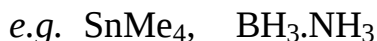


Electron Counting in Organometallic Chemistry

1. The 18-Electron Rule; definition & rationalisation

The constitution and structure of main group element complexes can be predicted and rationalised by a combination of the "Octet Rule" and VSEPR.

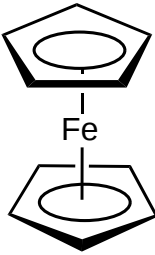


In transition metal (TM) complexes, the "18 Electron Rule" generally applies.

"A stable TM complex is formed when the sum of d-electrons, donated ligand electrons and charge on complex = 18."

(In a d-block metal the 9 valence orbitals (the five d-orbitals, the three p-orbitals and the single s-orbital) can combine with ligand orbitals to make 9 bonding combinations and 9 antibonding combinations. Thus filling all the bonding orbitals with electron pairs gives 18 bonding electrons).

Classically, the number of valence electrons (VE) in complexes are counted by using one of two conventions *e.g.* in the familiar example of ferrocene;

	<i>ionic</i>	<i>covalent</i>
	$[\text{C}_5\text{H}_5]^-$ 6 VE	$[\text{C}_5\text{H}_5]^\bullet$ 5 VE
	$[\text{Fe}]^{2+}$ 6 VE	$[\text{Fe}]^0$ 8 VE
	$[\text{C}_5\text{H}_5]^-$ 6 VE	$[\text{C}_5\text{H}_5]^\bullet$ 5 VE
	18 VE	18 VE

The ionic counting system is misleading; organometallics usually have a large amount of covalent character. The covalent counting system is similarly misleading, but more particularly it does not help us to describe the electronic structure of the molecule. A more instructional "classification" of organometallic compounds has been suggested by Green. We will describe this in some detail later.

Why don't classical coordination compounds obey the 18e rule?

In order to answer that we have to look more closely at what makes the 18e rule work in the first place. Firstly, we can classify *all* complexes into the following groups;

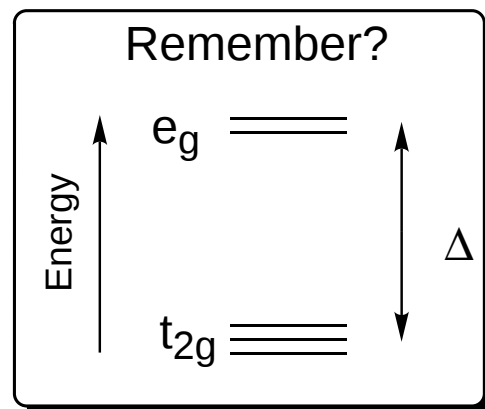
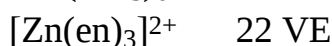
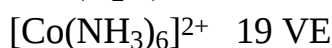
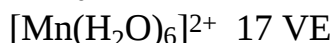
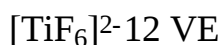
Class 1

number of valence electrons $\geq$ or $\leq$ 18,

First row TM,

Δ small, *i.e.* **weak field** ligands like F^- , Cl^- , H_2O , NH_3 . Hence, t_{2g} non-bonding and e_g weakly antibonding and so it's not so important how many electrons are in these orbitals.

NB, electron count could be accidentally 18!



What determines the number of VE in Class 1 complexes?

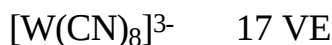
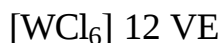
Class 2

number of valence electrons $\leq$ 18,

Second/third row TM,

Δ large

Hence, t_{2g} non-bonding (0-6e allowed) and e_g antibonding (0e preferred).



Class 3

number of valence electrons = 18,

Organometallics,

Δ large *i.e.* **strong field** organometallic ligands like CO , C_2H_4 , C_5H_5 (π -acceptors which stabilise t_{2g} orbitals- see Coordination Chemistry Handout page 27!)

