INORGANIC AND METAL-ORGANIC SYNTHESIS

Fausto Calderazzo
University of Pisa, Italy

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Contents

Summary

The fundamental properties of the elements in their physical state of monoatomic gases, namely, their electronic configuration, ionization energy, and electron affinity, are considered first. In their combinations with other elements of the Periodic Table, metals may form compounds that fall within the classification of inorganic systems. A specific area of inorganic chemistry deals with organometallic compounds (i.e., those containing at least one metal–carbon bond in their composition). Bonds within inorganic compounds can be, to a first approximation, classified into two main categories: ionic and coordinative. The former type of bond is normally representative of elements from opposite areas of the Periodic Table that combine with each other, the energy expenditure for ionization being compensated by the electrostatic lattice energy. Metals combine with ligands in the so-called coordinative bond, thus spanning coordination numbers from four (tetrahedral and square planar) to six (octahedral) and higher for lanthanide elements. Stable compounds are formed when the molecular orbitals of lower energy are filled, low-oxidation state systems leading, usually, to spin-paired

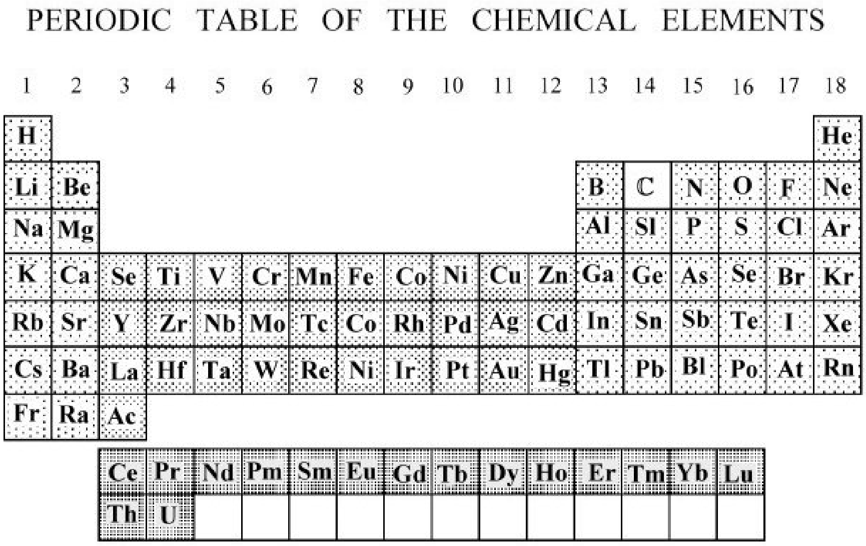
complexes. Starting from some fundamental properties of metals, in particular from the enthalpy of formation of gaseous atoms in their standard state − $\Delta H^0_{(g)}$, kJ mol^{-1}, which measure the cohesive strength in the condensed phase − considerations about the strength of metal–ligand bonds are presented, depending on the position of the element in the Periodic Table. Some kinetic data concerning ligand substitution in, presumably, unimolecular processes, are presented as a function of the position of the central metal atom in the Periodic Table. The descriptive chemistry of some representative elements –hydrogen, carbon, nitrogen, phosphorus, oxygen, sulfur, and halogens − is presented, taking into account the fact that examples are selected using the criterion that systems are arranged according to the metal-coordinated atom.

1. Introduction

About 70% of the 92 chemically relevant elements of the Periodic Table have metallic properties in the bulk (i.e., high electrical and thermal conductivities, high reflectivity, mechanical strength, or ductility) (see *Chemical Matter: Elements and their Classification through the Periodic System*). Metals can combine with other metallic elements forming alloys or with nonmetallic elements forming numerous classes of compounds. Inorganic chemistry deals with the properties of metals in the bulk, and with the synthesis and properties of the compounds formed by metals with nonmetallic elements. This article will be restricted to this class of compounds, and within this class particular stress will be given to compounds of low nuclearity. The coordinating properties of the central metal atom are more easily visualized in compounds of low nuclearity.

