COORDINATION COMPOUNDS

1. Introduction

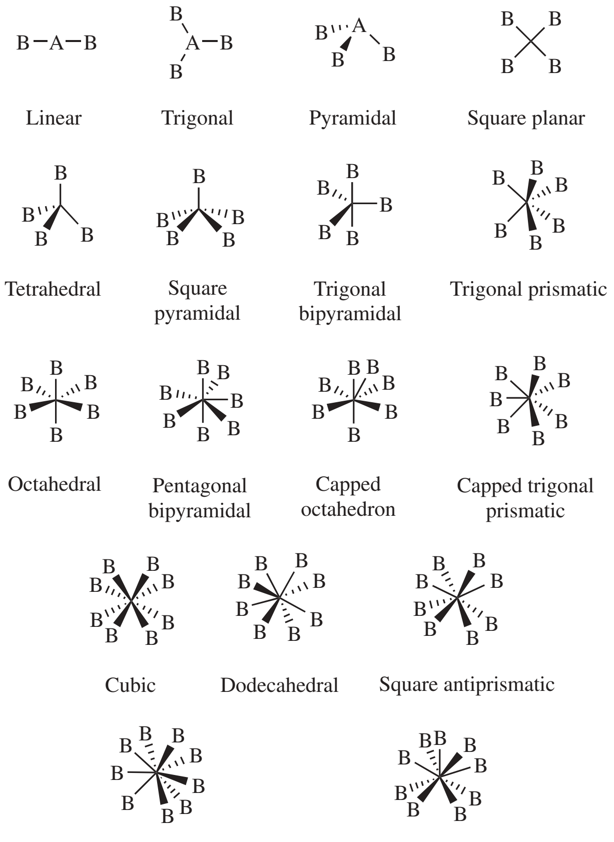
(Normal) Coordination Compounds: A coordination compound typically consists of a metal atom or ion (Lewis acid) surrounded by a number of electron-pair donors (Lewis bases) called ligands.

Inverse Coordination Compounds: More rare are the coordination compounds with inversed polarity, in which anions (Lewis bases) are surrounded by ligands with positively polarized atoms (Lewis acids).

Coordination compounds of the first type, also known as metal complexes, are pervasive throughout chemistry, biochemistry, and chemical technology. The metallic elements, which constitute 80% of the Periodic Table, exhibit predominantly coordination chemistry. Whereas the ligands may have charges equal in magnitude and opposite in sign to the charge of the metal ion, in which case a neutral coordination compound or inner complex results, often the metal plus ligands result in a charged entity or complex ion. In these situations, the coordination compound may include neutral ligands or counterions, either simple or complex. Generally, coordination compounds have properties, which are unique relative to both the ligands and the metal ion itself.

Coordination compounds are used as catalysts in nature, ie, metal enzymes, and in industry in situations where the metal ion or ligand would not work alone. The ligands often modify the properties of the metals or metal ions and vice versa. For example, the metal deactivators in gasoline modify the chemistry of dissolved copper to the extent that the copper does not promote gum formation. Complexation of iron in heme allows us to render iron ions soluble in human blood, and thus they are bioavailable for oxygen transport in living organisms. Some ligands react with different metal ions such that selective analysis of metallic elements is possible through coordination followed by solvent extraction, spectroscopy, gravimetry, electrochemistry, etc. Furthermore, complexes of copper and zinc in water allow brass to be electroplated. Conversely, metals are sometimes used to modify the properties of ligands. For example, azo dyes are metalated to give more permanence and/or alter color tones; the coordination of zinc to bactericides modifies the properties of the bactericides. The modification includes template and neighboring group effects, promotion of nucleophilic substitution, enhanced ligand acidity, and strain modification (1). Common geometries for coordination numbers from two through nine are shown in Figure 1, with International Union of Pure and Applied Chemistry (IUPAC) (2) and American Chemical Society (ACS) (3) polyhedral symbols for the geometries provided in Table 1.

Supramolecular compounds are a recent development of coordination chemistry. Their formation is based on the principle of molecular recognition, and they are characterized by the energy and information contained in the formed bonds as well as in their selectivity. Metal and ligand must be complementary in their stereochemical preferences, steric constraints, and coordination energies (thermodynamically). This systematic was called the key-and-lock principle by Emil



Linear

Trigonal

Pyramidal

Square planar

Tetrahedral

Square pyramidal

Trigonal bipyramidal

Trigonal prismatic

Octahedral

Pentagonal bipyramidal

Capped octahedron

Capped trigonal prismatic

Cubic

Dodecahedral

Square antiprismatic

Tricapped trigonal prismatic

Capped square antiprismatic

Fig. 1. Common geometries for metal coordination numbers from two through nine (see Table1), A represents the metal and B, a ligand donor atom. For higher coordination numbers, A is in the center of the structure. The principal axis orientation is vertical.

Table 1. **Polyhedral Symbols for Common Coordination Geometries**[a]

Coordination geometry	Coordination number	Polyhedral symbols	
		IUPAC[b]	ACS[c]
linear	2	L-2	L-2
triangular plane	3	TP-3	TP-3
tetrahedron	4	T-4	T-4
square plane	4	SP-4	SP-4
trigonal bipyramid	5	TBPY-5	TB-5
square or tetragonal pyramid	5	SPY-5	SP-5
octahedron	6	OC-6	OC-6
trigonal prism	6	TPR-6	TP-6
pentagonal bipyramid	7	PBPY-7	PB-7
octahedron, face capped	7	OCF-7	OCF-7
trigonal prism, square face monocapped	7	TPRS-7	TPS-7
cubic	8	CU-8	CU-8
dodecahedral	8	DD-8	DD-8
square antiprism	8	SAPR-8	SA-8
trigonal prism, square face tricapped	9	TPRS-9	TPS-9

[a] See Figure 1.
[b] Ref. 2.
[c] Ref. 3.

Fischer in 1894. Supramolecular chemistry and the corresponding compounds will be treated in more detail in another article of this series, and only a few examples will be given in this article (4,5).

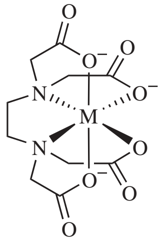
2. Definitions

2.1. Classification of Ligands.

The ligands can be classified as follows:

Unidentate ligands coordinate to the metal ion via one donor atom featuring at least one electron pair. Typical unidentate ligands are H_2O, NH_3 or phosphanes. They can act as terminal or as bridging ligands. In the latter case, they usually possess more than one lone electron pair, so that each pair can coordinate to a different metal ion.

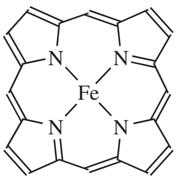
Chelating [(greek) = pincer, claw] ligands possess more than one donor atom and can coordinate a metal ion by two or more donor atoms. Usually, the more stable five- and six-membered rings are formed on coordination. Coordination compounds with chelating ligands are usually more stable than unidentate ligands if the same donor atoms are concerned. This chelate effect is due to a gain in enthalpy ($\Delta H<0$) as well as in entropy ($\Delta S>0$), the latter being predominant. Typical chelating ligands are bidentate ethylene diamine, polydentate polyethyleneglycol dimethyl ethers, as well as the hexadentate ethylenediaminetetraacetate, known as EDTA^{4-} (**1**).



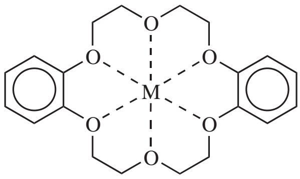
(**1**)

The latter plays a predominant role for the efficient complexation of metal ions with an octahedral coordination sphere, and is used to prevent precipitation of metal salts, ie., in water treatment (bathroom cleaners, eg.) for complexing calcium and magnesium ions, to prevent blood clots, to remove heavy metals from the body on poisoning, to solubilize iron in plant fertilizers, or to remove the iron taste from mayonnaise.

Macrocyclic ligands are chelating ligands, that are closed to a ring. Compounds in which the metal ion is coordinated by a macrocycle are more stable than compounds in which the metal ion is coordinated by the analogue open chelating ligand. The gain in energy is mainly entropic and due to the preorganization of the ligand. A typical example for a macrocyclic ligand is the porphyrin [101-60-6] (**2**), whose derivative forms the heme with iron in human blood, and cyclic polyethers such as dibenzo-[18]-crown-6 [14187-32-7] (**3**), which are used as extraction agents for metal ions and in biomimetics as compound mimicking ion transport through a cell membrane. The size of the macrocyclic ligand can be used as a selective tool in extraction and separation processes in industry.

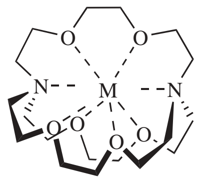


(**2**)



(**3**)

Cryptates are macropolycyclic ligands, and their size plays an important role as to which metal ions they are capable of complexing. The coordination compounds formed are usually more stable than the corresponding macrocyclic ones. This phenomenon is called the cryptate effect. A typical example is the [2,2,2]-cryptate [23978-09-8] (**4**), the numbers in brackets indicating the number of oxygen atoms present in the chain connecting two bridgehead nitrogen atoms.



(**4**)

Inversing the polarity of the donor atoms of a ligand will lead to coordination compounds of anions. One of the most common examples is the protonation or quaternization of macrocyclic amines, leading to the formation of Lewis acid nitrogen atoms. The interaction of such a ligand with anions is, however, generally weaker than the one found in metal coordination compounds. Chelate, macrocyclic, and cryptate effects are observed as well in these inverse anion coordination compounds, but are less important than in metal complexes.

2.2. Nomenclature.

Coordination compounds are named systematically beginning with the ligands. Ligands are listed alphabetically using prefixes that are Latin based (di, tri, tetra, etc, for 2, 3, 4, etc) for identical ligands, or Greek based (bis, tris, tetrakis, etc, for 2, 3, 4, etc) for identical multicomponent or complicated ligands that are placed in parentheses. The name of the metal follows, also using di, tri, etc, prefixes if polynuclear, or ending in -ate if the overall species is anionic. Then, in parentheses, comes either the overall charge of the species, if any, using an Arabic number followed by a plus or minus sign (Ewens-Bassett nomenclature), or the oxidation number of the metal represented by a Roman numeral or Arabic zero (Stock nomenclature). Examples of simple coordination species, including names, are given in Table 2.

