

A Thousand Manipulatable Inorganic Electron-Counting Problems from Crystallography

George Lisensky, Beloit College

One thousand interactive organometallic and coordination complexes have been selected and prepared for practice and discovery in electron counting problems. The structures can be displayed and manipulated without requiring software installation using a web browser with JavaScript and JSmol. The user can drag to rotate, shift-drag vertical to zoom, and shift-drag horizontal to turn the structure.

The problems are numbered alphabetically with **four** structures in each problem for small group work. Each member could present their electron count for one of the four. Sometimes a set designated by { } will contain more than one structure. In such cases the electron-count work is identical for all of them, for example {Co, Rh, Ir} or {Cl, Br, I} or {*cis*, *trans*} or {*fac*, *mer*}.

Selected display options are retained while on a given page. The user can switch a given view to another representation (e.g. space-filling or ball&stick) or label atoms. One display option is to display the metal-metal distance but double-clicking can also be used to measure observed distances and angles between atoms.

The displayed structures are derived from crystallographic results. If the hydrogen atom positions were not reported, then hydrogen atoms have been added and their positions energy-minimized. Any disorder is not shown. Counter ions may or may not be included; overall charge of the displayed portion is shown in the upper right of the JSmol window. Small deviations from ideal geometry may be due to crystal packing. See the link at the bottom of each page for the original references and cif files.

Later pages use ligands from earlier pages so examining the pages in order is helpful. The bottom of each page has links to all the other pages.

- [Metal Carbonyl Complexes](#)

Does observed geometry match 18-electron count predictions?

The metal carbonyl complexes are classic examples that follow a count of eighteen electrons around the metal atom with filled t_{2g} bonding orbitals. I begin the discussion of this topic using the ones at the top in bold. See below for a presentation outline. Additional electron counting problems follow the carbonyl-only ligand structures. These problems are useful in introducing the mechanics of student group work. The last problem could be used later since it introduces Cp and μ_2 -CO and μ_3 -CO bridging ligands. Counter ions are not shown.

I use a one page handout included below to introduce the closed shell ligand and neutral ligand methods of electron counting. An [additional booklet](#) goes into greater detail for each ligand (2.2MB).

- [Metal Nitrogen Complexes](#)

What is the metal [electron count](#)? Should these follow the EAN rule?

The metal nitrogen complexes have electron counts of 12-22e⁻ with filled bonding orbitals and possibly filled nonbonding t_{2g} and low-lying antibonding e_g^* orbitals. They are examples of the 18-electron rule *not* being useful. Counter ions are not shown.

- [Metal Nitrosyl Complexes](#)

Does observed geometry match 18-electron count predictions?

Nitrosyl is an interesting ligand since, depending on the M-N-O bond angle, it can be either a 1 or 3 neutral-ligand electron donor or either an NO⁺ or NO⁻ closed-shell-ligand electron donor. It really helps to be able to rotate the molecule to examine whether the NO is linear or bent. Counter ions are not shown.

- [Metal Carbon Complexes](#)

Which observed complexes have the expected [electron count](#) in each set?

Carbon ligands include metal single-bonded CN, Ph, Me and PhCO; metal double-bonded PhCH and Ph₂C; and metal triply-bonded PhC, MeC, ^tBuC and PhCOC.

Counter ions might be included, especially for singly charged complexes. Look for unconnected portions in uncharged molecules as in Co(en)(CN)₄ PPh₄ or AuPh₄ NBu₄ or Au(CN)₄ NBu₄ or K Mn(CH₂CH₂CH₂CH₂)₂(py) or Co(CH₂CH₂CH₂CH₂)(bipy)₂ ClO₄ or Re(MeC)(PMe₃)₄Cl PF₆ or W(PhCO)(CO)₅ NMe₄ or Mn(PhCO)(MeCO)(CO)₄ NMe₄.

- [Metal Alkene Complexes](#)

- [Metal Sandwich Complexes](#)

- [Metal Sandwich Complexes \(part 2\)](#)

Which observed complexes have the expected [electron count](#) in each set?

Coordination to unsaturated ligands can be displayed three ways: with and without bonds to each ligand atom or with one bond to each π system. Counter ions might be included, especially for singly charged complexes. Look for unconnected portions in uncharged molecules.

The alkene page includes alkene, alkyne, and allyl ligands.

