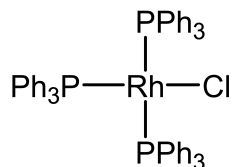


- 4/7: 1. For each complex, provide the (i) oxidation state, (ii) d^n configuration, and (iii) NVE (number of valence electrons, or electron count) at the metal. Provide this information for both metals and provide the number of M–M bonds in the bimetallic cases.

1)

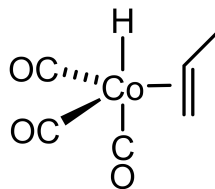


Answer.

- (i) Rh^+ (each phosphine is L-type; the chlorine is X-type).
- (ii) Rh^+ is d^8 .
- (iii) Each phosphine is a 2-electron donor, and the chlorine is a 1-electron donor. Thus, the ligands donate $3 \cdot 2 + 1 \cdot 1 = 7$ electrons in total. This combined with the above results yields $7 + 9 = 16$ as the electron count.

□

2)

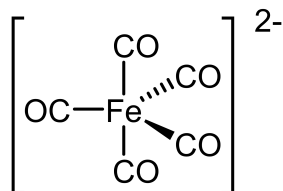


Answer.

- (i) Co^+ (each carbonyl is L-type; the hydride is X-type; the propene is L-type).
- (ii) Co^+ is d^8 .
- (iii) Each carbonyl is a 2-electron donor, the hydrogen is a 1-electron donor, and propene is a 2-electron donor. Thus, the ligands donate $3 \cdot 2 + 1 \cdot 1 + 1 \cdot 2 = 9$ electrons in total. This combined with the above result yields $9 + 9 = 18$ as the electron count.

□

3)

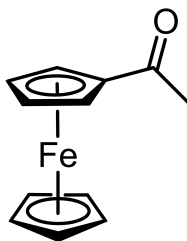


Answer.

- (i) Fe^{2-} (each carbonyl is L-type; the charge is 2-).
- (ii) Fe^{2-} is d^{10} .
- (iii) Each carbonyl is a 2-electron donor. Thus, the ligands donate $5 \cdot 2 = 10$ electrons in total. This combined with the above results yields $10 + 8 - (-2) = 20$ as the electron count.

□

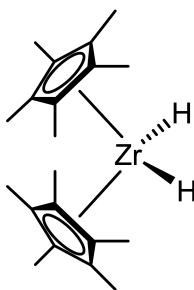
4)

*Answer.*

- (i) Fe^{2+} (both ligands are X-type).
- (ii) Fe^{2+} is d^6 .
- (iii) Both ligands are 5-electron donors. Thus, the ligands donate $2 \cdot 5 = 10$ electrons in total. This combined with the above results yields $10 + 8 = 18$ as the electron count.

□

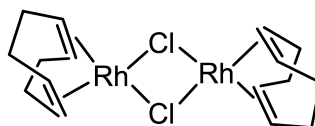
5)

*Answer.*

- (i) Zr^{4+} (all ligands are X-type).
- (ii) Zr^{4+} is d^0 .
- (iii) Both pentamethylcyclopentadienyl (Cp^*) groups are 5-electron donors, and both hydrogens are 1-electron donors. Thus, the ligands donate $2 \cdot 5 + 2 \cdot 1 = 12$ electrons in total. This combined with the above results yields $12 + 4 = 16$ as the electron count.

□

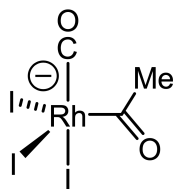
6)

*Answer.*

- (i) Both metals are Rh^+ (both cycloocta-1,5-dienyl (COD) groups are L_2 -type; both bridging chlorines are LX -type [they can be thought of as bonding covalently to one rhodium and datively to the other, so when the bonds are cleaved, each chlorine steals one covalent electron from a rhodium and reclaims its two dative electrons]).
- (ii) Rh^+ is d^8 .
- (iii) Both COD groups are 4-electron donors, and both bridging chlorines are 3-electron donors. Thus, the ligands donate $2 \cdot 4 + 2 \cdot 3 = 14$ electrons in total. This combined with the above results yields $\frac{14+2 \cdot 9}{2} = 16$ as the electron count at each rhodium. It follows that there should be $\frac{36-2 \cdot 16}{2} = 2$ Rh–Rh bonds.