In chemical formulas, the coordination compound or metal complex is written in square brackets with the charge of the complex given as a superscript outside at the end of the compound if written alone. Bridging ligands are designated as μ or μ^n, where n is the number of metal atoms bonded by the bridging ligand if n is >2. Such bridging ligands donate electron pairs to two or more metal ions simultaneously; eg, the $W_2Cl_9^{3-}$ ion of $K_3W_2Cl_9$ has three bridging chloro ligands, and the potassium salt can be named as potassium tri-μ-chlorohexachloroditungstate(3−) [23403-17-0], $K_3W_2Cl_9$. Alternatively, the Ewens-Bassett (3−) can be replaced by (III) if the Stock nomenclature is used. The direct metal−metal bonded $[Re_2Cl_8]^{2-}$ ion is named octachlorodirhenate(2−)(Re−Re) [19584-24-8] [or (III) may be used instead of (2−)]. The 1990 IUPAC *Nomenclature of Inorganic Chemistry* volume recommends that chelating ligands having 2, 3, 4, 5, 6, etc, donors bonded to the same metal atom be termed didentate, tridentate, tetradentate, pentadentate, hexadentate, etc, analogous to the prefixes used to designate identical ligands bonded to a metal center (2,6,7). More complicated nomenclature referring to heteronuclear polyanions, ring and chain compounds, intercalation, and polymer compounds can be found in the 2000 IUPAC *Nomenclature of Inorganic Chemistry II* (7).

Isomerism. Two or more different compounds having the same formula are called isomers. Two principal types of isomerism are known among

Table 2. **Coordination Compounds Possessing Unidentate Ligands**

Name[a]	CAS Registry number	Molecular formula	Coordination number	Typical use
		Common coordination numbers		
dicyanoargentate(I)	[15391-88-5]	$[Ag\,(CN)_2]^-$	2	recovery of silver
tetraamminecopper (II)	[16828-95-8]	$[Cu(NH_3)_4]^{2+}$	4	dissolution of copper (II) in basic soln
tetracarbonylnickel (0)	[13463-39-3]	$[Ni(CO)_4]$	4	separation of nickel from metals
hexafluorosilicate (IV)	[17084-08-1]	$[SiF_6]^{2-}$	6	dissolution of silicon (IV) in hydrolytic media
		Less common coordination numbers		
tricyanocuprate(I)	[16593-63-8]	$[Cu(CN)_3]^{2-}$	3	brass plating bath component
pentacarbonyl-manganate(-I)	[14971-26-7]	$[Mn(CO)_5]^-$	5	composite polymer–metal particle synthesis
heptafluorozirconate (IV)	[27679-73-8]	$[ZrF_2]^{3-}$	7	fluoride extractive metallurgy
octacyanotungstate (IV)	[18177-17-8]	$[W(CN)_8]^{4-}$	8	light sensitzer for TiO_2
nonaaquaneodymium (III)	[54375-24-5]	$[Nd(H_2O)_9]^{3+}$	9	aqueous ion in Nd laser synthesis

[a] Stock nomenclature.

coordination compounds: stereoisomerism and structural isomerism. Stereoisomers have the same atoms, same sets of bonds, but differ in the relative orientation of these bonds. They can be divided into geometrical isomers (possible for square planar and octahedral complexes, but not tetrahedral ones), and optical isomers (possible for tetrahedral and octahedral compounds, but not square planar ones). Structural isomers can involve coordination, ionization, hydrate, or linkage isomerism.

Octahedral arrangements are most common for coordination compounds, so a short overview of the most important possible stereoisomers will be given (2). Octahedral coordination compounds with at least two unidentate ligands can have two isomers, one called cis if the two unidentate ligands are placed in vicinal positions, the other called trans for the two ligands in opposite sites of the octahedron. A tridentate ligand can coordinate to a metal ion by occupying three positions forming a triangular face of the octahedron, and is then called *facial* (fac). If the ligand coordinates in a linear way, it is called *meridional* (mer). Three bidentate ligands lead to a helicoidal coordination of the metal ion. The left- and right-turning helices are called by the Greek letters, lambda ($\lambda-$) and delta ($\Delta-$) forms, respectively. These prefixes are placed before the chemical names and formula of the compounds. See Figure 2.

Examples for structural isomerism concerning coordination, ionization, hydrate, or linkage are in the order: $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Co(C_2O_4)_3]$

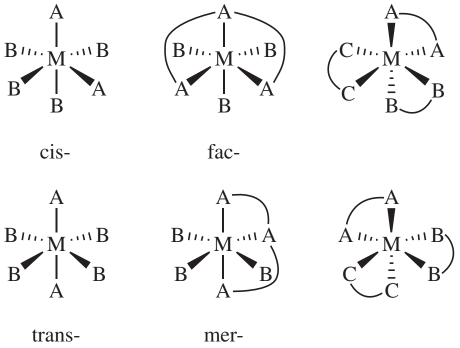


Fig. 2. Most frequent isomeries for octahedral complexes with mono-, tri-, and bidentate ligands.

$[Cr(NH_3)_6]$, $[Pt(NH_3)_3Br]NO_2$ and $[Pt(NH_3)_3NO_2]Br$, $[Cr(H_2O)_4Cl_2]$ Clú$2H_2O$ (bright-green), $[Cr(H_2O)_5Cl]Cl_2$úH_2O (gray-green) and $[Cr(H_2O)_6]Cl_3$ (violet), and $[Co(NH_3)_5(ONO)]$ and $[Co(NH_3)_5NO_2]$ with the NO_2 group once linked via the oxygen, once via the nitrogen atom.

Depending on the isomers, the compounds can have very different chemical and physical properties.

3. Examples of Coordination Compounds

3.1. Hydrides. Whereas dihydrogen was formerly thought to be bonded to metals only as the dissociated hydrido (H^-) species, a number of η^2-H_2 complexes are known (8). The η^2-H_2 designation implies the H−H bond is still intact and both hydrogen atoms are coordinated to the metal. Discovery of these dihydrogen species altered the thinking of chemists not only with regard to hydrogenation processes but even regarding the very nature of bonding between metals and ligands (8). Transition metal hydrides can be used as ligands for other metal ions, ie, in $\{[(PPh_3)_3IrH(\mu\text{-}H)_2]Ag\}(CF_3SO_3)$ (9).

3.2. Groups 1 (I A) and 2 (II A) Coordination Compounds. Ethers, polyethers, and especially the cyclic polyethers are ideal ligands for coordinating the alkali and alkaline earth metal ions. The macrocycle 18-crown-6 and its derivatives show bonding constants that increase in the order $Li^+ < Na^+$, $Cs^+ < Rb^+ < K^+$.Depending on the size of the cryptant, certain metal ions can be extracted via size exclusion. In biology, coordination of group, 1 (IA) (Na^+, K^+) and Group 2 (II A) metal ions (Mg^{2+}, Ca^{2+}) with cyclic polypeptides play an important role in the metal-ion transport through cell membranes. Such biological systems, ie, nonactine, can be modeled by macrocyclic polyethers or calixarenes (3) (10). See Figure 3.

Coordination compounds of Group 1 (IA) with main group element ligands can also afford polynuclear species, which are best studied for the smaller ions Li^+, Na^+, Mg^{2+}, and Ca^{2+}, due to their use in other fields of chemistry such as organic synthesis. They possess mainly polymeric ladder or cluster-type cage structures (11–13).

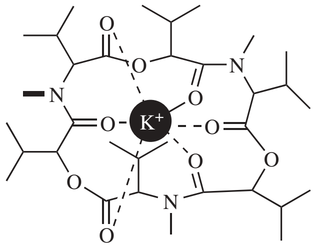


Fig. 3. Structure of the potassium complex with [D-hydroxyisovalericacid-*N*-methyl-L-valine]$_3$, the natural antibiotic enniatin B [917-13-5].

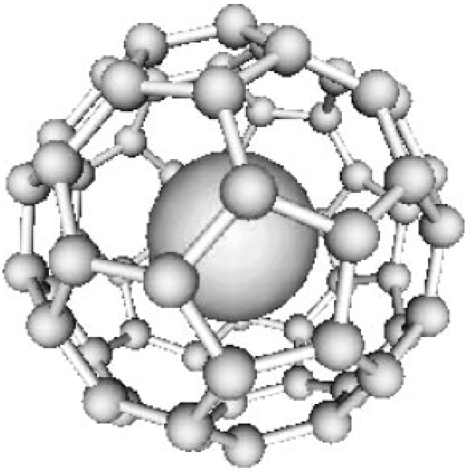
Coordination compounds of beryllium, a highly toxic element to living organisms, have been studied recently due to the increasing use of beryllium in materials like windows for X-rays or alloys with improved properties, and exhibit mainly a coordination number of 4 for the metal ion (14).

3.3. Main Group Metal Coordination Compounds.

Main group elements show a neat tendency to form element–element bonds, and this is expressed in their coordination compounds. The more electronegative the elements, the better donor ligands they are in their anionic form, and the less tendency they show for being coordinated themselves.

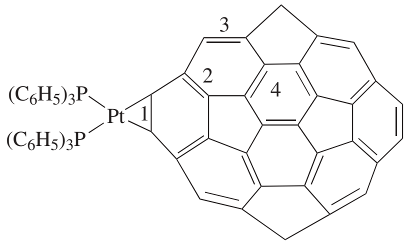
Group 13 (III A). Organometallic compounds are as well known as coordination compounds of the electron poor Group 3 (III B) ions with classical Lewis base donor ligands, such as in the boron–nitrogen compounds (aminoboranes) or the $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ anion with a metalloid center. Transition-metal complexes with boron are well described in a recent review (15). RAl or RGa [$R = Cp^*$, $C(SiMe_3)_3$ or other bulky fragments] can be used as ligands on transition-metal ions such as chromium, iron, nickel, and cobalt (16). The Tl^+ ion has a similar ionic radius to K^+. It may replace the latter in certain enzymes and is very toxic.