The sandwich page includes C₄H₄, C₄Me₄, C₄Ph₄, C₅H₅, C₅Me₅, C₆H₆, C₇H₇, C₈H₈, and C₉H₉ ligands. Part 2 adds other carbon and NO ligands. Conjugated pi systems can accommodate gaining and losing electrons so the 18-count does not always hold.

- [Metal-Metal Bonds](#)

- [Metal-Metal Bonds \(part 2\)](#)

What is the [M-M bond](#) order based on the [electron count](#)?

Is the geometry staggered or eclipsed? Are multiple bonds shorter?

Electron counts are often used to suggest a bond order for metal-metal bonds. Geometry and distance measurements can then be made to support the suggestion of multiple bonding. Counter ions might be included, especially for singly charged complexes. Look for unconnected portions in uncharged molecules.

It is possible to have up to 1 sigma, 2 pi, and 2 delta bonds using *d*-orbitals but the orbitals for one of the later are often used for ligand bonds in a stacked square planar geometry. See the [ligand geometry](#) page, also linked from "M-M bond" at the top of the metal-metal bonds pages.

Part 2 includes ligands with more than one atom forming the bridge between the metal atoms. While all the pages have common formula abbreviations below the display options, this list is especially important for the less well-known M-M bonding ligands in part 2. Their structural formulas are also provided on the reference page.

- **Z Ligands**

What is the **electron count**?

Which bonds to group 13 elements are coordination and which are covalent?

The Z-ligands page begins with Group 13 elements and classic Lewis Dot electron counting. This group would make 3 covalent bonds and might have a coordination bond to a lone pair to reach an octet electron count. In the structures with transition metal atoms it is important to pay attention to whether the Group 13 element is making one of its three covalent bonds to the transition metal or whether the metal is supplying a pair of electrons to the Group 13 element to form the bond, $M \rightarrow Z$. Structures with Cp and Cp* are grouped at the end so Z ligands could be introduced earlier if only the first dozen groups were used. Counter ions are not shown. On this page the displayed portion of the periodic table includes Group 13.

Evaluation and Learning Goals

Students should be able to do problems by both the neutral ligand and closed shell methods. Remember that the names of these methods tell what you need to do to the ligand (use its neutral or closed shell form). For determining oxidation state, you have to use the closed shell method since oxidation states assume closed shell ligands.

For the closed shell method, remember to show the charges on each ligand!

For the neutral ligand method, remember to show the electron count from each ligand!

A thousand problems are probably more than you want to assign, but they have been useful for in-class or online groups of four working together. The goal is to do these problems as quickly as you do Lewis octet problems to begin to understand the bonding. This takes lots of practice.

Links embedded above

<https://chem.beloit.edu/classes/structure/EAN/carbonyl.html>
<https://chem.beloit.edu/classes/structure/EAN/nitrogen.html>
<https://chem.beloit.edu/classes/structure/EAN/nitrosyl.html>
<https://chem.beloit.edu/classes/structure/EAN/carbon.html>
<https://chem.beloit.edu/classes/structure/EAN/alkene.html>
<https://chem.beloit.edu/classes/structure/EAN/sandwich.html>
<https://chem.beloit.edu/classes/structure/EAN/sandwich2.html>
<https://chem.beloit.edu/classes/structure/EAN/MM.html>
<https://chem.beloit.edu/classes/structure/EAN/MM2.html>
<https://chem.beloit.edu/classes/structure/EAN/Z.html>
<https://chem.beloit.edu/classes/structure/ligandfield.html>
<https://chem.beloit.edu/classes/structure/EAN/EAN.pdf>
https://chem.beloit.edu/classes/structure/EAN/EAN_booklet.pdf

References

JSmol: an open-source HTML5 viewer for chemical structures in 3D

<https://wiki.jmol.org/index.php/JSmol>

<https://wiki.jmol.org/index.php/Literature>

Electron Counting

Stable compounds are formed when each atom has the same number of electrons around it as the next noble gas element.

- I. Application to first row: He is $1s^2$ so 2 valence electrons preferred and H_2 is predicted.
 II. Application to second row: Ne is $[He]2s^22p^6$ so 8 valence electrons are preferred.