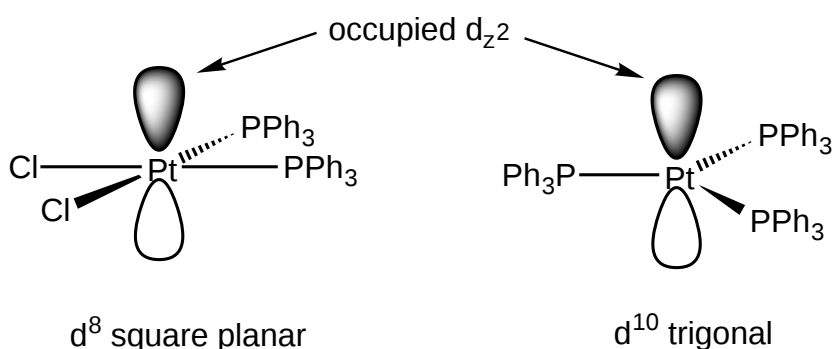
Hence, t_{2g} now bonding (fully occupied, 6e) and e_g antibonding (unoccupied).

Exceptions to the 18e Rule

There are quite a few examples of organometallics which have 16 VE. As with all chemistry, the excuse is either electronic or steric (or both).

(i) Electronic effects

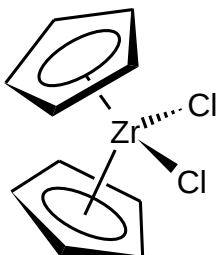
Late TM with d^8 electron configurations[†] *e.g.* Rh(I), Ir(I), Pd(II), Pt(II) have a strong tendency to form square planar 16 VE complexes. Similarly, d^{10} complexes tend to form trigonal 16 VE complexes. As the atomic number Z increases, the d -shell is stabilised (lowers in energy). The occupied d_{z^2} orbital (perpendicular to the plane) is no longer involved in ligand bonding.



or...

(ii) Steric Effects

Early TM have fewer d -electrons to start with than the middle and late TM, so they must achieve their 18e count by coordination of a larger number of ligands. If the ligands involved are too bulky, then low-electron count complexes are formed.



The 16e "Zirconocene dichloride."

[†] 4s is ALWAYS above 3d in complexes, hence although the electronic configuration of *e.g.* Ti atoms is usually given as $[\text{Ar}]3d^2 4s^2$, in Ti complexes it is always $[\text{Ar}]3d^4$. That also makes $\text{Rh(I)} = d^8$.

2. The Green Guide To Electron Counting

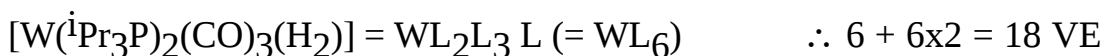
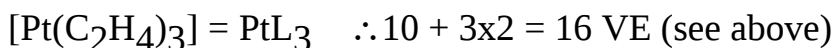
The basic principle of this method of counting electrons in organometallic compounds is that all ligands and the metal centre are counted as *neutral*. Ligands are divided into two main classes:

L ligands which contribute 2 electrons
X ligands which contribute 1 electron

L Ligands

These are the conventional neutral ligands which bond *via* lone pair donation or donation from a π -system, e.g. PR_3 , N_2 , C_2H_4 , H_2 (molecular hydrogen), CO , RNC , C_2H_2 .

Examples:



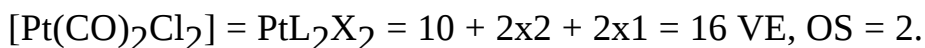
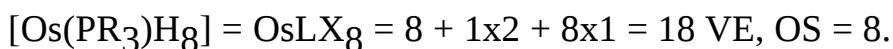
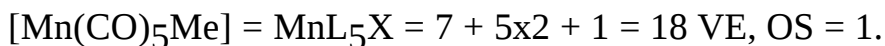
X Ligands

These are ligands which, in real life, have charges. In this scheme we count them as *radicals* (*i.e.* neutral) and therefore contributing one electron,[‡] e.g. H, X (X = halide), R (alkyl), Ar (aryl), RCO, OR, NR_2 , SH. Note that these are only simple X ligands when they are terminal - see later for bridging.

Oxidation State (OS)

In neutral compounds, the number of X ligands = the oxidation state of the metal, but see later for anionic and cationic complexes.