Group 14 (IV A). Carbon has a chemistry on its own, termed "organic chemistry" and is mainly based on covalent bonds. However, it may also act as a ligand. Metals bonded to hydrocarbons through carbon atoms are normally termed organometallics. Some examples will be given in the transition-metal examples. The metal fullerenes are newer (17). A large number of metal encapsulated fullerenes, ie, three-dimensional (3D) C_x polytopal cage derivatives, have been observed, such as the number of $M@C_{60}$ (**5**) species. The @ indicates the metal is inside the C_{60} polytope, known as a fullerene. Smaller $M@C_{28}$ species for $M = Ti$, Zr, Hf, and U, are thought to be stabilized by these tetravalent metals. External mono- and multimetallic fullerene complexes, eg, $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$ (**6**) or $[C_{60}\{M(PEt_3)_2\}_6]$, $M = Ni$, Pd, Pt (17) are also known where the η^2 indicates that two of the carbons in the C_{60} are bonded to the platinum. Additionally, alkali metal doped fullerenes having several metal atoms per fullerene show interesting properties. For example, Rb_3C_{60} becomes superconducting at 28 K. Another class of 3 D structures are the icosohedral metallocarbohedranes such as M_8C_{12}, where $M = Ti$, Zr, or Hf.



(5)

and



(6)

$SnCl_4$ [7646-78-8] is a good Friedel-Crafts catalyst, and $[Pb_2(OOCCH_3)_4]$ is used in chemistry as a strong but selective oxidizing agent. Polymeric fluorosilanes $Si_{16}F_{34}$, tin clusters $[Sn_3(OH)_4]^{2+}$, and lead clusters $[Pb_6O(OH)_6]^{4+}$ show the general tendency to form element-element bonds.

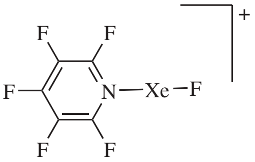
Group 15 (V A). Nitrogen-containing compounds are usually good ligands in coordination compounds, whereas nitrogen itself or its derivatives are rarely found complexed by ligands. So are the phosphines. For the heavier Group 5 (VB) elements, complexes do exist, such as $[Sb(C_2O_4)_3]^{3-}$ with an incomplete pentagonal-bipyramidal structure with a lone pair at one axial position. The tartrate complexes of antimony(III) have been used medicinically as “tartar emeric” for >300 years. Only bismuth features a real cationic chemistry in this group, and hexameric species predominate in solution, ie, $[Bi_6O_6(OH)_3]^{3+}$. The coordination chemistry of Bi(III) is surveyed by Briand and co-workers (18).

Group 16 (VI A). Whereas compounds of oxygen with more electronegative elements are rare, some inverse coordination compounds are known in which an oxide (O^{2-}) or peroxide (O_2^{2-}) anion is coordinated octahedrally by six cations such as alkali (Li^+) or alkaline earth metal (Ba^{2+}) cations in cluster compounds. On the other hand are the oxygen atoms containing ligands well suited to act as terminal and/or bridging ligands. Dioxygen itself can be found as a ligand, and can coordinate to a metal ion in four ways: terminally (= end-on, like in hemoglobin), side-on, linearly, or side-on bridging.

Sulfur, selenium, and tellurium form homo- and heteropolycations as well as polyanions with themselves. The former can react with Lewis bases to form monomeric species, the latter are ideal Lewis-basic ligands for transition-metal ions of the second and third row, due to their soft character.

Group 17 (VII A). Whereas fluoride, chloride, and bromide are strong ligands for many metal ions, iodide in its elemental form can act as a ligand for polar molecules as it is very soft and thus polarizable. Its charge-transfer complexes can be written as $I_2^-X^+$ (for X = element less electronegative than iodide, ie, S). It also has a tendency to form polyanions with itself, or the other halides. The heavier halogen atoms can be coordinated by oxygen to form hypohalite, halites, halates, and perhalates. Inverse complexes, in which anions, especially halides, are coordinated by ligands, are of interest in water treatment. Recent developments are the synthesis of amide groups containing macrocyclic and cryptate-like species that can be attached to the surface of a substrate in order to extract anions (19).

Group 18 (VIII A). The noble gases are usually inert, however, some rare coordination compounds are known that involve fluoride and oxide anions. Thus, complexes like $[Xe_2F_3]^+$ can be isolated and are used as fluoride transfer agents. The compound Rb_2XeF_8 is stable and decomposes only above 400°C. Recently, more classical coordination compounds like $[C_5F_5N{-}XeF]^+$ [114481-53-7] (**7**) were found to be stable at −30°C and could be isolated as $[AsF_6]^-$ salts from BrF_5 solution. Even organometallic coordination compounds like $[C_6F_5Xe]$ exist at low temperatures. For the heavier noble gas elements, $[HRnO_3]^+$, $[HRnO_4]^-$, and $[RnO_3F]$ have been reported (20).



(**7**)

3.4. Transition-Metal Coordination Compounds. *Group 3 (III B) + Lanthanum + Actinium.* Group 3 (III B) elements can have very high coordination numbers, up to 12 for lanthanum in $[La_2(SO_4)_3\,(H_2O)_9]$, 10 in $[Y(NO_3)_5]^{2-}$, and 9 for $[Sc(NO_3)_5]^{2-}$, the nitrate ligands binding as bidentate ligands except for one in the latter compound. This is due to their hard character, their ionic radius being rather small, and the ion being highly charged.

Group 4 (IV B). Still highly charged in their higher oxidation state, these metal ions prefer a high coordination number, ie, eight in $Ti(NO_3)_4$. Clusters via bridging ligands are known as well, such as in $[Ti(OEt)_4]_4$. Octahedral coordination is preferred for the oxidation states + III and + II. Nitrogen-donor ligands such as bipyridine can stabilize unusual oxidation states of Group 4 (IV B) metals, such as 0, -I, and -II, as in $Li_2[M(bpy)_3]$ formally (bpy = 2,2′-bipyridine.

These metals are then so strongly reducing that they can attack the ligands. The Ti(IV) coordination compounds are used in the Ziegler-Natta catalysis for the industrial synthesis of polypropylene.

Group 5 (V B). Having a wide range of oxidation states at their disposition, the coordination geometry varies from trigonal planar to square antiprismatic. These elements show a tendency to form polyoxometallates and clusters with bridging halide ligands. Metal organic compounds are known as well. The cluster chemistry of these and Group 6 (VI B) elements is vast, and was recently resumed by Prokopuk and Shriver (21).

Group 6 (VI B). A wide redox chemistry allows for coordination compounds with coordination numbers from 3 to 12 and 13. Similar to Group 5 (V B) elements, organometallic compounds are found as well as polyoxometallates with as much as 248 molybdenum atoms. The synthesis of unnatural amino acids is a very special example for the use of (chiral) organochromium carbenes (22).

Heteropolymetallates are known for their colorful species and applications in the synthesis of tungsten bronzes. Low-valent compounds compensate their electron poor configuration by sharing electrons in a metal–metal bond. Metal clusters containing molybdenum are found in numerous enzymes. In particular, the Mo–S bonds play an important role in biological systems, and therefore, the chemistry of Mo–S containing compounds has been widely investigated (23).

Group 7 (VII B). With a wide range of oxidation states, the possible coordination numbers in coordination compounds vary from 4 to 11. Mono- and polynuclear clusters are formed for halides as ligands, and mainly octahedral coordination compounds exist for these metal ions. Metal–metal bonds can be found in polynuclear clusters with a mainly octahedral geometry at each metal ion.

Group 8 (VIII). Coordination compounds with coordination numbers of 3–10 are known for these metal ions. For M(II)/M(III), the redox potentials change dramatically with the ligands used for their coordination. This implies changes in the ligand field and color transitions. Thus, in the late eighteenth century, cobalt coordination compounds were discovered to possess a variety of different colors depending on the ligands and isomers. Rhodium and iridium complexes find their application as catalysts in organic and pharmaceutical synthesis. Metal complexes of the cobalt group were found to activate dioxygen, which makes them potential candidates for biological applications (24). For metal ions with a d^4, d^5, d^6, or d^7 electronic configuration, the possibility of spin crossover is given for coordination compounds, making them interesting materials for information storage and switches. The Ni(II) coordination compounds are very frequent, and are interesting due to their magnetic properties. Macrocyclic N-donor ligands are known to stabilize Ni(III) and Ni(I), allowing a wide redox chemistry. Such compounds are used in catalytic reactions such as olefin epoxidation and electrochemical reduction of alkyl halide and carbon dioxide. Partially oxidized cyano coordination compounds of Pt(II), the so-called Krogmann's and Wolfram's salts, were shown to possess a one-dimensional (1 D) structure with conducting properties along the polymer axis. A similar structure is proposed for the so-called platinum blue "Platinblau" (25). Pt(II) and Pd(II) usually possess a coordination number of 4 in the form of quadratic planar complexes.

The trans-effect, a phenomenon in which the ligand in the trans position to a studied ligand is destabilized, has been investigated on behalf of the platinum compounds. In biochemistry, iron-containing proteins, namely, hemoglobine, myoglobine, cytochrome, and iron–sulfur proteins, play the role of oxygen transporters and storage as well as electron- transfer systems. Cobalt as a biologically essential element is found coordinated in vitamin B*12*. The organometallic chemistry of these elements is also a very wide subject, mainly covering carbonyl- and cyclopentadienyl-containing coordination compounds. Alkene and alkyne complexes of many of these metal ions find applications as catalysts.

Group 9 (VIII). Coordination numbers for Group 9 (VIII) elements vary from 2 to 12. Coordination compounds of M(I, II, III) are known. Copper plays an important role in biochemistry, where it is found coordinated by hemocyanine, the blood of many mollusks. Blue proteins are known in plants in which redox chemistry of Cu(II)/Cu(I) is involved (26). Silver finds its application in black and white photography. Most interesting is the coordination chemistry of gold clusters with metal–metal bonds that can be used to make gold colloid particles whose color is dependent of the particle size.

Group 10 (VIII). Coordination numbers between 2 and 8 are found for these elements. Their coordination chemistry is characterized by the M(II) cations, however, Hg(I) species are known in halide complexes. Zinc is one of the most important metal ions in biological systems. For example, in carboxypeptidase A, it catalyzes the hydrolysis of terminal peptide bonds during digestion. Compounds of cadmium and mercury, however, are among the most toxic ones for living organisms.

