

## INORGANIC SYNTHESIS

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**Keywords:** coordination chemistry, metal carbonyls, ligand exchange, metals, nitrogen-containing ligands, organometallic chemistry, periodic properties, reactivity of metal complexes, transition elements

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### Summary

After a short introduction to the Periodic Table and to the transition metals, some general features of the coordination compounds are discussed aimed to introduce the reader to the most important features of this class of compounds. For sake of clarity, distinction is made between classical Werner complexes and transition metal organometallic compounds, i.e., complexes containing at least one metal-carbon bond. A Section is devoted to the reactivity of coordination compounds and some of the most important reaction modes involving the central metal atom have been considered.

### 1. Introduction

Any approach to the synthesis of chemical compounds must face the main question concerning the properties of the elements involved in the process, thus a general view of the properties of the transition elements will be given first.

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, high melting and boiling points) and most of these metals are known as transition elements. Strictly speaking [Cotton F.A. et al., 1999] a transition element is a substance which, as element, has partially filled *d* or *f* shells. However, a slightly broader definition is generally adopted and includes also elements that have partially filled *d* or *f* shells in any of their commonly occurring oxidation states. For this reason copper(II) and gold(III) are considered transition metals.

This large number of transition elements is divided into three groups: a) the main transition elements, b) the lanthanide elements and c) the actinide elements.

I will focus the attention on the main transition elements or *d*-block which includes the elements that have partially filled *d* shells only, Figure 1. Throughout this article, the classification of chemical elements in Groups from 1 to 18 inclusive will be adopted [Fluck E., 1988; Leigh G.J., 1990]. The lightest element is scandium ( $3d^14s^2$ ) and the eight succeeding elements, titanium to copper, form the first transition series. The second transition series starts with yttrium ( $4d^15s^2$ ) and finishes with silver. Silver is followed by a sequence of elements in which there are no *d*-shell vacancies under chemically significant conditions until lanthanum ( $5d^16s^2$ ) is reached. With lanthanum, *f*-orbitals have become slightly more stable than the *d*-ones, thus electrons fill the *f*-orbitals until lutetium. Although lanthanum and lutetium might be considered as transition elements because they have partially filled *d*-orbitals, for chemical reasons lanthanum is considered the prototypal of a series of 14 elements called lanthanides. Hafnium may be thus considered as the first member of the third transition series.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra																
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Figure 1. The Periodic Table of the chemical elements disposed according to Groups (from 1 to 18) and Periods (from 1 to 7).

The three series of elements described above, exhibit a number of characteristic properties which together distinguish them from other groups of elements:

- Most of them display numerous oxidation states. An important characteristic of transition metal chemistry is the formation of compounds with low (often zero or negative) oxidation states which has little parallel outside the transition elements.
- They have high propensity to give coordination compounds with Lewis bases. This is due to the ability of transition metal cations to behave as Lewis acids, i.e., to accept electron pairs.
- One of the consequences of the open (incompletely filled)  $d^n$  configuration of a transition metal ion is the presence of one or more unpaired electrons which produces magnetically active coordination compounds (paramagnetic species).
- A striking feature of transition metals is the color which generally characterizes their compounds, which again has no correspondence for main group metal compounds.

It is generally accepted that compounds containing at least one carbon atom and no metals are classified in the area of organic chemistry. By contrast, compounds containing one or more metal atoms are considered to be inorganic. The coordination compounds therefore belong to the inorganic derivatives. For sake of clarity, I will divide metal coordination compounds into two groups: A) *Werner complexes* and B) *Organometallic compounds*. This classification places all the compounds that do not contain a M–C bond and the cyanides in group A, while group B includes derivatives containing at least one metal-carbon bond thus representing an interface between classical organic and inorganic chemistry.

## 2. Coordination Compounds: Generality

Coordination compounds play an essential role in the chemical industry and in life itself. The 1963 Nobel Prize in Chemistry was awarded jointly to Karl Ziegler (Max Planck Institute für Kohlenforschung, Mannheim, Germany) and to Giulio Natta (University of Milan, Italy) "for their discoveries in the field of the chemistry and technology of high polymers". The Ziegler-Natta catalyst for this polymerization reaction is a complex of aluminum and titanium.