We predict $H\cdot$ will react with $\cdot\dot{C}\cdot$ $\cdot\ddot{N}\cdot$ $\cdot\ddot{O}\cdot$ $\cdot\ddot{F}\cdot$ to produce $\begin{array}{c} H \\ | \\ H:\dot{C}:H \\ | \\ H \end{array}$ $\begin{array}{c} H \\ | \\ H:\ddot{N}:H \\ | \\ H \end{array}$ $\begin{array}{c} H \\ | \\ H:\ddot{O}:H \\ | \\ H \end{array}$ $\begin{array}{c} H \\ | \\ H:\ddot{F}: \\ | \\ H \end{array}$

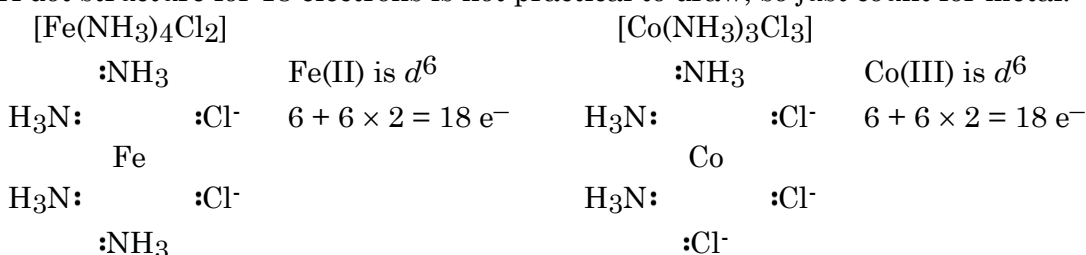
but unsaturated $\begin{array}{c} H \\ | \\ H:\dot{B}: \\ | \\ H \end{array}$ will react with $\begin{array}{c} H \\ | \\ H:\ddot{N}:H \\ | \\ H \end{array}$ to form complex $\begin{array}{c} H & H \\ | & | \\ H:\dot{B}:\ddot{N}:H \\ | & | \\ H & H \end{array}$

III. Types of electron pair σ bonds

An ordinary covalent bond has one electron from each atom, so radical species result when the bond is broken, $CH_4 \rightarrow CH_3\cdot + \cdot H$, with -yl nomenclature.

Coordination bond has both electrons from one atom, so stable species result when the bond is broken, $H_3B:NH_3 \rightarrow H_3B + \cdot NH_3$

- IV. Application to third row: $[Kr]$ is $[Ar]3s^24d^{10}3p^6$ so 18 valence electrons are preferred. A dot structure for 18 electrons is not practical to draw, so just count for metal.



V. Structural predictions for $M(CO)_n$ agree with observed geometries.

Cr(0)	d^6	18-6=12 from 6 ligands.	Predict $Cr(CO)_6$	
Fe(0)	d^8	18-8=10 from 5 ligands.	Predict $Fe(CO)_5$	
Ni(0)	d^{10}	18-10=8 from 4 ligands.	Predict $Ni(CO)_4$	Predictions
Mn(I)	d^6	18-6=12 from 6 ligands.	Predict $Mn(CO)_6^+$	are correct!
Mn(-I)	d^8	18-8=10 from 5 ligands.	Predict $Mn(CO)_5^-$	

What do we get for Mn(0) and Co(0)? $d^7 + 5 CO = 17 e^-$ and $d^9 + 4 CO = 17 e^-$.

One more electron is needed. We expect free-radicals like $\cdot CH_3$ to dimerize and give H_3C-CH_3 . We get $(CO)_5Mn-Mn(CO)_5$ and $(CO)_4Co-Co(CO)_4$

VI. Effective atomic number (EAN) rule in italics at the top of this page.

- Allows systematization and prediction of structures and reactivities.
- Doesn't always hold
 - Fill all bonding, maybe fill nonbonding t_{2g} and low-lying antibonding e_g^* orbitals, yields a 12-22 e^- count.
 - Fill all bonding, maybe fill nonbonding t_{2g} orbitals, yields 12-18 e^- count.
 - Fill all bonding, including π back-bonding t_{2g} orbitals, yields 18 e^- count.
- Steric crowding or high oxidation states can prevent reaching an 18 e^- count.
- The most common exception to 18 electrons is 16 electrons for d^8 second and third row species or intermediates (square planar complexes).
 Sometimes called the *16 and 18 electron rule*.

