

Electron Counting, Formal Oxidation States and the 18 Electron Rule in Transition Metal Chemistry

The 18 Electron Rule

In 1927 Sidgwick proposed that the coordinate bond arises from donation of an electron pair from the ligand to the metal ion. Since noble gases are inert (relatively !!) and have filled s, p, and d shells for a total of 18 electrons in the 9 valence orbitals, he reasoned that metal complexes with 18 electrons might also exhibit particularly high stability. This "18 electron rule" (also called the *effective atomic number rule*) is analogous to the octet rule discussed in earlier courses and is essentially *kinetic in origin*. This is because a compound which makes full use of its valence orbitals has no low lying vacant orbitals into which electrons can be promoted to initiate thermal decomposition or into which donation can occur in the case of nucleophilic attack.

We can understand the effectiveness of the 18 electron rule by considering the simple molecular orbital diagram of an octahedral complex ML_6 . The 18 electron rule is of limited use in ionic systems because the HOMO-LUMO gap is small (another way of stating this is to say that Δ_o , from crystal field theory, is small) (Fig. 1a below). As the covalent character of the metal ligand bonding increases, the size of the HOMO-LUMO gap also increases (because e_g^* is higher in energy when the orbital overlap is better) (Fig. 1b, 1c and Fig. 2) and therefore the 18 electron rule becomes more important. Finally, in cases where the ligands can function as π -acceptors as well as σ -donors, the interaction of the t_{2g} set of orbitals (remember these are σ -nonbonding) with the ligand π -symmetry orbitals results in an effective increase in the HOMO-LUMO gap (Δ_o in Fig. 3a) and we would expect the 18 electron rule to hold best for these types of complexes. This is indeed the case and, as we shall see in carbonyl complexes, the rule is seldom violated in stable covalent complexes with π -acceptor ligands (Table 1).

Figure 1 Interaction diagram for metal and ligand orbitals

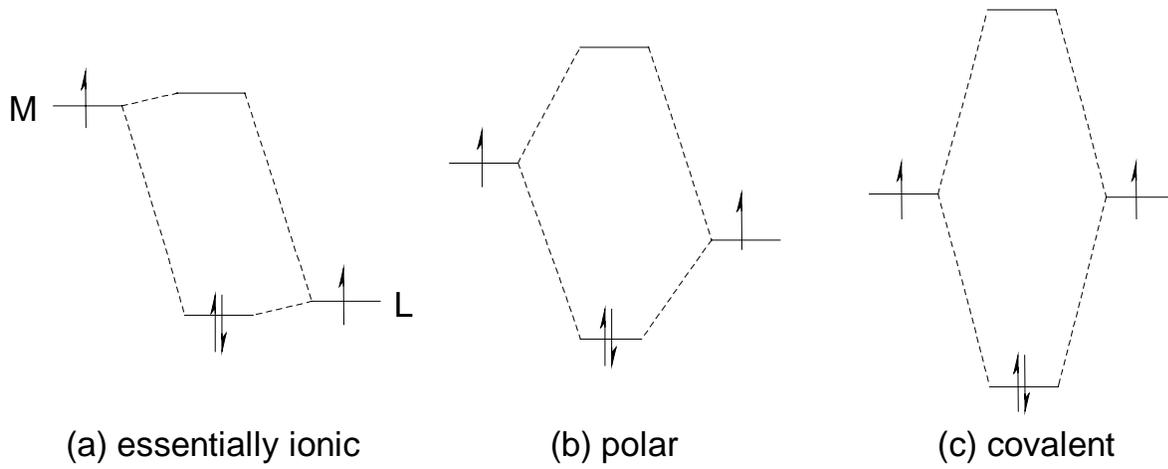


Figure 2 Qualitative M.O. diagram for an octahedral ML_6 complex where only σ -bonding is considered

