroxo bridge.

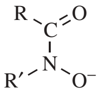


(**16**)

4.4. Siderophores. Iron is not readily available at physiological pH because it is present as the insoluble hydrated iron(III) oxide, which has $K_{sp} \sim 10^{-39}$. Bacteria synthesize chelating agents to facilitate the solubilization of iron from the environment, transport into the organism, and release of iron. Most contain negatively charged oxygen-donor groups which preferentially complex iron(III) and afford octahedral, high spin complexes called siderophores (28, 29). The two principal classes of donor groups employed are catecholates (**17**) and hydroxamates (**18**).



(**17**)



(**18**)

Enterobactin (ent), the cyclic triester of 2,3-dihydroxy-*N*-benzoyl-1-serine, uses three catecholate dianions to coordinate iron. The iron(III)-enterobactin complex [62280-34-6] has extraordinary thermodynamic stability. For $Fe^{3+} + ent^{6-}$, the estimated formal stability constant is 10^{49} and the reduction potential is approximately -750mV at pH 7 (29). Several catecholate-containing synthetic analogues of enterobactin have been investigated and found to have lesser, but still impressively large, formation constants.

Two types of hydroxamate-containing siderophores are known. Ferrichromes are cyclic polypeptides that have three appended hydroxamic acid side chains. Ferrioxamines, which may be linear or cyclic compounds, contain three hydroxamic acids as an integral part of the main backbone rather than as appended side chains. Variants of these compounds, which differ in their substituent groups, can be isolated from different bacteria. The formation constants of these iron(III) complexes typically approach 10^{30}. The free ligand of the complex is designated by adding the prefix deferri- to its name. One of these ligands, deferriferrioxamine B, is marketed as Desferal and is used to treat iron overload from accidental poisoning, chronic transfusions, or Cooley's anemia.

Although high spin iron(III) complexes are usually kinetically labile, siderophores are inert and can be resolved into individual optical isomers. An important issue, then, is how the microorganism releases iron from the siderophore. The redox potential of iron-enterobactin is probably too negative for reduction to iron(II), which would be more labile, to occur under physiological conditions. Suggestions include cleavage of the siderophore backbone and protonation of the chelate groups.

5. Economic Aspects

Prices of representative iron compounds in 2003 U.S. dollars are listed in Table 1. Suppliers include Aldrich, Alfa/Aesar, Cerac, Fisher, GFS Chemicals, and Pressure Chemical, among others.

5.1. Iron Oxide Pigments. U. S. output of finished natural (mined) iron oxide pigments sold by processors in 2002 was 60,000 t. This represented 14% less than the amount produced in 2001. Output of finished synthetic iron oxide pigments was 54,600 t, which was a decrease of 16% from 2001. The largest use for iron oxide pigments in 2002 was construction (34%) and coatings (21%). Transparent iron oxide pigments are used for automotive applications. Transparent pigments in coatings protect against uv light exposure (30).

Average prices for year end 2002 were \$2.07/kg for black, \$1.16–2.14/kg for natural, buff domestic, and \$2.25–2.34/kg for synthetic yellow. These prices are gerneral guidelines for bags, per truckload, fob warehouse (30).

5.2. Ferric Chloride. U. S. producers prepared 421,755 t of ferric chloride in 2002. The growth rate for the period 1997–2002 was 1.2% per year. Growth is projected at 2.0% per year through the year 2006. Ferric chloride's biggest use is in water treatment as follows: municipal wastewater treatment (60%); municipal potable wter treatment (20%), industrial water treatment (8%). Use in treatment of industrial water has advanced at a modest rate of 0.5%. Ferric chloride is acidic and less corrosive materials are preferred in this market (12).

Historical price information for 1997–2002 was \$290–340/t. Current price range is \$340–360/t (12).

5.3. Ferrous Sulfate. U. S. producers prepared 207,703 t of ferrous sulfate in 2002. Growth for the period 1997–2002 was 0%. Growth was projected at 2.0% through 2003. Dry ferrous sulfate's primary uses are in animal feeds (30%), water treatment (30%), and fertilizers (25%). Moist and liquid ferrous sulfate is used in the production of iron oxide (60%), and water treatment (30%). The uses in animal feeds and as fertilizers represent stable markets (16).

Historical price information for 1997–2002 was \$160–175/t heptahydrate. Current price is \$175/t. Bulk price for the monohydrate powder is \$265/t, \$300/t for granular monohydrate. The price for the moist product is \$15/t (16).

