Chapter 24

THE ELEMENTS OF THE FIRST TRANSITION SERIES

As we have seen from their position in the periodic table (Section 2-5), the metals of the first transition series show variable valency. In this chapter we first discuss some of their common features and then consider the chemistry of individual elements.

24-1 The Metals

The metals are hard, refractory, electropositive, and good conductors of heat and electricity. The exception is copper, a soft and ductile metal, relatively noble, but second only to Ag as a conductor of heat and electricity. Some properties are given in Table 24-1. Manganese and iron are attacked fairly readily but the others are generally unreactive at room temperature. All react on heating with halogens, sulfur, and other nonmetals. The carbides, nitrides, and borides are commonly nonstoichiometric, interstitial, hard, and refractory.

24-2 The Lower Oxidation States

The oxidation states are given in Table 24-2, the most common and important (especially in aqueous chemistry) in bold type. Table 24-2 also gives the *d* electron configurations. Their chemistry can be classified on this basis; for example, the d^6 series is V^{-I}, Cr^0, Mn^I, Fe^{II}, Co^{III}, and Ni^{IV}. Comparisons of this kind can occasionally emphasize similarities in spectra and magnetic properties. However, the differences in properties of the d^n species due to differences in the nature of the metal, its energy levels, and especially the charge on the ion, often exceed the similarities.

1. The oxidation states less than II. With the exception of copper, where copper(I) binary compounds and complexes and the Cu^+ ion are known, the chemistry of the I, 0, –I, and –II formal oxidation states is entirely concerned with:

- (a) π-Acid ligands such as CO, NO, PR_3, CN^-, and bpy.
- (b) Organometallic chemistry in which alkenes, acetylenes, or aromatic systems, such as benzene, are bound to the metal.

Table 24-1 Some Properties of the First Transition Series Metals

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
mp(°C)	1668	1890	1875	1244	1537	1493	1453	1083
Properties	Hard, corrosion resistant	Hard, corrosion resistant	Brittle, corrosion resistant	White, brittle, reactive	Lustrous, reactive	Hard, bluish color	Quite corrosion resistant	Soft and ductile, reddish color
Density ($g\ cm^{-3}$)	4.51	6.11	7.19	7.18	7.87	8.90	8.91	8.94
E^0 (V^a)	—[b]	−1.19	−0.91	−1.18	−0.44	−0.28	−0.24	+0.34
Solubility in acids	Hot HCl, HF	HNO_3, HF, concentrated H_2SO_4	dilute HCl, H_2SO_4	dilute HCl, H_2SO_4, and so on	dilute HCl, H_2SO_4, and so on	Slowly in dilute HCl	dilute HCl, H_2SO_4	HNO_3, hot concentrated H_2SO_4

[a] For $M_{aq}^{2+} + 2\ e^- = M(s)$.

[b] No + 2 ion in aqueous solution.

Table 24-2 Oxidation States of First Series Transition Elements[a]

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	0 d^5	0 d^6	0 d^7	0 d^8	0 d^9	**0** d^{10}	
	1 d^4	1 d^5	**1** d^6		**1** d^8	1 d^9	**1** d^{10}
2 d^2	2 d^3	**2** d^4	**2** d^5	**2** d^6	**2** d^7	**2** d^8	**2** d^9
3 d^1	**3** d^2	**3** d^3	**3** d^4	**3** d^5	**3** d^6	3 d^7	3 d^8
4 d^0	**4** d^1	4 d^2	4 d^3	**4** d^4	4 d^5	4 d^6	
	5 d^0	5 d^1	5 d^2		5 d^4		
		6 d^0	6 d^1	6 d^2			
			7 d^0				

[a] Formal negative oxidation states are known in compounds of π-acid ligands, for example, Fe^{-II} in $[Fe(CO)_4]^{2-}$, Mn^{-1} in $[Mn(CO)_5]^-$, and so on.

There is an extensive chemistry of mixed compounds such as $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ or $(\eta^4\text{-}C_4H_6)Fe(CO)_3$. These topics are described in Chapters 28 and 29. Some organometallic compounds in higher oxidation states are known, however, mainly for the cyclopentadienyl ligand as in $(\eta^5\text{-}C_5H_5)_2Ti^{IV}Cl_2$, $(\eta^5\text{-}C_5H_5)_2Fe^{II}$, and $[(\eta^5\text{-}C_5H_5)_2Co^{III}]^+$. With π-acid or organic ligands, transition metals also form many compounds with bonds to hydrogen, for example, $H_2Fe(PF_3)_4$. Compounds with M—H bonds are very important in certain catalytic reactions (Chapter 30).

2. The II oxidation state. The binary compounds in this state are usually ionic. The metal oxides are basic; they have the NaCl structure but are often nonstoichiometric, particularly for Ti, V, and Fe. The *aqua ions,* $[M(H_2O)_6]^{2+}$, except for the unknown Ti^{2+} ion, are well characterized in solution and in crystalline solids. The potentials and colors are given in Table 24-3. Note that the V^{2+}, Cr^{2+}, and Fe^{2+} ions are oxidized by air in acidic solution.

The aqua ions may be obtained by dissolution of the metals, oxides, carbonates, and so on, in acids and by electrolytic reduction of M^{3+} salts. Hydrated salts with noncomplexing anions usually contain $[M(H_2O)_6]^{2+}$; typical ones are

$$Cr(ClO_4)_2 \cdot 6H_2O \qquad Mn(ClO_4)_2 \cdot 6H_2O \qquad FeF_2 \cdot 8H_2O \qquad FeSO_4 \cdot 7H_2O$$

However, certain *halide hydrates* do *not* contain the aqua ion. Thus $VCl_2 \cdot 4H_2O$ is *trans*-$VCl_2(H_2O)_4$, and $MnCl_2 \cdot 4H_2O$ is a polymer with *cis*-$MnCl_2(H_2O)_4$ units; the diaqua species of Mn, Fe, Co, Ni, and Cu have a linear polymeric edge-shared chain structure with *trans*-$[MCl_4(H_2O)_2]$ octahedra. The $FeCl_2 \cdot 6H_2O$ compound contains *trans*-$FeCl_2(H_2O)_4$ units.

The water molecules of $[M(H_2O)_6]^{2+}$ can be displaced by ligands such as NH_3, en, $EDTA^{4-}$, CN^-, and acac. The resulting complexes may be cationic, neutral, or anionic depending on the charge of the ligands. For Mn^{2+} complexes, the formation constants in aqueous solution are low compared with those of the other ions, because of the absence of ligand field stabilization energy in the d^5 ion (Section 23-8). In complexes the ions are normally *octahedral,* but for the Cu^{2+} and Cr^{2+} ions two H_2O molecules in trans positions are much further from the metal than the other four equatorial ones, because of the Jahn–Teller effect (Section 23-8). For Mn, the complex $[Mn(edta)H_2O]$ is seven coordinate. With halide ions, SCN^-, and some other ligands, *tetrahedral* species MX_4^{2-} and MX_2L_2 may be formed, the tendency being greatest for Co, Ni, and Cu.

Addition of OH^- to the M^{2+} solutions gives *hydroxides,* some of which can be obtained as crystals. The compounds $Fe(OH)_2$ and $Ni(OH)_2$ have the brucite, $Mg(OH)_2$, structure. On addition of HCO_3^- the carbonates of Mn, Fe, Co, Ni, and Cu are precipitated.

24-3 The III Oxidation State

All of the elements form at least some compounds in this state but for Cu only a few complexes, not stable toward water, are known.

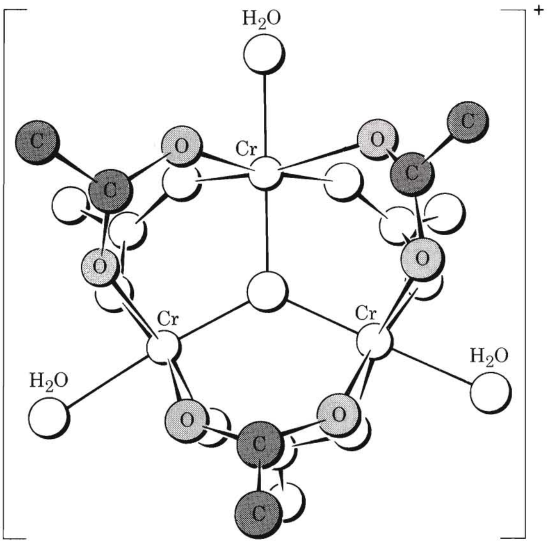
The fluorides (MF_3) and oxides (M_2O_3) are generally ionic but the chlorides, bromides, and iodides (where known), as well as sulfides and similar compounds, may have considerable covalent character.

The elements Ti to Co form octahedral ions, $[M(H_2O)_6]^{3+}$. The Co^{3+} and Mn^{3+} ions are very readily reduced by water (Table 24-3). The Ti^{3+} and V^{3+} ions are oxidized by air. In aqueous solution high acidities are required to prevent hydrolysis, for example,

$$[Ti(H_2O)_6]^{3+} = [Ti(H_2O)_5OH]^{2+} + H^+ \quad K = 1.3 \times 10^{-4} \qquad (24\text{-}3.1)$$

Addition of OH^- to the solutions gives *hydrous oxides* rather than true hydroxides. In fairly concentrated halide solutions, complexes of the type $[MCl(H_2O)_5]^{2+}$, $[MCl_2(H_2O)_4]^+$, and so on, are commonly formed, and crystalline chlorides of V, Fe, and Cr are of the type *trans*-$[VCl_2(H_2O)_4]^+Cl^- \cdot 2H_2O$. The alums, such as $CsTi(SO_4)_2 \cdot 12H_2O$, or $KV(SO_4)_2 \cdot 12H_2O$ contain the hexaaqua ion as do certain hydrates like $Fe(ClO_4)_3 \cdot 10H_2O$.

There are many anionic, cationic, or neutral M^{III} complexes, which are mostly *octahedral.* For Cr^{III} and, especially for Co^{III}, hundreds of octahedral com-



24-I

Table 24-3 Standard Potentials[a] (V, Acid Solution) and Colors for $[M(H_2O)_6]^{2+}$ and $[M(H_2O)_6]^{3+}$

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu[b]
$M^{2+} + 2\,e^- = M$	—	−1.19	−0.91	−1.18	−0.44	−0.28	−0.24	+0.34
$M^{3+} + e^- = M^{2+}$	−0.37	−0.25	−0.41	+1.59	+0.77	+1.84	—	—
Color M^{2+}(aq)	—	Violet	Sky blue	Pale pink	Pale green	Pink	Green	Blue green
Color M^{3+}(aq)	Violet	Blue	Violet	Brown	v. Pale purple	Blue	—	—

[a] Some potentials depend on acidity and complexing anions, for example, for Fe^{3+}—Fe^{2+} in 1 *M* acids: HCl, +0.70; $HClO_4$, +0.75; H_3PO_4, +0.44; 0.5 *M* H_2SO_4, +0.68 V.

[b] $Cu^{2+} + e^- = Cu^+$; $E_0 = +0.15$ V; $Cu^+ + e^- = Cu$; $E_0 = +0.52$V.

plexes that are substitutionally inert are known. Representative octahedral complexes are $[TiF_6]^{3-}$, $[V(CN)_6]^{3-}$, $Cr(acac)_3$, and $[Co(NH_3)_6]^{3+}$.

The halides (MX_3) act as Lewis acids and form adducts, such as $VX_3(NMe_3)_2$, and $CrCl_3(thf)_3$, as well as the ionic species $[VCl_4]^-$, $[CrCl_4]^-$, and so on.

A special feature of the M^{3+} ions is the formation of basic carboxylates in which an O atom is in the center of a triangle of metal atoms (Structure 24-I). The latter are linked by carboxylate bridge groups, and the sixth coordination position is occupied by a water molecule or other ligand. This oxo-centered unit has been proved for carboxylates of V, Cr, Mn, Fe, Co, Ru, Rh, and Ir.

24-4 The IV and Higher Oxidation States

The IV state is the most important state for Ti, where the main chemistry is that of TiO_2 and $TiCl_4$ and derivatives. Although there are compounds like VCl_4, the main V^{IV} chemistry is that of the oxovanadium(IV) or vanadyl ion VO^{2+}. This ion can behave like an M^{2+} ion, and it forms many complexes that may be cationic, neutral, or anionic, depending on the ligand.

For the remaining elements, the IV oxidation state is not very common or well established except in fluorides, fluorocomplex ions, oxo anions, and a few complexes. Some tetrahedral compounds with —OR, —NR_2, or —CR_3 groups are known for a few elements, notably Cr; examples are $Cr(OCMe_3)_4$ and $Cr(1\text{-norbornyl})_4$.

The oxidation states V and above are known for V, Cr, Mn, and Fe in fluorides, fluorocomplexes or oxo anions (e.g., CrF_5, $KMnO_4$, and K_2FeO_4). All are powerful oxidizing agents.

TITANIUM

24-5 General Remarks: The Element

Titanium has the electronic structure $3d^24s^2$. The energy of removal of four electrons is so high that the Ti^{4+} ion may not exist and titanium(IV) compounds are covalent. There are some resemblances between Ti^{IV} and Sn^{IV} and their radii are similar. Thus TiO_2 (rutile) is isomorphous with SnO_2 (cassiterite) and is similarly yellow when hot. Titanium tetrachloride, like $SnCl_4$, is a distillable liquid readily hydrolyzed by water, behaving as a Lewis acid, and giving adducts with donor molecules. The bromide and iodide, which form crystalline molecular lattices, are also isomorphous with the corresponding Group IVB(14) halides.

Titanium is relatively abundant in the earth's crust (0.6%). The main ores are *ilmenite* ($FeTiO_3$) and *rutile,* one of the several crystalline varieties of TiO_2. The metal cannot be made by reduction of TiO_2 with C because a very stable carbide is produced. The rather expensive Kroll process is used. Ilmenite or rutile is treated at red heat with C and Cl_2 to give $TiCl_4$, which is fractionated to free it from impurities, such as $FeCl_3$. The $TiCl_4$ is then reduced with molten Mg at about 800 °C in an atmosphere of argon. This gives Ti as a spongy mass from which the excess of Mg and $MgCl_2$ is removed by volatilization at 1000 °C. The sponge may then be fused in an electric arc and cast into ingots; an atmosphere of Ar or He must be used since Ti readily reacts with N_2 and O_2 when hot.

Titanium is lighter than other metals of similar mechanical and thermal properties and is unusually resistant to corrosion. It is used in turbine engines and industrial chemical, aircraft, and marine equipment. It is unattacked by dilute acids and bases. It dissolves in hot HCl giving Ti^{III} chloro complexes and in HF or HNO_3 + HF to give fluoro complexes. Hot HNO_3 gives a hydrous oxide.