The importance of coordination complexes becomes even clearer when one realizes that chlorophyll, which is vital to photosynthesis in plants, is a magnesium complex and that hemoglobin, the oxygen carrier in the animal cells, is an iron complex.

As cited in the Introduction, the formation of complexes is often accompanied by striking changes in color. For example, you can use aqueous solutions of  $\text{CoCl}_2$  as invisible ink; what is written with this solution does not turn visible until the paper is heated. A blue colored writing turns visible and slowly disappears. The phenomenon responsible for the appearance of the color is reported in Eq. (1). The pink aquo-complex  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is almost colorless when dilute, so the writing done with it is practically invisible. Upon heating, water is driven off, the blue complex  $[\text{CoCl}_4]^{2-}$  is

formed and the color turns sufficiently intense that the writing appears. Upon standing, water is taken up from the atmosphere and the original colorless writing is regenerated.



A useful concept in coordination chemistry is the “effective atomic number rule” (EAN rule), introduced by N.V. Sidgwick of the University of Oxford, UK [Sidgwick N.V., 1941]. This formalism can be considered an extension of 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: for this reason the EAN rule is also known as the “18-electron rule”. Transition metals acquire electrons to fill their valence orbitals by forming bonds to ligand molecules that act as electron donors. The 18-valence electrons are then the sum of the number of electrons initially present in the “bare” metal atom and the electrons donated by the ligands. Although organometallic complexes frequently obey the 18-electron rule, metals in Werner-type complexes frequently do not follow the rule. Generally, Werner complexes contain metal ions in relatively high oxidation state which means that there are relatively few electrons on the “bare” metal atom. When ligands coordinate to the metal ion, the preferred coordination number for the particular metal is reached before 18-valence electrons can be acquired. For example,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  contains a Ti(III) ion of  $d^1$  electronic configuration and six water molecules, each donating two electrons to titanium: the valence shell electron count is therefore 13. On the other hand, in many types of organometallic complexes, such as metal carbonyls (Section 2.2.4), the metals are in low oxidation state, i.e., a large number of valence electrons is present on the “bare” metal atom. Both the electron pairs donated by the ligands and the coordination number typical of the metal guarantee the complete filling of the valence shell. The 18-electron rule represents a useful tool in organometallic chemistry to decide whether a given  $d$ -block compounds is likely to be stable.

Some of the properties of transition metal coordination compounds can be rationalized on the basis of some bonding schemes. The first attempt was made through the valence bond (VB) theory [Pauling L., 1960], utilizing hybrid orbitals centered on transition  $d$  elements. For example, the octahedral and square-planar geometries were treated in terms of  $d^2sp^3$  and  $dsp^2$  hybridizations, respectively, of the empty valence orbitals of the metal accepting electron pairs from the ligands. This scheme, which is able to justify, in some cases, the magnetic properties of the complexes, cannot explain other important features of transition metal complexes such as their absorption spectra or, in other words, their colors.

The so-called Crystal Field Theory, initially introduced by H. Bethe, was used extensively by chemists [Van Vleck J.H., 1935]. This theory, as it was initially stated, considers the electrostatic effect of a given number of negative point charges around a metal cation of  $d^n$  electronic configuration. The five empty  $d$  orbitals have identical energies (they are degenerate). If the point charges are distributed along preferential directions in space, the orbitals will undergo an energy separation. If the charges are six, and the cartesian axes are chosen along the  $x$ ,  $y$ ,  $z$  directions corresponding to the vertices of an octahedron, two new sets of degenerate orbitals will originate, namely,

$d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  – called  $t_{2g}$  orbitals – at lower energy and  $d_{x^2-y^2}$ ,  $d_{z^2}$  – called  $e_g$  orbitals – at higher energy, due to the directional properties in space of the  $d$  orbitals. With the total energy being maintained, the energy splitting qualitatively shown in Figure 2 will result. Analogously, crystal field splittings can be obtained for other type of geometries (tetrahedral, square pyramidal....) [Huheey J.E., 1993].