3.5. Rare Earth Metal Coordination Compounds.

Lanthanides. Lanthanide coordination chemistry has been rediscovered lately as their coordination compounds can exhibit interesting properties such as luminescence and paramagnetism. Lanthanide ions have been mostly studied in their Ln^{3+} form for their luminescence properties. Coordination numbers vary from 6 to 10, ligands usually exchanging rapidly in solution (27–29). The chemistry of Ln^{2+} was manily studied at the solid state for the properties of doped-solid state materials as phosphors, but their solution chemistry is evolving (30).

Actinides. The state-of-the-art coordination chemistry of these radioactive elements has been recently resumed by Kharisov and Mendez-Rojas (31). Extraction of actinide ions from waste waters has been studied with calixarenes and porphyrins (28,32). Plutonium is one of the best studied elements of the 5*f* element's row, especially concerning its biouptake via trihydroxamate desferrioxamine siderophore complexes of plutonium, which are recognized by microbial metal-siderophore binding sites (33).

4. Coordination Theories and Bonding

The quest for a comprehensible theory of coordination chemistry has given rise to the use of valence-bond, crystal-field, ligand-field, and molecular orbital theories. Ligand-field theory incorporates covalency with the electrostatic crystal field. The symmetry-induced separation of energy levels that is perceived from the chemical and physical properties of coordination compounds is inherent in all

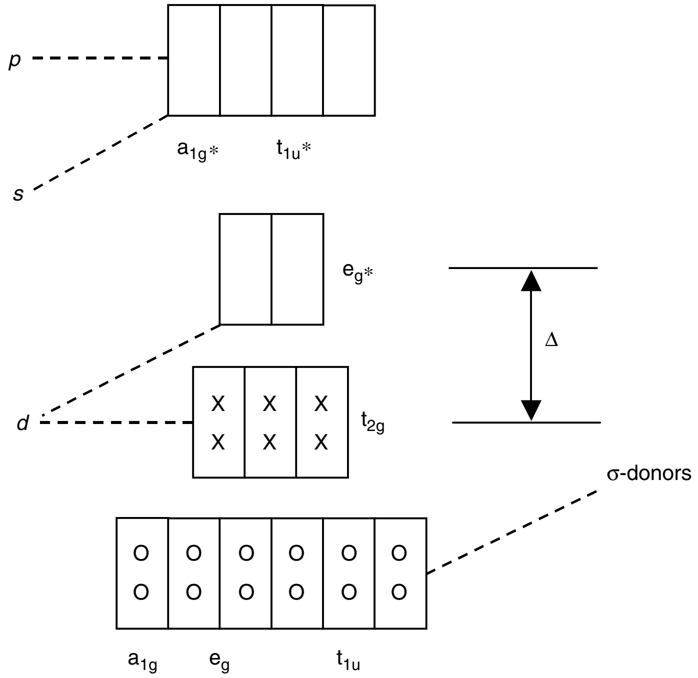


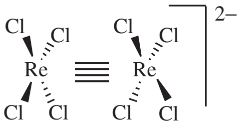
Fig. 4. Simplified molecular orbital diagram for a low spin octahedral d^6 complex, such as $[Co(NH_3)_6]^{3+}$, where $\Delta =$ energy difference; *a, e,* and *t* may be antisymmetric (subscript μ, ungerade) or centrosymmetric (subscript *g*, gerade) symmetry orbitals. (see text).

four theories, but symmetry effects are more apparent in the latter three. Excellent references on symmetry and group theory are available (34). Molecular orbital treatments of complexes range from the very simple semiempirical, such as Hückel, angular overlap, etc, through so-called *ab initio* methods (35,36).

A simplified energy-level diagram for octahedral complexes, the most common ones, is shown in Figure 4. The 12 electrons designated by circles are the electron-pair donors from the ligand-donor atoms; the electrons designated by *x* represent electrons from the *d* orbitals of a transition-metal ion. For octahedral metal ions having >3, but <8, *d* electrons, choices of spin states exist that are important in the kinetic, thermodynamic, spectroscopic, and magnetic properties of the octahedral species (see applications). In general, low spin octahedral complexes have a maximum number of electrons paired, and thus fewer antibonding electrons. Therefore, unless electron–electron repulsions predominate, the low spin state is more thermodynamically stable. Furthermore, low spin complexes are more kinetically inert.

Ligands having more than one electron pair can interact in a pi (π) sense as well as in the simple Lewis-base electron-pair sigma (σ) sense. Examples of π-donors include halide ions, oxygen donors, some nitrogen donors, such as NH_2^-, N_3^-, or β-ketoimines, and some sulfur donors, eg, S^{2-} and RS^-. Ligands such as the cyanide ion (cyano ligand) and carbon monoxide are considered to be π acceptors (π-acids) as a result of empty π* levels that have appropriate symmetry for π-type overlap with filled or partially filled metal orbitals, eg, the t_{2g} level of octahedral complexes (see CARBONYLS). This type of π interaction, also known as back-donation, helps relieve the buildup of electron density on the central metal atom that results from the ligand σ donation. Therefore, π-acceptor ligands stabilize low oxidation states.

Other types of bonding include donation by ligand π orbitals, as in the classical Zeiss's salt ion $[Pt(\eta^2\text{-}CH_2{=}CH_2)Cl_3]$ [12275-00-2] and sandwich compounds such as ferrocene. Another type is the delta (δ) bond, as in the $[Re_2Cl_8]^{2-}$ [19584-24-8] ion (**8**), which consists of two $ReCl_4$ squares with the Re−Re bonding and eclipsed chlorides. The Re−Re d bond makes the system quadruply bonded and holds the chlorides in sterically crowded conditions.



(**8**)

Numerous other coordination compounds contain two or more metal atoms having metal−metal bonds (37) and correspond therefore to cluster compounds in their strictest sense.

5. Properties

5.1. Stability. The thermodynamic stability of coordination compounds in solution has been extensively studied (38). The equilibrium constants may be reported as stability or formation constants.

$$M + n\,L \rightleftharpoons ML_n$$

This compound, ML_n, has a cumulative stability constant β_n related to the activities a of the species by

$$\beta_n = a_{ML_n} / \left(a_M a_L^n\right)$$

and the stepwise constant K_n

$$K_n = a_{ML_n} / (a_{ML_{n-1}} a_L)$$

Alternatively, instability or dissociation constants are sometimes used to describe compounds, and caution is necessary when comparing values from different sources.

Attempts have been made to categorize the interactions between metal ions and ligands. Whereas all metal ions interact more strongly with fluoride than with chloride in the gas phase, in aqueous solution a number of exceptions occur. Metal ions that have the normal (class **a**) aqueous solution stability order of $F \gg Cl > (Br > I$ also have $N \gg P > As > Sb$ and $O \gg S > Se > Te$ donor stability order (39). The inverse (class **b**) aqueous solution stability

Table 3. **Classification of Donors, Acceptors, and Solvents Based on Polarizability**

Class a, Nonpolarizable or Hard	Borderline	Class b, Polarizable or Soft[a]
	Metallic ions	
$H^+, Li^+, Na^+, K^+, Rb^+$,	Cs^+	
$Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$		
Sc^{3+}, Y^{3+}, La^{3+}, (lanthanides)$^{3+}$		
$Ti^{4+}, Zr^{4+}, Hf^{4+}$		
$VO^{2+}, Cr^{3+}, {UO_2}^{2+}, Pu^{4+}$,		
$Mn^{2+}, Fe^{3+}, Co^{3+}$	Fe^{2+}, Co^2	$Co(CN)_5^{2-}, Co(DMG))_2CH_3^+$
$Rh(NH_3)_5^{3+}$, $Ir(NH_3)_5^{3+}$		$Rh(CN)_5^{2-}$, $Ir(CN)_5^{2-}$, Rh^+, Ir^+
	Ni^{2+}, Cu^2	Pd^{2+}, Pt^{2+}, Cu^+, Ag^+, $Au^{+,3+}$
Al^{3+}, Ga^{3+}, In^{3+}	Zn^{2+}	Cd^{2+}, Hg_2^{2+}, Hg^{2+}, $Tl^{+,3+}$
Si^{4+}, Sn^{2+}, 4^+, As^{3+}	Pb^{2+}	
metals in oxidation state 4 + or higher[b]		metal in oxidation state 0 or lower
	Ligands	
F^-, O donors		H^-, CO,CO^-, R^- alkide ions, olefins aromatics
	N donors	P, As, Sb, Bi donors
	Cl^-, Br^-	S, Se, Te donors, I^-
	Solvents	
HF, H_2O, ROH	NH_3	$(CH_3)_2CO$, $(CH_3)_2SO$, $(CH_2)_4SO_2$, nitroparaffins, DMF

[a] DMG = dimethylglyoxime; DMF = dimethylformamide.

[b] Exceptions exist if a large number of soft bases are coordinated to the metal.

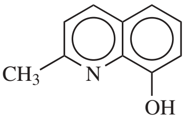
donor orders are $F \ll Cl < Br < I$, $N \ll P > As > Sb$, and $O \ll S \cong Se \cong Te$. This inverse order has long been considered related to the polarizability of the ligand.

Bases of low polarizability such as fluoride and the oxygen donors are termed hard bases. The corresponding class **a** cations are called hard acids; the class **b** acids and the polarizable bases are termed soft acids and soft bases, respectively. The general rule that hard prefers hard and soft prefers soft prevails. A classification is given in Table 3. Whereas the divisions are arbitrary, the trends are important. Attempts to provide quantitative gradations of "hardness and softness" have appeared (40). Another generality is the usual increase in stability constants for divalent 3*d* ions that occurs across the row of the Periodic Table through copper and then decreases for zinc (41).

Chelating or multidentate ligands are usually more stable than the analogous unidentate ligands, and this gives rise to the chelate effect. This effect is particularly evident for the formation of five-membered rings, anionic ligands, and aromatic donors. Larger rings, unless rigid, lose appreciable entropy on coordination; anionic ligands displace large quantities of oriented solvent molecules; and aromatic ring donors are normally rigid. Detailed quantitative considerations between similar systems is often difficult, however, because the ΔH and ΔS changes are normally a very small fraction of the enthalpies involved in the coordination bonds.