TITANIUM COMPOUNDS

The most important stereochemistries in titanium compounds are the following:

Ti^{II}	Octahedral	in most compounds and in solution
Ti^{III}	Octahedral	
Ti^{IV}	Tetrahedral	in $TiCl_4$, $Ti(CH_2C_6H_5)_4$, and so on
	Octahedral	in TiO_2 and Ti^{IV} complexes

24-6 Binary Compounds of Titanium

Titanium tetrachloride, a colorless liquid (bp 136 °C), has a pungent odor, fumes strongly in moist air, and is vigorously, though not violently, hydrolyzed by water.

$$TiCl_4 + 2\ H_2O = TiO_2 + 4\ HCl \qquad (24\text{-}6.1)$$

Partially hydrolyzed species are formed with a deficit of water or on addition of $TiCl_4$ to aqueous HCl.

Titanium oxide has three crystal forms—rutile (see Fig. 4-1), anatase, and brookite—all of which occur in nature. The dioxide that is used in large quantities as a white pigment in paints is made by vapor phase oxidation of $TiCl_4$ with oxygen. The precipitates obtained by addition of OH^- to Ti^{IV} solutions are best regarded as hydrous TiO_2, not a true hydroxide. This material is amphoteric and dissolves in concentrated NaOH.

Materials called "titanates" are of technical importance, for example, as ferroelectrics. Nearly all of them have one of the three major mixed metal oxide structures (Section 4-8). Indeed, the names of two of the structures are those of the titanium compounds that were the first found to possess them: $FeTiO_3$ (*ilmenite*) and $CaTiO_3$ (*perovskite*).

24-7 Titanium(IV) Complexes

Aqueous Chemistry: Oxo Salts

There is no firm evidence for the Ti^{4+} aqua ion. In aqueous solutions of Ti^{IV} there are only oxo species; basic oxo salts or hydrated oxides may be precipitated. These oxo salts have formulas such as $TiOSO_4 \cdot H_2O$ and $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$, and have chains or rings, $(Ti—O—Ti—O—)_x$. There is spectroscopic evidence for TiO^{2+} only in 2 M $HClO_4$ solution, although some compounds with a Ti=O group have been characterized.

Anionic Complexes

The solutions obtained by dissolving the metal or hydrous oxide in aqueous HF contain fluoro complex ions, mainly $[TiF_6]^{2-}$, which can be isolated as crystalline salts. In aqueous HCl, $TiCl_4$ gives yellow oxo complex anions but from solutions saturated with gaseous HCl, salts of the $[TiCl_6]^{2-}$ ion may be obtained.

Adducts of TiX_4

The halides form adducts, TiX_4L or TiX_4L_2, which are crystalline solids that are often soluble in organic solvents. These adducts are invariably *octahedral.* Thus $[TiCl_4(OPCl_3)]_2$ and $[TiCl_4(CH_3COOC_2H_5)]_2$ are dimeric, with two chlorine bridges, while $TiCl_4(OPCl_3)_2$ has octahedral coordination with *cis*-$OPCl_3$ groups.

Peroxo Complexes

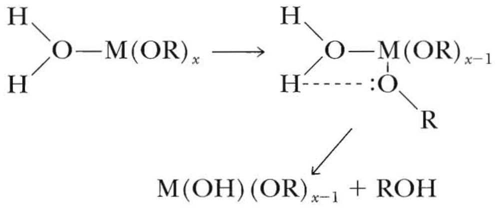
One of the most characteristic reactions of aqueous Ti solutions is the development of an intense orange color on addition of H_2O_2. This reaction can be used for the colorimetric determination of either Ti or of H_2O_2. Below pH 1, the main species is $[Ti(O_2)(OH)]^+(aq)$.

Solvolytic Reactions of $TiCl_4$: Alkoxides and Related Compounds

Titanium tetrachloride reacts with compounds containing active hydrogen atoms with loss of HCl. The replacement of chloride is usually incomplete in the absence of an HCl acceptor such as an amine or alkoxide ion. The *alkoxides* are typical of other transition metal alkoxides, which we shall not discuss. They can be obtained by reactions such as

$$TiCl_4 + 4\ ROH + 4\ R'NH_2 \longrightarrow Ti(OR)_4 + 4\ R'NH_3Cl \qquad (24\text{-}7.1)$$

The alkoxides are liquids or solids that can be distilled or sublimed. They are soluble in organic solvents such as benzene, but are exceedingly readily hydrolyzed by even traces of water, to give polymeric species with —OH— or —O— bridges. The initial hydrolytic step probably involves coordination of water to the metal; a proton on H_2O could then interact with the oxygen of an OR group through hydrogen bonding, leading to hydrolysis:



(24-7.2)

Although monomeric species can exist, for example, when made from secondary and tertiary alcohols, and in dilute solution, alkoxides are usually polymers. Solid $Ti(OC_2H_5)_4$ is a tetramer, with the structure shown in Fig. 24-1. The alkoxides are often referred to as "alkyltitanates" and under this name they are used in heat-resisting paints, where eventual hydrolysis to TiO_2 occurs.

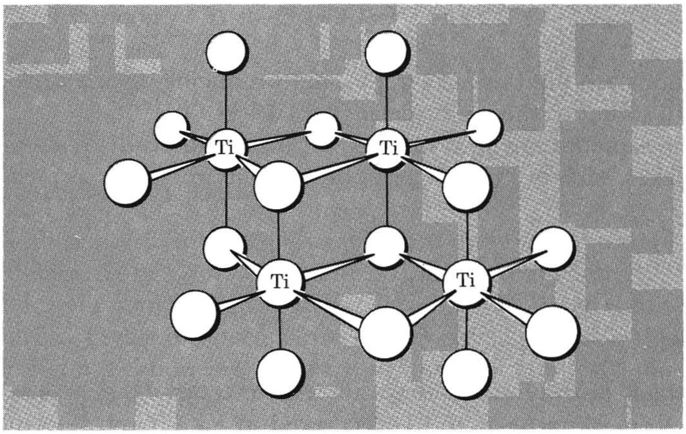


Figure 24-1 The tetrameric structure of $Ti(OC_2H_5)_4$. Only Ti and O atoms are shown. Each Ti is octahedrally coordinated.

Another class of titanium compounds, the *dialkylamides,* are also representative of similar compounds of other transition metals. These are liquids or volatile solids readily hydrolyzed by water. Unlike the alkoxides they are not polymeric. They are made by reaction of the metal halide with lithium dialkylamides:

$$TiCl_4 + 4\ LiNEt_2 = Ti(NEt_2)_4 + 4\ LiCl \tag{24-7.3}$$

Such amides can undergo a wide range of "insertion" reactions (Section 30-3); thus with CS_2, the dithiocarbamates are obtained.

$$Ti(NEt_2)_4 + 4\ CS_2 = Ti(S_2CNEt_2)_4 \tag{24-7.4}$$

24-8 The Chemistry of Titanium(III), d^1, and Titanium(II), d^2

Binary Compounds

Titanium trichloride ($TiCl_3$) has several crystalline forms. The violet α form is made by H_2 reduction of $TiCl_4$ vapor at 500–1200 °C. The reduction of $TiCl_4$ by aluminum alkyls (Section 30-10) in inert solvents gives a brown β form that is converted into the α form at 250–300 °C. The α form has a layer lattice containing $TiCl_6$ groups. The β-$TiCl_3$ is fibrous with single chains of $TiCl_6$ octahedra sharing edges. This structure is of particular importance for the stereospecific polymerization of propene using $TiCl_3$ as catalyst (Ziegler–Natta process) (Section 30-9).

The *dichloride* is obtained by high temperature syntheses:

$$TiCl_4 + Ti = 2\ TiCl_2 \tag{24-8.1}$$

or

$$2\ TiCl_3 = TiCl_2 + TiCl_4 \tag{24-8.2}$$

Aqueous Chemistry and Complexes

Aqueous solutions of the $[Ti(H_2O)_6]^{3+}$ ion are obtained by reducing aqueous Ti^{IV} either electrolytically or with zinc. The violet solutions reduce O_2 and, hence, must be handled in a N_2 or H_2 atmosphere.

$$\text{“TiO}^{2+}\text{(aq)”} + 2\,\text{H}^+ + e^- = \text{Ti}^{3+} + \text{H}_2\text{O} \qquad E^\circ = \text{about } 0.1\text{ V} \quad (24\text{-}8.3)$$

The Ti^{3+} solutions are used as fairly rapid, mild reducing agents in volumetric analysis. In HCl solutions the main species is $[TiCl(H_2O)_5]^{2+}$.

There is no aqueous chemistry of Ti^{II} because of its ready oxidation, but a few Ti^{II} complexes, such as $[TiCl_4]^{2-}$, can be made in nonaqueous media.

VANADIUM

24-9 The Element

Vanadium is widely distributed but there are few concentrated deposits. It occurs in petroleum from Venezuela, and is recovered as V_2O_5 from flue dusts after combustion.

Very pure vanadium is rare because, like titanium, it is quite reactive toward O_2, N_2, and C at the elevated temperatures used in metallurgical processes. Since its chief commercial use is in alloy steels and cast iron, to which it lends ductility and shock resistance, commercial production is mainly as an iron alloy, *ferrovanadium.*

Vanadium metal is not attacked by air, alkalis, or nonoxidizing acids other than HF at room temperature. It dissolves in HNO_3, concentrated H_2SO_4, and aqua regia.

VANADIUM COMPOUNDS

The stereochemistries for the most important classes of vanadium compounds are the following:

V^{II} } Octahedral as in $[V(H_2O)_6]^{2+}$
V^{III} } $VF_3(s)$ or $[V(ox)_3]^{3-}$
Tetrahedral as in VCl_4 or $V(CH_2SiMe_3)_4$
V^{IV} { Square pyramidal in $O{=}V(acac)_2$
{ Octahedral in VO_2, K_2VCl_6, $O{=}V(acac)_2py$, and so on
V^{V} { Octahedral as in $[VO_2(ox)_2]^{3-}$, $VF_5(s)$

24-10 Binary Compounds

Halides

In the highest oxidation state only VF_5 is known. The colorless liquid (bp 48 °C) has a high viscosity (cf. SbF_5, Section 17-4) and has chains of VF_6 octahedra linked by *cis*-V—F—V bridges; it is monomeric in the vapor.

The *tetrachloride* is obtained from $V + Cl_2$ or from CCl_4 on red-hot V_2O_5. It is a dark red oil (bp 154 °C), which is violently hydrolyzed by water to give solutions of oxovanadium(IV) chloride. It has a high dissociation pressure and loses chlorine slowly when kept, but rapidly on boiling, leaving violet VCl_3. The latter may be decomposed to pale green VCl_2, which is then stable.

$$2\ VCl_3(s) \longrightarrow VCl_2(s) + VCl_4(g) \qquad (24\text{-}10.1)$$

$$VCl_3(s) \longrightarrow VCl_2(s) + \tfrac{1}{2}\ Cl_2(g) \qquad (24\text{-}10.2)$$

Vanadium(V) Oxide

Addition of dilute H_2SO_4 to solutions of ammonium vanadate gives a brick-red precipitate of V_2O_5. This oxide is acidic and dissolves in NaOH to give colorless solutions containing the *vanadate* ion, $[VO_4]^{3-}$. On acidification, a complicated series of reactions occurs involving the formation of hydroxo anions and polyanions (cf. Section 5-4). In very strong acid solutions, the *dioxovanadium(V) ion* (VO_2^+) is formed.

24-11 Oxovanadium Ions and Complexes

The two oxo cations VO_2^+ and VO^{2+} have an extensive chemistry and form numerous complex compounds. All of the compounds show IR and Raman bands that are characteristic for M=O groups. The VO_2^+ group is angular. Examples of complexes are *cis*-$[VO_2Cl_4]^{3-}$, *cis*-$[VO_2\text{edta}]^{3-}$, and *cis*-$[VO_2(\text{ox})_2]^{3-}$. The cis arrangement for dioxo compounds of metals with no *d* electrons is preferred over the trans arrangement that is found in some other metal dioxo systems (e.g., $[RuO_2]^{2+}$) because the strongly π-donating O ligands then have exclusive use of one $d\pi$ orbital each (d_{xz}, d_{yz}) and share a third one (d_{xy}), whereas in the trans configuration they would have to share two $d\pi$ orbitals and leave one unused.

The oxovanadium(IV) or vanadyl compounds are among the most stable and important of vanadium species, and the VO unit persists through a variety of chemical reactions. Solutions of V^{3+} are oxidized in air, while V^V is readily reduced by mild reducing agents to form the blue oxovanadium(IV) ion, $[VO(H_2O)_5]^{2+}$:

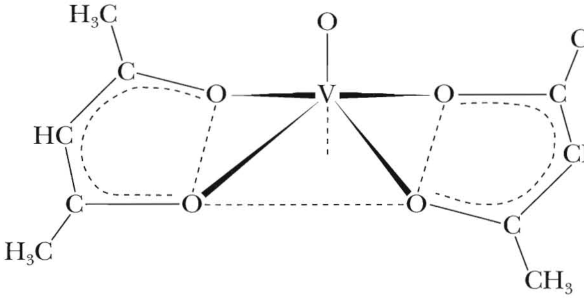
$$VO^{2+} + 2\ H^+ + e^- = V^{3+} + H_2O \qquad E^\circ = 0.34\ V \qquad (24\text{-}11.1)$$

$$VO_2^+ + 2\ H^+ + e^- = VO^{2+} + H_2O \qquad E^\circ = 1.0\ V \qquad (24\text{-}11.2)$$

Addition of base to $[VO(H_2O)_5]^{2+}$ gives the yellow hydrous oxide $VO(OH)_2$, which redissolves in acids giving the cation.

Oxovanadium(IV) compounds are usually blue green. They may be either five-coordinate square pyramidal (Structure 24-II) or six-coordinate with a distorted octahedron. Examples are $[VO(\text{bpy})_2Cl]^+$, $VO(\text{acac})_2$, and $[VO(NCS)_4]^{2-}$. The VO bonds are short (1.56–1.59 Å), and can properly be regarded as multiple ones, the π component arising from electron flow $O(p\pi) \rightarrow V(d\pi)$. Even in VO_2, which has a distorted rutile structure, one bond (1.76 Å) is conspicuously shorter than the others in the VO_6 unit (note that in TiO_2 all Ti—O bonds are substantially equal).

All of the five-coordinate complexes, such as Structure 24-II, take up a sixth ligand quite readily, becoming six coordinate.