(Throughout this chapter, the classification of chemical elements in Groups from 1 to 18 inclusive will be adopted [Fluck, E.; Leigh, G. J.]. Each element, independent of its name and symbol, can be identified by two numbers specifying Period and Group in that order. For example, carbon, represented by symbol C, could be defined as the element 2-14; gallium (Ga) is element 4-13; and hafnium (Hf) is element 6-4.)

Figure 1 displays the chemical elements, including those belonging to the d and f transition series. Within the $5f$ series, the transuranic elements have been omitted.



PERIODIC TABLE OF THE CHEMICAL ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Se	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Co	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Ni	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	U														

Figure 1. The Periodic Table of the chemical elements, each identified by a symbol and numerically disposed according to Groups (from 1 to 18) and Periods (from 1 to 7).

The elements of the so-called Main Groups possess $\mathrm{n}s - \mathrm{n}p$ valence orbitals. The intermediate area defines the transition d metals, which have $(\mathrm{n}-1)\,d - \mathrm{n}s - \mathrm{n}p$ valence orbitals. Carbon (i.e., element 2-14) occupies a special position for reasons that will soon appear clear. Chemical elements are arranged in a numerical sequence that is of universal validity. In all parts of the Universe under the conditions of temperature and pressure available in our laboratories or in our environment, only the chemical elements of the Periodic Table can exist. This comes from their physical nature, the atomic number Z being defined by the elementary positive (protons) and negative (electrons) particles of each atomic system.

Chemical elements in their physical state of monoatomic gases have characteristic properties, namely, the electronic configuration, the ionization energy, and the electron affinity. These quantities are defined in the Glossary.

By considering the properties according to Groups, elements with an $\mathrm{n}s - \mathrm{n}p$ valence electron configuration have a constant distribution of the electrons independent of the Period n. For example, both boron (Period 2) and aluminum (Period 3) of Group 13 have the electronic configuration $\mathrm{n}s^2 - \mathrm{n}p^1$; nitrogen and bismuth, respectively, in Periods 2 and 6 of Group 15, have the electronic configurations $\mathrm{n}s^2 - \mathrm{n}p^2$. On the other hand, within the transition *d* elements, the electronic distribution may vary within the same Group. For example, the electronic distribution of the 10 valence electrons for the elements of Group 10 is $\mathrm{Ni}: 3d^8,\ 4s^2 - \mathrm{Pd}:\ 4d^{10} - \mathrm{Pt}: 5d^9, 6s^1$. The electronic configuration of each atom derives from the relative energy of the orbitals and from the pairing energy, which depends on the atomic number Z. Thus, in the case of palladium, the $4d$ orbital is sufficiently low in energy to allow all the valence electrons to be paired up.

It is important to notice that carbon occupies a special position within the Periodic Table, see Figure 1; it is an element of Period 2 and has as many electrons –four (i.e., $2s^2 - 2p^2$) – as valence orbitals. Moreover, the orbitals of the valence shell 3 (i.e., of Period 3) are far away in energy and thus unable to take any consistent part in chemical bonding. Thus, carbon is frequently tetracoordinated in the tetrahedral geometry (sp^3 hybridization), although planar (sp^2 hybridization) or linear geometries (sp hybridization) are also possible. Catenation (i.e., the formation of element–element single bonds in sequence) is particularly favorable for carbon, the $\mathrm{C-C}$ bond enthalpy being estimated to be $356\ \mathrm{kJ\ mol^{-1}}$. Carbon can assume a coordination number higher than four, e.g., in some dinuclear aluminum-alkyls, i.e., $\mathrm{R_2Al(\mu-R)_2AlR_2}$: the dinuclear molecule contains two bridging alkyl groups, $\mu-\mathrm{R}$, each containing pentacoordinated carbon, the nearest neighbors of carbon being represented by the two aluminum atoms, in addition to the covalent bonds within the R group. In some inorganic metal-containing clusters, a carbon atom may be encapsulated by a number of metal atoms higher than four.

