



Coordination Compounds in Chemistry

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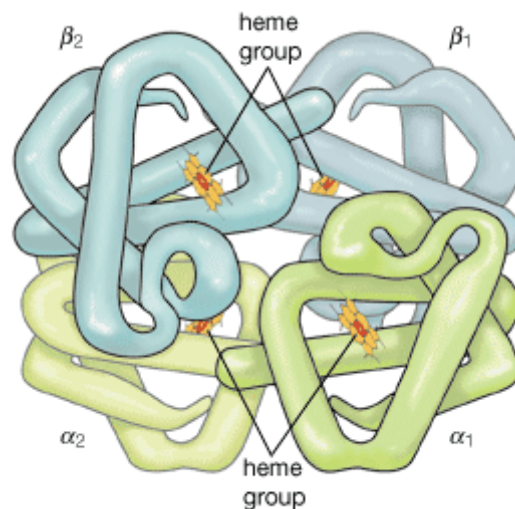
ABSTRACT: Coordination compounds are any of a class of substances with chemical structures in which a central metal atom is surrounded by nonmetal atoms or groups of atoms, called ligands, joined to it by chemical bonds. Coordination compounds include such substances as vitamin B₁₂, hemoglobin, and chlorophyll, dyes and pigments, and catalysts used in preparing organic substances. A major application of coordination compounds is their use as catalysts, which serve to alter the rate of chemical reactions. Certain complex metal catalysts, for example, play a key role in the production of polyethylene and polypropylene. In addition, a very stable class of organometallic coordination compounds has provided impetus to the development of organometallic chemistry. Organometallic coordination compounds are sometimes characterized by “sandwich” structures, in which two molecules of an unsaturated cyclic hydrocarbon, which lacks one or more hydrogen atoms, bond on either side of a metal atom. This results in a highly stable aromatic system.

KEYWORDS: coordination, compounds, metal, non-metal, organometallic, hydrocarbon, catalysts

I. INTRODUCTION

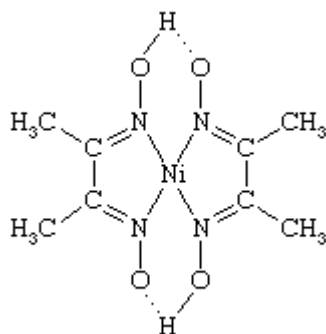
Naturally occurring coordination compounds are vital to living organisms. Metal complexes play a variety of important roles in biological systems. Many enzymes, the naturally occurring catalysts that regulate biological processes, are metal complexes (metalloenzymes); for example, ¹carboxypeptidase, a hydrolytic enzyme important in digestion, contains a zinc ion coordinated to several amino acid residues of the protein. Another enzyme, catalase, which is an efficient catalyst for the decomposition of hydrogen peroxide, contains iron-porphyrin complexes. In both cases, the coordinated metal ions are probably the sites of catalytic activity. Hemoglobin ²also contains iron-porphyrin complexes, its role as an oxygen carrier being related to the ability of the iron atoms to coordinate oxygen molecules reversibly. Other biologically important coordination compounds include chlorophyll (a magnesium-porphyrin complex) and vitamin B₁₂, ³a complex of cobalt with a macrocyclic ligand known as corrin.

The applications of coordination compounds in chemistry and technology are many and varied. The brilliant and intense colours of many coordination compounds, ⁴such as Prussian blue, render them of great value as dyes and pigments. Phthalocyanine complexes (e.g., copper phthalocyanine), containing large-ring ligands closely related to the porphyrins, constitute an important class of dyes for fabrics. ⁵Several important hydrometallurgical processes utilize metal complexes. Nickel, cobalt, and copper can be extracted from their ores as ammine complexes using aqueous ammonia ⁶. Differences in the stabilities and solubilities of the ammine complexes can be utilized in selective precipitation procedures that bring about separation of the metals. ⁷The purification of nickel can be effected by reaction with carbon monoxide to form the volatile tetracarbonylnickel complex, which can be distilled and thermally decomposed to deposit the pure metal. Aqueous cyanide solutions usually are employed to separate gold from its ores in the form of the extremely stable dicyanoaurate(-1) complex. Cyanide complexes also find application in electroplating. ⁸