6. Analytical Methods

6.1. Gravimetric. Soluble iron samples may be analyzed by precipitation of iron(III) as the hydrated oxide, followed by heating to 900–1000°C to achieve a constant weight of anhydrous Fe_2O_3. The sample must be free of interfering ions, eg, those of aluminum, chromium, titanium, and manganese. The sample is first heated with nitric acid to convert all iron present to iron(III) and then is treated with an excess of ammonia to precipitate hydrated iron(III) oxide as a gelatinous mass. The precipitate is collected on ashless filter paper and is washed with hot 1% ammonium nitrate solution. Paper and precipitate are transferred to a porcelain crucible and ignited.

6.2. Volumetric. Analysis of iron solutions requires reduction of all of the iron present to iron(II). This is often accomplished by use of a Jones reductor. The solution of iron(II) may then be titrated with a standardized solution of potassium permanganate, potassium dichromate, cerium(IV) sulfate, or cerium(IV) perchlorate. Titration with permanganate can be complicated by its tendency to oxidize chloride ion, by the temporal instability of permanganate solutions, and by the possibility of uncertain stoichiometry in the reaction. These problems are eliminated by titration with cerium(IV), but it is considerably more expensive, must be used in acidic solution, and requires an indicator such as 1,10-phenanthroline. An indicator, usually diphenylaminesulfonic acid, is also required for titration with potassium dichromate. Dichromate is not as strong an oxidant as either permanganate or cerium(IV) and sometimes may react sluggishly. An advantage of potassium dichromate standard solutions is that they may be prepared directly by weight from the primary standard salt.

6.3. Colorimetric. A sensitive method for the determination of small concentrations of dissolved iron is the spectrophotometric determination of the orange-red tris(1,10-phenanthroline)iron(II) complex. Other substituted phenanthrolines can be even more sensitive. Only the iron(II) complexes of these ligands are highly colored. The sample is first treated with an excess of reducing agent. The complexes are stable from pH 2–9 and analysis preferably is done at about pH 3.5.

Small concentrations of iron can also be determined by flame atomic absorption and inductively coupled plasma emission spectroscopies (see SPECTROSCOPY, OPTICAL).

7. Health and Safety Factors

Most iron salts and compounds may be safely handled following common safe laboratory practices. Some compounds are irritants. A more serious threat is ingestion of massive quantities of iron salts which results in diarrhea, hemorrhage, liver damage, heart damage, and shock. A lethal dose is 200–250 mg/kg of body weight. The majority of the victims of iron poisoning are children under five years of age.

Two compounds associated with particular industrial risks are iron(III) oxide, Fe_2O_3, and iron pentacarbonyl, $Fe(CO)_5$. Chronic inhalation of iron(III) oxide leads to siderosis. Adequate ventilation and mechanical filter respirators should be provided to those exposed to the oxide. Iron pentacarbonyl is volatile and highly toxic.

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Table 1. **U.S. Prices for Iron Compounds, 2003**