Compounds containing one or more metal atoms are considered to be inorganic. Within this category, compounds with at least one metal–carbon bond are classified as organometallic. By contrast, compounds containing at least one carbon atom and no metals are classified in the area of organic chemistry.

Metals of Groups 1 and 2 form essentially ionic compounds with elements on the opposite side of the Periodic Table – especially with elements belonging to Groups 16 and 17, in Periods 2 and 3. Important within this category are halides or oxides of metals in relatively low oxidation states, +I for alkali metals or +II for earth-alkali metals. In these systems the components are held together by essentially electrostatic forces (e.g., NaCl forms a ionic crystal containing both $\mathrm{Na^+}$ and $\mathrm{Cl^-}$). From a didactic viewpoint, sodium chloride can be considered to derive from the direct combination of the elements. The reaction is thermodynamically favored, the experimental ΔH_f^0 corresponding to $-411\ \mathrm{kJ\ mol^{-1}}$. The enthalpy-based Born–Haber cycle of Figure 2 describes the transformation from the chemical element M (an alkali metal) and a halogen in the appropriate stoichiometric ratio, to give the ionic metal halide, reagents and products being in their standard states (see *Molecular Energetics: Valence Bond and Molecular Orbital Methods* and *Density Functional Theory of Atoms and Molecules*).

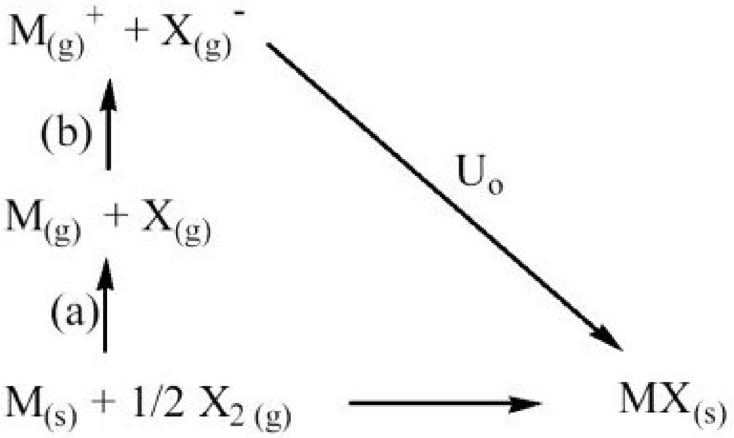


Figure 2. The Born–Haber cycle for the formation of a uni-univalent ionic compound; specifically, a halide of a Group 1 metal. Step (a) contains the atomization enthalpy of the metal and half the dissociation enthalpy of the halogen. Step (b) contains the ionization energy of the metal and the electron affinity of the halogen.

Most important in the definition of the thermodynamic parameters of Figure 2 is U_0, currently named lattice energy, whose formula is given by Eq. (1), the corresponding quantities being:

- e = unitary charge;
- N = Avogadro number, 6.02×10^{23};
- A = Madelung constant, a numerical factor (e.g., 1.75 for NaCl) that takes care of both attractive and repulsive electrostatic interactions within the ions constituting the crystal;
- $|\mathrm{Z_i}|$ and $|\mathrm{Z_j}|$ absolute values of the cationic and anionic charges;
- r_0 = interionic equilibrium distance (i.e., the sum of the radii of both cation and anion);
- n = Born exponent.

The last item is a numerical factor, i. e. 5 (He), 7 (Ne), 9 (Ar), 10 (Kr), 12 (Xe) − that depends on the electronic configurations of both cation and anion (e.g., for $\mathrm{NaF_{(s)}}$ containing the isoelectronic $\mathrm{Na^+}$ and $\mathrm{F^-}$ ions, both possessing the electronic configuration of Ne, the numerical factor is 7).

$$\mathrm{U_0} = -e^2 NA\,|\mathrm{Z_i}|\,|\mathrm{Z_j}|\,(1 - 1/n)/r_0 \qquad (1)$$

The treatment of the ionic bond is relatively simple, and usually the model based on electrostatic interactions gives satisfactory agreement between calculated and estimated – by difference from the other quantities – $\mathrm{U_0}$'s, no direct experimental determination of lattice energy being intrinsically possible.