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There are a number of ways in which coordination compounds are used in the analysis of various substances. These include (1) the selective precipitation of metal ions as complexes—for example, nickel(2+) ion as the



dimethylglyoxime complex⁹

(2) the formation of coloured complexes, such as the tetrachlorocobaltate(2-) ion, which can be determined spectrophotometrically—that is, by means of their light absorption properties, and (3) the preparation of complexes, such as metal acetylacetonates, which can be separated from aqueous solution by extraction with organic solvents.¹⁰

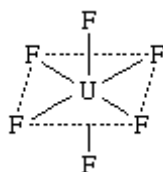
In certain circumstances, the presence of metal ions is undesirable, as, for example, in water, in which calcium (Ca²⁺) and magnesium (Mg²⁺) ions cause hardness. In such cases the undesirable effects of the metal ions frequently can be eliminated by “sequestering” the ions as harmless complexes through the addition of an appropriate complexing¹¹ reagent. Ethylenediaminetetraacetic acid (EDTA) forms very stable complexes, and it is widely used for this purpose.¹² Its applications include water softening (by tying up Ca²⁺ and Mg²⁺) and the preservation of organic substances, such as vegetable oils and rubber, in which case it combines with traces of transition metal ions that would catalyze oxidation of the organic substances.¹³

A technological and scientific development of major significance was the discovery in 1954 that certain complex metal catalysts—namely, a combination of titanium trichloride, or TiCl₃, and triethylaluminum, or Al(C₂H₅)₃—bring about the polymerizations of organic compounds with carbon-carbon double bonds under mild conditions to form polymers of high molecular weight and highly ordered (stereoregular) structures. Certain of these polymers are of great commercial importance because they are used to make many kinds of fibres, films, and plastics.¹⁴ Other technologically important processes based on metal complex catalysts include the catalysis by metal carbonyls, such as hydridotetracarbonylcobalt, of the so-called hydroformylation of olefins—i.e., of their reactions with hydrogen and carbon monoxide to form aldehydes—and the catalysis by tetrachloropalladate(2-) ions of the oxidation of ethylene in aqueous solution to acetaldehyde.¹⁵

II.DISCUSSION

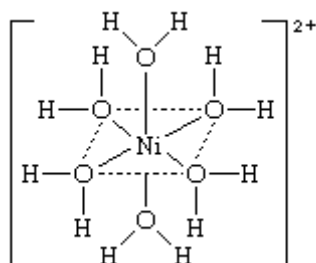
Coordination compounds have been studied extensively because of what they reveal about molecular structure and chemical bonding, as well as because of the unusual chemical nature and useful properties of certain coordination compounds. The general class of coordination compounds—or complexes, as they are sometimes called—is extensive and diverse. The substances in the class may be composed of electrically neutral molecules or of positively or negatively charged species (ions).¹⁶

Among the many coordination compounds having neutral molecules is uranium(+6) fluoride, or uranium hexafluoride (UF₆). The structural formula of the compound represents the actual arrangement of atoms in the molecules:



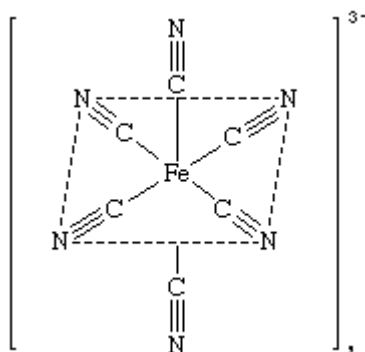
In this formula the solid lines, which represent bonds between atoms, show that four of the fluorine (F) atoms are bonded to the single atom of uranium (U) and lie in a plane with it, the plane being indicated by dotted lines (which do not represent bonds), whereas the remaining two fluorine atoms (also bonded to the uranium atom) lie above and below the plane, respectively.¹⁷

An example of an ionic coordination complex is the hydrated ion of nickel, (Ni), hexaaquanickel(2+) ion, [Ni(H₂O)₆]²⁺, the structure of which is shown below. In this structure, the symbols and lines are used as above, and the brackets and the “two plus” (2+) sign show that the double positive charge is assigned to the unit as a whole.¹⁸



The central metal atom in a coordination compound itself may be neutral or charged (ionic). The coordinated groups—or ligands—may be neutral molecules such as water (in the above example), ammonia (NH₃), or carbon monoxide (CO); negatively charged ions (anions) such as the fluoride (in the first example above) or cyanide ion (CN⁻); or, occasionally, positively charged ions (cations) such as the hydrazinium (N₂H₅⁺) or nitrosonium (NO⁺) ion.¹⁹