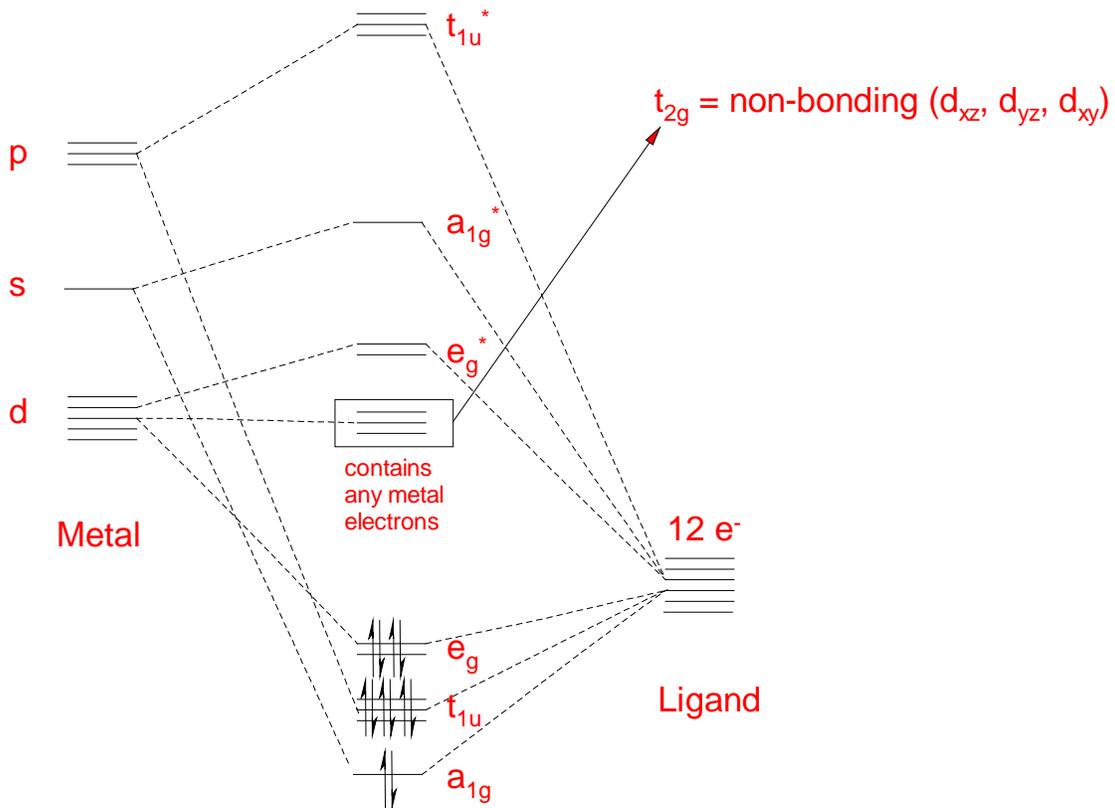


Figure 3 Effect of π -bonding on separation.
 (a) π -acceptor ligands (b) π -donor ligands