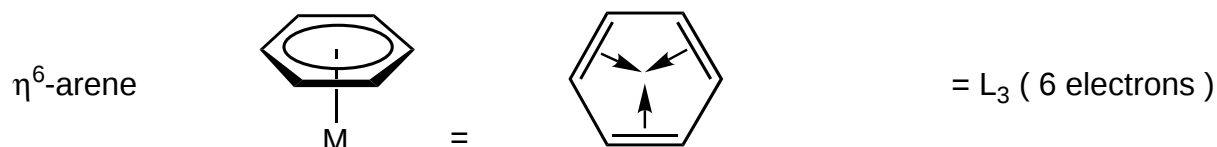
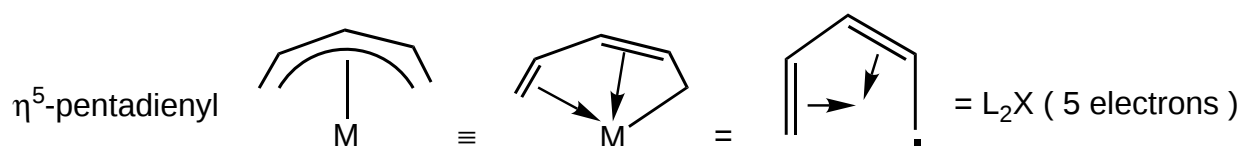
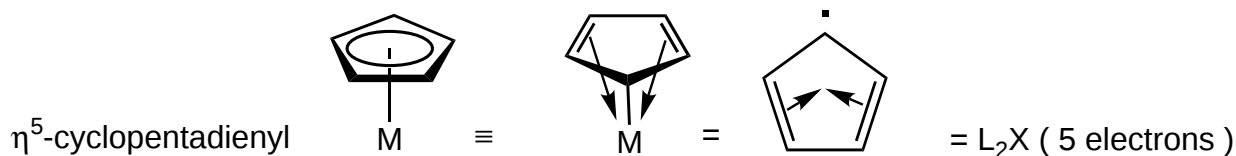
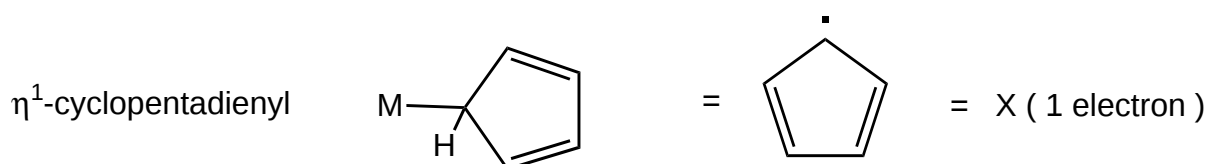
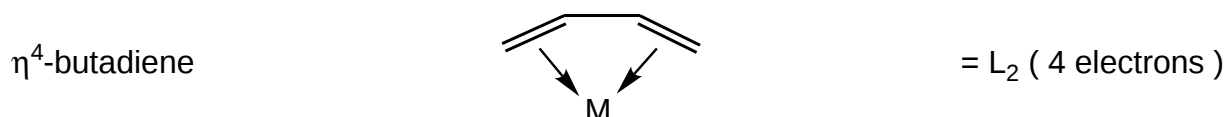
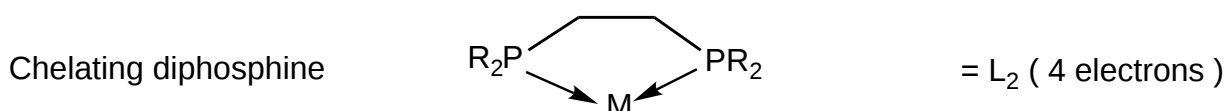
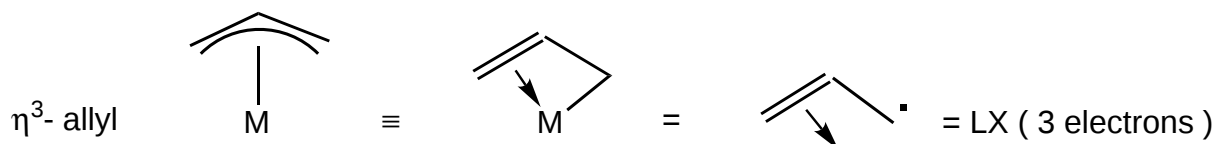
Examples:



[‡] This avoids problems with charge assignment (Ph^+ or Ph^- ?).