On the contrary, for compounds characterized by a predominant covalent bond the theoretical treatment is more sophisticated and the reader is referred to specialized compendia for further information. Here, only the qualitative results obtained with some of the available methods will be discussed.

For elements belonging to Groups higher than 1 and 2, the covalent character becomes important and, within the same metal, as the oxidation state increases (e.g., positive oxidation states are known for manganese ranging from +VII to +II); a ionic description of the bond is considered to be more appropriate for $MnCl_2$ than for MnO_4^-, the ligand being, respectively, $Cl(-I)$ or $O(-II)$).

The elements of Period 3 (from Na to Ar) are characterized by the filling of the appropriate $3s-3p$ orbitals. However, at aluminum the energy of the $3d$ orbitals is close enough to possibly become involved in the formation of chemical bonds (e.g., in AlF_6^{3-}).

Period 2:	BCL_3	CF_4	CO_2	NF_3	OF_2	O_2
Period 3:	$Al_2Cl_{6(g)}$	SiF_6^{2-}	SiO_2	$PF_{5(g)}$ PF_6^-	SF_6	S_8

Consequently, the compounds formed by elements of Period 3 may perform coordination numbers of the central metal atom higher than the corresponding analogs of Period 2 in the same Group − boron in BCL_3 is tricoordinated trigonal-planar − , while aluminum in Al_2Cl_6 (in the gas phase) is tetracoordinated; carbon in CF_4 is tetracoordinated, while silicium is hexacoordinated in SiF_6^{2-}; and oxygen is bicoordinated in OF_2, while sulfur is hexacoordinated in SF_6.

Also, the molecular complexity increases on going from Period 2 to Period 3. Thus, for example, CO_2 is a gas at 298 K and melts at 216.6 K (at p = 5.1 atm), while SiO_2 (cristobalite, $d = 2.33\ g \times cm^{-3}$) is a solid, mp 1986 K with an extended structure, see Section 3.5 . The lower degree of aggregation for the elements of Period 2 is attributed to their higher tendency to form multiple bonds by π overlap of p orbitals. A major contrast of aggregation is offered by the elements of Group 16. As a matter of fact, O_2 is a stable species, while O_3 is thermodynamically unstable with respect to the former species (see Eq. (2)) (see *Statistical Approach to Thermodynamics*).

$$3/2\ O_2 \rightleftarrows O_3 \tag{2}$$

$$[\Delta H^0 = +143\ kJ\ mol^{-1}; \Delta G^0 = +163\ kJ\ mol^{-1}]$$

On the other hand, the stable octanuclear molecule of sulfur, S_8, partially decomposes to the binuclear species, S_2, only at about 1000 K. Sulfur is the next element beside carbon to give catenation, the $S-S$ single bond enthalpy being $226\,\mathrm{kJ\,mol^{-1}}$. Accordingly, octasulfur is a cyclic molecule with a $S-S$ distance of $2.06\,\text{Å}$ and an angle at sulfur of 108°.