24-II

24-12 The Vanadium(III) Aqua Ion and Complexes

The electrolytic or chemical reduction of acid solutions of vanadates or V^{IV} solutions gives solutions of V^{III} that are quite readily reoxidized to VO^{2+}. Crystalline salts can be obtained. Addition of OH^- precipitates the hydrous oxide V_2O_3.

24-13 Vanadium(II)

When V^{III} solutions are reduced by Zn in acid, violet air-sensitive solutions of $[V(H_2O)_6]^{2+}$ are obtained. These are oxidized by water with evolution of hydrogen despite the fact that the V^{3+}/V^{2+} potential (Table 24-3) suggests otherwise. Vanadium(II) solutions are often used to remove traces of O_2 from inert gases.

The salt $[V(H_2O)_6]SO_4$ is obtained as violet crystals on addition of ethanol to reduced sulfate solutions. Because of its d^3 configuration the $[V(H_2O)_6]^{2+}$ ion like $[Cr(H_2O)_6]^{3+}$ is kinetically inert, and its substitution reactions are relatively slow.

CHROMIUM

24-14 The Element Chromium

Apart from stoichiometric similarities, chromium resembles the Group VIB(16) elements of the sulfur group only in the acidity of CrO_3 and the covalent nature and ready hydrolysis of CrO_2Cl_2 (cf. SO_3, SO_2Cl_2).

The chief ore is *chromite*, $FeCr_2O_4$, which is a spinel with Cr^{III} on octahedral sites and Fe^{II} on the tetrahedral ones. It is reduced by C to the carbon-containing alloy ferrochromium.

$$FeCr_2O_4 + 4\ C \xrightarrow{\text{heat}} Fe \cdot 2Cr + 4\ CO \qquad (24\text{-}14.1)$$

When pure Cr is required, the chromite is first treated with molten NaOH and O_2 to convert the Cr^{III} to CrO_4^{2-}. The melt is dissolved in water and sodium dichromate is precipitated. This precipitate is then reduced.

$$Na_2Cr_2O_7 + 2\ C \xrightarrow{\text{heat}} Cr_2O_3 + Na_2CO_3 + CO \qquad (24\text{-}14.2)$$

Next, the oxide is reduced.

$$Cr_2O_3 + 2\,Al \xrightarrow{\text{heat}} Al_2O_3 + 2\,Cr \qquad (24\text{-}14.3)$$

Chromium is resistant to corrosion, hence its use as an electroplated protective coating. It dissolves fairly readily in HCl, H_2SO_4, and $HClO_4$, but it is passivated by HNO_3.

CHROMIUM COMPOUNDS

The most common stereochemistries for chromium compounds are the following:

Cr^{II}, Cr^{III} Octahedral as in $[Cr(H_2O)_6]^{2+}$ (distorted) or $[Cr(NH_3)_6]^{3+}$

Cr^{IV} Tetrahedral as in $Cr(O\text{-}t\text{-}Bu)_4$

Cr^{V}, Cr^{VI} Tetrahedral as in $[CrO_4]^{3-}$, $[CrO_4]^{2-}$, CrO_3

24-15 Binary Compounds

Halides

The anhydrous Cr^{II} halides are obtained by action of HCl, HBr, or I_2 on the metal at 600–700 °C or by reduction of the trihalides with H_2 at 500–600 °C. $CrCl_2$ dissolves in water to give a blue solution of the Cr^{2+} ion.

The red-violet trichloride, $CrCl_3$, is made by the action of $SOCl_2$ on the hydrated chloride. The flaky form of $CrCl_3$ is due to its layer structure.

Chromium(III) chloride forms adducts with donor ligands. The violet tetrahydrofuranate, *fac*-$CrCl_3(thf)_3$, which crystallizes from solutions formed by the action of a little zinc on $CrCl_3$ in thf, is a particularly useful material for the preparation of other chromium compounds, such as carbonyls or organometallic compounds.

Oxides

The green α-Cr_2O_3 (corundum structure) is formed on burning Cr in O_2, on thermal decomposition of CrO_3, or on roasting the hydrous oxide ($Cr_2O_3 \cdot nH_2O$). The latter, commonly called "chromic hydroxide," although its water content is variable, is precipitated on addition of OH^- to solutions of Cr^{III} salts. The hydrous oxide is amphoteric, dissolving readily in acid to give $[Cr(H_2O)_6]^{3+}$, and in concentrated alkali to form "chromites."

Chromium oxide and chromium supported on other oxides, such as Al_2O_3, are important catalysts for a wide variety of reactions.

Chromium(VI)oxide, CrO_3, is obtained as an orange-red precipitate on adding sulfuric acid to solutions of $Na_2Cr_2O_7$. It is thermally unstable above its melting point (197 °C), losing O_2 to give Cr_2O_3. The structure consists of infinite chains of CrO_4 tetrahedra sharing corners. This oxide is soluble in water and is highly poisonous.

Interaction of CrO_3 and organic substances is vigorous and may be explosive, but CrO_3 is used in organic chemistry as an oxidant, usually in acetic acid as solvent.

24-16 The Chemistry of Chromium(II), d^4

Aqueous solutions of the blue *chromium(II) ion* are best prepared by dissolving electrolytic Cr metal in dilute mineral acids. The solutions must be protected from air (Table 24-3)—even then, they decompose at rates varying with the acidity and the anions present, by reducing water with liberation of H_2.

The mechanisms of reductions of other ions by Cr^{2+} have been extensively studied, since the resulting Cr^{3+} complex ions are substitution inert. Much information regarding ligand-bridged transition states (Section 6-5) has been obtained in this way.

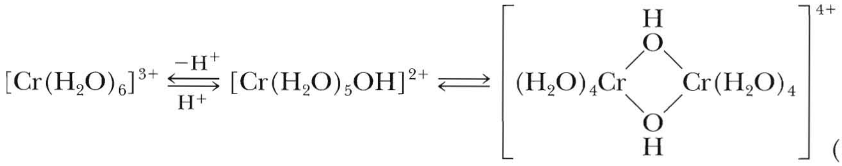
Chromium(II) *acetate,* $Cr_2(O_2CCH_3)_4(H_2O)_2$, is precipitated as a red solid when a Cr^{2+} solution is added to a solution of sodium acetate. Its structure is typical of carboxylate-bridged complexes with water end groups (Structure 24-X). The short Cr—Cr bond (2.36 Å) and diamagnetism are accounted for by the existence of a quadruple Cr—Cr bond, consisting of a σ, two π, and a δ component. This was the first compound containing a quadruple bond to be discovered (1844).

24-17 The Chemistry of Chromium(III), d^3

Chromium(III) Complexes

There are thousands of chromium(III) complexes which, with a few exceptions, are all six coordinate. The principal characteristic is their relative kinetic inertness in aqueous solutions. It is because of this that so many complex species can be isolated, and why much of the classical complex chemistry studied by early workers, notably S. M. Jørgensen and A. Werner, involved chromium. These complexes persist in solution, even where they are thermodynamically unstable.

The hexaaqua ion, $[Cr(H_2O)_6]^{3+}$, occurs in numerous salts, such as the violet hydrate, $[Cr(H_2O)_6]Cl_3$, and alums, $M^ICr(SO_4)_2 \cdot 12H_2O$. The chloride has three isomers, the others being the dark green *trans*-$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, which is the usual form, and pale green $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$. The ion is acidic and the hydroxo ion condenses to give a dimeric hydroxo bridged species.


(24-17.1)

On addition of further base, soluble polymeric species of high-molecular weight and eventually dark green gels of the hydrous oxide are formed.

The most numerous complexes are those of amine ligands. These ligands provide examples of virtually all the kinds of isomerism possible in octahedral complexes. In addition to the mononuclear species, for example, $[Cr(NH_3)_5Cl]^{2+}$, there are many polynuclear complexes in which two or sometimes more metal atoms are bridged by hydroxo groups or, less commonly, oxygen in a linear Cr—O—Cr group. A representative example is $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$.

24-18 The Chemistry of Chromium(IV), d^2, and Chromium(V), d^1

The most readily accessible of these rare oxidation states are those with bonds to C, N, and O. A representative synthesis is

$$CrCl_3(thf)_3 + 4\ LiCH_2SiMe_3 \xrightleftharpoons{\text{ether}} Li[Cr^{III}(CH_2SiMe_3)_4] + 3\ LiC \qquad (24\text{-}18.1)$$

$$[Cr(CH_2SiMe_3)_4]^- \rightleftharpoons Cr(CH_2SiMe_3)_4 + e^- \qquad (24\text{-}18.2)$$

The oxidation of the green Cr^{III} anion to the purple, petroleum-soluble Cr^{IV} compound can be made by air. The alkoxides and dialkylamides are similarly made from *fac*-$CrCl_3(thf)_3$; one example is the dark blue $Cr(OCMe_3)_4$.

For Cr^V some chromites containing CrO_4^{3-} are known. Reduction of CrO_3 with concentrated HCl in the presence of alkali ions at 0 °C gives salts $M_2[Cr^VOCl_5]$.

24-19 The Chemistry of Chromium(VI), d^0

Chromate and Dichromate Ions

In basic solutions above pH 6, CrO_3 forms the tetrahedral yellow *chromate* ion, CrO_4^{2-}. Between pH 2 and 6, $HCrO_4^-$ and the orange-red *dichromate* ion, $Cr_2O_7^{2-}$, are in equilibrium. At pH values below 1 the main species is H_2CrO_4. The equilibria are

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K = 10^{-5.9} \qquad (24\text{-}19.1)$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K = 4.1 \qquad (24\text{-}19.2)$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ HCrO_4^- \qquad K = 10^{-2.2} \qquad (24\text{-}19.3)$$

In addition, there are the base-hydrolysis equilibria

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-} \qquad (24\text{-}19.4)$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O \qquad (24\text{-}19.5)$$

The CrO_4^{2-} ion is tetrahedral; $Cr_2O_7^{2-}$ has the structure shown in Fig. 24-2.

The pH-dependent equilibria are quite labile and on addition of cations that form insoluble chromates (e.g., Ba^{2+}, Pb^{2+}, and Ag^+), the chromates and not the dichromates are precipitated. Only for HNO_3 and $HClO_4$ are the equilibria as given previously. When HCl is used, there is essentially quantitative conversion into the *chlorochromate* ion, while with sulfuric acid a sulfato complex results.

$$CrO_3(OH)^- + H^+ + Cl^- \longrightarrow CrO_3Cl^- + H_2O \qquad (24\text{-}19.6)$$

$$CrO_3(OH)^- + HSO_4^- \longrightarrow CrO_3(OSO_3)^{2-} + H_2O \qquad (24\text{-}19.7)$$

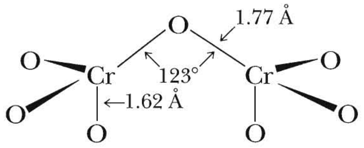


Figure 24-2 The structure of the dichromate ion as found in $Na_2Cr_2O_7$.

Acid solutions of dichromate are strong oxidants:

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- = 2\ Cr^{3+} + 7\ H_2O \qquad E^\circ = 1.33\ V \qquad (24\text{-}19.8)$$

In alkaline solution, the chromate ion is much less oxidizing:

$$CrO_4^{2-} + 4\ H_2O + 3\ e^- = Cr(OH)_3(s) + 5\ OH^- \qquad E^\circ = 0.13\ V \qquad (24\text{-}19.9)$$

Chromium(VI) does not give rise to the extensive and complex series of polyacids and polyanions characteristic of the somewhat less acidic oxides of V^V, Mo^{VI}, and W^{VI}. The reason for this is perhaps the greater extent of multiple bonding (Cr=O) for the smaller chromium ion.

Chromyl chloride (CrO_2Cl_2), a deep-red liquid, is formed by the action of HCl on chromium(VI) oxide:

$$CrO_3 + 2\ HCl \longrightarrow CrO_2Cl_2 + H_2O \qquad (24\text{-}19.10)$$

or on warming dichromate with an alkali metal chloride in concentrated sulfuric acid:

$$K_2Cr_2O_7 + 4\ KCl + 3\ H_2SO_4 \longrightarrow 2\ CrO_2Cl_2 + 3\ K_2SO_4 + 3\ H_2O \qquad (24\text{-}19.11)$$

It is photosensitive but otherwise rather stable, vigorously oxidizes organic matter, and is hydrolyzed by water to CrO_4^{2-} and HCl.

24-20 Peroxo Complexes of Chromium(IV), (V), and (VI)

Like other transition metals, notably Ti, V, Nb, Ta, Mo, and W, chromium forms peroxo compounds in the higher oxidation states. These complexes are all more or less unstable both in and out of solution, decomposing slowly with the evolution of O_2. Some are explosive or flammable in air.

When acid dichromate solutions are treated with H_2O_2, a deep blue color rapidly appears.

$$HCrO_4^- + 2\ H_2O_2 + H^+ \longrightarrow CrO(O_2)_2 + 3\ H_2O \qquad (24\text{-}20.1)$$

The blue species decomposes fairly readily, giving Cr^{3+}, but it may be extracted into ether where it is more stable. On addition of pyridine to the ether solution, the compound (py)CrO_5 is obtained. The pyridine complex has the bisperoxo structure shown in Fig. 24-3(*a*).

Treatment of alkaline chromate solutions with 30% H_2O_2 gives the red-brown peroxochromates, $M^I_3CrO_8$ [Fig. 24-3(*b*)], which are paramagnetic with one unpaired electron.

MANGANESE

24-21 The Element

The highest oxidation state of manganese corresponds to the total number of 3*d* and 4*s* electrons. It occurs in the oxo compounds MnO_4^-, Mn_2O_7, and MnO_3F and in amido complexes(Section 24-25). These compounds show some similarity to corresponding compounds of the halogens.

Manganese is relatively abundant, and occurs in substantial deposits, mainly oxides, hydrous oxides, or the carbonate. From them, or the Mn_3O_4 obtained by roasting them, the metal can be obtained by reduction with Al.

Manganese is quite electropositive, and readily dissolves in dilute, nonoxidizing acids.