5.2. Steric Selectivity. In addition to the normal regularities that can be rationalized by electronic considerations, steric factors are important in coordination chemistry. To illustrate, at 100°C 8-hydroxyquinoline, or 8-quinolinol

(Hq) [148-24-3], precipitates both Mg^{2+} and Al^{3+} from aqueous solution as hydrated $Mg(q)_2$ (formulated as $Mg(q)_2(H_2O)_2$ [56531-18-1]) and as $Al(q)_3$ [2085-33-8], respectively. 2-Methyl-8-hydroxyquinoline [826-81-3] (**9**),



(**9**)

however, precipitates only Mg^{2+} from aqueous solution. The 2-methyl group prevents three of the methyl-substituted ligands from coordinating to Al^{3+} in water. By varying ring sizes and donor atoms of the macrocyclic crown ethers and the fused ring cryptates, different metal ions can be selectively accommodated. The crown ethers, such as 18-crown-6 or eicosahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecin [14187-32-7] (2) are highly selective for K^+ relative to Na^+. However, the cryptate 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacoxane [23978-09-8] (4) is selective for the sodium ion (see CATALYSIS, PHASE-TRANSFER).

Another example of steric selectivity involves the homopoly and heteropoly ions of molybdenum, tungsten, etc. Each molybdenum(VI) and tungsten(VI) ion is octahedrally coordinated to six oxygen (oxo) ligands. Chromium(VI) is too small and forms only the well-known chromate-type species having four oxo ligands. The ability of other cations to participate in stable heteropoly ion formation is also size related.

Coordination stereochemistry (including various forms of isomerization) is an area of significant research interest. This aspect of coordination is important for stereospecific catalytical applications.

5.3. Reactivity. Coordination species are often categorized in terms of the rate at which they undergo substitution reactions. Complexes that react with other ligands to give equilibrium conditions almost as fast as the reagents can be mixed by conventional techniques and are termed labile. Included are most of the complexes of the alkali metals, the alkaline earths, the aluminum family, the lanthanides, the actinides, and some of the transition-metal complexes. On the other hand, numerous transition-metal complexes that kinetically resist substitution reactions are termed inert. These terms refer to substitution reactivity and not to thermodynamic properties. As an illustration, the reaction rates, k, and activation parameters, ΔH^*, $(S^*$, and ΔV^*, of solvent-exchange for some of the aquated cations of the first-row transition elements are listed in Table 4. Although vanadium(II) and nickel(II) react more slowly than the other ions of oxidation state II listed, they are labile by the operational definition. On the other hand, chromium(III) and cobalt(III) complexes are inert. Iron(III), however, is labile even though iron lies between chromium and cobalt in the Periodic Table.

In general, octahedral complexes of transition-metal ions possessing 0, 1, or 2 electrons beyond the electronic configuration of the preceding noble gas, ie, d^0, d^1, d^2 configurations, are labile. The d^3 systems are usually inert; the relative lability of vanadium(II) may be charge and/or redox related. However, high spin

Table 4. **Water Exchange Rates and Activation Parameters of Hexaaqua Complexes at 25°C**[a,b]

Ion	k_1, s^{-1}	ΔH^*, kJ/mol[c]	ΔS^*, J/(K · mol)c	ΔV^*, cm^3/mol	Electron configuration[d]
V^{2+}	8.9×10^1	62	−0.4	−4.1	d^3
Cr^{2+}	7×10^9				d^4
Mn^{2+}	2.1×10^7	33	6	−5.4	d^5
Fe^{2+}	4.4×10^6	41	21	3.8	d^6
Co^{2+}	3.2×10^6	47	37	6.1	d^7
Ni^{2+}	3.2×10^4	57	32	7.2	d^8
Cu^{2+}	8×10^9	20			d^9
Ti^{3+}	1.8×10^5	43	1	−12.1	d^1
V^{3+}	5.0×10^2	49	−28	−8.9	d^2
Cr^{3+}	2.4×10^{-6}	109	12	−9.6	d^3
Fe^{3+}	1.6×10^2	64	12	−5.4	d^5
$CrOH^{2+}$	1.8×10^{-4}	110	55	2.7	d^3
$FeOH^{2+}$	1.2×10^5	42	5	7.0	d^5

[a] Ref. 1, unless noted otherwise.
[b] For the reaction $M(H_2O)_6^{n+} + H_2^{18}O \longrightarrow M(H_2O)_5(H_2^{18}O)^{n+} + H_2O$.
[c] To convert from J to cal, divide by 4.184.
[d] The de^4 (Cr^{2+}) and d^9(Cu^{2+}) complexes have distorted octahedra.

d^4, d^5, and d^6 species, which possess 4, 5, and 4 unpaired electrons, respectively, are labile, as are d^7 through d^{10} octahedral complexes. In addition to the inert d^3 systems, low spin d^4, d^5, and d^6 complexes are inert to rapid substitution. The d^8 species are the least labile of the configurations classed as labile.

Spin-paired octahedral d^6 ions and spin-free octahedral d^8 ions appear to react by largely dissociative (D or I_d) reactions, eg,

$$ML_n \longrightarrow ML_{n-1} + L \quad \text{followed by} \quad ML_{n-1} + L' \longrightarrow ML_{n-1}L'$$

although d^6 complexes THAT are just barely spin paired, such as tri-1,10-phenanthroline-iron(II) [14708-99-7] and ethylenediaminetetraacetatocobalt(III) [15136-66-0], appear to undergo associative (A or I_a) reactions, with good nucleophiles.

$$ML_n + L' \longrightarrow ML_nL' \longrightarrow ML_{n-1}L' + L$$

Discernible associative character is operative for divalent 3d ions through manganese and the trivalent ions through iron, as is evident from the volumes of activation in Table 4. However, deprotonation of a water molecule enhances the reaction rates by utilizing a conjugate base π- donation dissociative pathway. As can be seen from Table 4, there is a change in sign of the volume of activation ΔV^*. Four-coordinate square-planar molecules also show associative behavior in their reactions.

For many species, the effective atomic number (EAN) or 18- electron rule is helpful. Low spin transition-metal complexes having the EAN of the next noble gas (Table 5), which have 18 valence electrons, are usually inert, and normally

Table 5. **Complexes Having Effective Atomic Numbers (EAN) of a Noble Gas**[a]

Name	CAS Registry number	Molecular formula	Coordination number	EAN
nickel tetracarbonyl	[13463-39-3]	$Ni(CO)_4$	4	36
iron pentacarbonyl	[13463-40-6]	$Fe(CO)_5$	5	36
chromium hexacarbonyl	[13007-92-6]	$Cr(CO)_6$	6	36
hexaammineplatinum(IV)	[16893-12-2]	$Pt(NH_3)^{4+}{}_6$	6	86
tricarbonyldichlorobis-(triphenylphosphine)-molybdenum(II)	[17250-39-4]	$Mo(CO)_3Cl_2[P(C_6H_5)_3]_2$	7	54
tetrakis(8-quinolinolato) · tungsten(IV)	[17499-74-0]	$W(C_9H_6NO)_4$	8	86
nonahydridorhenate(VII)	[44863-47-0]	$[ReH_9]^{2-}$	9	86

[a] 18-Electron species.

react by dissociation. Each normal donor is considered to contribute two electrons; the remainder are metal valence electrons. Sixteen-electron complexes are often inert, if these are low spin and square planar, but can undergo associative substitution and oxidative–addition reactions.

Oxidation–Reduction. Redox or oxidation(reduction reactions are often governed by the hard–soft base rule. For example, a metal in a low oxidation state (relatively soft) can be oxidized more easily if surrounded by hard ligands or a hard solvent. Metals tend toward hard-acid behavior on oxidation. Redox rates are often limited by substitution rates of the reactant so that direct electron transfer can occur (42). If substitution is very slow, an outer sphere or tunneling reaction may occur. One-electron transfers are normally favored over multielectron processes, especially when three or more species must aggregate prior to reaction. However, oxidative addition

$$[Ir^{I}(P(C_6H_5)_3)_2(CO)Cl] + CH_3I \longrightarrow [Ir^{III}(P(C_6H_5)_3)_2(CO)(CH_3)ClI]$$

oxygen atom transfer

$$[M^{n+}L_x] + ClO^- \longrightarrow [M^{n+2}OL_x] + Cl^-$$

where M is a metal ion of charge n^+ and L is a ligand, are considered complementary two-electron transfers that are second only to one-electron processes in general. The distinction between atom and electron transfer is academic when a bridging atom moves from one species to another during a redox reaction:

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow_{H_2O} [Cr(H_2O)_5Cl]^{2+} + [Co(H_2O)_6]^{2+} + 5\,NH_3$$

In effect, the atom is transferred by internal sphere.

Coordination species that coordinate an organometallic ligand in catalytic processes often cycle between 16- and 18-electron systems, although ligand substitution also participates. For example, the first step in the well-studied olefin hydrogenation by chlorotris–(triphenylphosphine)rhodium(I) [14694-95-2] is now thought to be solvation followed by oxidative addition of hydrogen because the phosphine is somewhat labile and the solvated species adds hydrogen $\sim 10^7$ times as fast as the original complex and goes from a 16-electron rhodium(I) species to an 18- electron rhodium(III) species (43):

$$[RhCl\{P(C_6H_5)_3\}_3] + \text{solvent} \longrightarrow [RhCl\{P(C_6H_5)_3\}_2(\text{solv})] + P(C_6H_5)_3$$

$$[RhCl\{P(C_6H_5)_3\}_2(\text{solv})] + H_2 \longrightarrow [Rh(H)_2Cl\{P(C_6H_5)_3\}_2(\text{solv})]$$

where solv is solvent. An olefin, R, such as cyclohexene, substitutes for the solvent on the dihydride.

$$[Rh(H)_2Cl\{P(C_6H_5)_3\}_2(\text{solv})] + \text{olefin} \longrightarrow [Rh(H)_2Cl\{P(C_6H_5)_3\}_2(\eta^2 - R)] + \text{solvent}$$

This equilibrium is followed by a rate-determining tautomeric shift (18 → 16 electrons) to give a coordinated alkyl group:

$$[Rh(H)_2Cl\{P(C_6H_5)_3\}_2(\eta^2 - R)] \longrightarrow [Rh(RH)(H)Cl\{P(C_6H_5)_3\}_2]$$

where RH = alkyl. These last two steps are often called an olefin insertion. Addition of solvent gives the 18-electron complex, $[Rh(R')(H)Cl(P(C_6H_5)_3)_2(\text{solv})]$, and reductive elimination produces the original 16-electron solvated catalyst:

$$[Rh(R')(H)Cl(P(C_6H_5)_3)_2(\text{solv})] \longrightarrow [RhCl(P(C_6H_5)_3)_2(\text{solv})] + R'H$$

This catalytic cycle is related to some stereoselective industrial catalysis.