□

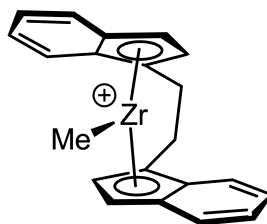
7)

*Answer.*

- (i) Rh^{3+} (the carbonyl is L-type; each iodide is X-type; the other ligand is X-type; the charge is 1-).
- (ii) Rh^{3+} is d^6 .
- (iii) The carbonyl is a 2-electron donor, each iodide is a 1-electron donor, and the other ligand is a 1-electron donor. Thus, the ligands donate $1 \cdot 2 + 3 \cdot 1 + 1 \cdot 1 = 6$ electrons in total. This combined with the above results yields $6 + 9 - (-1) = 16$ as the electron count.

□

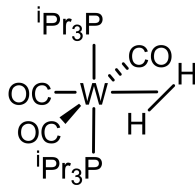
8)

*Answer.*

- (i) Zr^{4+} (the methyl is X-type; the other ligand is X_2 -type; the charge is 1+).
- (ii) Zr^{4+} is d^0 .
- (iii) The methyl is a 1-electron donor, and the other ligand is a 10-electron donor. Thus, the ligands donate $1 \cdot 1 + 1 \cdot 10 = 11$ electrons in total. This combined with the above results yields $11 + 4 - 1 = 14$ as the electron count.

□

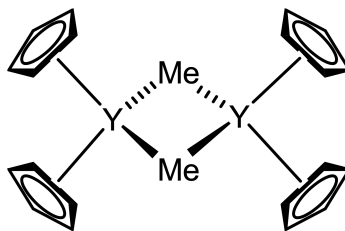
9)

*Answer.*

- (i) W^0 (each carbonyl is L-type; both phosphines are L-type; the other ligand is L-type).
- (ii) W^0 is d^6 .
- (iii) Each carbonyl is a 2-electron donor, both phosphines are 2-electron donors, and the other ligand is a 2-electron donor. Thus, the ligands donate $3 \cdot 2 + 2 \cdot 2 + 1 \cdot 2 = 12$ electrons in total. This combined with the above results yields $12 + 6 = 18$ as the electron count.

□

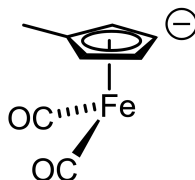
10)

*Answer.*

- (i) Y^{3+} (each Cp is X-type; each bridging methyl is LX-type).
- (ii) Y^{3+} is d^0 .
- (iii) Each Cp is a 5-electron donor, and each methyl is a 3-electron donor. Thus, the ligands donate $4 \cdot 5 + 2 \cdot 3 = 26$ electrons in total. This combined with the above results yields $\frac{26+2 \cdot 3}{2} = 16$ as the electron count at each yttrium. It follows that there should be $\frac{36-2 \cdot 16}{2} = 2$ Y–Y bonds.

□

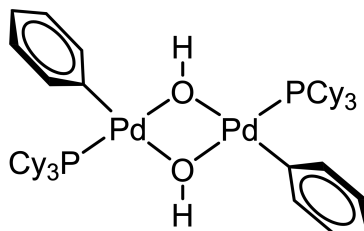
11)

*Answer.*

- (i) Fe^0 (both carbonyls are L-type; the other ligand is X-type; the charge is $1-$).
- (ii) Fe^0 is d^8 .
- (iii) Both carbonyls are 2-electron donors, and the methylcyclopentadienyl group is a 5-electron donor. Thus, the ligands donate $2 \cdot 2 + 1 \cdot 5 = 9$ electrons in total. This combined with the above results yields $9 + 8 - (-1) = 18$ as the electron count.

□

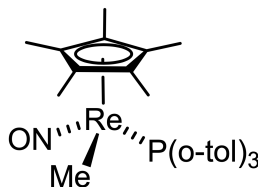
12)

*Answer.*

- (i) Pd^{2+} (both benzenes are X-type; both phosphines are L-type; both bridging hydroxides are LX-type).
- (ii) Pd^{2+} is d^8 .
- (iii) Both benzenes are 1-electron donors, both phosphines are 2-electron donors, and both bridging hydroxides are 3-electron donors. Thus, the ligands donate $2 \cdot 1 + 2 \cdot 2 + 2 \cdot 3 = 12$ electrons in total. This combined with the above results yields $\frac{12+2 \cdot 10}{2} = 16$ as the electron count at each palladium. It follows that there should be $\frac{36-2 \cdot 16}{2} = 2$ Pd–Pd bonds.