Coordination chemistry originates from the studies of Alfred Werner (1866–1919), who received the Nobel Prize for Chemistry in 1913 for his work on the compounds formed by transition *d* elements with molecules containing nitrogen (e.g., ammonia, NH_3, or secondary amines, R_2NH); or oxygen (e.g., water); or halides as donor atoms [Werner A. 1904; Werner A. 1919; Schwarzenbach G. 1966]. Eqs. (3)–(5) correspond to the synthesis of typical Werner's compounds:

$$[Cr(H_2O)_6]^{3+} + 3\ en \longrightarrow [Cr(en)_3]^{3+} + 6\ H_2O \qquad (3)$$

$$[Fe(H_2O)_6]^{3+} + 3\ acacH \longrightarrow Fe(acac)_3 + 6\ H_2O + 3\ H^+ \qquad (4)$$

$$[PtCl_6]^{2-} + 6\ NH_3 \longrightarrow [Pt(NH_3)_6]Cl_4 + 2\ Cl^-. \qquad (5)$$

$[en = H_2NCH_2CH_2NH_2;\ acacH = meC(O)CH_2C(O)Me;\ acac = MeC(O)CHC(O)Me^-]$

Pure reasoning, intuition, and experimental ability led Werner to the correct conclusions about the tridimensional disposition of the donor atoms around the central metal atom (see *History of Chemistry*). In simple terms, metallic elements are able to coordinate (i.e., to bind) monoatomic (e.g., Cl^- as in $[PtCl_6]^{2-}$) or polyatomic ligands (e.g., the ammonia and water ligands in the complexed ions $[Pt(NH_3)_6]^{4+}$ or $[Cr(H_2O)_6]^{3+}$), thus forming a metal–ligand combination. The metal–ligand bond is realized through the dative (coordinated) bond between lone pairs on the donor and empty orbitals of the metal.

The studies by Werner were restricted to donor atoms belonging to Groups from 15 to 17 inclusive. The compounds studied by Werner mainly involved transition *d* metals, although not exclusively. Werner should be considered the founder of coordination chemistry. Due to the availability of an expanded shell of valence orbitals, more complex geometries than those already known at that time for carbon were detected. In addition to the tetrahedral geometry $(CN = 4)$, others were discovered, namely, square-planar $(CN = 4)$ and octahedral $(CN = 6)$. The most common coordination polyhedra are shown in Figure 3. The inner position is occupied by the metal, while the vertices identify the donor atom of the ligand.

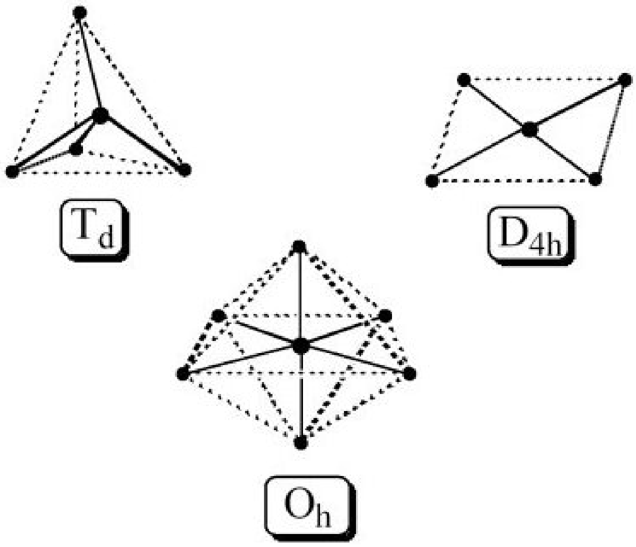


Figure 3. The most common coordination polyhedra.

The first polyhedron, on the left-hand side – T_d, in the notation of group theory – is the well-established tetrahedron typical of carbon. Tetrahedral coordination is also found in numerous compounds within transition d elements, although it is less common than the octahedral (O_h) one. Also square-planar coordination is frequent for transition d metals, which use the dsp^2 hybridization, especially in their $4d^8$[Rh(I), Pd(II)] and $5d^8$[Ir(I), Pt(II), Au(III)] electronic configurations.

With square-planar and octahedral coordinations, geometrical isomers are expected. On the other hand, for hexacoordinated and tetrahedral complexes, optical isomers should exist with the appropriate set of ligands. Werner was able to isolate both types of isomers: geometrical isomers are usually distinguished by their colors and optical isomers are distinguished by their capacity to rotate the plane of polarized light. Geometrical and optical isomerisms, which depend on the overall tridimensional symmetry, are ubiquitous properties along the Periodic Table with the appropriate set of ligands and/or substituents. The discoveries by Werner were later confirmed through X-ray diffraction methods.