An interpretation of both the absorption spectra and the magnetic properties of transition metal complexes is now available. As a matter of fact, the low-energy, threefold-degenerate set  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  can be used to locate the  $n$  electrons of the  $d^n$  configuration. For example, for a coordination compound of vanadium(II) of  $3d^3$  electronic configuration containing six ligands L (i.e.,  $[\text{VL}_6]^{2+}$ ), only one possibility exists of filling the low-energy  $t_{2g}$  set with the three unpaired electrons, according to the Hund rule. However, if a fourth electron is added, such as, for example, in the case of the derivative of  $3d^4$  chromium(II),  $[\text{CrL}_6]^{2+}$ , two possibilities arise: the fourth electron may be positioned in the  $e_g$  set, giving rise to an electronic configuration  $t_{2g}^3 e_g^1$  (high-spin) or be paired up in the lower energy level, as  $t_{2g}^4$  (low-spin). The choice between the two possibilities will depend on the relative amount of two quantities: the energy splitting  $\Delta_o$  and the spin-pairing energy  $P$ . The high-spin and low-spin configurations correspond to different magnetic properties; this can be verified experimentally by measuring the magnetic susceptibility of a solid sample of a given substance; low-spin configurations correspond to a relatively low magnetic susceptibility or to a completely diamagnetic behavior.

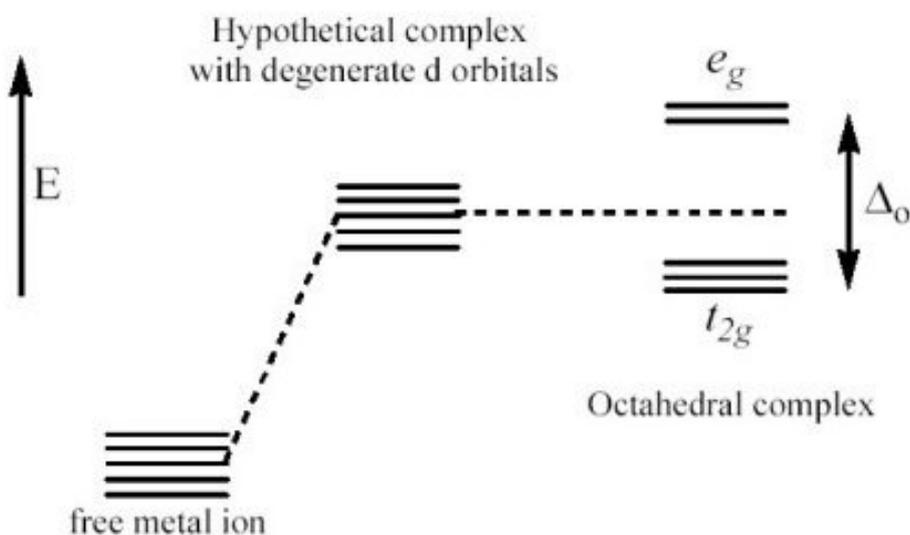


Figure 2. Crystal field splittings of the  $d$  orbitals for an octahedral complex.

A more sophisticated treatment of transition metal complexes is based on the combination of ligands and metal orbitals to give molecular orbitals (MO). For an octahedral system, the energy-level diagram is represented in Figure 3. The orbitals of the six ligands combine with the metal-based orbitals of appropriate symmetry giving rise to an equal number of bonding and antibonding orbitals. The  $t_{2g}$  orbitals have no ligand orbitals of appropriate symmetry to combine with, and therefore are not

modified. Within this bonding scheme,  $\Delta_o$  now corresponds to the energy separation between the nonbonding  $t_{2g}$  orbitals and the antibonding  $e_g$  orbitals. As it can be seen from Figure 3, different ligands ( $F^-$  vs.  $NH_3$ ) determine a different  $\Delta_o$  thus causing the formation of high- or low-spin complexes.

The orbital-splitting  $\Delta_o$  can be measured experimentally and ligands can be arranged in the so-called spectrochemical series according to their capacity to induce the orbital separation. Part of the spectrochemical series is represented below, showing induction of larger  $\Delta_o$  by ligands from left to right.