□

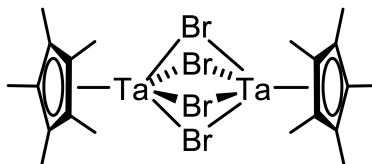
13)

*Answer.*

- (i) Re^+ (the [linear] nitrosyl group is L-type but takes on a positive charge during bond cleavage; the methyl group is X-type; the phosphine is L-type; the Cp^* group is X-type).
- (ii) Re^+ is d^6 .
- (iii) The nitrosyl group is a 3-electron donor (assuming it bonds linearly), the methyl group is a 1-electron donor, the phosphine is a 2-electron donor, and the Cp^* is a 5-electron donor. Thus, the ligands donate $1 \cdot 3 + 1 \cdot 1 + 1 \cdot 2 + 1 \cdot 5 = 11$ electrons in total. This combined with the above results yields $11 + 7 = 18$ as the electron count.

□

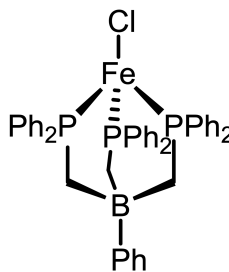
14)

*Answer.*

- (i) Ta^{3+} (both Cp^* groups are L-type; each bridging bromine is LX-type).
- (ii) Ta^{3+} is d^2 .
- (iii) Both Cp^* groups are 5-electron donors, and each bridging bromine is a 3-electron donor. Thus, the ligands donate $2 \cdot 5 + 4 \cdot 3 = 22$ electrons in total. This combined with the above results yields $\frac{22+2 \cdot 5}{2} = 16$ as the electron count at each tantalum. It follows that there should be $\frac{36-2 \cdot 16}{2} = 2$ Ta-Ta bonds.

□

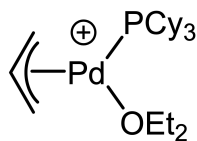
15)

*Answer.*

- (i) Fe^{2+} (the chloride is X-type; the other ligand is L_3 -type but carries a negative formal charge).
- (ii) Fe^{2+} is d^6 .
- (iii) The chlorine is a 1-electron donor, and the other ligand is a 5-electron donor (3 dative bonds minus a single negative formal charge on the boron). Thus, the ligands donate $1 \cdot 1 + 1 \cdot 5 = 6$ electrons in total. This combined with the above results yields $6 + 8 = 14$ as the electron count.

□

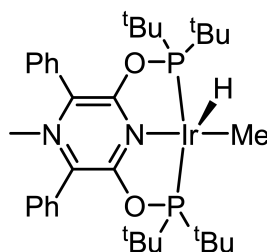
16)

*Answer.*

- (i) Pd^0 (the phosphine is L-type; the ether is L-type; the other ligand is L-type but takes on a positive charge during bond cleavage; the charge is 1+).
- (ii) Pd^0 is d^{10} .
- (iii) The phosphine is a 2-electron donor, the ether is a 2-electron donor, and the other ligand is a 3-electron donor. Thus, the ligands donate $1 \cdot 2 + 1 \cdot 2 + 1 \cdot 3 = 7$ electrons in total. This combined with the above result yields $7 + 10 - 1 = 16$ as the electron count.

□

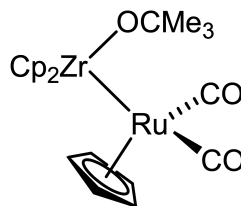
17)

*Answer.*

- (i) Ir^{2+} (the methyl is X-type; the hydride is X-type; the other ligand is L_3 -type).
- (ii) Ir^{2+} is d^7 .
- (iii) The methyl group is a 1-electron donor, the hydrogen is a 1-electron donor, and the other ligand is a 7-electron donor (3 dative bonds plus a single positive formal charge on the leftmost nitrogen in the above picture). Thus, the ligands donate $1 \cdot 1 + 1 \cdot 1 + 1 \cdot 7 = 9$ electrons in total. This combined with the above result yields $9 + 9 = 18$ as the electron count.

□

18)

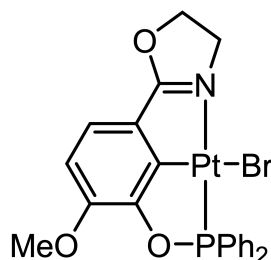
*Answer.*

- (i) Zr^{3+} (the *t*-butoxide is X-type; both Cp groups are X-type; the Zr–Ru bond makes no contribution), and Ru^+ (both carbonyls are L-type; the Cp is X-type; the Zr–Ru bond makes no contribution).
- (ii) Zr^{3+} is d^1 , and Ru^+ is d^7 .