MANGANESE COMPOUNDS

The most common stereochemistries of manganese compounds are the following:

$$\left.\begin{array}{l}\mathrm{Mn^{II}}\\ \mathrm{Mn^{III}}\\ \mathrm{Mn^{IV}}\end{array}\right\}\ \text{Octahedral as in } [\mathrm{Mn(H_2O)_6}]^{2+},\ [\mathrm{Mn(ox)_3}]^{3-} \text{ and } [\mathrm{MnCl_6}]^{2-}$$

$$\left.\begin{array}{l}\mathrm{Mn^{VI}}\\ \mathrm{Mn^{VII}}\end{array}\right\}\ \text{Tetrahedral as in } [\mathrm{MnO_4}]^{2-} \text{and } \mathrm{MnO_4^-}$$

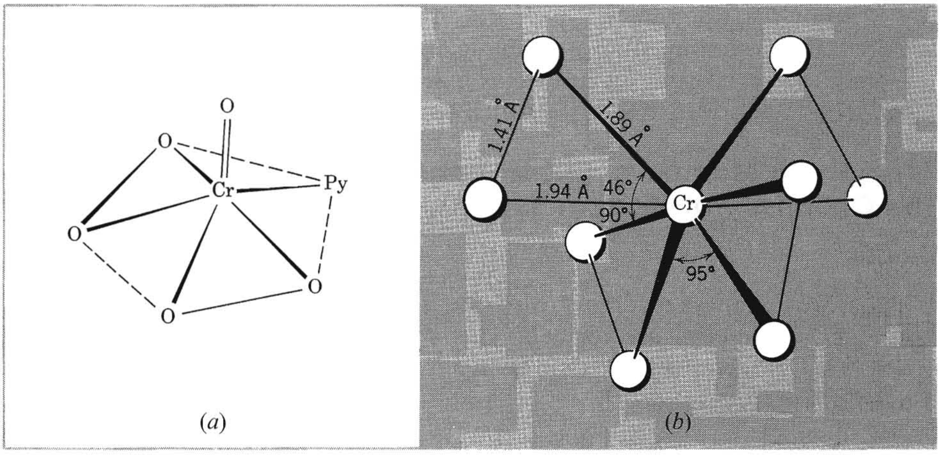


Figure 24-3 (*a*) The structure of $CrO(O_2)_2py$. The coordination polyhedron is approximately a pentagonal pyramid with the oxide ligand at the apex. (*b*) The dodecahedral structure of the CrO_8^{3-} ion, a tetraperoxide complex.

24-22 The Chemistry of Manganese(II), d^5

Manganese(II) salts are mostly water soluble. Addition of OH^- to Mn^{2+} solutions produces the gelatinous white *hydroxide.* This compound rapidly darkens in air due to oxidation, as shown by the base potentials:

$$MnO_2 \xrightarrow{-0.1\ V} Mn_2O_3 \xrightarrow{-0.2\ V} Mn(OH)_2 \qquad (24\text{-}22.1)$$

Addition of SH^- gives hydrous MnS, which also oxidizes becoming brown in air; on boiling in the absence of air the salmon pink material changes into green crystalline MnS. The sulfate, $MnSO_4$, is very stable and may be used for Mn analysis as it can be obtained on fuming down sulfuric acid solutions to dryness. The phosphate and carbonate are sparingly soluble. The equilibrium constants for the formation of manganese(II) complexes are relatively low as the Mn^{2+} ion has no ligand field stabilization energy (Section 23-8). However, chelating ligands, such as en, ox, or $EDTA^{4-}$, form complexes isolable from aqueous solution.

In aqueous solution the formation constants for halogeno complexes are very low, for example,

$$[Mn_{(aq)}]^{2+} + Cl^- \rightleftharpoons MnCl^+_{(aq)} \qquad K \approx 4 \qquad (24\text{-}22.2)$$

but in ethanol or acetic acid, salts of complex anions of varying types may be isolated, such as

MnX_3^-	Octahedral with perovskite structure
$[MnX_4]^{2-}$	Tetrahedral (green yellow) or polymeric octahedral with halide bridges (pink)
$[MnCl_6]^{4-}$	Only Na and K salts known; octahedral

The Mn^{2+} ions may occupy tetrahedral holes in certain glasses and substitute for Zn^{II} in ZnO. Tetrahedral Mn^{II} has a green-yellow color, far more intense than the pink of the octahedrally coordinated ion, and it very often exhibits intense yellow-green fluorescence. Most commercial phosphors are manganese-activated zinc compounds, wherein Mn^{II} ions are substituted for some of the Zn^{II} ions in tetrahedral surroundings as, for example, in Zn_2SiO_4.

Only the very strong ligand fields give rise to spin pairing as in the ions $[Mn(CN)_6]^{4-}$ and $[Mn(CNR)_6]^{2+}$, which have only one unpaired electron.

24-23 The Chemistry of Manganese(III), d^4

Oxides

When any manganese oxide or hydroxide is heated at 1000 °C, black crystals of Mn_3O_4 (*haussmannite*) are formed. This compound is a spinel, $Mn^{II}Mn^{III}_2O_4$. When $Mn(OH)_2$ is allowed to oxidize in air, a hydrous oxide is formed that gives MnO(OH) on drying.

Manganese(III) Aqua Ion

The manganese(III) ion can be obtained by electrolytic or peroxodisulfate oxidation of Mn^{2+} solutions or by reduction of MnO_4^-. It cannot be obtained in high concentrations as it is reduced by water (Table 24-3). It also has a strong tendency to hydrolyze and to disproportionate in weakly acid solution.

$$2\ \mathrm{Mn}^{3+} + 2\ \mathrm{H_2O} = \mathrm{Mn}^{2+} + \mathrm{MnO_2(s)} + 4\ \mathrm{H}^+ \qquad K \approx 10^9 \qquad (24\text{-}23.1)$$

The dark brown crystalline *acetylacetonate* Mn(acac)$_3$ is readily obtained by oxidation of basic solutions of Mn^{2+} by O_2 or Cl_2 in the presence of acetylacetone.

The basic-oxo centered acetate (Structure 24-I), which is obtained by the action of $KMnO_4$ on $\mathrm{Mn^{II}}$ acetate in acetic acid, will oxidize alkenes to lactones. It is used industrially for oxidation of toluene to phenol.

Manganese(III) and (IV) complexes are probably important in photosynthesis, where oxygen evolution depends on manganese.

24-24 The Chemistry of Manganese(IV), d^3, and Manganese(V), d^2

The most common compound of $\mathrm{Mn^{IV}}$ is *manganese dioxide,* a gray to black solid found in nature as *pyrolusite.* When made by the action of oxygen on manganese at a high temperature it has the rutile structure found for many other dioxides, for example those of Ru, Mo, W, Re, Os, Ir, and Rh. However, as normally made, for example, by heating $\mathrm{Mn(NO_3)_2{\cdot}6H_2O}$ in air, it is nonstoichiometric. A hydrated form is obtained by reduction of aqueous $KMnO_4$ in basic solution.

Manganese dioxide is inert to most acids except when heated, but it does not dissolve to give $\mathrm{Mn^{IV}}$ in solution; instead, it functions as an oxidizing agent, the exact manner of this depending on the acid. With HCl, chlorine is evolved.

$$\mathrm{MnO_2(s)} + 4\ \mathrm{H}^+ + 4\ \mathrm{Cl}^- = \mathrm{Mn}^{2+} + 2\ \mathrm{Cl}^- + \mathrm{Cl_2} + 2\ \mathrm{H_2O} \qquad (24\text{-}24.1)$$

With sulfuric acid at 110 °C, oxygen is evolved and an $\mathrm{Mn^{III}}$ acid sulfate is formed. Hydrated manganese dioxide is used in organic chemistry for the oxidation of alcohols and other compounds.

Manganese(IV) is known in $\mathrm{MnF_6^{2-}}$ and, like $\mathrm{Mn^{VI}}$, in compounds with Mn=O groups. Manganese(V) is little known except in bright blue "hypomanganates" that are formed by the reduction of permanganate with an excess of sulfite.

24-25 The Chemistry of Manganese(VI), d^1, and Manganese(VII), d^0

Manganese(VI) is found in the deep green *manganate* ion, $\mathrm{MnO_4^{2-}}$. This ion is formed on oxidizing MnO_2 in fused KOH with KNO_3 or air.

The manganate ion is stable only in very basic solutions. In acid, neutral, or slightly basic solutions it readily disproportionates according to the equation

$$3\ \mathrm{MnO_4^{2-}} + 4\ \mathrm{H}^+ = 2\ \mathrm{MnO_4^-} + \mathrm{MnO_2(s)} + 2\ \mathrm{H_2O} \qquad K \approx 10^{58} \qquad (24\text{-}25.1)$$

Manganese(VII) is best known in the form of salts of the *permanganate ion.* The compound $KMnO_4$ is manufactured by electrolytic oxidation of a basic solution of K_2MnO_4. Aqueous solutions of $\mathrm{MnO_4^-}$ may be prepared by oxidation of solutions of the $\mathrm{Mn^{II}}$ ion with very powerful oxidizing agents such as PbO_2 or

$NaBiO_3$. The ion has an intense purple color, and crystalline salts appear almost black.

Solutions of permanganate are intrinsically unstable, decomposing slowly but observably in acid solution.

$$4\ MnO_4^- + 4\ H^+ \longrightarrow 3\ O_2(g) + 2\ H_2O + 4\ MnO_2(s) \qquad (24\text{-}25.2)$$

In neutral or slightly alkaline solutions in the dark, decomposition is immeasurably slow. It is catalyzed by light so that standard permanganate solutions should be stored in dark bottles.

In *basic* solution, permanganate is a powerful oxidant.

$$MnO_4^- + 2\ H_2O + 3\ e^- = MnO_2(s) + 4\ OH^- \qquad E^\circ = +1.23\ V \qquad (24\text{-}25.3)$$

In very strong base and with an excess of MnO_4^-, however, manganate ion is produced.

$$MnO_4^- + e^- = MnO_4^{2-} \qquad E^\circ = +0.56\ V \qquad (24\text{-}25.4)$$

In *acid* solution permanganate is reduced to Mn^{2+} by an excess of reducing agent:

$$MnO_4^- + 8\ H^+ + 5\ e^- = Mn^{2+} + 4\ H_2O \qquad E^\circ = +1.51\ V \qquad (24\text{-}25.5)$$

but because MnO_4^- oxidizes Mn^{2+},

$$2\ MnO_4^- + 3\ Mn^{2+} + 2\ H_2O = 5\ MnO_2(s) + 4\ H^+ \qquad E^\circ = +0.46\ V \qquad (24\text{-}25.6)$$

the product in the presence of an excess of permanganate is MnO_2. The addition of $KMnO_4$ to concentrated H_2SO_4 gives stoichiometrically:

$$2\ KMnO_4 + 3\ H_2SO_4 \rightleftharpoons 2\ K^+ + Mn_2O_7 + H_3O^+ + 3\ HSO_4^- \qquad (24\text{-}25.7)$$

the dangerous explosive oil, Mn_2O_7. This can be extracted into CCl_4 or chlorofluorocarbons in which it is reasonably stable and safe.

Until recently, only oxo compounds of Mn^{VI} and Mn^{VII} were known, but now the compound $Mn^{VII}(N\text{-}t\text{-}Bu)_3Cl$ has been shown to be stable (mp 94–95 °C), whereas its oxo analog $MnClO_3$ detonates above 0 °C. A great many derivatives of $Mn(N\text{-}t\text{-}Bu)_3Cl$ have also been prepared, examples being $Mn(N\text{-}t\text{-}Bu)_3Br$ (mp 105–107 °C), $Mn(N\text{-}t\text{-}Bu)_3(O_2CCH_3)$ (mp 49–59 °C), $Mn(N\text{-}t\text{-}Bu)_3(OC_6F_5)$ (mp 95–97 °C), and $Mn(N\text{-}t\text{-}Bu)_3(NH\text{-}t\text{-}Bu)$, which is an unstable oil. Reduction of the chloride with sodium amalgam in THF gives the Mn^{VI} dimer $[(N\text{-}t\text{-}Bu)_2Mn(\mu\text{-}N\text{-}t\text{-}Bu)]_2$.

IRON

24-26 The Element Iron

Beginning with this element, there is no oxidation state equal to the total number of valence-shell electrons, which in this case is eight. The highest oxidation state is VI, and it is rare. Even the trivalent state, which rose to a peak of importance at chromium, now loses ground to the divalent state.

Iron is the second most abundant metal, after Al, and the fourth most abundant element in the earth's crust. The core of the earth is believed to consist mainly of Fe and Ni. The major ores are Fe_2O_3 (*hematite*), Fe_3O_4 (*magnetite*), FeO(OH) (*limonite*), and $FeCO_3$ (*siderite*).

Pure iron is quite reactive. In moist air it is rather rapidly oxidized to give a hydrous iron(III) oxide (rust) that affords no protection, since it flakes off, exposing fresh metal surfaces. Finely divided iron is pyrophoric.

The metal dissolves readily in dilute mineral acids. With nonoxidizing acids and in the absence of air, Fe^{II} is obtained. With air present or when warm dilute HNO_3 is used, some of the iron goes to Fe^{III}. Very strongly oxidizing media, such as concentrated HNO_3 or acids containing dichromate, passivate iron. Air-free water and dilute air-free solutions of OH^- have little effect, but iron is attacked by hot concentrated NaOH (see the following section).

IRON COMPOUNDS

The main stereochemistries of iron compounds are as follows:

Fe^{II}	Octahedral as in $Fe(OH)_2$, $[Fe(H_2O)_6]^{2+}$, and $[Fe(CN)_6]^{4-}$
Fe^{III}	Octahedral as in $[Fe(H_2O)_6]^{3+}$ and $Fe(acac)_3$

24-27 Binary Compounds

Oxides and Hydroxides

The addition of OH^- to Fe^{2+} solutions gives the pale green *hydroxide,* which is very readily oxidized by air to give red-brown hydrous iron(III) oxide.

The compound $Fe(OH)_2$, a true hydroxide with the $Mg(OH)_2$ structure, is somewhat amphoteric. Like Fe, it dissolves in hot concentrated NaOH, from which solutions, blue crystals of $Na_4[Fe^{II}(OH)_6]$ can be obtained.

The *oxide,* FeO, may be obtained as a black pyrophoric powder by ignition of Fe^{II} oxalate: It is usually nonstoichiometric, $Fe_{0.95}O$, which means that some Fe^{III} is present. The addition of OH^- to iron(III) solutions gives a red-brown gelatinous mass commonly called iron(III) hydroxide, but it is best described as a *hydrous oxide* ($Fe_2O_3 \cdot nH_2O$). This has several forms; one, FeO(OH), occurs in the mineral *lepidocrocite* and can be made by high-temperature hydrolysis of iron(III) chloride. On heating at 200 °C the hydrous oxides form red-brown α-Fe_2O_3, which occurs as the mineral *hematite.* This has the corundum structure with an hcp array of O, with Fe^{3+} in the octahedral interstices.

The black crystalline oxide Fe_3O_4, a mixed Fe^{II}–Fe^{III} oxide, occurs in nature as *magnetite.* It can be made by ignition of Fe_2O_3 above 1400 °C. It has the inverse spinel structure (Section 4-8).