The useful concept of the “effective atomic number” (EAN) was introduced by N.V. Sidgwick (1873–1952) of the University of Oxford, UK [Sidgwick N.V.]. This formalism in extremely simple terms extends the well–known “octet rule” of Period 2 (from Li to Ne) to the elements of the longer Periods from 4 (from K to Kr) to 6 (from Cs to Rn) inclusive. As a matter of fact, it is easily shown (see Table 1) that in some cases, the sum of the electrons contributed by the central metal atom – once its oxidation state is taken into consideration – and by the lone pairs of the ligands corresponds to the number of electrons of the next inert gas within the same Period.

Table 1 reports some examples of hexacoordinated nd^6 metal complexes reaching a closed-shell configuration by ligand coordination.

Species	**M$_{(g)}$** [*a*]	**ON**	**N. e.** [*b*]	**L** [*c*]	**EAN**
$Fe(CN)_6^{4-}$	$3d^6 4s^2$	II	6	12	18
$Co(NH_3)_6^{3+}$	$3d^7 4s^2$	II	6	12	18
$PtCl_6^{2-}$	$5d^9 6s^1$	IV	6	12	18

[*a*] Electronic configuration of the metal as the monoatomic gas-phase species.

[*b*] Number of residual electrons of the metal, once its oxidation number (ON) is taken into consideration. All metal cations in this Table have the electronic configuration nd^6.

[*c*] Electronic contribution from the six electron pairs of the ligands.

Table 1. Formal electronic configuration or effective atomic number (EAN) of the central metal atom on coordination of the set of six ligands L.

After Werner’s pioneering work, coordination compounds were studied, particularly in aqueous solution, and a set of important thermodynamic data relating to the formation constants was collected, covering a subject that is still actively pursued [Cox J.D. et al.]. Coordination chemistry underwent a further important stage in its progress with the discovery and rationalization of a completely unexpected compound, namely, biscyclopentadienyliron(II), abbreviated as ferrocene, of formula $Fe(\eta^5-C_5H_5)_2$, and of other compounds containing carbocycles as ligands (see below).

The preparation of the iron derivative was initially carried out under strictly anhydrous conditions in an ether solvent by treating the cyclopentadienyl-Grignard reagent, C_5H_5MgX, with an anhydrous iron(III) halide (see Eq. (6)). The product was isolated and purified, after separation from the magnesium-containing coproduct, by crystallization or by sublimation.

$$3\ C_5H_5MgX + FeX_3 \longrightarrow Fe(C_5H_5)_2 + 3\ MgX_2 + \{C_5H_5\} \qquad (6)$$

$(X = Cl \text{ or } Br)$

The preparation of ferrocene was the starting point for the discovery of organometallics of transition elements. Geoffrey Wilkinson and Ernst Otto Fischer shared the 1973 Nobel Prize for “their pioneering work, performed independently, on the chemistry of the organometallics so-called sandwich compounds.” For transition metals, the erroneous belief existed that compounds containing a metal–carbon σ–bond would not be intrinsically stable. As a matter of fact, alkyl– and aryl derivatives of transition metals were substantially unknown [Cotton F. A. 1955; Uhlig E. 1993], due to the lack of appropriate synthetic procedures.