The Two Methods of Electron Counting

CLOSED SHELL LIGAND (IONIC)	NEUTRAL LIGAND (COVALENT)
<i>All ligands are closed shell.</i>	<i>All ligands are neutral.</i>
1. Metal ligand bonds are all coordination bonds and all contribute two electrons.	1. Ordinary covalent bonds contribute one electron, and coordination bonds contribute two electrons.
2. Find number of electrons on metal from the formal oxidation state (based on ligand and complex charges.)	2. Use the number of valence electrons on the neutral metal atom (count from the left edge of periodic table.)
3. Each M-M bond contributes 1 electron.	3. Subtract the charge on the complex.
<i>Show the charges on each ligand!</i>	<i>Show the electron count from each ligand!</i>
Examples	
$\begin{array}{ccccccc} \text{:CH}_3^- & \text{:H}^- & \text{:C}_6\text{H}_5^- & & & & \\ \text{:C}\equiv\text{N:}^- & \text{:}\ddot{\text{Br}}\text{:}^- & \text{:}\ddot{\text{O}}\text{H}^- & \text{:}\ddot{\text{N}}=\ddot{\text{O}}\text{:}^- & \text{:N}\equiv\text{O:}^+ & & \\ & & \text{bent} & \text{linear} & & & \end{array}$ $\begin{array}{ccccccc} \text{:NH}_3 & \text{:PR}_3 & \text{:C}\equiv\text{O:} & \text{:N}\equiv\text{N:} & \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \end{array} & & \\ \text{Allyl} & \text{H}_2\text{C}=\text{CH}-\text{CH}_2^- & 4e^- \text{ donor} & & & & \end{array}$ $\begin{array}{ccccccc} \text{H}_2\text{N:} & \text{:NH}_2 & \text{R}_2\text{P:} & \text{:PR}_2 & \text{alkene} & & \\ 2e^-/\text{N} & & 2e^-/\text{P} & & 2e^-/\text{alkene} & & \end{array}$	$\begin{array}{ccccccc} \cdot\text{CH}_3 & \cdot\text{H} & \cdot\text{C}_6\text{H}_5 & & & & \\ \cdot\text{C}\equiv\text{N:} & \cdot\ddot{\text{Br}}\text{:} & \cdot\ddot{\text{O}}\text{H} & \cdot\ddot{\text{N}}=\ddot{\text{O}}\text{:} & & & \\ & & 1e^- \text{ bent,} & 3e^- \text{ linear} & & & \\ \text{:NH}_3 & \text{:PR}_3 & \text{:C}\equiv\text{O:} & \text{:N}\equiv\text{N:} & \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \end{array} & & \\ \text{Allyl} & \text{H}_2\text{C}=\text{CH}-\text{CH}_2 & 3e^- \text{ donor} & & & & \end{array}$ $\begin{array}{ccccccc} \text{H}_2\text{N:} & \text{:NH}_2 & \text{R}_2\text{P:} & \text{:PR}_2 & \text{alkene} & & \\ 2e^-/\text{N} & & 2e^-/\text{P} & & 2e^-/\text{alkene} & & \end{array}$
[Co(CN) ₂ (CO)(PEt ₃) ₂] ⁻	
$\begin{array}{ll} 2 \text{ :CN}^- & 4 \\ \text{:CO} & 2 \\ 2 \text{ :P} & 4 \\ \text{Co(I)} & \underline{8} \\ & 18e^- \end{array}$	$\begin{array}{ll} 2 \cdot\text{CN} & 2 \\ \text{:CO} & 2 \\ 2 \text{ :P} & 4 \\ \text{Co(0)} & 9 \\ 1e^- & -(-1) \\ & 18e^- \end{array}$
Os(CO) ₄ (CH ₃) ₂	
$\begin{array}{ll} 4 \text{ :CO} & 8 \\ 2 \text{ :CH}_3^- & 4 \\ \text{Os(II)} & \underline{6} \\ & 18e^- \end{array}$	$\begin{array}{ll} 4 \text{ :CO} & 8 \\ 2 \cdot\text{CH}_3 & 2 \\ \text{Os(0)} & \underline{8} \\ & 18e^- \end{array}$
Co(CO) ₃ H(CH ₂ =CH ₂)	
$\begin{array}{ll} 3 \text{ :CO} & 6 \\ \text{:H}^- & 2 \\ \text{://} & 2 \\ \text{Co(I)} & \underline{8} \\ & 18e^- \end{array}$	$\begin{array}{ll} 3 \text{ :CO} & 6 \\ \cdot\text{H} & 1 \\ \text{://} & 2 \\ \text{Co(0)} & \underline{9} \\ & 18e^- \end{array}$

You should be able to do problems by both the neutral ligand and closed shell methods. Remember that the names of these methods tell what you need to do to the ligand (use its neutral or closed shell form). For determining oxidation state, you have to use the closed shell method since oxidation states assume closed shell ligands.