Complex ions—that is, the ionic members of the family of coordination substances—may exist as free ions in solution, or they may be incorporated into crystalline materials (salts) with other ions of opposite charge. In such salts, the complex ion may be either the cationic (positively charged) or the anionic (negatively charged) component (or, on occasion, both). The hydrated nickel ion (above) is an example of a cationic complex. An anionic complex is the hexacyanide of the ferric iron (Fe⁺³) ion, the hexacyanoferrate²⁰(3-) ion, [Fe(CN)₆]³⁻, or



Crystalline salts containing complex ions include potassium hexacyanoferrate(3⁻) (potassium ferricyanide), $K_3[Fe(CN)_6]$, and the hexahydrate of nickel chloride, hexaaquanickel(2+) chloride, $[Ni(H_2O)_6]Cl_2$. In each case the charge on the complex ion is balanced by ions of opposite charge. In the case of potassium ferricyanide, three positively charged potassium ions, K^+ , balance the negative charge on the complex, and in the nickel complex the positive charges are balanced by two negative chloride ions,²¹ Cl^- . The oxidation state of the central metal is determined from the charges on the ligands and the overall charge on the complex. For example, in hexaaquanickel(2+), water is electrically neutral and the charge on the complex ion is +2; thus, the oxidation state of Ni is +2. In hexacyanoferrate(3⁻), all six cyano ligands have a charge of -1; thus, the overall charge of -3 dictates that the oxidation state of Fe is +3.²²

The distinction between coordination compounds and other substances is, in fact, somewhat arbitrary. The designation coordination compound, however, is generally restricted to substances whose molecules or ions are discrete entities and in which the central atom is metal. Accordingly, molecules such as sulfur(+6) fluoride (sulfur hexafluoride; SF_6) and carbon(+4) fluoride (carbon tetrafluoride; CF_4) are not normally considered coordination compounds, because sulfur (S) and carbon (C) are nonmetallic elements. Yet there is no great difference between these compounds and, say, uranium hexafluoride. Furthermore, such simple ionic salts as sodium chloride ($NaCl$) or nickel(+2) fluoride (nickel difluoride; NiF_2) are not considered coordination compounds, because they consist of continuous ionic lattices rather than discrete molecules. Nevertheless, the arrangement (and bonding) of the anions surrounding the metal ions in these salts is similar to that in coordination compounds. Coordination compounds generally display a variety of distinctive physical and chemical properties, such as colour, magnetic susceptibility, solubility and volatility, an ability to undergo oxidation-reduction reactions, and catalytic activity.²³

A coordination compound is characterized by the nature of the central metal atom or ion, the oxidation state of the latter (that is, the gain or loss of electrons in passing from the neutral atom to the charged ion, sometimes referred to as the oxidation number), and the number, kind, and arrangement of the ligands. Because virtually all metallic elements form coordination compounds—sometimes in several oxidation states and usually with many different kinds of ligands—a large number of coordination compounds are known.

III.RESULTS

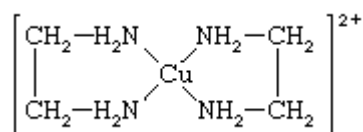
Coordination number is the term proposed by Werner to denote the total number of bonds from the ligands to the metal atom. Coordination numbers generally range between 2 and 12, with 4 (tetra-coordinate) and 6 (hexa-coordinate) being the most common. Werner referred to the central atom and the ligands surrounding it as the coordination sphere. Coordination number should be distinguished from oxidation number (defined in the previous paragraph). The oxidation number, designated by an Arabic number with an appropriate sign (or, sometimes, by a Roman numeral in parentheses), is an index derived from a simple and formal set of rules and is not a direct indicator of electron distribution or of the charge on the central metal ion or compound as a whole. For the hexaamminecobalt(3+) ion, $[Co(NH_3)_6]^{3+}$, and the neutral molecule triamminetritinitrocobalt(3+), $[Co(NO_2)_3(NH_3)_3]$, the coordination number of cobalt is 6 while its oxidation number is +3.