Composite Ligands

We can use combinations of L and/or X to classify more complicated ligands, still treating them as neutral, *e.g.*:



The η -nomenclature

The prefix η^n for π -ligands means:

The number of carbons (n) bound to the metal centre

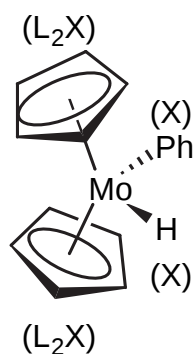
N.B. η with no superscript n means n is taken as the maximum for that ligand

Coordination Number (CN)

This is the sum of L and X ligands, not the number of ligand atoms bonded to the metal.

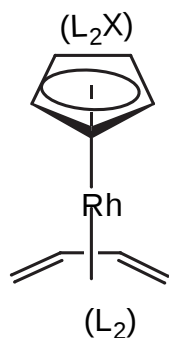
For the complex ML_nX_m , $CN = n + m$

Examples:



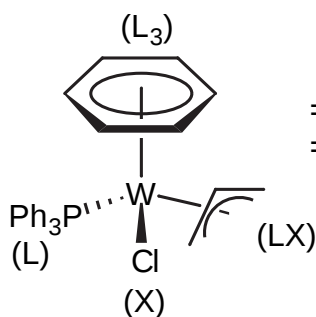
$$= Mo(L_2X)_2(X)(X) = MoL_4X_4 = 6 + 4 \times 2 + 4 \times 1$$

$$= 18 \text{ VE, OS} = 4, \text{ CN} = 8$$



$$= Rh(L_2X)(L_2) = RhL_4X = 9 + 4 \times 2 + 1$$

$$= 18 \text{ VE, OS} = 1, \text{ CN} = 5$$



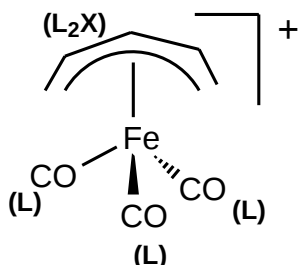
$$= W(L_3)(LX)(L)(X) = WL_5X_2 = 6 + 5 \times 2 + 2 \times 1$$

$$= 18 \text{ VE, OS} = 2, \text{ CN} = 7$$

Cationic And Anionic Complexes

These are counted in exactly the same way, except that in a cation we have to subtract one from the electron count for each positive charge and add one to the number of Xs to get the oxidation state.

Example:

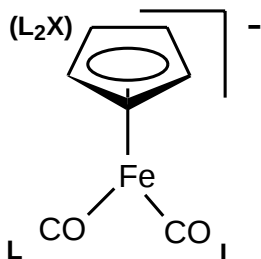


$$= \text{Fe}(\text{L}_2\text{X})(\text{L})_3^+ = \text{FeL}_5\text{X}^+ = 8 + 5 \times 2 + 1 - 1$$

$$= 18 \text{ VE, OS} = 2, \text{CN} = 6$$

Similarly, in *anionic* complexes we have to add one to the electron count for each negative charge and subtract one from the number of Xs to get the oxidation state.

Example:



$$= \text{Fe}(\text{L}_2\text{X})(\text{L})_2^- = \text{FeL}_4\text{X}^- = 8 + 4 \times 2 + 1 \times 1 + 1$$

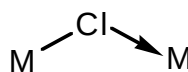
$$= 18 \text{ VE, OS} = 0, \text{CN} = 5$$

Hence,

$\text{Oxidation state} = (\text{number of X ligands}) + (\text{charge on complex})$
--

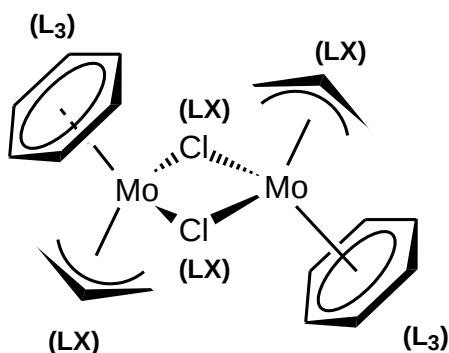
Bridging Ligands

Halides often bridge between two metal centres using a lone pair, *i.e.*



so they count as LX, X for the σ bond and L for the donor bond.