Chlorides are used as source material for the synthesis of other iron compounds. Anhydrous *iron(II) chloride* can be made by passing HCl gas over heated iron powder, by reducing $FeCl_3$ with Fe(s) in THF or by refluxing $FeCl_3$ in chlorobenzene. It is a very pale green, almost white, solid.

Iron(III) chloride is obtained by the action of chlorine on heated iron as almost black, red-brown crystals. Although in the gas phase there are dimers, Fe_2Cl_6, in the crystal the structure is nonmolecular and there are Fe^{III} ions occupying two thirds of the octahedral holes in alternate layers of Cl^- ions.

Iron(III) chloride quite readily hydrolyzes in moist air. It is soluble in ethers and other polar solvents.

Ferrites such as $M^{II}Fe_2O_4$ are important mixed oxide materials used in magnetic tapes for recording purposes.

24-28 Chemistry of Iron(II), d^6

The iron(II) ion, $[Fe(H_2O)_6]^{2+}$, gives many crystalline salts. Mohr's salt, $(NH_4)_2[Fe(H_2O)_6](SO_4)_2$, is reasonably stable toward air and loss of water, and is commonly used to prepare standard solutions of Fe^{2+} for volumetric analysis and as a calibration substance in magnetic measurements. By contrast, $FeSO_4 \cdot 7H_2O$ slowly effloresces and turns brown-yellow when kept in air.

Addition of HCO_3^- or SH^- to aqueous solutions of Fe^{2+} precipitates $FeCO_3$ and FeS, respectively. The Fe^{2+} ion is oxidized in acid solution by air to Fe^{3+}. With ligands other than water present, substantial changes in the potentials may occur, and the Fe^{II}–Fe^{III} system provides an excellent example of the effect of ligands on the relative stabilities of oxidation states.

$$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-} \qquad E^\circ = 0.36\text{ V} \qquad (24\text{-}28.1)$$

$$[Fe(H_2O)_6]^{3+} + e^- = [Fe(H_2O)_6]^{2+} \qquad E^\circ = 0.77\text{ V} \qquad (24\text{-}28.2)$$

$$[Fe(phen)_3]^{3+} + e^- = [Fe(phen)_3]^{2+} \qquad E^\circ = 1.12\text{ V} \qquad (24\text{-}28.3)$$

Complexes

Octahedral complexes are generally paramagnetic, and quite strong ligand fields are required to cause spin pairing. Diamagnetic complex ions are $[Fe(CN)_6]^{4-}$ and $[Fe(dipy)_3]^{2+}$. Formation of the red 2,2′-bipyridine and 1,10-phenanthroline complexes is used as a test for Fe^{2+}.

Some tetrahedral complexes like $[FeCl_4]^{2-}$ are known. Among the most important complexes are those involved in biological systems (Chapter 31) or models for them. An important iron(II) compound is ferrocene (Section 29-14).

24-29 The Chemistry of Iron(III), d^5

Iron(III) occurs in crystalline salts with most anions other than those, such as iodide, that are incompatible because of their reducing properties:

$$Fe^{3+} + I^- = Fe^{2+} + \tfrac{1}{2} I_2 \qquad (24\text{-}29.1)$$

Salts containing the ion $[Fe(H_2O)_6]^{3+}$, such as $Fe(ClO_4)_3 \cdot 10H_2O$, are pale pink to nearly white and the aquo ion is pale purple. Unless Fe^{3+} solutions are quite strongly acid, hydrolysis occurs and the solutions are commonly yellow because of the formation of hydroxo species that have charge-transfer bands in the UV region tailing into the visible region.

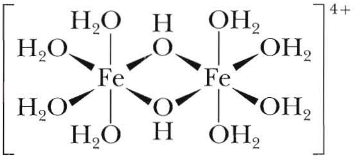
The initial hydrolysis equilibria are

$$[Fe(H_2O)_6]^{3+} = [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad K = 10^{-3.05} \tag{24-29.2}$$

$$[Fe(H_2O)_5(OH)]^{2+} = [Fe(H_2O)_4(OH)_2]^+ + H^+ \qquad K = 10^{-3.26} \tag{24-29.3}$$

$$2[Fe(H_2O)_6]^{3+} = [Fe(H_2O)_4(OH)_2Fe(H_2O)_4]^{4+} + 2\,H^+ \qquad K = 10^{-2.91} \tag{24-29.4}$$

The binuclear species in Reaction 24-29.4 probably has the Structure 24-III.



24-III

From the constants it is clear that, even at pH values of 2–3, hydrolysis is extensive. In order to have solutions containing say, about 99% $[Fe(H_2O)_6]^{3+}$ the pH must be around zero. As the pH is raised to about 2–3, more highly condensed species than the dinuclear one are formed, attainment of equilibrium becomes sluggish, and soon colloidal gels are formed. Ultimately, hydrous Fe_2O_3 is precipitated.

Iron(III) ion has a strong affinity for F^-

$$Fe^{3+} + F^- = FeF^{2+} \qquad K_1 \approx 10^5 \tag{24-29.5}$$

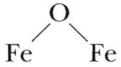
$$FeF^{2+} + F^- = FeF_2^+ \qquad K_2 \approx 10^5 \tag{24-29.6}$$

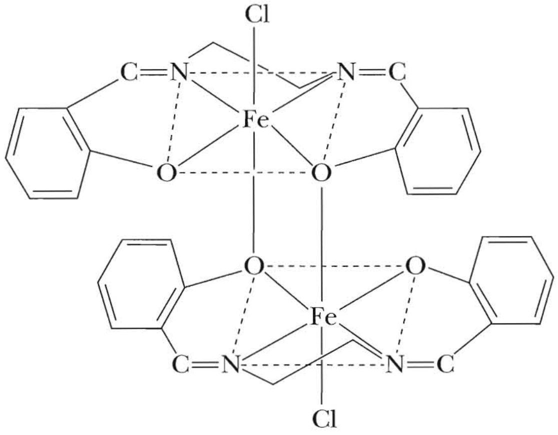
$$FeF_2^+ + F^- = FeF_3 \qquad K_3 \approx 10^3 \tag{24-29.7}$$

The corresponding constants for chloro complexes are only about 10, 3, and 0.1, respectively. In very concentrated HCl the tetrahedral $FeCl_4^-$ ion is formed, and its salts with large cations may be isolated. Complexes with SCN^- are an intense red, and this serves as a sensitive qualitative and quantitative test for ferric ion; $Fe(SCN)_3$ and/or $Fe(SCN)_4^-$ may be extracted into ether. Fluoride ion, however, will discharge this color. In the solid state, $[FeF_6]^{3-}$ ions are known but in solutions only species with fewer F atoms occur.

The hexacyanoferrate ion, $[Fe(CN)_6]^{3-}$, in contrast to $[Fe(CN)_6]^{4-}$, is quite poisonous because the CN^- ions rapidly dissociate, whereas $[Fe(CN)_6]^{4-}$ is not labile.

The affinity of Fe^{III} for NH_3 and amines is low except for chelates, such as $EDTA^{4-}$; 2,2′-bipyridine and 1,10-phenanthroline, which produce ligand fields strong enough to cause spin pairing (cf. Fe^{II}) and form quite stable ions that can be isolated with large anions.

A number of hydroxo- and oxygen-bridged species, one of which has been mentioned previously, are of interest because they may show unusual magnetic properties due to coupling between the iron atoms via the bridges. One example is the complex of salen [bis(salicylaldehyde)ethylenediiminato], [Fe(salen)]$_2$O, which has a nonlinear  group, while Fe(salen)Cl can form both mononuclear and binuclear complexes (Structure 24-IV). The latter has marked antiferromagnetic coupling between the Fe atoms.



24-IV

24-30 The Chemistry of Iron(IV) and (VI)

There are only a few complexes, such as [Fe(S$_2$CNR$_2$)$_3$]$^+$ and [Fe(diars)$_2$Cl$_2$]$^{2+}$, for Fe^{IV}, and the unusual hydrocarbon soluble alkyl, Fe(1-norbornyl)$_4$ (Section 29-11). No stable Fe^{V} compounds are known.

The best known compound of iron(VI) is the oxo anion, [FeO$_4$]$^{2-}$, which is obtained by chlorine oxidation of suspensions of Fe$_2$O$_3$·nH$_2$O in concentrated NaOH or by fusing Fe powder with KNO$_3$. The red-purple ion is paramagnetic with two unpaired electrons. The Na and K salts are quite soluble but the Ba salt can be precipitated. The ion is relatively stable in basic solution but decomposes in neutral or acid solution according to the equation

$$2[\mathrm{FeO_4}]^{2-} + 10\ \mathrm{H^+} = 2\ \mathrm{Fe^{3+}} + \tfrac{3}{2}\,\mathrm{O_2} + 5\ \mathrm{H_2O} \qquad (24\text{-}30.1)$$

It is an even stronger oxidizing agent than MnO$_4^-$ and can oxidize NH$_3$ to N$_2$, Cr^{II} to CrO$_4^{2-}$, and also primary amines and alcohols to aldehydes.

COBALT

24-31 The Element Cobalt

The trends toward decreased stability of the very high oxidation states and the increased stability of the II state relative to the III state, which occur through the series Ti, V, Cr, Mn, and Fe, persist with Co. The highest oxidation state is now IV, and only a few such compounds are known. Cobalt(III) is relatively unstable in simple compounds, but the low-spin complexes are exceedingly numerous and stable, especially where the donor atoms (usually N) make strong contributions to the ligand field. There are also numerous complexes of Co^I. This oxidation state is better known for cobalt than for any other element of the first transition series except copper. All Co^I complexes have π-acid ligands (Chapter 28).

Cobalt always occurs in association with Ni and will usually occur also with As. The chief sources of Co are "speisses," which are residues in the smelting of arsenical ores of Ni, Cu, and Pb.

Cobalt is relatively unreactive, although it dissolves slowly in dilute mineral acids.

COBALT COMPOUNDS

The main stereochemistries found in cobalt compounds are the following:

Co^{II}	Tetrahedral as in $[CoCl_4]^{2-}$ and $CoCl_2(PEt_3)_2$ Octahedral as in $[Co(H_2O)_6]^{2+}$
Co^{III}	Octahedral as in $[Co(NH_3)_6]^{3+}$

24-32 Chemistry of Cobalt(II), d^7

The dissolution of Co, or the hydroxide or carbonate, in dilute acids gives the pink aqua ion, $[Co(H_2O)_6]^{2+}$, which forms many hydrated salts.

Addition of OH^- to Co^{2+} gives the *hydroxide,* which may be blue or pink depending on the conditions; it is weakly amphoteric dissolving in very concentrated OH^- to give a blue solution containing the $[Co(OH)_4]^{2-}$ ion.

Complexes

The most common Co^{II} complexes may be either octahedral or tetrahedral. There is only a small difference in stability and both types, with the same ligand, may be in equilibrium. Thus for water there is a very small but finite concentration of the tetrahedral ion:

$$[Co(H_2O)_6]^{2+} \rightleftharpoons [Co(H_2O)_4]^{2+} + 2\ H_2O \qquad (24\text{-}32.1)$$

Addition of excess Cl^- to pink solutions of the aqua ion readily gives the blue tetrahedral species:

$$[Co(H_2O)_6]^{2+} + 4\ Cl^- = [CoCl_4]^{2-} + 6\ H_2O \qquad (24\text{-}32.2)$$

Tetrahedral complexes, $[CoX_4]^{2-}$, are formed by halide, pseudohalide, and OH^- ions. Cobalt(II) forms tetrahedral complexes more readily than any other transition metal ion. The Co^{2+} ion is the only d^7 ion of common occurrence. For a d^7 ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent (see Table 23-4) than for any other $d^n (1 \leq n \leq 9)$ configuration. This argument is valid only in comparing the behavior of one metal ion with another and not for assessing the absolute stabilities of the configurations for any particular ion.

24-33 The Chemistry of Cobalt(III), d^6

In the absence of complexing agents, the oxidation of $[Co(H_2O)_6]^{2+}$ is very unfavorable (Table 24-3) and Co^{3+} is reduced by water. However, electrolytic or O_3 oxidation of cold acidic solutions of $Co(ClO_4)_2$ gives the aqua ion, $[Co(H_2O)_6]^{3+}$, in equilibrium with $[Co(OH)(H_2O)_5]^{2+}$. At 0 °C, the half-life of these diamagnetic ions is about a month. In the presence of complexing agents, such as NH_3, the stability of Co^{III} is greatly improved.

$$[Co(NH_3)_6]^{3+} + e^- = [Co(NH_3)_6]^{2+} \qquad E^\circ = 0.1\ V \qquad (24\text{-}33.1)$$

In the presence of OH^- ion, cobalt(II) hydroxide is readily oxidized by air to a black hydrous oxide.

$$CoO(OH)(s) + H_2O + e^- = Co(OH)_2(s) + OH^- \qquad E^\circ = 0.17\ V \quad (24\text{-}33.2)$$

The Co^{3+} ion shows a particular affinity for N donors, such as NH_3, en, edta, and NCS^-, and complexes are exceedingly numerous. They generally undergo ligand-exchange reactions relatively slowly, like Cr^{3+} and Rh^{3+}. Hence, they have been extensively studied since the days of Werner and Jørgensen. A large part of our knowledge of the isomerism, modes of reaction, and general properties of octahedral complexes as a class is based on studies of Co^{III} complexes. Almost all Co^{III} complexes are octahedral.