Each molecule or ion of a coordination compound includes a number of ligands, and, in any given substance, the ligands may be all alike, or they may be different. The term ligand was proposed by the German chemist Alfred Stock in 1916. Attachment of the ligands to the metal atom may be through only one atom, or it may be through several atoms. When only one atom is involved, the ligand is said to be monodentate; when two are involved, it is didentate,

and so on. In general, ligands utilizing more than one bond are said to be polydentate. Because a polydentate ligand is joined to the metal atom in more than one place, the resulting complex is said to be cyclic—i.e., to contain a ring of atoms.²² Coordination compounds containing polydentate ligands are called chelates (from Greek chele, “claw”), and their formation is termed chelation. Chelates are particularly stable and useful. An example of a typical chelate is bis(1,2-ethanediamine)copper(2+), the complex formed between the cupric ion (Cu^{2+}) and the organic compound ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, often abbreviated as en in formulas). The formula of the complex is



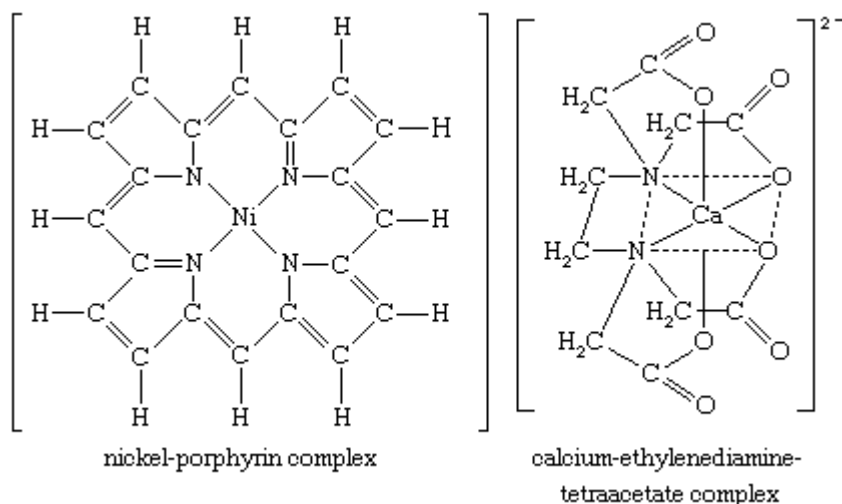
and the structural formula is



Mononuclear, monodentate

The simplest types of coordination compounds are those containing a single metal atom or ion (mononuclear compounds) surrounded by monodentate ligands. Most of the coordination compounds already cited belong to this class. Among the ligands forming such complexes are a wide variety of neutral molecules (such as ammonia, water, carbon monoxide, and nitrogen), as well as monoatomic and polyatomic anions (such as the hydride, fluoride, chloride, oxide, hydroxide, nitrite, thiocyanate, carbonate, sulfate, and phosphate ions). Coordination of such ligands to the metal virtually always occurs through an atom possessing an unshared pair of electrons, which it donates to the metal to form a coordinate bond with the latter. Among the atoms that are known to coordinate to metals are those of virtually all the nonmetallic elements (such as hydrogen, carbon, oxygen, nitrogen, and sulfur), with the exception of the noble gases (helium [He], neon [Ne], argon [Ar], krypton [Kr], and xenon [Xe]). Polydentate²⁰

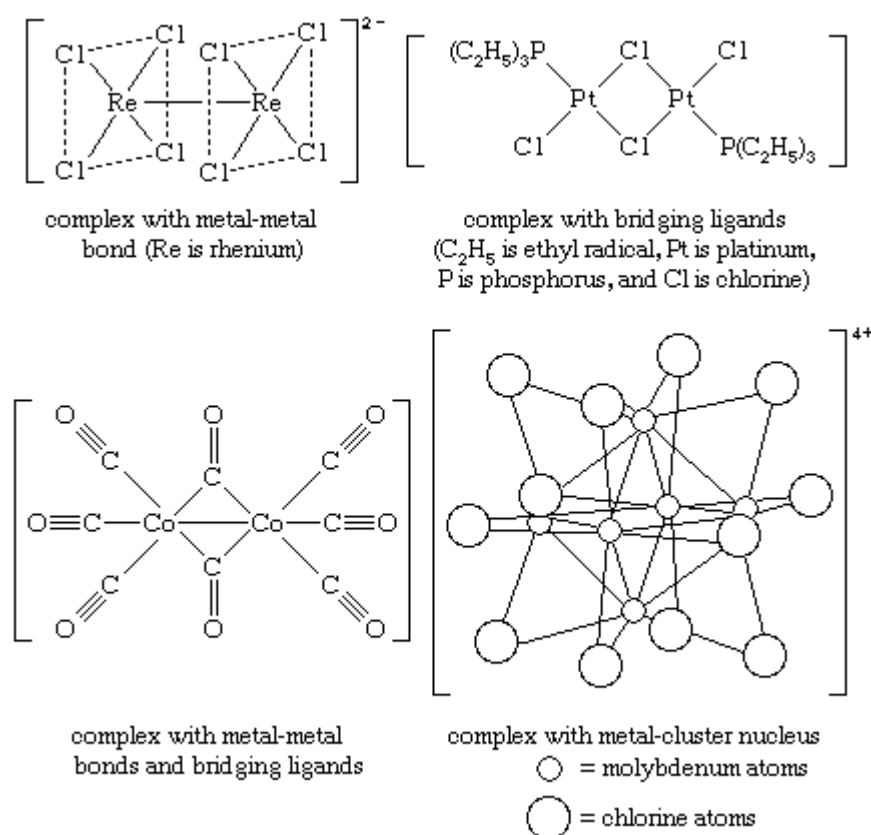
The chelate complex of a copper ion and ethylenediamine mentioned above is an example of a compound formed between a metal ion and a didentate ligand. Two further examples of chelate complexes are shown below.



