

5.2: Counting Electrons in Transition Metal Complexes

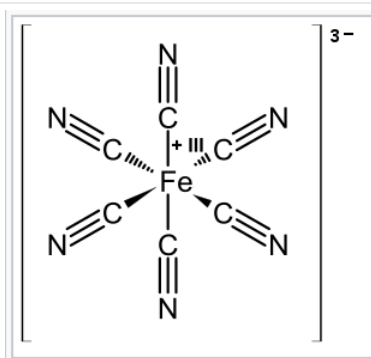
The d-orbitals are the frontier orbitals (the HOMO and LUMO) of transition metal complexes. Many of the important properties of complexes - their shape, color, magnetism, and reactivity - depend on the electron occupancy of the metal's d-orbitals. To understand and rationalize these properties it is important to know how to count the d-electrons.

Because transition metals are generally less electronegative than the atoms on the ligands (C, N, O, Cl, P...) that form the metal-ligand bond, our convention is to assign **both electrons** in the bond to the **ligand**. For example, in the ferricyanide complex $[\text{Fe}(\text{CN})_6]^{3-}$, if the cyanide ligand keeps both of its electrons it is formulated as CN^- . By difference, iron must be Fe^{3+} because the charges ($3^+ + 6(1^-)$) must add up to the overall -3 charge on the complex.

The next step is to determine how many d-electrons the Fe^{3+} ion has. The rule is to count **all** of iron's valence electrons as **d-electrons**. Iron is in group 8, so

$$\text{group 8} - 3^+ \text{ charge} = d^5 \text{ (or } 3d^5\text{)}$$

$$8 - 3 = 5$$

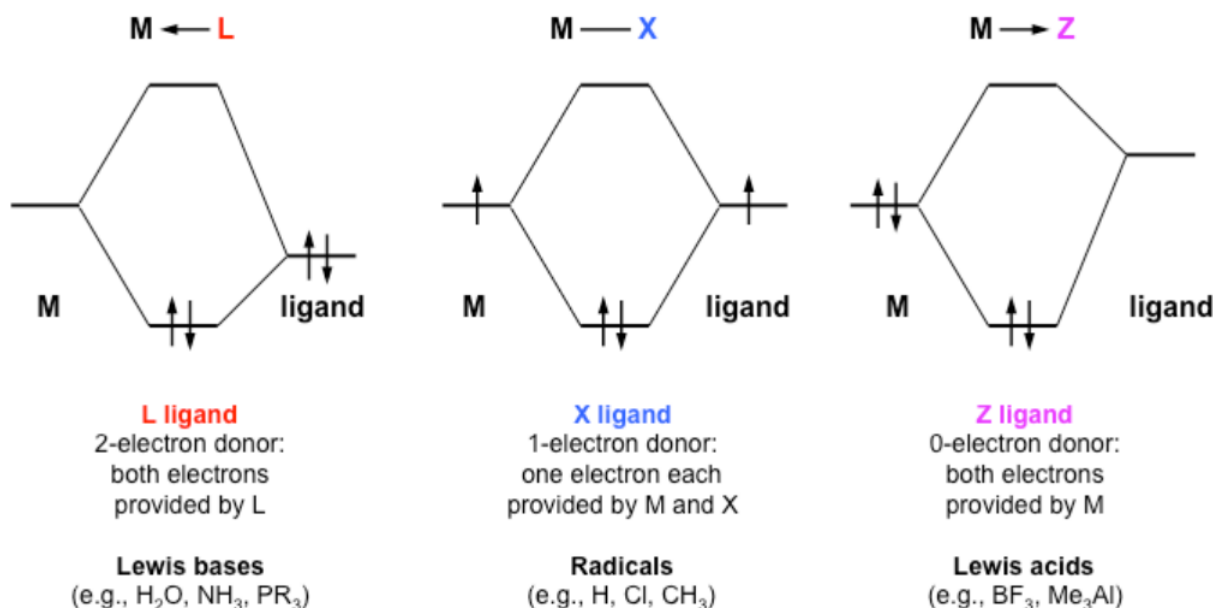


Structure of the octahedral ferricyanide anion. Because the overall charge of the complex is 3^- , Fe is in the $+3$ oxidation state and its electron count is $3d^5$.