Photochemistry. Substitution rates of many complexes are enhanced by irradiation of the low energy d–d transitions, such as $t_{2g} \rightarrow e_g$ in octahedral coordination compounds (see 2). Quantum yields, Φ, defined as the ratios of moles of product formed (or reactant depleted) to the moles of photons absorbed, vary from very good, eg, chromium(III) ~0.5, to poor, eg, cobalt(III) (0.01, for ligand substitution (44). The substituted ligand is normally the stronger of the two on the axis with the weakest net pair of ligands as determined by spectrochemical relationships, ie, $CN^- > NO_2 > NH_3 > H_2O$, $F^- > Cl^-$. Exceptions do occur. Photochemical ligand dissociation is useful in the synthesis of multinuclear metal complexes such as diiron nonacarbonyl [15321-51-4] from iron pentacarbonyl [13463-40-6]

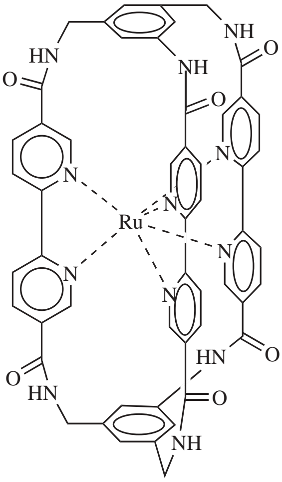
$$2[Fe(CO)_5] \xrightarrow{h\nu} [Fe_2(CO)_9] + CO$$

Or conversely, active radicals can be obtained by irradiating certain metal–metal bonded species:

$$[Mn_2(CO)_{10}] \xrightarrow{h\nu} 2[Mn(CO)_5]$$

Irradiation of coordination compounds in the charge-transfer spectral region can often enhance redox reactions. The quantum yields are variable.

The use of photochemical redox for practical energy transfer is being actively pursued (see HYDROGEN;HYDROGEN ENERGY). For example, sufficient energy is available in visible photons to split water into hydrogen and oxygen (45). Whereas derivatives of $[Ru(bpy)_3]^{2+}$ [15158-62-0], have been at the forefront of this area, a small amount of decomposition during the photochemical cycles had precluded commercialization of such systems. However, the encapsulated ruthenium(II) [116970-07-1] found in structure (**10**), is claimed to be 10^4 times more stable than $[Ru(bpy)_3]^{2+}$ (46).



(**10**)

Magnetism. Many coordination compounds are paramagnetic, ie, they have unpaired electrons. Combining several metal ions in one coordination compound can lead to a coupling of the individual magnetic moments. Their interaction depends on the distance between the magnetic ions and on the orientation of the magnetic moments. The magnetic moments can become aligned parallel to each other via exchange coupling below the Curie temperature, in which case one obtains ferromagnetism, or antiparallel to each other, leading to antiferromagnetism. Nonparallel alignment leads to ferrimagnetism. Magnetism of a compound can be measured with a Faraday or Gouy balance, with a superconducting quantum interference device (SQUID)-magnetometer or with nuclear magnetic resonance (NMR) methods for paramagnetic compounds, and the values obtained have to be corrected for the diamagnetic contribution.

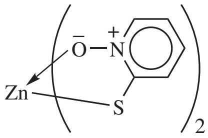
For metal ions with 4, 5, 6, or 7 d-electrons in octahedral symmetry, two configurations are possible: low spin with the maximum of electrons paired, or high spin with a maximum of unpaired electrons. Considering, eg, a d^6 metal ion such as Co^{3+}, it can have, depending on the ligand field, no unpaired electrons, as in $[Co(H_2O)_6]^{3+}$ [15275-05-5] or four unpaired electrons, as in $[CoF_6]^{3-}$ [15318-87-3] per ion, corresponding to a low spin, respectively a high spin octahedral complex. If the two spin states are close in energy, they can be populated differently depending on the temperature. Having different magnetic properties, the high spin–low spin distribution can easily be monitored via the effective magnetic moment or color changes.

Spin frustration can occur upon antiferromagnetic coupling in confined cluster compounds of three or more metal ions, when the magnetic moments of the ions cannot be arranged antiparallel to all other neighbors. Then, a total magnetic moment is observed, and molecular magnets are obtained that are currently subject to research (see the Applications section). The interested reader can refer to O. Kahn's book on molecular magnetism (see General References) and its mathematical explanation via the Van Vleck equation.

6. Applications

6.1. Bactericides and Fungicides.

Among marketed bactericides is the sodium salt of 2-pyridinethiol-1-oxide [3811-73-2], C_5H_5NOSNa. However, because this material is a strong skin irritant, the milder zinc chelate [13463-41-7] (**11**) is used in shampoos (see ANTIBACTERIAL AGENTS, HAIR PREPARATIONS) and also has been used in wood protection. The plant fungicides zineb [2122-67-7], $Zn(S_2CNHCH_2CH_2HCS_2)$, and maneb [12427-38-2], $Mn(S_2CNHCH_2CH_2NH CS_2)$, are polymeric chelates (see FUNGICIDES, AGRICULTURAL). A number of other coordination compounds, especially copper derivatives, are used as bactericides, fungicides, and disinfectants (47) (see DISINFECTANTS AND ANTISEPTICS). Some chelating agents used in the past, eg, ligands derived from 8-quinolinol, are no longer in use because of concern over their ability to facilitate unwanted metal-ion transport.



(**11**)

6.2. Catalysis.

Hydrogenation reactions can be catalyzed by a wide variety of coordination compounds (48) (see CATALYSIS). For example, dicobalt octacarbonyl [10210-68-1], $Co_2(CO)_8$, has been suggested to be a suitable catalyst for the hydrogenation of olefins to alkanes, aldehydes to alcohols, acid anhydrides to acids and aldehydes, as well as for the selective hydrogenation of polyenes to monoenes, and for the hydrogenation and isomerization of unsaturated fats (see also OXO PROCESS). The list for chlorotris(triphenylphospine)rhodium(I) [14694-95-2], Wilkinson's catalyst is even longer (49). On the other hand, a number of chromium tricarbonyl arene derivatives such as benzenetricarbonylchromium [12082-08-5], $C_6H_6Cr(CO)_3$, appear to be quite selective for the hydrogenation of 1,3- and 1,4-dienes to form cis-monoenes by 1,4-addition. Other homogeneous hydrogenation catalysts include coordination compounds of Fe, Ru, Ir, Ni, Pd, Pt, Os, and Cu. Probably the most important homogeneous hydrogenation application has been the Monsanto asymmetric (or enantioselective) synthesis of L-dopa [59-92-7], $C_9H_{11}NO_4$, a chiral amino acid used to treat Parkinson's disease, using a rhodium(I) catalyst containing a chiral phosphine (50).

The palladium chloride process for oxidizing olefins to aldehydes in aqueous solution (Wacker process) apparently involves an intermediate anionic complex such as dichloro-(ethylene)hydroxopalladate(II) or else a neutral aqua complex $PdCl_2(CH_2{=}CH_2)(H_2O)$ [165824-16-8]. The coordinated $PdCl_2$ is reduced to a Pd(0) species during the olefin oxidation and is reoxidized by the cupric–cuprous chloride couple, which in turn is reoxidized by oxygen, and the net reaction for any olefin ($RCH{=}CH_2$) is then

$$2\ RCH{=\!=}CH_2 + O_2 \xrightarrow{PdCl_2-CuCl_2} 2\ RCH_2CHO$$

Whereas this reaction was used to oxidize ethylene to acetaldehyde, which in turn was oxidized to acetic acid, the direct carbonylation of methanol to acetic acid has largely replaced the Wacker process industrially (see ACETIC ACID AND DERIVATIVES). A large number of other oxidation reactions of hydrocarbons by oxygen involve coordination compounds as detailed elsewhere (51).

The oxo reaction or hydroformylation converts an olefin to an aldehyde containing one or more carbon atoms, using tetracarbonylhydrocobalt [16842-03-8], $CoH(CO)_4$. Phosphine substitution lowers the pressure required for the hydroformylation. Rhodium coordination species are also used for this purpose and give a higher normal to branched aldehyde ratio in the hydroformylation of alkenes, and both rhodium and platinum species appear useful for asymmetric hydroformylation (52). The carbonylation of methanol by CO to acetic acid is catalyzed by coordination compounds of all three Group 9 (VIII) metals (Co, Rh, and Ir); however, the Monsanto process using rhodium complexes allows the use of lower CO pressures and is used worldwide. Adiponitrile is prepared industrially by the hydrocyanation (addition to two moles of HCN) to butadiene using a $Ni[P(OC_6H_5)_3]_4$ [14221-00-2] catalyst.

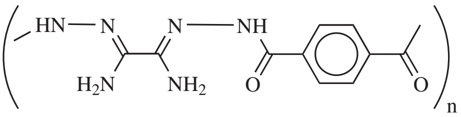
Metal coordination compounds may also provide alternatives to the heterogeneous catalysts used for the water gas shift reaction. In fact, Ru, Rh, Ir, and Pt coordination compounds have all shown some promise (53).

The stereospecific polymerization of alkenes is catalyzed by coordination compounds such as Ziegler-Natta catalysts, which are heterogeneous $TiCl_3$–Al alkyl complexes. Cobalt carbonyl is a catalyst for the polymerizations of monoepoxides; several rhodium and iridium coordination compounds catalyze certain polymerizations; and nickel complexes can initiate living polymers. Cyclooligomerization is promoted by coordination compounds of nickel, as well. The products depend on the sites available for coordination; eg, complexes having four octahedral sites available for coordination by acetylene produce cyclooctatetraene, three facial sites yield benzene, etc. Other transition-metal species catalyze similar cyclizations to obtain benzene.