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 < \text{pyridine} < 2,2'$ -  
bipyridyl  $\ll CN^-, CO, PR_3$

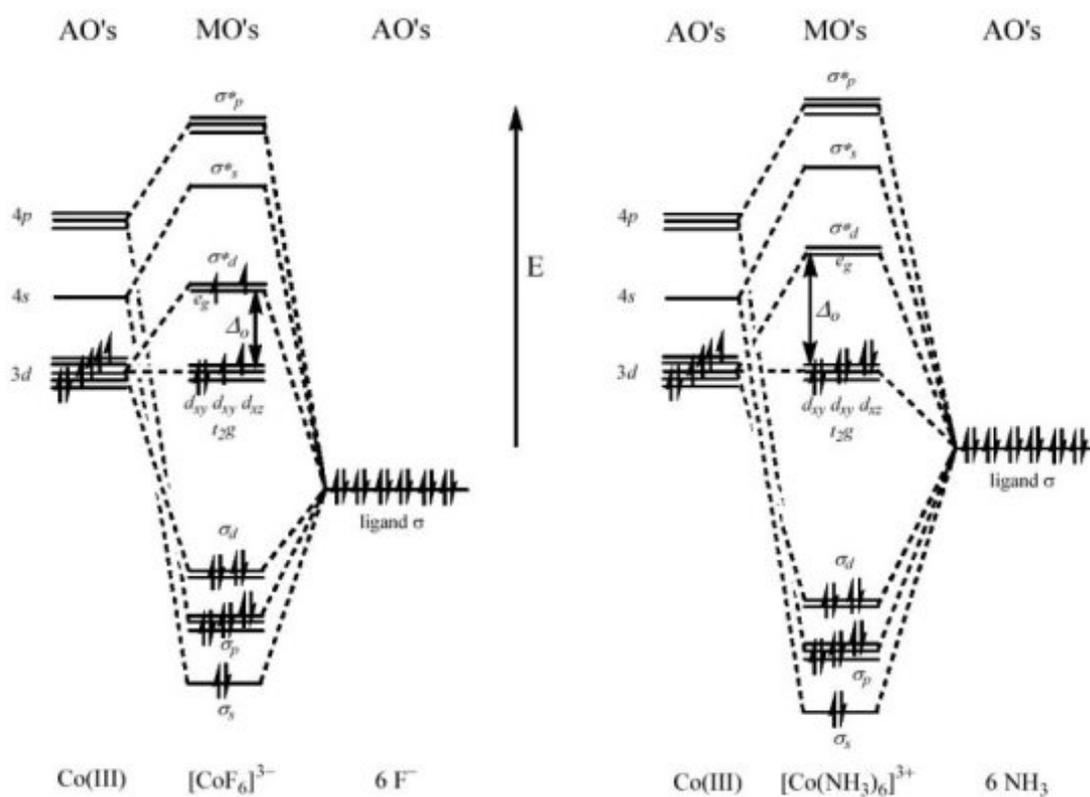


Figure 3. MO diagrams for high-spin  $[CoF_6]^{3-}$  and low-spin  $[Co(NH_3)_6]^{3+}$  complex ions.

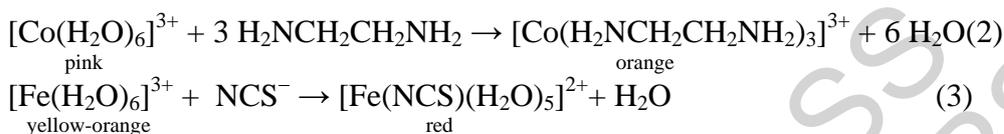
Crystal Field Theory (CFT) and Molecular Orbital (MO) theory, confirmed by some supporting experimental evidence, allow some generalization to be made when  $d$  transition metal cations belonging to the same Group are considered:

- The orbital splitting  $\Delta$  increases in the sequence  $3d < 4d < 5d$ .
- Because of the increase of the field splitting, metal cations of the Periods 5 and 6 (i.e., of the second and third transition  $d$  series) will tend to pair their electrons and to give low-spin complexes.