Cobalt(III) complexes are synthesized by oxidation of Co^{2+} in solution in the presence of the ligands. Oxygen or hydrogen peroxide and a catalyst, such as activated charcoal, are used. For example,

$$4\ Co^{2+} + 4\ NH_4^+ + 20\ NH_3 + O_2 \longrightarrow 4[Co(NH_3)_6]^{3+} + 2\ H_2O \quad (24\text{-}33.3)$$

$$4\ Co^{2+} + 8en + 4enH^+ + O_2 = 4[Co(en)_3]^{3+} + 2\ H_2O \quad (24\text{-}33.4)$$

The green salt, *trans*-$[Co(en)_2Cl_2][H_5O_2]Cl_2$, is obtained from a reaction similar to Reaction 24-33.4 in the presence of HCl. This salt may be isomerized to the purple racemic cis isomer on evaporation of a neutral aqueous solution at 90–100 °C. Both the cis and the trans isomer are aquated when heated in water:

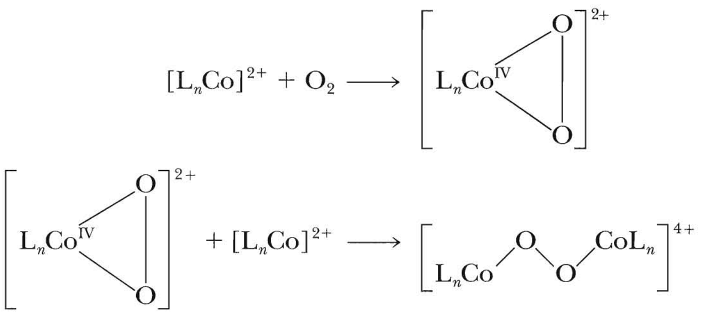
$$[Co(en)_2Cl_2]^+ + H_2O \longrightarrow [Co(en)_2Cl(H_2O)]^{2+} + Cl^- \quad (24\text{-}33.5)$$

$$[Co(en)_2Cl(H_2O)]^{2+} + H_2O \longrightarrow [Co(en)_2(H_2O)_2]^{3+} + Cl^- \quad (24\text{-}33.6)$$

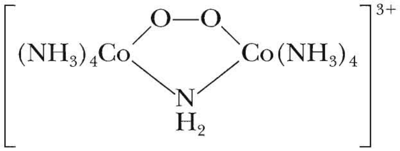
and on treatment with solutions of other anions are converted into other $[Co(en)_2X_2]^+$ species, for example,

$$[Co(en)_2Cl_2]^- + 2\ NCS^- \longrightarrow [Co(en)_2(NCS)_2]^+ + 2\ Cl^- \quad (24\text{-}33.7)$$

The initial reaction of Co^{II} with oxygen may involve oxidative–addition (Section 30-2) of O_2 to Co^{II} to give a transient Co^{IV} species that then reacts with another Co^{II} to produce a binuclear *peroxo-bridged* species:



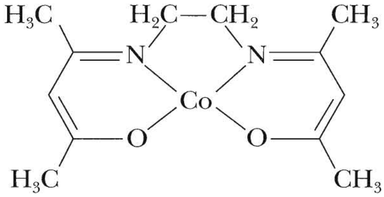
Complexes such as $[(NH_3)_5CoOOCo(NH_3)_5]^{4+}$ or $[(NC)_5CoOOCo(CN)_5]^{6-}$ have been isolated, although these ions decompose fairly readily in water or acids. The open-chain species $[(NH_3)_5CoOOCo(NH_3)_5]^{4+}$ can be cyclized in the presence of base to



Such peroxo species, open chain or cyclic, contain low-spin Co^{III} and bridging peroxide (O_2^{2-}) ions.

The O_2-bridged binuclear complexes can often be oxidized in a one-electron step. The resulting ions were first prepared by Werner, who formulated them as peroxo-bridged complexes of Co^{III} and Co^{IV}. However, ESR data have shown that the single unpaired electron is distributed equally over *both* cobalt ions, and is best regarded as belonging formally to a superoxide (O_2^-) ion but delocalized over the planar $Co^{III}—O—O—Co^{III}$ group. The structures (Fig. 24-4) show that the O—O distance is close to that for the O_2^- ion (1.28 Å) and much shorter than the distance (1.47 Å) in the peroxo complexes.

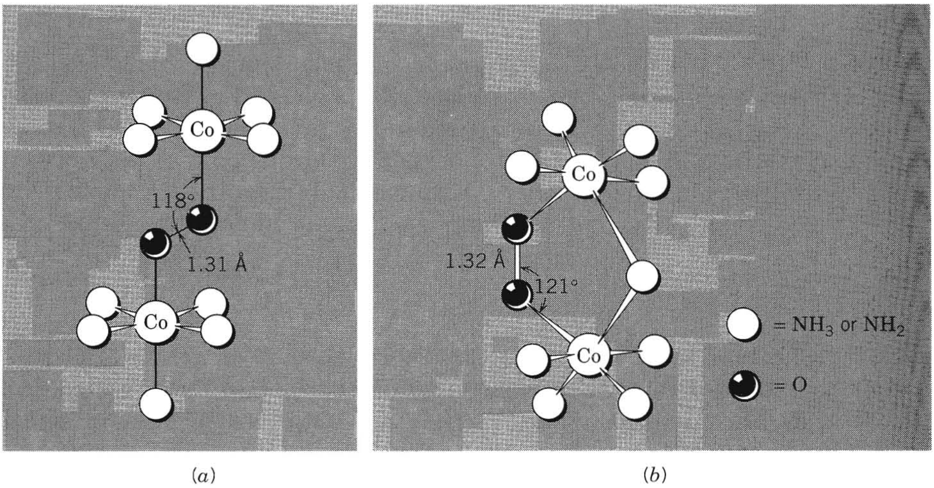
Although no cobalt-containing complex is known to be involved in oxygen metabolism, there are several that provide models for metal-to-oxygen binding in biological systems. Of greatest interest are those that undergo *reversible* oxygenation and deoxygenation in solution. The Schiff base complexes such as Co(acacen) (Structure 24-V) in DMF or py take up O_2 reversibly below 0 °C, for example,



24-V

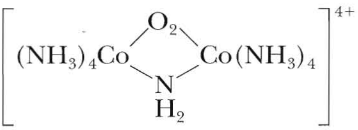
$$+ \text{DMF} + O_2 \longrightarrow \text{Co(acacen)(dmf)}O_2 \qquad K = 2.1 \text{ at } -10\ °C \qquad (24\text{-}33.10)$$

The initial complex has one unpaired electron, and so also do the oxygen adducts, but ESR data indicate that in the latter the electron is heavily localized on the oxygen atoms. There is also an IR absorption band due to an O—O stretching vibration. The adducts can be formulated as octahedral, low-spin Co^{III}



(a) (b)

Figure 24-4 The structures of (a) $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$, and

(b)


There is octahedral coordination about each cobalt ion and the angles and distances shown are consistent with the assumption that there are bridging superoxo groups. The five-membered ring in (b) is essentially planar.

complexes containing a coordinated superoxide (O_2^-) ion. The Co—O—O chain is bent. A second type of complex involves the reversible formation of oxygen bridges (Co—O—O—Co), which are similar to those discussed previously.

Finally, we note in connection with oxidation that in acid solutions, cobalt(III) carboxylates catalyze the oxidation not only of alkyl side chains in aromatic hydrocarbons, but even of alkanes themselves. A cobalt catalyzed process is used commercially for oxidation of toluene to phenol. The actual nature of "cobaltic acetate," a green material made by ozone oxidation of Co^{2+} acetate in acetic acid is uncertain; it can, however, be converted by pyridine to an oxo centered species similar to those known for other M^{III} carboxylates (Structure 24-I).

24-34 Complexes of Cobalt(I), d^8

With the exception of reduced vitamin B_{12} and models for this system (Section 31-8), which appear to be Co^I species, all Co^I compounds involve ligands of the π-acid type (Chapter 28). The coordination is trigonal bipyramidal or tetrahedral. The compounds are usually made by reducing $CoCl_2$ in the presence of the ligand by agents such as N_2H_4, Zn, $S_2O_4^{2-}$, or Al alkyls.

Representative examples are $CoH(N_2)(PPh_3)_3$, $[Co(CNR)_5]^+$, $CoCl(PR_3)_3$.

NICKEL

24-35 The Element

The trend toward decreased stability of higher oxidation states continues, so that only Ni^{II} normally occurs with a few compounds *formally* containing Ni^{III} and Ni^{IV}. The relative simplicity of nickel chemistry in terms of oxidation number is balanced by considerable complexity in coordination numbers and geometries.

Nickel occurs in combination with arsenic, antimony, and sulfur as in *millerite* (NiS) and in *garnierite,* a magnesium-nickel silicate of variable composition. Nickel is also found alloyed with iron in meteors; the interior of the earth is believed to contain considerable quantities. In general, the ore is roasted in air to give NiO, which is reduced to Ni with C. Nickel is usually purified by electrodeposition but some high purity nickel is still made by the carbonyl process. Carbon monoxide reacts with impure nickel at 50 °C and ordinary pressure or with nickel–copper matte under more strenuous conditions, giving volatile $Ni(CO)_4$, from which metal of 99.90 to 99.99% purity is obtained on thermal decomposition at 200 °C.

Nickel is quite resistant to attack by air or water at ordinary temperatures when compact and is, therefore, often electroplated as a protective coating. It dissolves readily in dilute mineral acids. The metal or high Ni alloys are used to handle F_2 and other corrosive fluorides. The finely divided metal is reactive to air and may be pyrophoric. Nickel absorbs considerable amounts of hydrogen when finely divided and special forms of Ni (e.g., Raney nickel) are used for catalytic reductions.

NICKEL COMPOUNDS

24-36 The Chemistry of Nickel(II), d^8

The binary compounds, such as NiO and $NiCl_2$, need no special comment.

Nickel(II) forms a large number of *complexes* with coordination numbers six, five, and four having all the main structural types: octahedral, trigonal bipyramidal, square pyramidal, tetrahedral, and square. It is characteristic that complicated equilibria, which are generally temperature dependent and sometimes concentration dependent, often exist between these structural types.

Six-Coordinate Complexes

The commonest six-coordinate complex is the green aqua ion, $[Ni(H_2O)_6]^{2+}$, that is formed on dissolution of Ni, $NiCO_3$, and so on, in acids and gives salts like $NiSO_4 \cdot 7H_2O$.

The water molecules in the aqua ion can be readily displaced especially by amines to give complexes, such as *trans*-$[Ni(H_2O)_2(NH_3)_4]^{2+}$, $[Ni(NH_3)_6]^{2+}$, or $[Ni(en)_3]^{2+}$. These amine complexes are usually blue or purple because of shifts in absorption bands when H_2O is replaced by a stronger field ligand (Section 23-6).

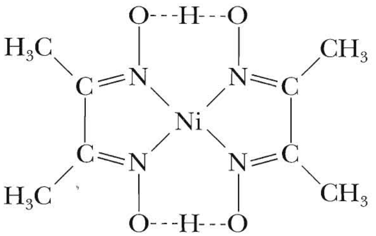
Four-Coordinate Complexes

Most of the four-coordinate complexes are square. This is a consequence of the d^8 configuration, since the planar ligand set causes one of the d orbitals ($d_{x^2-y^2}$)

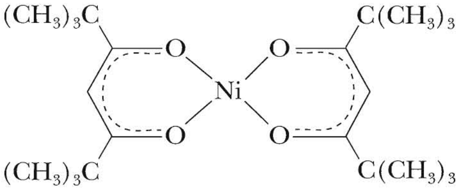
to be uniquely high in energy, and the eight electrons can occupy the other four *d* orbitals but leave this strongly antibonding one vacant. In tetrahedral coordination, on the other hand, occupation of antibonding orbitals is unavoidable. With the congeneric d^8 systems Pd^{II} and Pt^{II} this factor becomes so important that no tetrahedral complex is formed.

Planar complexes of Ni^{II} are thus invariably diamagnetic. They are frequently red, yellow, or brown owing to the presence of an absorption band of medium intensity ($\epsilon \approx 60$) in the range 450–600 nm.

Probably the best known example is the red *bis(dimethylglyoximato)nickel(II)*, $Ni(dmgH)_2$, which is used for the gravimetric determination of nickel; it is precipitated on addition of ethanolic $dmgH_2$ to ammoniacal nickel(II) solutions. It has Structure 24-VI, where the hydrogen bond is symmetrical, but these units are *stacked* one on top of the other in the crystal. Here, and in similar square compounds of Pd^{II} and Pt^{II} (Section 25-28), there is evidence of metal-to-metal interaction, even though the distance in the stack is too long for true bonding.



24-VI



24-VII

Similar square complexes are given by certain β-ketoenolates (e.g., Structure 24-VII), as well as by unidentate π-acid ligands [e.g., $NiBr_2(PEt_3)_2$], and by CN^- and SCN^-. The cyano complex, $[Ni(CN)_4]^{2-}$, is readily formed on addition of CN^- to Ni^{2+} (aq). The green $Ni(CN)_2$ which is first precipitated redissolves to give the yellow ion, which can be isolated as, for example, $Na_2[Ni(CN)_4]\cdot 3H_2O$. On addition of an excess of CN^- the red ion, $[Ni(CN)_5]^{3-}$, is formed, which can be precipitated only by use of large cations.

Tetrahedral Complexes

Tetrahedral complexes are less common than planar complexes, and are all paramagnetic. These complexes are of the types $[NiX_4]^{2-}$, NiX_3L^-, NiL_2X_2, and $Ni(L—L)_2$ where X is halogen, L is a neutral ligand (e.g., R_3P or R_3PO), and L—L is a bidentate uninegative ligand, $[NiL_4]^{2+}$, is known, where L = hexamethylphosphoramide.

Five-Coordinate Complexes

Five-coordinate complexes usually have trigonal-bipyramidal geometry but some are square pyramidal. Many contain the tetradentate "tripod" ligands, such as $N[CH_2CH_2N(CH_3)_2]_3$ (see Structures 6-XVa and 6-XVb).

24-37 Conformational Properties of Nickel(II) Complexes

The main structural and conformational changes that nickel(II) complexes undergo are the following:

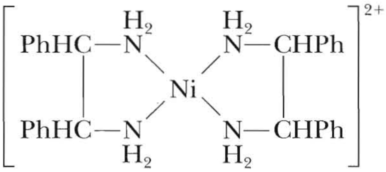
1. *Formation of five- and six-coordinate complexes results from the addition of ligands to square complexes.* For *any* square complex NiL_4 the following equilibria with additional ligands (L′) must in principle exist:

$$ML_4 + L' = ML_4L' \tag{24-37.1}$$

$$ML_4 + 2\,L' = ML_4L_2' \tag{24-37.2}$$

Where L = L′ = CN^-, only the five-coordinate species is formed, but in most systems in which L′ is a good donor such as py, H_2O and C_2H_5OH, the equilibria lie far in favor of the six-coordinate species. These have a trans structure and a high-spin electron configuration; many may be isolated as pure compounds. Thus, the β-diketone complex (Structure 24-VII) is normally prepared in the presence of water and/or alcohol and is first isolated as the green, paramagnetic dihydrate or dialcoholate, from which the red, square complex is then obtained by heating to drive off the solvent.

Another type of square complex that picks up H_2O, anions, or solvent is shown in Structure 24-VIII.