Olefin isomerization can be catalyzed by a number of catalysts such as molybdenum hexacarbonyl [13939-06-5], $Mo(CO)_6$. This compound has also been found to catalyze the photopolymerization of vinyl monomers, the cyclization of olefins, the epoxidation of alkenes and peroxo species, the conversion of isocyanates to carbodiimides, etc. Rhodium carbonylhydrotris(triphenylphosphine) [17185-29-4], $RhH(CO)[P(C_6H_5)_3]_3$, is a multifunctional catalyst that accelerates the isomerization and hydroformylation of alkenes.

These applications are mostly examples of homogeneous catalysis. Coordination catalysts that are attached to polymers via phosphine, siloxy, or other side chains have also shown promise. The catalytic specificity is often modified by such immobilization. Metal enzymes are, from this point of view, anchored coordination catalysts immobilized by the protein chains. Even multistep syntheses are possible using alternating catalysts along polymer chains. Other polynuclear coordination species, such as the homopoly and heteropoly ions, also have applications in reaction catalysis.

6.3. Coordination Polymers. In addition to catalysts, polymeric coordination compounds have applications in high temperature coatings and lubricants utilizing poly(metal phosphinates) LUBRICATION AND LUBRICANTS), and also in the chelated fiber called Enkatherm, which is the zinc chelate of (polyterephythaloyl oxalic-bis-amidrazone), PTO (**12**). Enkatherm has been said to resist temperatures of up to 1500°C, and to be superior to any other flame-resistant fiber (54) (see FLAME RETARDANTS FOR TEXTILES). Sensitivity to acid solutions, poor long-term stability, and photosensitivity have limited the use of such materials. On the other hand, there are a large number of potential uses for metal coordination polymers (55), including use as high energy lithographic resists (56).

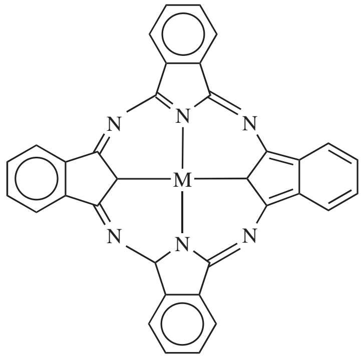


(**12**)

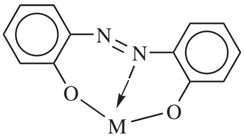
Polyelectrolytes, charged polymer chains based on metal ion coordination, are not only of fundamental interest but exhibit unique properties due to their viscosity and high charge, so that they are used for the formation of functional coatings and micelles, modified membranes and structured surfaces, as well as support for functional groups and devices.

In supramolecular chemistry, metal–ion coordination is used in combination with other noncovalent bonding types for the construction of low dimensional functional devices. For example, in combination with hydrogen bonding or π stacking, nanoporous materials can be obtained. Depending on the metal ions employed, optical and magnetic properties can be introduced into the polymers.

6.4. Dyes and Pigments. Several thousand metric tons of metalated or metal coordinated phthalocyanine dyes (**13**) are sold annually in the United States. The partially oxidized metalated phthalocyanine dyes are good conductors and are called molecular metals (see SEMICONDUCTORS, ORGANIC COMPOUND SEMICONDUCTORS; PHTHALOCYANINE COMPOUNDS; COLORANTS FOR PLASTICS). Azo dyes (qv) are also often metalated. The basic unit for a 2,2(-azobisphenol dye is shown as structure (**14**). Sulfonic acid groups are used to provide solubility, and a wide variety of other substituents influence color and stability. Such complexes have also found applications as analytical indicators, pigments, ie, for cosmetics, and paint additives.



(13)

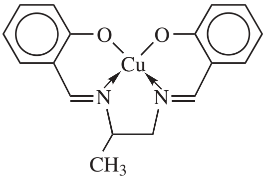


(14)

6.5. Photography. Coordination chemistry is important in classical black and white silver photographic systems, color photography, and in other special photographic areas (see PHOTOGRAPHY) (57). In order to have silver halide grains of appropriate size, silver halides are ripened by solutions containing a silver complexing agent. For example, $[AgX_2]^-$, where X is a halide, or $[Ag(NH_3)_2]^+$ [16972-61-5] can be used to partially dissolve and, through dilution, reprecipitate the silver halides in the gelatin emulsion. In fact, a light-insensitive emulsion consisting of $(NH_4)_2[AgBr_3]$ becomes light-sensitive AgBr when moistened with water or alcohol. Silver halides have increased light sensitivity when sensitized using 10^{-5} moles of a gold(I) or gold(III) coordination compound, such as ammonium dithiocyanatoaurate(I) [15066-31-6], $NH_4[Au(SCN)_2]$, or sodium tetrachloroaurate(III) [15189-51-2], $Na[AuCl_4]$, per mole of silver halide. Coordination compounds are used as emulsion stabilizers, developers, and are formed with the well-known thiosulfate fixers. Silver halide diffusion transfer processes and silver image stabilization also make use of coordination phenomena. A number of copper and chromium azo dyes have found use in diffusion transfer systems developed by Polaroid (see COLOR PHOTOGRAPHY, INSTANT). Coordination compounds are also important in a number of commercial photothermography and electrophotography applications as well as in the classic iron cyano blueprint images, a number of chromium systems, etc (58).

6.6. Electroplating. Aluminum can be electroplated by the electrolytic reduction of cryolite, which is trisodium aluminum hexafluoride [13775-53-6], Na_3AlF_6, containing alumina. Brass (see CAST COPPER ALLOYS) can be electroplated from aqueous cyanide solutions that contain cyano complexes of zinc(II) and copper(I). The soft CN^- stabilizes the copper as copper(I) and the two cyano complexes have comparable potentials. Without CN^- the potentials of aqueous zinc(II) and copper(I), as well as those of zinc(II) and copper(II), are >1V apart; thus only the copper plates out. Careful control of concentration and pH also enables brass to be deposited from solutions of citrate and tartrate. The noble metals are often plated from solutions in which coordination compounds help provide fine, even deposits (see ELECTROPLATING).

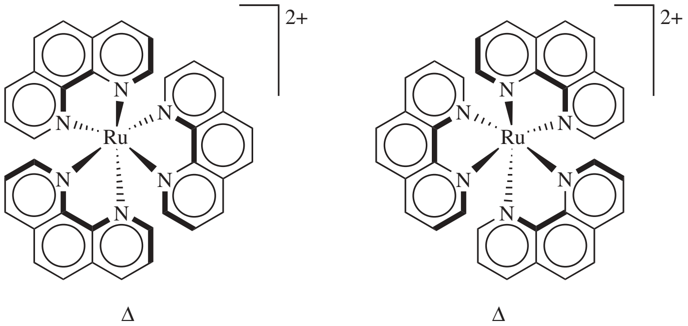
6.7. Fuel Additives. Antiknock fuel additives include lanthanide β-diketones, several mixed-ligand manganese carbonyl complexes, and tetraethyllead. Coordination compounds have been suggested as fuel oil additives. Metal deactivators for gasoline include Schiff-base ligands that minimize oxidation state changes in the traces of copper dissolving from fuel lines. For example, the planar copper(II) chelate [14522-52-2] (**15**) resists reduction to copper(I) in gasoline (see GASOLINE AND OTHER MOTOR FUELS).



(**15**)

6.8. Medical Applications. Calcium ethylenediaminetetraacetate [38620-52-9] is used to treat lead poisoning; the free ligand causes calcium loss (see LEAD COMPOUNDS, TOXICOLOGY). Many metal (main group as well as transition metal) coordination compounds show anticancer activity, among them Cp_2MCl_2 (M = Ti, V) as well as ionic species $[Cp_2MCl_2]^{n+}$ (M = Nb, Re, Mo), soluble ruthenium(II–IV) complexes used as antimetastatic agents, bis(β-diketonato)Ti(IV) compounds with aromatic substituents on the β-diketoiminato ligands active in the treatment of colon cancer, and the best known cisplatin, *cis*-dichlorodiammineplatinum(II) [15663-27-1], *cis*-$Pt(NH_3)_2Cl_2$, whose activity was discovered in 1971 (59,60) (see CHEMOTHERAPEUTICS, ANTICANCER). A number of other neutral coordination compounds of platinum(II) and (IV), and of other metals, are also under investigation. The improved cancer cure rates using combined chemotherapy and radiotherapy is leading to the development of Auger-emitting therapeutic drugs.

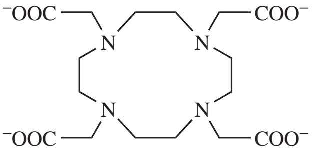
Radiopharmaceuticals based on a wide range of metal radionucleotides are used in diagnostics as well as therapy (61). Technetium-99m coordination compounds are used very widely as noninvasive imaging tools (62) (see IMAGING TECHNOLOGY; RADIOACTIVE TRACERS). Different coordination species concentrate in different organs. Several of the $[Tc^{V}O(chelate)_2]^{n}$ types have been used. In fact, the large majority of nuclear medicine scans in the United States are of technetium-99m complexes. Moreover, chiral transition-metal complexes have been used to probe nucleic acid structure (see NUCLEIC ACIDS). For example, the two chiral isomers of tris(1,10-phenanthroline)ruthenium(II) [24162-09-2] (**16**) interact differently with DNA. These compounds are enantioselective and provide an additional tool for DNA structural interpretation (63).



(**16**)

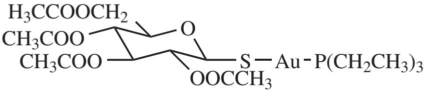
High throughput screening of immunoassays for the detection of antigens is available with water soluble and stable lanthanide complexes of Eu(III) and Tb(III) based on cryptates or multipodal ligands, which recognize antigens via specific binding sites and transfer energy after Ultraviolet radiation to a visible light emitting molecule.

Detection of abnormal tissue is realized by magnetic resonance imaging (mri), with contrast agents based on high spin Gd(III), Mn(II), and Fe(III) coordination compounds with a high number of unpaired electrons and long electron spin relaxation times. One of the best known is the coordination compound of gadolinium with DOTA [60239-18-1] (**17**), Na[Gd(DOTA)(H_2O)] used for the detection of blood–brain barrier abnormalities.



(**17**)

Anti infective, anti inflammatory and, anti arthritic agents are based mainly on transition metal complexes, whereas neurologically active compounds are based on lithium ion Gastrointestinal disorders are treated with Bi(III) coordination compounds. Gold complexes, such as (**18**) [34031-32-8], have been used to treat rheumatoid arthritis since 1935, and copper complexes may also be of some benefit as antiinflammatory drugs. There are many other examples available in the literature (64).