These are a nickel complex with a tetradentate large-ring ligand, known as a porphyrin, and a calcium complex with a hexadentate ligand, ethylenediaminetetraacetate (EDTA). Because metal-ligand attachment in such chelate complexes is through several bonds, such complexes tend to be very stable.

The commonest and most stable complexes of the lanthanoid metals (the series of 14 f-block elements following lanthanum [atomic number 57]) are those with chelating oxygen ligands, such as EDTA-type anions or hydroxy acids (e.g., tartaric or citric acids). The formation of such water-soluble complexes is employed in the separation of lanthanoids by ion-exchange chromatography. Lanthanoid β -diketonates are well known because some fluorinated β -diketonates yield volatile complexes amenable to gas-chromatographic separations. Neutral complexes can complex further to yield anionic species such as octacoordinated tetrakis(thenoyltrifluoroacetato)neodymate(1-), $[\text{Nd}(\text{CF}_3\text{COCHCOCF}_3)_4]^-$.

Certain ligands may be either monodentate or polydentate, depending on the particular compound in which they occur. The carbonate ion, $(\text{CO}_3)^{2-}$, for example, is coordinated to the cobalt (Co^{3+}) ions in two cobalt complexes, pentaamminecarbonatocobalt(+), $[\text{Co}(\text{CO}_3)(\text{NH}_3)_5]^+$, and tetraamminecarbonatocobalt(+), $[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]^+$, through one and two oxygen atoms, respectively.²⁴

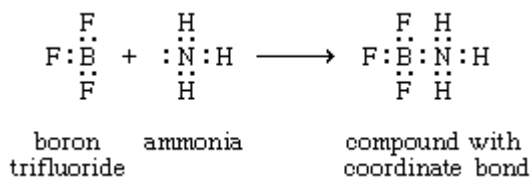


Polynuclear complexes are coordination compounds containing two or more metal atoms, or ions, in a single coordination sphere. The two atoms may be held together through direct metal-metal bonds, through bridging ligands, or both. Examples of each are shown above along with a unique metal-cluster complex having six metal atoms in its nucleus

IV. CONCLUSIONS

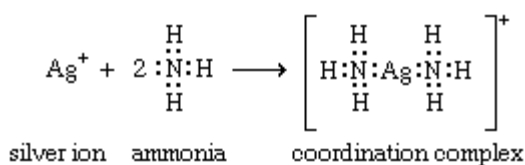
Structure and bonding of coordination compounds

Werner originally postulated that coordination compounds can be formed because the central atoms carry the capacity to form secondary, or coordinate, bonds, in addition to the normal, or valence, bonds. A more complete description of coordinate bonding, in terms of electron pairs, became possible in the 1920s, following the introduction of the concept that all covalent bonds consist of electron pairs shared between atoms, an idea advanced chiefly by the American physical chemist Gilbert N. Lewis. In Lewis's formulation, when both electrons are contributed by one of the atoms, as in the boron-nitrogen bond formed when the substance boron trifluoride (BF_3) combines with ammonia, the bond is called a coordinate bond:



In Lewis's formulas, the valence (or bonding) electrons are indicated by dots, with each pair of dots between two atomic symbols representing a bond between the corresponding atoms.