24-VIII

2. **Monomer-polymer equilibria** can occur. Four-coordinate complexes may associate or polymerize, to give five- or six-coordinate species. In some cases, the association is very strong and the four-coordinate monomers are observed only at high temperatures. In others the position of the equilibrium is such that both red, diamagnetic monomers, and green or blue, paramagnetic polymers, are present in a temperature- and concentration-dependent equilibrium around room temperature. A clear example of this situation is provided by the *acetylacetonate* (Fig. 24-5). As a result of the sharing of some oxygen atoms, each nickel atom achieves octahedral coordination. This trimer is very stable, and detectable quantities of monomer appear only at temperatures around 200 °C in a noncoordinating solvent. It is, however, readily cleaved by donors, such as H_2O or py, to give six-coordinate monomers. When the methyl groups of the acetylacetonate ligand are replaced by the very bulky $C(CH_3)_3$ groups, trimerization is completely prevented and the planar monomer (Structure 24-VII) results. When groups sterically intermediate between CH_3 and $C(CH_3)_3$ are used, temperature- and concentration-dependent monomer–trimer equilibria are observed in noncoordinating solvents.

3. **Square-tetrahedral equilibria and isomerism** can occur. Complexes, such as NiL_2X_2, where L represents a mixed alkylarylphosphine exist in solution in an

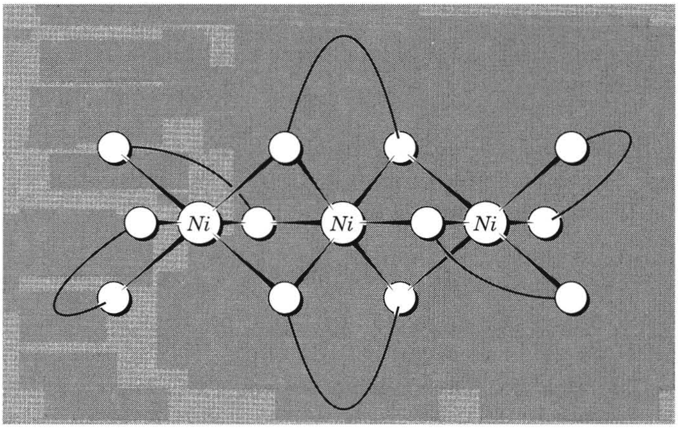


Figure 24-5 Sketch indicating the trimeric structure of nickel acetylacetonate. The unlabeled circles represent oxygen atoms, and the curved lines connecting them in pairs represent the remaining portions of the acetylacetonate rings. (Reproduced by permission from J. C. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **1965,** *4,* 456 © American Chemical Society.)

equilibrium distribution between the tetrahedral and square forms. In some cases it is possible to isolate two crystalline forms of the compound, one yellow-red and diamagnetic, the other green or blue with two unpaired electrons. There is even a case, $Ni[C_6H_5CH_2)(C_6H_5)_2P]_2Br_2$, in which *both* tetrahedral and square complexes are found together in the same crystalline substance.

24-38 Higher Oxidation States of Nickel

Oxides and Hydroxides

The action of Br_2 on alkaline solutions of Ni^{2+} gives a black hydrous oxide, NiO(OH). Other black substances can be obtained by electrolytic oxidation; some of them contain alkali metal ions.

The Edison or nickel-iron battery, which uses KOH as the electrolyte, is based on the reaction

$$\mathrm{Fe} + 2\,\mathrm{NiO(OH)} + 2\,\mathrm{H_2O} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Fe(OH)_2} + 2\,\mathrm{Ni(OH)_2} \qquad (\sim 1.3\ \mathrm{V}) \quad (24\text{-}38.1)$$

but the mechanism and the true nature of the oxidized nickel species are not fully understood.

Complexes

There are several authentic complexes of *nickel(III)*. Oxidation of $NiX_2(PR_3)_2$ with the appropriate halogen gives $NiX_3(PR_3)_2$.

Nickel(IV) complexes are even rarer, and the dithiolene complexes (Section 28-18), which could formally be regarded as containing Ni^{4+} and $S_2CR_2^{2-}$ ligands, are best regarded as Ni^{II} complexes.

COPPER

24-39 The Element

Copper has a single *s* electron outside the filled $3d$ shell. It has little in common with the alkalis except formal stoichiometries in the +1 oxidation state. The filled *d* shell is much less effective than is a noble gas shell in shielding the *s* electron from the nuclear charge, so that the first ionization potential of Cu is higher than those of the alkalis. Since the electrons of the *d* shell are also involved in metallic bonding, the heat of sublimation and the melting point of copper are also much higher than those of the alkalis. These factors are responsible for the more noble character of copper. The effect is to make compounds more covalent and to give them higher lattice energies, which are not offset by the somewhat smaller radius of Cu^+ (0.93 Å) compared with Na^+ (0.95 Å) and K^+ (1.33 Å).

The second and third ionization potentials of Cu are very much lower than those of the alkalis and account in part for the transition metal character.

Copper is not abundant (55 ppm) but is widely distributed as a metal, in sulfides, arsenides, chlorides, and carbonates. The commonest mineral is chalcopyrite, $CuFeS_2$. Copper is extracted by oxidative roasting and smelting, or by microbial-assisted leaching, followed by electrodeposition from sulfate solutions.

Copper is used in alloys such as brass and is completely miscible with gold. It is very slowly superficially oxidized in moist air, sometimes giving a green coating of hydroxo carbonate and hydroxo sulfate (from SO_2 in the atmosphere).

Copper readily dissolves in nitric acid and in sulfuric acid in the presence of oxygen. It is also soluble in KCN or ammonia solutions in the presence of oxygen, as indicated by the potentials:

$$Cu(s) + 2\,NH_3 \xrightarrow{-0.12\ V} [Cu(NH_3)_2]^+ \xrightarrow{-0.01\ V} [Cu(NH_3)_4]^{2+} \quad (24\text{-}39.1)$$

COPPER COMPOUNDS

The stereochemistry of the more important copper compounds is as follows:

Cu^I	Tetrahedral as in CuI(s) or $[Cu(CN)_4]^{3-}$
	Square as in CuO(s), $[Cu(py)_4]^{2+}$, or $[CuCl_4]^{2-}$
Cu^{II}	Distorted octahedral with two longer trans bonds, for example, $[Cu(H_2O)_6]^{2+}$, $CuCl_2(s)$

24-40 The Chemistry of Copper(I), d^{10}

Copper(I) compounds are diamagnetic and, except where color results from the anion or charge-transfer bands, are colorless.

The relative stabilities of the Cu^{I} and Cu^{II} states are indicated by the potentials:

$$Cu^{+} + e^{-} = Cu(s) \qquad E° = 0.52\ V \qquad (24\text{-}40.1)$$

$$Cu^{2+} + e^{-} = Cu^{+} \qquad E° = 0.153\ V \qquad (24\text{-}40.2)$$

From these we have

$$Cu(s) + Cu^{2+} = 2\ Cu^{+} \qquad E° = -0.37\ V \qquad (24\text{-}40.3)$$

$$\frac{[Cu^{2+}]}{[Cu^{+}]^{2}} = \sim 10^{6} \qquad (24\text{-}40.4)$$

The relative stabilities depend very strongly on the nature of anions or other ligands present, and vary considerably with solvent or the nature of neighboring atoms in a crystal.

In *aqueous* solution only low equilibrium concentrations of Cu^{+} ($<10^{-2}$ M) can exist (see the following section). The only copper(I) compounds that are stable to water are the highly insoluble ones, such as CuCl or CuCN. This instability toward water is due partly to the greater lattice and solvation energies and higher formation constants for complexes of the Cu^{2+} ion so that ionic Cu^{I} derivatives are unstable.

The equilibrium $2\ Cu^{I} \leftrightharpoons Cu + Cu^{II}$ can readily be displaced in either direction. Thus, with CN^{-}, I^{-}, and $(CH_3)_2S$, Cu^{II} reacts to give the Cu^{I} compound. The Cu^{II} state is favored by anions that cannot give covalent bonds or bridging groups (e.g., ClO_4^{-} and SO_4^{2-}) or by complexing agents that have their greater affinity for Cu^{II}. Thus ethylenediamine reacts with copper(I) chloride in aqueous potassium chloride solution.

$$2\ CuCl + 2en = [Cu(en)_2]^{2+} + 2\ Cl^{-} + Cu^{0} \qquad (24\text{-}40.5)$$

The latter reaction also depends on the chelate nature of the ligand. Thus for ethylenediamine, K is about 10^{7}; for pentamethylenediamine (which does not chelate) K is 3×10^{-2}; and for ammonia K is 2×10^{-2}. Hence, in the last case the reaction is

$$[Cu(NH_3)_4]^{2+} + Cu^{0} = 2[Cu(NH_3)_2]^{+} \qquad (24\text{-}40.6)$$

The lifetime of the Cu^{+} ion in water is usually very short (<1 s), but dilute solutions from reduction of Cu^{2+} with V^{2+} or Cr^{2+} may last for several hours in the absence of air.

An excellent illustration of how the stability of the Cu^{I} ion relative to that of the Cu^{II} ion may be affected by the solvent is the case of acetonitrile. The Cu^{I} ion is very effectively solvated by CH_3CN, and the halides have relatively high solubilities (e.g., CuI, 35 g/kg CH_3CN) versus negligible solubilities in H_2O. The Cu^{I} ion is more stable than Cu^{II} in CH_3CN, and Cu^{II} acts as a comparatively powerful oxidizing agent.

Copper(I) Binary Compounds

The *oxide* and *sulfide* are more stable than the corresponding Cu^{II} compounds at high temperatures. Cu_2O is made as a yellow powder by controlled reduction of an alkaline solution of a copper(II) salt with hydrazine or, as red crystals, by thermal decomposition of CuO. Copper(I) sulfide (Cu_2S) is a black crystalline solid prepared by heating copper and sulfur in the absence of air; it is, however, markedly nonstoichiometric.

Copper(I) chloride and *bromide* are made by boiling an acidic solution of the copper(II) salt with an excess of copper; on dilution, white CuCl or pale yellow CuBr is precipitated. Addition of I^- to a solution of Cu^{2+} forms a precipitate that rapidly and quantitatively decomposes to CuI and iodine. CuF is unknown. The halides have the zinc blende structure (tetrahedrally coordinated Cu^+). They are insoluble in water, but the solubility is enhanced by an excess of halide ions owing to formation of, for example, $[CuCl_2]^-$, $[CuCl_3]^{2-}$, and $[CuCl_4]^{3-}$.

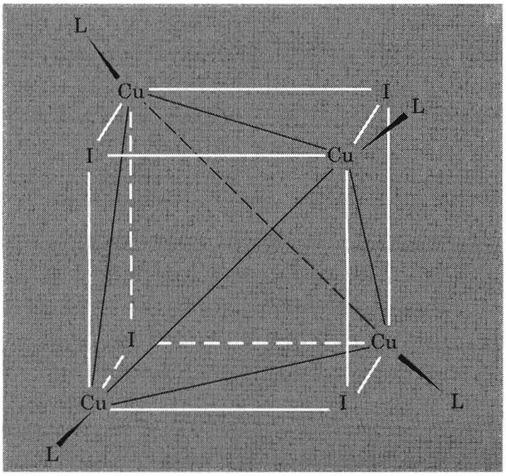
Copper(I) Complexes

The most common types of Cu^I complexes are those of simple halide or amine ligands and are usually *tetrahedral.* Even those with stoichiometries such as K_2CuCl_3 still have tetrahedral coordination as there are chains sharing halide ions.

Copper(I) also forms several kinds of polynuclear complexes in which four Cu atoms lie at the vertices of a tetrahedron. In $Cu_4I_4L_4$ (L = R_3P or R_3As) species, there is a triply bridging I atom on each face of the Cu_4 tetrahedron and one ligand (L) is coordinated to a Cu atom at each vertex (Structure 24-IX).

24-41 The Chemistry of Copper(II), d^9

Most Cu^I compounds are fairly readily oxidized to Cu^{II}, but further oxidation to Cu^{III} is difficult. There is a well-defined aqueous chemistry of Cu^{2+}, and a large



24-IX

number of salts of various anions, many of which are water soluble, that exist in addition to a wealth of complexes.

Before we discuss copper(II) chemistry, it is pertinent to note the stereochemical consequences of the d^9 configuration of Cu^{II}. This makes Cu^{II} subject to distortions (Section 23-8) if placed in an environment of cubic (i.e., regular octahedral or tetrahedral) symmetry. The result is that Cu^{II} is nearly always found in environments appreciably distorted from these regular symmetries. The characteristic distortion of the octahedron is such that there are *four short* Cu—L *bonds in the plane and two trans long ones.* In the limit, this elongation leads to a situation indistinguishable from square coordination, as found in CuO and many discrete complexes of Cu^{II}. Thus the cases of tetragonally distorted "octahedral" coordination and square coordination cannot be sharply differentiated.

Some distorted tetrahedral complexes, such as $M^I_2CuX_4$, are also known provided M is large like cesium. The compound $(NH_4)_2CuCl_4$ has a planar anion.

Binary Compounds

Black crystalline CuO is obtained by pyrolysis of the nitrate or other oxo salts; above 800 °C it decomposes to Cu_2O. The *hydroxide* is obtained as a blue bulky precipitate on addition of NaOH to Cu^{2+} solutions; warming an aqueous slurry dehydrates this to the oxide. The hydroxide is readily soluble in strong acids and also in concentrated NaOH, to give deep blue anions, probably of the type $[Cu_n(OH)_{2n-2}]^{2+}$. In ammoniacal solutions the deep blue tetraammine complex, $[Cu(NH_3)_4]^{2+}$, is formed.

The common *halides* are the yellow chloride and the almost black bromide, having structures with infinite parallel bands of square CuX_4 units sharing edges. The bands are arranged so that a tetragonally elongated octahedron is completed about each copper atom by halogen atoms of neighboring chains. Both $CuCl_2$ and $CuBr_2$ are readily soluble in water, from which hydrates may be crystallized, as well as in donor solvents, such as acetone, alcohol, and pyridine.