(**18**)

6.9. Chemosensors. Many coordination compounds are now constructed for their specific function arising from the combination of the metal ion with the ligand. The changes in the chemical and physical properties of complexes compared to their building blocks can be used in message transfers. For example, a lumophore can be attached to a metal-ion receptor unit via a spacer. Irradiating the lumophore without any metal ion fixed in the receptor, quenching by, ie, photoinduced electron transfer (PET) can occur, which means that the receptor is oxidized and the luminophore reduced. After complexation of a metal ion by the receptor, quenching is not possible any longer, and the lumophore will emit a characteristic luminescence on irradiation, indicating the presence of the specific metal ion (Fig. 5)(65–67).

Similar signaling devices have been developed for metal ions as well as anions. Anion receptors are, eg, metallacrown- or metallocenium-substituted macrocycles, and their binding can have an influence on the electrochemistry and the luminescence of the system. (68–70) Cooperativity is observed in systems that are able to recognize not only one specie, but also its counterion, eg, as it is the case for KI in a receptor cage formed by a Zn-porphyrine and a derived calix[4]arene (71). Luminescent lanthanide sensors can detect pH, pO_2, or selected anions (72).

6.10. Electronic Materials. Chemical vapor deposition (CVD) has become the method of choice in the growth of thin films of conductors, semi- or superconductors over a very large substrate area. The precursors for the preparation of such materials via CVD is mostly based on organometallic and inorganic chemistry. Especially the alkoxide coordination chemistry of Group 2 (II A) and transition metal ions yields soluble and volatile precursors suitable for CVD. For example, single source precursors for superconductors, containing Ba, Cu, and Y were in the focus of research for quite some time in order to obtain the high T_c–$YBa_2Cu_3O_{7-\delta}$.

With the aim to miniaturize electronic circuits, rod like molecular wires of nanometric dimension (**19**) have been designed based on metal ion complexation

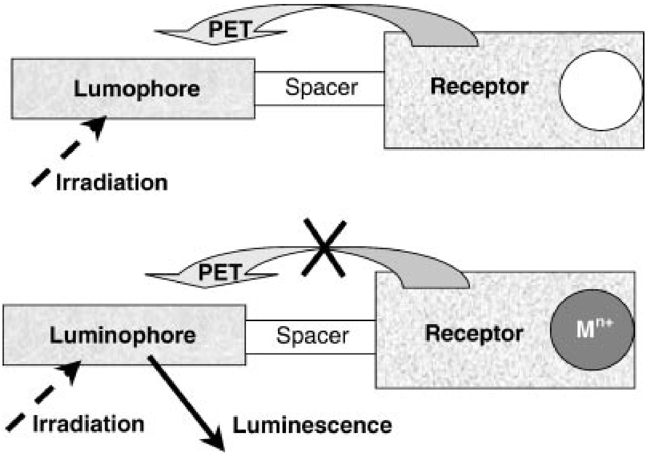
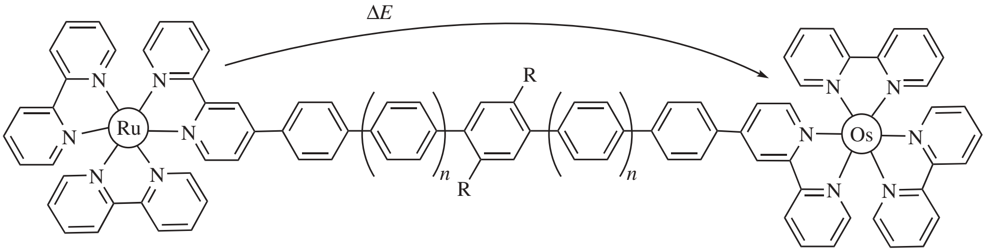


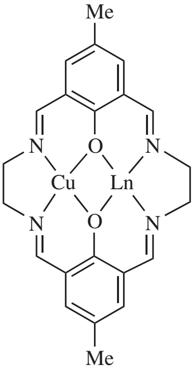
Fig. 5. Scheme showing the principle of a chemosensor based on blocking of luminescence via photo electron transfer when the receptor is empty and luminescence switched on in the presence of a metal ion in the receptor unit. [Based on A. P. de Silva and coworkers., *Coord. Chem. Rev.* **205**, 41–57 (2000)].

in order to transfer energy electronically (73).



(**19**)

6.11. Magnetic Materials. In multinuclear coordination compounds, metal ions can communicate with each other magnetically via space (dipole–dipols) and/or orbitals of the ligands. In particular, metal complexes were investigated due to their physicochemical properties arising from the presence of dissimilar metal ions in close proximity. Unique magnetic properties are obtained by the combination of paramagnetic d and f metal ions within one ligand [212895-01-7] (**20**). The field of molecular magnets has galned enormous attention in the last few years, and coordination chemists are challenged by the synthesis of such potentially magnetic switches (74,75).



(**20**)

6.12. Mimetics of Biological Systems. Manganese is one of several first-row transition elements that are employed in biological systems to play a variety of metabolic and structural roles. One is the oxygen-evolving complex OEC, which oxidizes water to oxygen during photosynthesis, manganese catalase, manganese superoxide dismutase, arginase, and manganese ribonucleotide reductase. In order to model nature, numerous coordination compounds of manganese and other metal ions in various oxidation states have been synthesized. One example out of many is the dinuclear [Mn(2-OHsalpn)](2-OHsalpn – *N*,*N*′-(salicylidenimine)-1,3-diaminopropan-2-ol)$_2$, which is active in hydrogen peroxide disproportionation (76). The proposed mechanism for its activity is outlined in Figure 6.

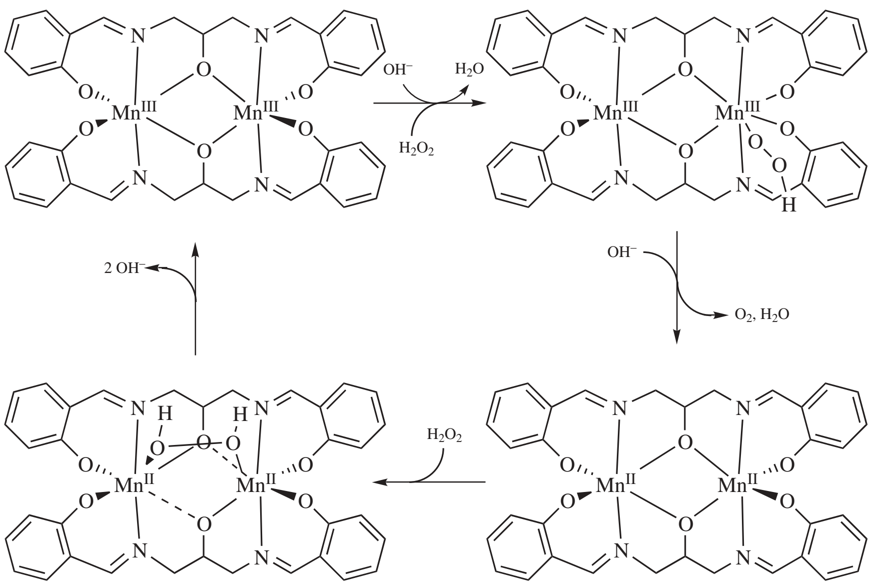


Fig. 6. Proposed mechanism of hydrogen peroxide disproportionation by the [Mn(2-OH-salpn)]$_2$ system.

6.13. Liquid Crystals. Metal-containing liquid crystals, metallomesogens, are used in the synthesis of flat screens with liquid crystal displays (LCDs). Due to their high anisotropy in structure, these compounds show birefringence (Fig. 7) and can be studied by polarized microscopy (77).

6.14. Miscellaneous. Numerous other applications of coordination compounds exist and may be found throughout this *series*. Tetrahedral cobalt(II) units are incorporated in cobalt blue glass (see COBALT AND COBALT ALLOYS; COLORANTS FOR CERAMICS; GLASS). Tetrahedral to octahedral coordination and the

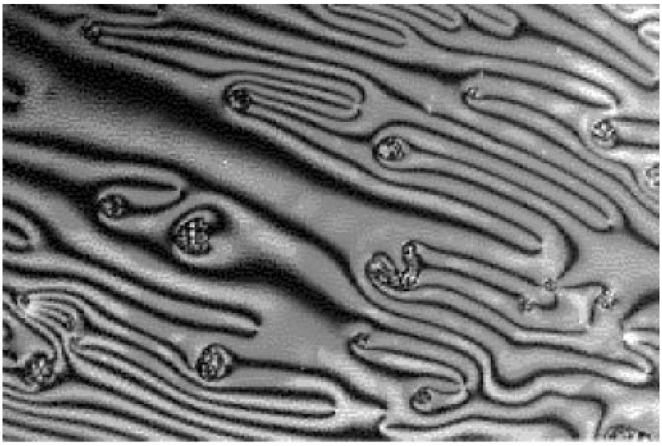


Fig. 7. Nematic mesophase of an organomanganese complex.

concurrent blue to pink indicator color change is obtained from moisture on cobalt(II) chloride (see DESICCANTS; DRYING). Nickel cyano clathrates are used for organic isomer separation, and the closely related zeolites as catalysts (78) and as porous molecular sieves (see INCLUSION COMPOUNDS). A number of dioxygen complexes are being considered for artificial blood applications (see BLOOD, ARTIFICIAL); tetrakis(β-diketonato) anionic chelates of europium are employed in laser applications (see LASERS); the neutral tris(β-diketonato) lanthanide chelates are used as nmr shift reagents (see MAGNETIC SPIN RESONANCE); and coordination compound membranes are under consideration for ion-selective electrodes (see ELECTROANALYTICAL TECHNIQUES). The use of coordination compounds in extractive metallurgy includes complexes in leaching, solvent-extraction, ion-exchange, precipitation, and electrochemical processes (see METALLURGY SURVEY, EXTRACTIVE METALLURGY) (79). Similarly, nuclear fuel cell preparation and reprocessing use coordination compounds (80) (see NUCLEAR REACTORS CHEMICAL REPROCESSING NUCLEAR FUEL RESERVES).

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