Compounds	Formula	CAS Registry number	Price,[a] $/kg
iron(II) acetate[b]	$Fe(C_2H_3O_2)_2$	[3094-87-9]	2180
iron(III) acetate (basic)	[c]	[10450-55-2]	408
iron(III) ammonium citrate	[c]	[1185-57-5]	48
iron(II) bromide[d]	$FeBr_2$	[7789-46-0]	1210
iron(II) bromide hydrate	$FeBr_2 \cdot xH_2O$	[13463-12-2]	1160
iron(III) bromide[e]	$FeBr_3$	[10031-26-2]	1920
iron pentacarbonyl[d]	$Fe(CO)_5$	[13463-40-6]	90
diiron nonacarbonyl[e]	$Fe_2(CO)_9$	[15321-51-4]	1620
triiron dodecacarbonyl[f]	$Fe_3(CO)_{12}$	[17685-52-8]	2460
iron(II) chloride[d]	$FeCl_2$	[7758-94-3]	626
iron(II) chloride tetrahydrate[e]	$FeCl_2 \cdot 4H_2O$	[13478-10-9]	91
iron(III) chloride[g]	$FeCl_3$	[7705-08-0]	16
iron(III) chloride hexahydrate[b]	$FeCl_3 \cdot 6H_2O$	[10025-77-1]	60
potassium ferrocyanide trihydrate	$K_4[Fe(CN)_6] \cdot 3H_2O$	[14459-95-1]	92
potassium ferricyanide[e]	$K_3[Fe(CN)_6]$	[13746-66-2]	69
sodium pentacyanonitrosylferrate[e]	$Na_2[Fe(CN)_5NO] \cdot 2H_2O$	[13755-38-9]	382
Prussian Blue (ferric ferrocyanide)	$Fe_4[Fe(CN)_6]_3$[b]	[25869-98-1]	580
iron(II) fluoride[e]	FeF_2	[7798-28-8]	2440
iron(III) fluoride[e]	FeF_3	[7783-50-8]	1360
iron(III) fluoride trihydrate[g]	$FeF_3 \cdot 3H_2O$	[15469-38-2]	616
iron(II) iodide[d]	FeI_2	[7783-86-0]	2028
iron(II) iodide tetrahydrate[e]	$FeI_2 \cdot 4H_2O$	[13492-45-0]	2662
iron(III) nitrate nonahydrate[g]	$Fe(NO_3)_3 \cdot 9H_2O$	[7782-61-8]	21
iron(II) oxalate dihydrate[e]	$FeC_2O_4 \cdot 2H_2O$	[6047-25-2]	48
iron(III) oxalate hexahydrate	$Fe_2(C_2O_4)_3 \cdot 6H_2O$	[19469-07-9]	1850
iron(II) oxide[d]	FeO	[1345-25-1]	1956
iron(III) oxide[h]	Fe_2O_3	[1309-37-1]	10
iron(II,III) oxide[g]	Fe_3O_4	[1317-61-9]	12
iron(III) 2,4-pentanedionate[e]	$Fe(C_5H_7O_2)_3$	[14024-18-1]	168
iron(II) perchlorate hexahydrate	$Fe(ClO_4)_2 \cdot 6H_2O$	[13933-23-8]	83
iron(III) perchlorate hexahydrate	$Fe(ClO_4)_3 \cdot 6H_2O$	[13537-24-1]	69
iron(II) phthalocyanine[i]	$Fe(C_{32}H_{16}N_8)$	[132-16-1]	4800
iron(II) sulfate · heptahydrate[e]	$FeSO_4 \cdot 7H_2O$	[7782-63-0]	63
iron(III) sulfate-hydrate	$Fe_2(SO_4)_3 \cdot xH_2O$	[15244-10-7]	59
iron(II) ammonium sulfate	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	[7783-85-9]	84
iron(II) sulfide[e]	FeS[b]	[1317-37-9]	122
iron disulfide[h]	FeS_2	[12068-85-8]	1464
ferrocene[e]	$Fe(C_5H_5)_2$	[102-54-5]	120

[a] Retail price in U.S. $ from fine chemical supply houses. Price may be substantially discounted for larger quantities, and varies with grade.

[b] 97%.

[c] Nonstoichiometric compound.

[d] 99.5%.

[e] 99%.

[f] Stablized with 5–10% methanol.

[g] 98%.

[h] 99.9%.

[i] 95+%.

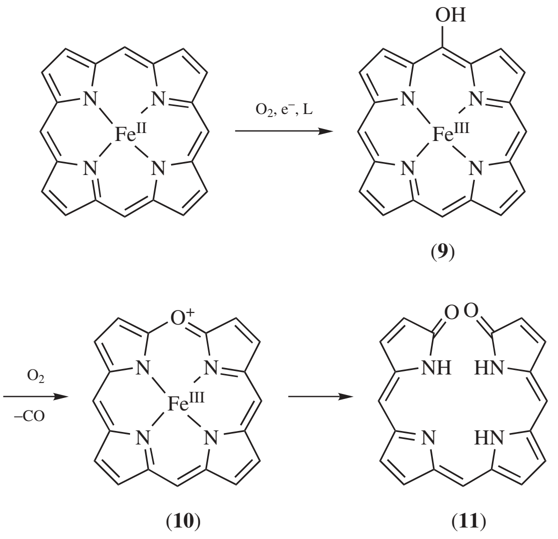

Fig. 1. Step-wise coupled oxidation of heme to meso-hydroxyheme (9), verdoheme (10), and verdin (11).

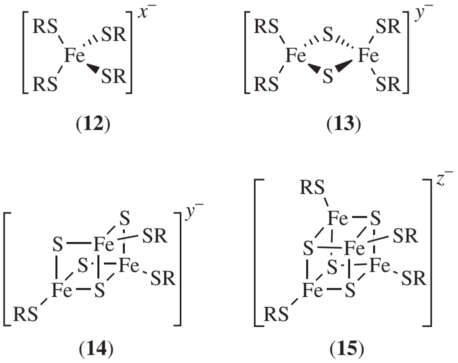

Fig. 2. Four important classes of iron compounds where x, y, and z represent 1 or 2, 2 or 3, and 1, 2, or 3, respectively. Structure (13) is a 2Fe–2S center; (14), a 3Fe–4S; and (15) a 4Fe–4S.