- Absorption spectra due to  $d \rightarrow d$  transitions will tend to shift towards high-energies (UV), on descending a vertical sequence of elements. Unless some charge transfer (CT) bands are present, the complexes of  $4d$  and  $5d$  transition metals frequently tend to be colorless.

## 2.1. Werner Complexes

Most of the early work on coordination compounds was done with ammonia and the resulting complexes were and are known as metal amines. It was also found that other amines and anions such as  $\text{CN}^-$ ,  $\text{NO}_2^-$ ,  $\text{NCS}^-$ ,  $\text{Cl}^-$ , form metal complexes. Eqs. (2)-(4) correspond to the synthesis of typical Werner's compounds.



Our present understanding about the nature of metal complexes is due to Alfred Werner, professor of chemistry in Zurich, and winner of the Nobel Prize in 1913 "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry". He proposed what is currently known as Werner's coordination theory which consists of three postulates [Werner A., 1919]:

- Most elements exhibit a primary and a secondary valence (oxidation state and coordination number, respectively, according to the modern terminology);
- Every element tends to satisfy both its primary and secondary valence;
- The secondary valence is directed towards fixed positions in the space.

According to the theory, the compound previously described with the formulation  $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$  was formulated as  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$ : the primary valence of cobalt, i.e., the oxidation state, is three (the three chloride ions saturate the primary valence). The secondary valence, or coordination number, of Co(III) is six and it is saturated by the ammonia molecules, so that the chloride ions are not bonded to cobalt. The solution of  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$  contains 4 ions, three  $\text{Cl}^-$  ions and the complex cation  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ .

Postulate three of Werner's theory deals specifically with the stereochemistry of metal complexes. Werner started with the assumption that a six-coordinated complex has a structure in which six ligands are situated at positions symmetrically equidistant from the central atom. Due to the availability of an expanded shell of valence orbitals, typical of transition metals, more complex geometries than those already known at that time for carbon were detected. In addition to the tetrahedral one (Figure 4A), other geometries were discovered, namely, square-planar (Figure 4B) and octahedral (Figure 4C). As a matter of fact, based on the number of isomers for a given compound, Werner was able to demonstrate that a six coordinate complex should have an octahedral structure, i.e., the six M–L bonds are directed towards the vertices of an octahedron.

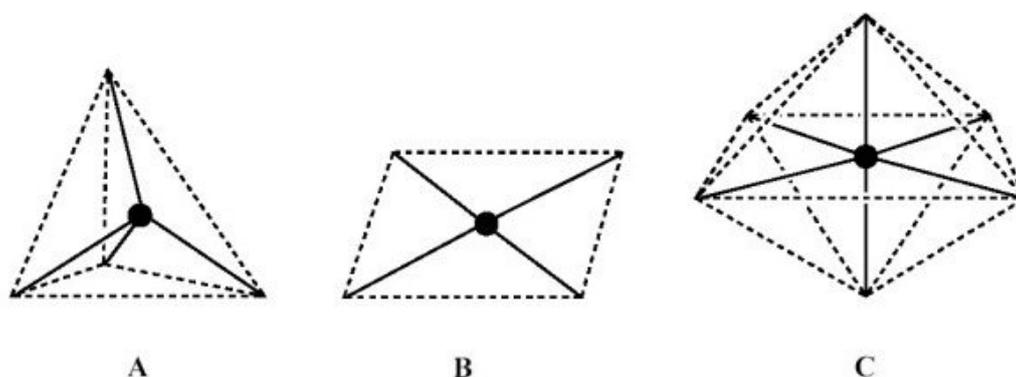


Figure 4. The most common coordination polyhedra.

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### Biographical Sketch

**Guido Pampaloni.** Born in 1955, he received the Degree in Chemistry from the University of Pisa in 1979. After a post-doctoral fellowship in Aachen (Germany) with Prof. G.E. Herberich (1979-1980), he came back to Pisa and in 1983 he received the Ph.D. in Chemistry from the Scuola Normale Superiore of Pisa. Since 1992, G. Pampaloni is associate professor at the Dipartimento di Chimica e Chimica Industriale of the University of Pisa. His main interests concern the synthesis and the reactivity of inorganic and organometallic compounds of early transition elements.