Following Lewis's ideas, the suggestion was made that the bonds between metals and ligands were of this same type, with the ligands acting as electron donors and the metal ions as electron acceptors. This suggestion provided the first electronic interpretation of bonding in coordination compounds. The coordination reaction between silver ions and ammonia illustrates the resemblance of coordination compounds to the situation in the boron-nitrogen compound. According to this view, the metal ion can be regarded as a so-called Lewis acid and the ligands as Lewis bases:



A coordinate bond may also be denoted by an arrow pointing from the donor to the acceptor.
Geometry

Many coordination compounds have distinct geometric structures. Two common forms are the square planar, in which four ligands are arranged at the corners of a hypothetical square around the central metal atom, and the octahedral, in which six ligands are arranged, four in a plane and one each above and below the plane. Altering the position of the ligands relative to one another can produce different compounds with the same chemical formula. Thus, a cobalt ion linked to two chloride ions and four molecules of ammonia can occur in both green and violet forms according to how the six ligands are placed. Replacing a ligand also can affect the colour. A cobalt ion linked to six ammonia molecules is yellow. Replacing one of the ammonia molecules with a water molecule turns it rose red. Replacing all six ammonia molecules with water molecules turns it purple.

Among the essential properties of coordination compounds are the number and arrangement of the ligands attached to the central metal atom or ion—that is, the coordination number and the coordination geometry, respectively. The coordination number of a particular complex is determined by the relative sizes of the metal atom and the ligands, by spatial (steric) constraints governing the shapes (conformations) of polydentate ligands, and by electronic factors, most notably the electronic configuration of the metal ion. Although coordination numbers from 1 to 16 are known, those below 3 and above 8 are rare. Possible structures and examples of species for the various coordination numbers are as follows: three, trigonal planar ($[\text{Au}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]^+$); four, tetrahedral ($[\text{CoCl}_4]^{2-}$) or square planar ($[\text{PtCl}_4]^{2-}$); five, trigonal bipyramid ($[\text{CuCl}_5]^{3-}$) or square pyramid ($\text{VO}(\text{acetylacetonate})_2$); six, octahedral ($[\text{Co}(\text{NO}_2)_6]^{3-}$) or trigonal prismatic ($[\text{Re}\{\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2\}_3]$); seven, pentagonal bipyramid ($\text{Na}_5[\text{Mo}(\text{CN})_7] \cdot 10\text{H}_2\text{O}$), capped trigonal prism (cation in $[\text{Ca}(\text{H}_2\text{O})_7]_2[\text{Cd}_6\text{Cl}_{16}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$), or capped octahedron (cation in $[\text{Mo}(\text{CNC}_6\text{H}_5)_7][\text{PF}_6]_2$); eight, square antiprism or dodecahedron ($[\text{Zr}(\text{acetylacetonate})_4]$); and nine, capped square antiprism ($\text{La}(\text{NH}_3)_9]^{3+}$) or tricapped trigonal prism ($[\text{ReH}_9]^{2-}$).

Coordination numbers are also affected by the 18-electron rule (sometimes called the noble gas rule), which states that coordination compounds in which the total number of valence electrons approaches but does not exceed 18 (the number of electrons in the valence shells of the noble gases) are most stable. The stabilities of 18-electron valence shells are also reflected in the coordination numbers of the stable mononuclear carbonyls of different metals that have oxidation number 0—e.g., tetracarbonylnickel, pentacarbonyliron, and hexacarbonylchromium (each of which has a valence shell of 18).



The 18-electron rule applies particularly to covalent complexes, such as the cyanides, carbonyls, and phosphines. For more ionic (also called outer-orbital) complexes, such as fluoro or aqua complexes, electronic factors are less important in determining coordination numbers, and configurations corresponding to more than 18 valence electrons are not uncommon. Several nickel(+2) complexes, for example—including the hexafluoro, hexaaqua, and hexaammine complexes—each have 20 valence electrons.

Any one metal ion tends to have the same coordination number in different complexes—e.g., generally six for chromium(+3)—but this is not invariably so. Differences in coordination number may result from differences in the sizes of the ligands; for example, the iron(+3) ion is able to accommodate six fluoride ions in the hexafluoro complex $[\text{FeF}_6]^{3-}$ but only four of the larger chloride ions in the tetrachloro complex $[\text{FeCl}_4]^-$. In some cases, a metal ion and a ligand form two or more complexes with different coordination numbers—e.g., tetracyanonickelate $[\text{Ni}(\text{CN})_4]^{2-}$ and pentacyanonickelate $[\text{Ni}(\text{CN})_5]^{3-}$, both of which contain Ni in the +2 oxidation state.²⁴

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