The same procedure can be applied to any transition metal complex. For example, consider the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Because ammonia is a neutral ligand, Cu is in the 2^+ oxidation state. Copper (II), in group 11 of the periodic table has 11 electrons in its valence shell, minus two, leaving it with 9 d-electrons ($3d^9$). In the neutral complex $[\text{Rh}(\text{OH})_3(\text{H}_2\text{O})_3]$, Rh is in the $+3$ oxidation state and is in group 9, so the electron count is $4d^6$. Zinc(II) in group 12 would have 10 d-electrons in $[\text{Zn}(\text{NH}_3)_4]^{2+}$, a full shell, and manganese (VII) has zero d-electrons in MnO_4^- . Nickel carbonyl, $\text{Ni}(\text{CO})_4$, contains the neutral CO ligand and Ni in the zero oxidation state. Since Ni is in group 10, we count the electrons on Ni as $3d^{10}$.

A frequent source of confusion about electron counting is the fate of the s-electrons on the metal. For example, our electron counting rules predict that Ti is $3d^1$ in the octahedral complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. But the electronic configuration of a free Ti atom, according to the Aufbau principle, is $4s^23d^2$. Why is the Ti^{3+} ion $3d^1$ and not $4s^1$? Similarly, why do we assign Mn^{2+} as $3d^5$ rather than $4s^23d^3$? The short answer is that the metal s orbitals are higher in energy in a metal complex than they are in the free atom because they have antibonding character. We will justify this statement with a MO diagram in Section 5.2.

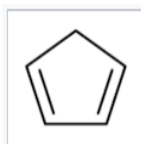
Covalent Bond Classification (CBC) Method. Although the electron counting rule we have developed above is useful and works reliably for all kinds of complexes, the assignment of all the shared electrons in the complex to the ligands does not always represent the true bonding picture. This picture would be most accurate in the case of ligands that are much more electronegative than the metal. But in fact, there are all kinds of ligands, including those such as H, alkyl, cyclopentadienide, and others where the metal and ligand have comparable electronegativity. In those cases, especially with late transition metals that are relatively electropositive, we should regard the metal-ligand bond as covalent. The CBC method, also referred to as LXZ notation, was introduced in 1995 by M. L. H. Green^[2] in order to better describe the different kinds of metal-ligand bonds. The molecular orbital pictures below summarize the difference between L, X, and Z ligands.^[3] Of these, L and X are the most common types.



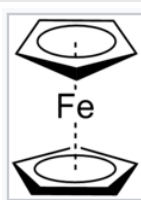
L-type ligands are Lewis bases that donate two electrons to the metal center regardless of the electron counting method being used. These electrons can come from lone pairs, pi or sigma donors. The bonds formed between these ligands and the metal are dative covalent bonds, which are also known as coordinate bonds. Examples of this type of ligand include CO , PR_3 , NH_3 , H_2O , carbenes ($=\text{CRR}'$), and alkenes.

X-type ligands are those that donate one electron to the metal and accept one electron from the metal when using the neutral ligand method of electron counting, or donate two electrons to the metal when using the donor pair method of electron counting.^[4] Regardless of whether it is considered neutral or anionic, these ligands yield normal covalent bonds. A few examples of this type of ligand are H , CH_3 , halogens, and NO (bent).

Z-type ligands are those that accept two electrons from the metal center as opposed to the donation occurring with the other two types of ligands. However, these ligands also form dative covalent bonds like the L-type. This type of ligand is not usually used, because in certain situations it can be written in terms of L and X. For example, if a Z ligand is accompanied by an L type, it can be written as X_2 . Examples of these ligands are Lewis acids, such as BR_3 .



Cp



Ferrocene

Some multidentate ligands can act as a combination of ligand types. A famous example is the cyclopentadienyl (or Cp) ligand, C_5H_5 . We would classify this neutral ligand as $[\text{L}_2\text{X}]$, with the two L functionalities corresponding to the two "olefinic" fragments while the X functionality corresponds to the CH "radical" carbon in the ring. The addition of one electron makes the Cp^- anion, which has six pi electrons and is thus planar and aromatic. In the ferrocene complex, Cp_2Fe , using the "standard" donor pair

counting method we can regard the two Cp^- ligands as each possessing six pi electrons, and by difference Fe is in the +2 oxidation state. The Fe^{2+} ion is d^6 . Thus the iron atom in the complex (regardless of the counting method) has $6+6+6=18$ electrons in its coordination environment, which is a particularly stable electron count for transition metal complexes.

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