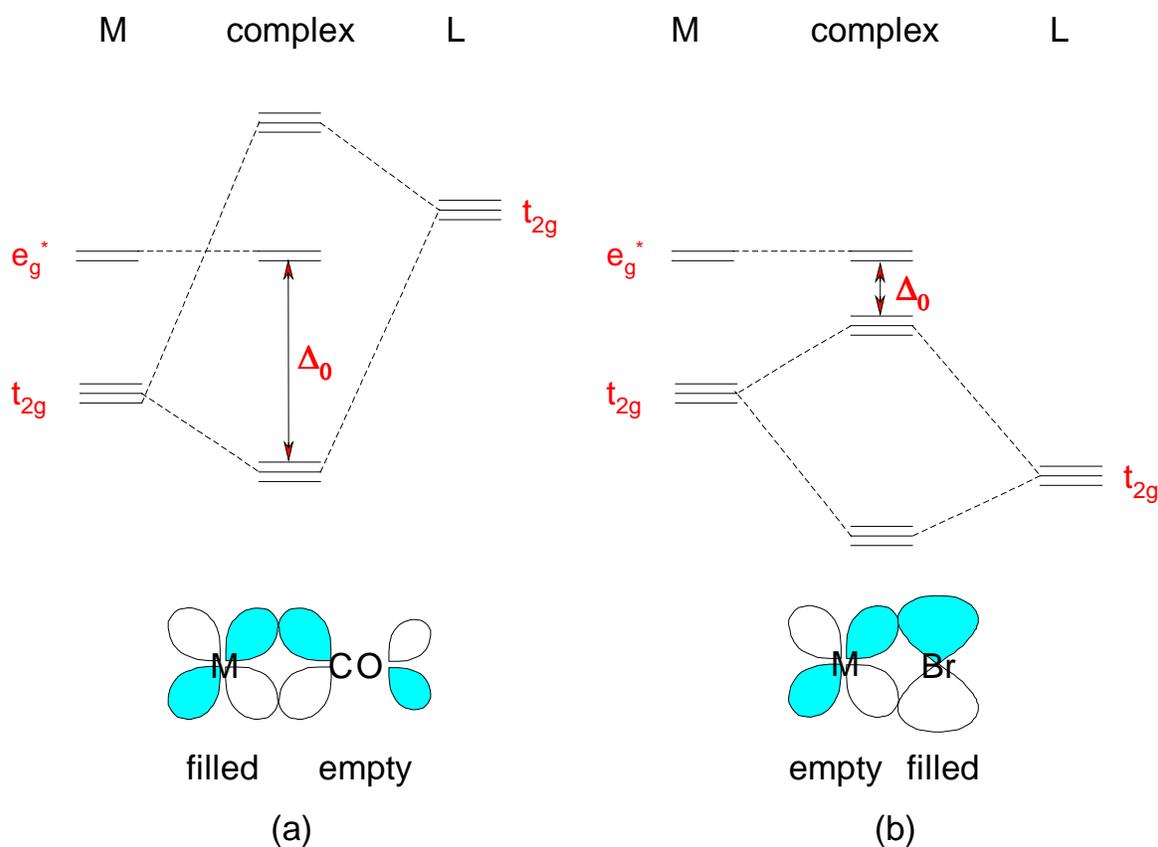


Table 1 Scope of the $18e^-$ rule

	18 e- rule useful	Intermediate	18 e- rule not useful
Ligands	CO, NO, N ₂ , CS, RNC ethene, alkenes, alkynes, PR ₃ (especially PF ₃)	H, CH ₃ , Ph, CN bipy, R ₂ S, RS ⁻	NH ₃ , H ₂ O, halide, OR

Electron Counting

Given the usefulness of the 18 electron rule, especially in organometallic chemistry where the bonding is predominantly polar covalent and often involves π -acceptor ligands, it is very important to be able to determine quickly how many electrons reside in the valence orbitals of the metal. Electron counting can be done by **either a neutral or charged** (with ligands negative where necessary in accord with general polarity considerations) **formalism**. The neutral scheme is more common in the literature and in texts but many will find the charged counting scheme somewhat easier to use. I will present both schemes below. It makes no difference which you adopt but you **MUST BE CONSISTENT** or you will make errors.

(a) neutral counting

By this method, the metal and its bonded ligands are all counted as neutral fragments. Thus a methyl group is considered to be a 1 electron ligand because $\bullet\text{CH}_3$ is the corresponding neutral fragment. Similarly, ligands which are already neutral in their free state (eg. CO, pyridine, PMe_3) are viewed as donating a pair of electrons to the metal. A few examples will help clarify this:

$\text{Ni}(\text{CO})_4$	Ni 10 e^- (group 10), CO 2 e^- each =	18 e^- total
$\text{PtCl}_2(\text{PMe}_3)_2$	Pt 10 e^- , Cl 1 e^- x 2, PMe_3 2 e^- x 2 =	16 e^-
TaMe_5	Ta 5 e^- (group 5), Me 1 e^- x 5 =	10 e^-
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$	Fe 8 e^- (group 8), $\eta^5\text{-C}_5\text{H}_5$ 5 e^- x 2 =	18 e^-
$\text{Co}(\eta^4\text{-C}_4\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)$	Co 9 e^- (group 9), $\eta^4\text{-C}_4\text{H}_6$ 4 e^- , $\eta^3\text{-C}_3\text{H}_5$ 3 e^- =	16 e^-

NB: $\eta^4\text{-C}_4\text{H}_6$ is butadiene $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ bonding through both C=C bonds (2 e^- each)

NB: for hydrocarbon ligands the haptic number equals the number of electrons donated in this counting scheme.

(b) charged counting (counting ligands as closed shell entities)

By this method, ligands are removed from the metal as closed shell species (no radicals). In the case of neutral Lewis bases such as pyridine this is the same as in (a) above (ie. it is still a $2 e^-$ ligand). However, species such as methyl groups and halides (X) are no longer removed as their neutral (radical) units (ie. $\bullet\text{CH}_3$ or $\text{X}\bullet$) but rather as closed shell species CH_3^- and X^- . In some ways this makes good chemical sense since CH_3 in metal complexes is generally nucleophilic (ie. has a partial negative charge) and X^- is the normal form of this ligand in all salts. *By convention, H is removed as H^- (hydride) rather than H^+ (proton).* After removal of the ligands, the metal is assigned a **formal charge** that will balance the overall charge on the complex. The number of electrons contributed by the metal to the bonding will then be the group number less the formal charge. Some examples:

$\text{Ni}(\text{CO})_4$	(same as above)	Ni^0 10 e^- (group 10), CO 2 e^- each =	18 e^-
$\text{PtCl}_2(\text{PMe}_3)_2$		Pt^{2+} 8 e^- , Cl^- 2 $e^- \times 2$, PMe_3 2 $e^- \times 2$ =	16 e^-
TaMe_5		Ta^{5+} 0 e^- (group 5), Me^- 2 $e^- \times 5$ =	10 e^-
$\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$		Fe^{2+} 6 e^- (group 8), $\eta^5\text{-C}_5\text{H}_5^-$ 6 $e^- \times 2$ =	18 e^-
$\text{Co}(\eta^4\text{-C}_4\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)$		Co^+ 8 e^- (group 9), $\eta^4\text{-C}_4\text{H}_6$ 4 e^- , $\eta^3\text{-C}_3\text{H}_5^-$ 4 e^- =	16 e^-

NB: the electron count must be the same regardless of how you count.