Wilkinson and Fischer and their students found out that carbon, when part of a cyclic structure (e.g., the cyclopentadienyl anion $C_5H_5^-$) [Wilkinson, G. et al. 1952; Cotton F.A. and Wilkinson G. 1952] or the neutral hexa-atomic ring of benzene C_6H_6, e.g., in bisbenzenechromium(0) [Fischer E.O. and Hafner W. 1955]] (see Eqs. (7) and (8)), can also perform as ligands for a transition d metal center.

$$\begin{gathered}3\,CrCl_3 + 2\,Al + AlCl_3 + 6\,C_6H_6 \longrightarrow \\ 3[Cr(\eta^6-C_6H_6)_2]AlCl_4\end{gathered} \tag{7}$$

$$[Cr(\eta^6-C_6H_6)_2]^+ + e^- \longrightarrow Cr(\eta^6-C_6H_6)_2 \tag{8}$$

Years before the timely review–article by Cotton [Cotton F. A., 1955], some alkyl and aryl derivatives of transition metals had been reported; however, some of them had been erroneously formulated [Hein, F.; Hein F. and Pauling, H.] as σ–aryl (or η^1–aryl) derivatives, and others, which have been later authenticated as genuine σ–alkyl compounds [Pope W. J. and Peachey S. J.], had not been pursued. The structures of $Fe(\eta^5-C_5H_5)_2$ and of $Cr(\eta^6-C_6H_6)_2$ are shown in Figure 4.

Figure 4. Schematic representation of: biscyclopentadienyliron(II), **A**, and bis(benzene)chromium(0), B. Each vertex of the pentagon or hexagon corresponds to a CH group.

It can be shown easily by an electron counting of the type indicated in Table 1 that both bis(cyclopentadienyl)iron(II) and bis(benzene)chromium(0) have an EAN of 18 electrons (i.e., by coordination of the carbon-containing ligands, the central metal atom acquires the electronic counting of the next inert gas (Kr) in both compounds). For example, in the formal electron counting for bis(benzene)chromium(0), each of the two hydrocarbon ligands uses its π-electron density, formally participating to the bond with six electrons. This chromium derivative is an example of a coordination compound in a low-oxidation state. Transition metal complexes in an usual oxidation state seldom fulfill the requirement of completing the valence shell. However, when a low oxidation state is considered, the electron counting is usually that of the next inert gas. Thus, for example, $MnX(CO)_5$ is a compound of manganese(I), of electronic configuration $3d^6$;

the addition of 12 electrons from the six ligands gives a total number of 18 electrons (i.e., the same as the next inert gas). Compounds of this type are generally characterized by a particularly high kinetic – they usually react by a ligand-dissociation mechanism – and thermodynamic – all the molecular orbitals of lower energy are filled – stabilities.

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Biographical Sketch

Fausto Calderazzo was a research associate from 1954–62 at the Istituto Chimica Industriale, Politecnico di Milano, Italy, and from 1960–1was A.P. Sloan Foundation fellow at Massachusetts Institute of Technology, Cambridge, MA, USA. He was then research associate (1963–5) and director of research (1965–8) at the Synthetic Inorganic Chemistry Group, Cyanamid European Research Institute, Geneva, Switzerland. Since 1968 he has been Professor of General and Inorganic Chemistry at the University of Pisa, Italy. He has published about 300 scientific papers on metal carbonyls of early and late transition metals, mechanism of insertion reactions in metal–carbon bonds, *N,N*-dialkylcarbamates of transition and Main Group elements, metal-arene and metal-cyclopentadienyl derivatives, and surface-coordination chemistry. He is a member of the following international scientific committees: the International Conferences of Organometallic Chemistry and the Advisory Board of International Symposia on Homogeneous Catalysis. He is also a present or past member of the editorial board of: *J. Chem. Soc., Dalton Trans*. (Royal Chemical Society), *Organometallics* (American Chemical Society), *Inorg. Syn*. (J. Wiley), and *Gazz. Chim. Italiana* (Società Chimica Italiana). Professor Calderazzo is a member of Istituto Lombardo di Scienze e Lettere and Accademia Nazionale dei Lincei (Membro Corrispondente) since 1989, honorary member of Società Chimica Italiana and Société Chimique de Belgique. He received awards from national institutions in 1988, 1990, and 1994, and was recipient of the L. Sacconi Medal in 1998. He has been a national member (Socio Nazionale) of Accademia Nazionale dei Lincei since November 1999.