Example:



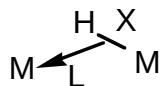
$$= \text{Mo}_2(\text{L}_3)_2(\text{LX})_2(\text{LX})_2 = \text{Mo}_2\text{L}_{10}\text{X}_4 = 2 \times 6 + 10 \times 2 + 4 \times 1$$

$$= 36 \text{ VE } i.e. 18 \text{ VE per Mo,}$$

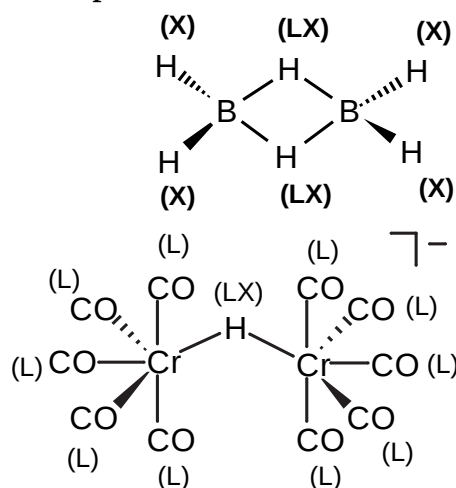
$$= 4 \text{ X ligands, } i.e. \text{ each Mo has OS} = 2,$$

$$= 14 \text{ L+X, } i.e. \text{ each MO has CN} = 7$$

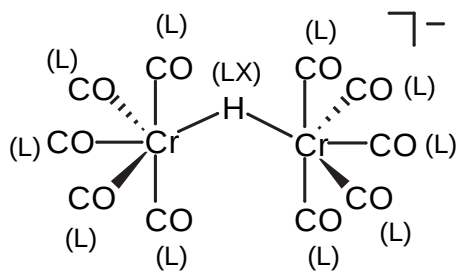
Bridging hydrogens are impossible to count conventionally, so we are not even going to attempt to do so! In this scheme we count them as LX, *i.e.*



Examples:



$$\begin{aligned}
 &= B_2 (LX)_2 X_4 = B_2 L_2 X_6 = 2 \times 3 + 2 \times 2 + 6 \times 1 \\
 &= 16 \text{ VE, } i.e. 8 \text{ VE per B,} \\
 &= 6 \text{ X ligands, } i.e. \text{ each B has OS} = 3, \\
 &= 8 \text{ L+X ligands, } i.e. \text{ each B has CN} = 4.
 \end{aligned}$$

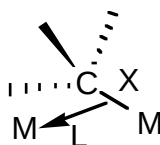


$$\begin{aligned}
 &= Cr_2 (L)_{10} LX^- = Cr_2 L_{11} X^- = 2 \times 6 + 11 \times 2 + 1 \times 1 + 1 \\
 &= 36 \text{ VE, } i.e. 18 \text{ VE per Cr} \\
 &= 1 \text{ X ligand} + (-1 \text{ charge}), i.e. \text{ each Cr has OS} = 0 \\
 &= 12 \text{ L+X ligands, } i.e. \text{ each Cr has CN} = 6
 \end{aligned}$$

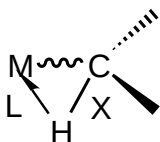
An advanced rule:

You may be able to see that $X^- = L$, thus $Cr_2 L_{11} X^- = Cr_2 L_{12}$

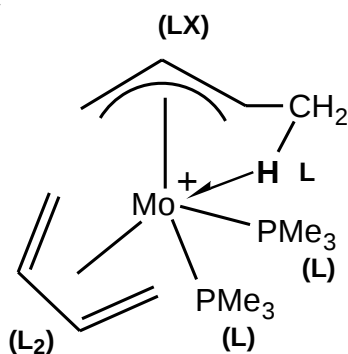
We count bridging alkyl groups in exactly the same way, as LX. *i.e.*



Agostic hydrogens are also bridging ligands in a sense and are classed as L, except that we use the *half-arrow* convention to indicate the agostic bond, *i.e.*



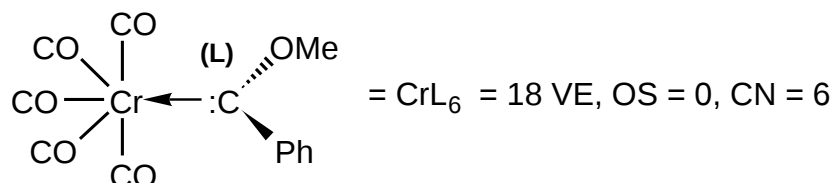
Example:



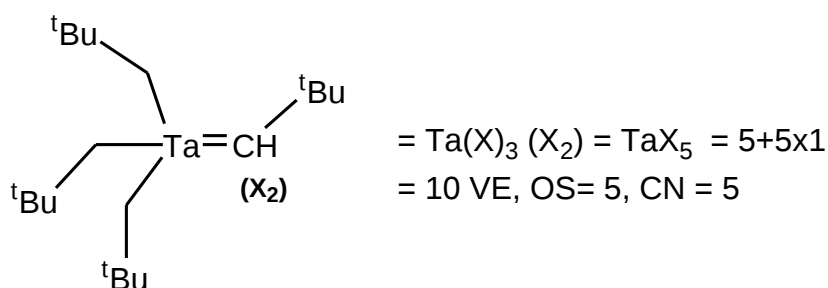
$$\begin{aligned}
 &= Mo(L_2)(L)_2 (LX)(L)^+ = MoL_6 X^+ = 6 + 6 \times 2 + 1 \times 1 - 1 \\
 &= 18 \text{ VE, OS} = 2, \text{ CN} = 7.
 \end{aligned}$$

Alkylidenes and Alkylidynes

There are two classes of alkylidenes: Fischer alkylidenes in which the alkylidene carbon is electrophilic, which are classed as L ligands, e.g.



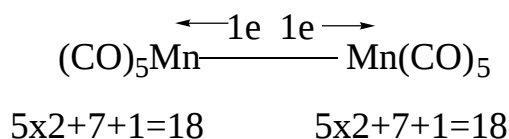
and Schrock alkylidene in which the alkylidene carbon is nucleophilic, which are classed as X_2 ligands, e.g.



Similarly, Fischer alkylidynes are classed as LX and Schrock alkylidynes as X_3 .

Metal-Metal Bonds

Here we assign one of the electrons of the electron pair in a single metal-metal bond to each of the metal centres e.g.

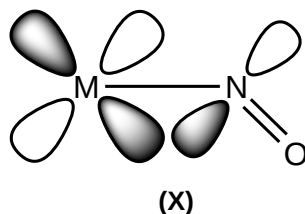


Metal-metal double, triple and quadruple bonds are treated in an analogous fashion by assigning 2, 3 or 4 electrons respectively to each metal.

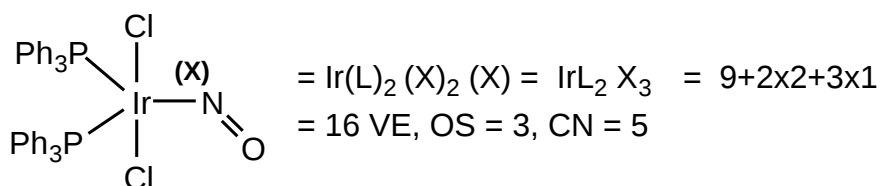
Nitrosyls

Remember that the neutral NO molecule is a radical with one unpaired electron, and can bind to a metal in a bent or linear fashion.

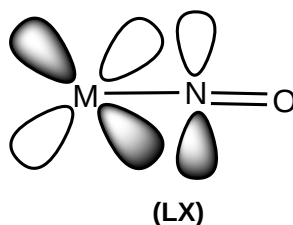
In a bent nitrosyl the NO is acting as a one electron X ligand and the lone pair on nitrogen is not being used in bonding (as a consequence of the bent geometry) *i.e.*



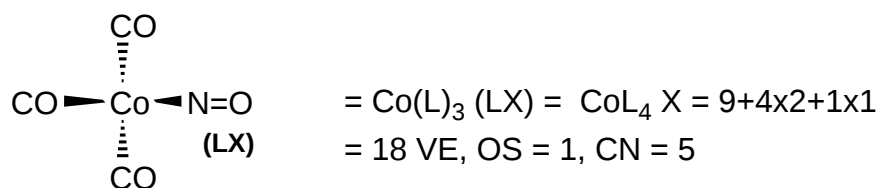
Example:



In linear nitrosyl complexes the lone pair on nitrogen can now donate to the metal (into an empty d orbital) as a result of the linear geometry, so that a linear nitrosyl counts as LX, *i.e.*



Example:



FGNC PROBLEM CLASS 1

Assuming the eighteen electron rule is obeyed, what are the values of t-z and the oxidation state of the metal in (a)-(g)?