The Aqua Ion and Aqueous Chemistry

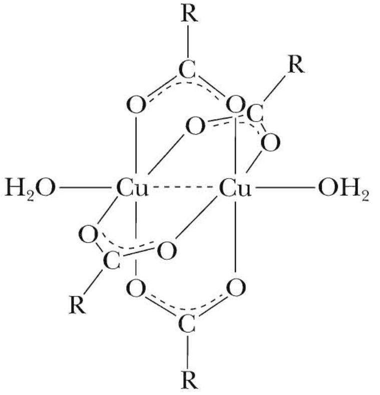
Dissolution of copper, the hydroxide, carbonate, and so on, in acids gives the blue-green aqua ion that may be written $[Cu(H_2O)_6]^{2+}$. Two of the H_2O molecules are further from the metal than the other four. Of the numerous crystalline hydrates the blue sulfate ($CuSO_4{\cdot}5H_2O$) is best known. It may be dehydrated to the virtually white anhydrous substance. Addition of ligands to aqueous solutions leads to the formation of complexes by successive displacement of water molecules. With NH_3, for example, the species $[Cu(NH_3)(H_2O)_5]^{2+} \cdots [Cu(NH_3)_4(H_2O)_2]^{2+}$ are formed in the normal way, but addition of the fifth and sixth molecules of NH_3 is difficult. The sixth can be added only in liquid ammonia. The reason for this unusual behavior is connected with the Jahn-Teller effect. Because of it, the Cu^{II} ion does not bind the fifth and sixth ligands strongly (even the H_2O). When this intrinsic weak binding of the fifth and sixth ligands is added to the normally expected decrease in the stepwise formation constants (Section 6-4), the formation constants (K_5 and K_6) are very small indeed. Similarly, it is found with ethylenediamine that $[Cu(en)(H_2O)_4]^{2+}$ and

$[Cu(en)_2(H_2O)_2]^{2+}$ form readily, but $[Cu(en)_3]^{2+}$ is formed only at extremely high concentrations of en.

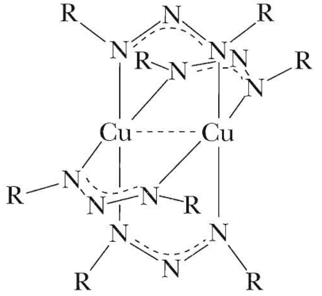
Multidentate ligands that coordinate through O or N, such as amino acids, form copper(II) complexes of considerable stability. The blue solutions formed by addition of tartrate to Cu^{2+} solutions (known as *Fehling's solution* when basic and when *meso*-tartrate is used) may contain monomeric, dimeric, or polymeric species at different pH values. The dimer, $Na_2[Cu\{(\pm)C_4O_6H_2\}]\cdot5H_2O$, has square Cu^{II} coordination, two tartrate bridges, and a Cu—Cu distance of 2.99 Å.

Polynuclear Compounds with Magnetic Anomalies

Copper forms many compounds in which the Cu—Cu distances are short enough to indicate significant M-M interaction, but in no case is there an actual bond. Particular examples are the bridged *carboxylates* and the related 1,3-triazenido complexes (Structures 24-X and 24-XI). Although in other cases of carboxylates with the same structure (Cr_2^{II}, Mo_2^{II}, Rh_2^{II}, or $Ru_2^{II,III}$) there is a definite M—M bond, this is *not* so for Cu. However, there is weak coupling of the unpaired electrons, one on each Cu^{II} ion, giving rise to a singlet ground state with a triplet state lying only a few kilojoules per mole above it; the latter state is thus appreciably populated at normal temperatures and the compounds are paramagnetic. At 25 °C, μ_{eff} is typically about 1.4 BM per Cu atom and the temperature dependence is very pronounced. The interaction involves either the $d_{x^2-y^2}$ orbitals of the two metal atoms directly or transmission through the π orbitals of the bridge group, or both.



24-X



24-XI

Catalytic Properties of Copper Compounds

Copper compounds catalyze an exceedingly varied array of reactions, heterogeneously, homogeneously, in the vapor phase, in organic solvents, and in aqueous solutions. Many of these reactions, particularly if in aqueous solutions, involve oxidation–reduction systems and a Cu^{I}-Cu^{II} redox cycle. Molecular oxygen can often be utilized as an oxidant, for example in copper-catalyzed oxidations of ascorbic acid and in the Wacker process (Section 30-11).

The oxidation probably involves an initial oxidative addition reaction (Section 30-2):

$$Cu^+ + O_2 = CuO_2^+ \qquad (24\text{-}41.1)$$

$$CuO_2^+ + H^+ = Cu^{2+} + HO_2 \qquad (24\text{-}41.2)$$

$$Cu^+ + HO_2 = Cu^{2+} + HO_2^- \qquad (24\text{-}41.3)$$

$$H^+ + HO_2^- = H_2O_2 \qquad (24\text{-}41.4)$$

Copper compounds have many uses in organic chemistry for oxidations, for example of phenols by Cu^{2+}-amine complexes, halogenations, coupling reactions, and the like. Copper(II) has considerable biochemical importance (see Chapter 31).

STUDY GUIDE

Scope and Purpose

We have presented a rather large amount of information in a somewhat traditional and descriptive fashion, namely, a steady "march" through the metals of the first transition series and their compounds. For each element we have presented the important or interesting properties of the element and its inorganic compounds. The student should find it satisfying that the descriptions of the compounds and their reactivities are readily set down in the same "language" and using the same theories as those developed earlier in the text.
*SG For each metal we have organized the presentation in terms of important oxidation states, coordination numbers, geometries, number of
d electrons, and types of compounds. We also mention, where appropriate, the various thermodynamic stabilities of the derivatives of a particular metal ion, as well as the kinetic and mechanistic aspects of the reactions. The principal inorganic binary compounds are given first for most elements, followed by the more complex derivatives of an essentially inorganic nature, organized by the important oxidation states of the element. We anticipate covering the metalloorganic compounds in later chapters.

Study Questions

A. Review

1. Write down the ground-state electron configurations for the ions and atoms Ti^{4+}, V^{2+}, Cr^{5+}, Mn^{6+}, Fe^0, Co^+, Ni^{2+}, Cu^{3+}, and Ti^{3+}.
2. Which of the ions in Question 1 typically form octahedral complexes, tetrahedral complexes, or five-coordinate complexes?
3. Which of the complexes of Question 2 would you expect to show Jahn-Teller distortions?
4. What is the chief structural difference between $TiOSO_4 \cdot H_2O$ and $VOSO_4 \cdot 5\ H_2O$?
5. List two examples each where the transition metal compounds MCl_4 and MCl_3 behave as Lewis acids.
6. Give two examples of disproportionation reactions that were presented in this chapter.
7. Explain why the V—O stretching frequency changes when bis(acetylacetonato)oxovanadium(IV) is dissolved in pyridine.

8. What happens when a solution of $K_2Cr_2O_7$ is added to solutions of (a) F^- (b) Cl^- (c) Br^- (d) I^- (e) OH^- (f) NO_2^- (g) SO_4^{2-} (h) H_2O_2.
9. Give two examples each of the spinels, perovskites, and alums.
10. Explain why the trivalent ions give acid solutions in water. Write balanced equations to illustrate your answer.
11. Draw the structures of $Cr_2(CO_2CH_3)_4(H_2O)_2$ and $Cr_3O(CO_2CH_3)_6(H_2O)_3Cl$. Classify each atom in these structures according to the AB_xE_y scheme of Chapter 3, and choose a hybridization for each nonmetal, nonterminal atom.
12. What are the structures of $[Ni(acac)_2]_3$, $CrCl_3(thf)_3$, and CrO_5py?
13. Why is it that the freshly prepared hydroxide (a) of Mn^{2+} is white, but turns dark brown in air, (b) of Co^{2+} is blue, but turns pink on warming, and (c) of Cu^{2+} is blue, but turns black on warming?
14. What is the number of unpaired electrons in complexes of (a) spin-paired Mn^{2+}, (b) tetrahedral Cr^{4+}, (c) tetrahedral Co^{2+}, (d) octahedral V^{3+}, (e) octahedral Co^{3+}, (f) low-spin Fe^{2+}, and (g) high-spin Mn^{2+}?
15. Give an example of a complex representing each case in Problem 14.
16. How is oxygen bound in the complexes (a) $Cs_3[TiO_2F_5]$, (b) $K_3[CrO_8]$, and (c) $[Co_2O_2(NH_3)_{10}](SO_4)_2$?
17. Enumerate the possible isomers of $[Co(en)_2(SCN)_2]^+$, and name each one according to proper nomenclature.

B. Additional Exercises

1. Draw the structures of each reactant and product found in Reactions 24-7.4, 24-14.2, 24-18.1, 24-25.7, and 24-33.7.
2. Most M—O—M bonds are angular but some are linear, namely, that in $[(NH_3)_5Cr—O—Cr(NH_3)_5]^{4+}$. Why?
3. The densities of the metals Ca, Sc, and Zn are, respectively, 1.54, 3.00, and 7.13 g cm^{-3}. Make a plot of these data along with those given in Table 24-1 for the first transition series, and explain the various features and trends that arise.
4. Dimethyl sulfoxide (DMSO) reacts with $Co(ClO_4)_2$ in absolute ethanol to form a pink product that is a 1:2 electrolyte, and that has a magnetic moment of 4.9 BM. The compound $CoCl_2$, however, reacts with DMSO to form a dark blue product with a magnetic moment (per Co) of 4.6 BM. The latter is a 1:1 electrolyte that has an empirical formula of $Co(dmso)_3Cl_2$. Suggest a formula and a structure for each compound.
5. $Mn(acac)_3$ has axial Mn—O bond lengths (~ 1.94 Å) that are shorter than the *equatorial* ones (~ 2.00 Å). Explain.
6. Write balanced chemical equations for
   (a) Reaction of the aqua ion of Co^{2+} with the disodium salt of EDTA.
   (b) Addition of sodium bicarbonate to aqueous Fe^{2+}.
   (c) Reduction of Mn^{3+} by water.
   (d) Air oxidation of $Fe^{2+}(aq)$.
   (e) Hydrolysis of $TiCl_4$.
   (f) Oxidation of Ti^{3+} by H_2O_2.
   (g) Dissolution of the acidic V_2O_5 into aqueous NaOH.
   (h) Dissolution of the hydrous oxide $VO(OH)_2$ in aqueous HNO_3.
   (i) Burning of Cr in air.
   (j) A preparation of CrO_3.

(k) Hydrolysis of CrO_2Cl_2.
(l) Oxidation of aqueous Mn^{2+} with PbO_2.
(m) A preparation of $[Co(NH_3)_6]^{3+}$.
(n) Addition of I^- to aqueous Cu^{2+}.
(o) Reaction of aqueous Cu^{2+} with cyanide.

7. How is the preferred tetrahedral coordination obtained in complexes with an apparent nontetrahedral stoichiometry, such as K_2CuCl_3?

8. Predict the number of unpaired electrons in $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$. Explain your reasoning.

9. Draw the structures of *cis*-$[VO_2Cl_4]^{3-}$ and *cis*-$[VO_2(ox)_2]^{3-}$.

10. Draw the structures of $[TiCl_4(OPCl_3)]_2$, $[TiCl_4(CH_3CO_2C_2H_5)]_2$, and $TiCl_4(OPCl_3)_2$. Classify each atom in the structures as AB_xE_y, and choose a hybridization for each nonterminal, nonmetal atom.

C. Problems from the Literature of Inorganic Chemistry

1. Consider the five-coordinate nickel(II) complex studied by K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **1968,** *7,* 1362–1372.
(a) What geometries are reported for the $[Ni(CN)_5]^{3-}$ ion?
(b) What hybridization should be chosen for each Ni^{II} ion? What crystal field diagrams should be drawn for each?
(c) How big an energy difference is there, apparently, between these two coordination geometries?
(d) What minimum sequence of atomic motions would be required to convert one geometry into the other?
(e) Write balanced equations for the synthesis of this compound from cobalt(II) chloride, ethylenediamine, $[Ni(CN)_4]^{2-}(aq)$, and KCN.

2. Titanium(IV) compounds are discussed in the article by T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, **1971,** *10,* 122–132.
(a) Write balanced equations for the syntheses of $[PCl_4]_2[Ti_2Cl_{10}]$ and $[PCl_4][Ti_2Cl_9]$, as performed in this work.
(b) Discuss the tendency for Ti^{IV} to be octahedrally coordinated, as illustrated by these two compounds.
(c) Explain the two reactions from the viewpoint of chloride ion transfer.
(d) How and why does the solvent (here either $SOCl_2$ or $POCl_3$) influence the formation of $[Ti_2Cl_{10}]^{2-}$ instead of $[Ti_2Cl_9]^-$?

3. Pentacoordinated copper(II) ions were reported by K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **1968,** *7,* 1111–1117.
(a) What geometry is reported for $[CuCl_5]^{3-}$ in this compound?
(b) Compare the geometries and the crystal field diagrams of $[Ni(CN)_5]^{3-}$, $[CuCl_5]^{3-}$, and $[MnCl_5]^{2-}$.
(c) Why are the axial Cu—Cl bond lengths in $[CuCl_5]^{3-}$ shorter than the equatorial ones?

4. Consider isomerism among nickel complexes as reported by R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **1965,** *4,* 1701–1706.
(a) For the complexes $NiX_2(PRPh_2)_2$, state the trend that is observed for isomer preference when $X = Cl^-$, Br^-, or I^-. When does the system prefer square planar or tetrahedral geometry?
(b) Which geometry should lead to paramagnetism and which should lead to diamagnetism? Explain with crystal field diagrams.

(c) How is isomer preference related to ligand field strength in the series of complexes with ligands $P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, $PC_2H_5(C_6H_5)_2$, and $P(C_6H_5)_3$ and for the series of complexes with ligands SCN^-, Cl^-, Br^-, and I^-?

5. Consider the adduct of oxovanadium(IV) dichloride as reported by J. E. Drake, J. Vekris, and J. S. Wood, *J. Chem. Soc. (A),* **1968,** 1000–1005.

(a) Write an equation for the synthesis in ammonia of the title compound.

(b) What is the significance of the magnetic susceptibility ($\mu_{eff} = 1.74$ BM) found for this compound?

(c) Describe the V—O multiple bond by showing orbital-overlap diagrams.

(d) How strong is the V—O π bond as judged by the V—O distance?

(e) Why, according to the authors, is the coordination geometry around this oxovanadium(IV) compound a trigonal bipyramid and not the usual square pyramid?

6. Consider the redox reactions reported by A. J. Miralles, R. E. Armstrong, and A. Haim, *J. Am. Chem. Soc.,* **1977,** *99,* 1416–1420.

(a) Prepare crystal field diagrams (with electrons properly configured) for $[Ru(NH_3)_5py]^{3+}$, $[Co(NH_3)_5py]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, and $[Ru(NH_3)_6]^{2+}$.

(b) How were these reactions shown to proceed via outer-sphere electron transfer mechanisms?

7. Consider the anation reactions studied by W. R. Muir and C. H. Langford, *Inorg. Chem.,* **1968,** *7,* 1032–1043.

(a) Why should exchange of dmso–ligand with DMSO-solvent be more rapid than anation? Explain by drawing the solvated activated complex along an I_d reaction pathway, and consider the probability of solvent versus anion entry into the first-coordination sphere.

(b) What evidence favoring an I_d mechanism for anation do the authors report?

(c) What evidence is cited in opposition to an associative mechanism?

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