- (iii) For the zirconium atom, the *t*-butoxide group is a 1-electron donor, both Cp groups are 5-electron donors, and the Zr–Ru bond is a 1-electron donor. Thus, the ligands donate $1 \cdot 1 + 2 \cdot 5 + 1 \cdot 1 = 12$ electrons in total to the zirconium atom. This combined with the above results yields $12 + 4 = 16$ as the electron count for the zirconium atom. For the ruthenium atom, both carbonyls are 2-electron donors, the Cp group is a 5-electron donor, and the Zr–Ru bond is a 1-electron donor. Thus, the ligands donate $2 \cdot 2 + 1 \cdot 5 + 1 \cdot 1 = 10$ electrons in total. This combined with the above results yields $10 + 8 = 18$ as the electron count for the ruthenium atom. It follows that there should be $\frac{36 - (16 + 18)}{2} = 1$ extra Zr–Ru bond beyond what is shown in the above picture (2 in total).

□

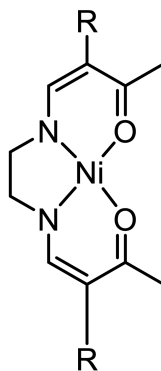
19)

*Answer.*

- (i) Pt^{2+} (the bromine is X-type; the other ligand is L_2X -type).
 (ii) Pt^{2+} is d^8 .
 (iii) The bromine is a 1-electron donor, and the other ligand is a 5-electron donor (2 dative bonds plus 1 covalent bond). Thus, the ligands donate $1 \cdot 1 + 1 \cdot 5 = 6$ electrons in total. This combined with the above result yields $6 + 10 = 16$ as the electron count.

□

20)

*Answer.*

- (i) Ni^{2+} (the ligand is L_2X_2 -type).
 (ii) Ni^{2+} is d^8 .
 (iii) The ligand is a 6-electron donor (2 dative bonds plus 2 covalent bonds). This combined with the above result yields $6 + 10 = 16$ as the electron count.

□

2. For the following pairs of complexes from problem 1, pick and justify based on the trend.

- a) Which complex is more basic and which is more acidic between 2 and 5 (Co and Zr)?

Answer. 5 is more acidic because it wants to gain two electrons to get to 18 to be more stable, whereas 2 already has 18 electrons, and thus is more basic relatively. \square

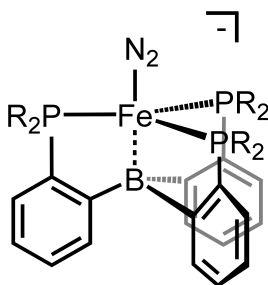
- b) Which complex is more likely to be reduced or oxidized between 4 and 15 (both Fe)?

Answer. 4 is more likely to be oxidized, and 15 is more likely to be reduced. 4 already has 18 electrons, so it won't want any more. 15 is at 14 electrons, so it would surely stabilize it to gain a few more. \square

- c) Which complex is more likely to have its M–C bond hydrolyze between 8 and 12 (Zr and Pd)?

Answer. 8 is more likely to have its M–C bond hydrolyze. In 12, benzene, because it is so stable, is not a great leaving group and the square planar geometry at each metal center is extra stable because of the 16 electron rule (or 18 electrons depending on Pd–Pd bonding). However, in 8, the M–CH₃ bond is highly unstable due to the electron count of 14. \square

3. Consider the following complex.



- a) Assign an oxidation state, d count, overall electron count, and “L/X/Z” formalism.

Answer. The oxidation state is Fe⁰ since all ligands form dative bonds.

The d count is d^8 .

With respect to the overall electron count, N₂ is a 2-electron donor and the bottom ligand is a 6-electron donor. Thus, the electron count is $(2 + 6) + (8) - (-1) = 17$.

The nitrogen is L-type, and the other ligand is L₃Z-type (assuming that there is a single Fe–B bond). \square

- b) Draw 3 different resonance structures for both the Fe–N₂ interaction and the Fe–B interactions in this compound (a total of 6) and explain how the oxidation state, d count, and “L/X/Z” formalism changes as a function of resonance structure.

Answer. Fe – N[⊕]≡N: will be our base Lewis structure of this type. This is an L-type ligand.

Fe = N[⊕]=N[⊖] exhibits no changes in oxidation state, d count, or type^[1].

Fe ≡ N[⊕]–N^{2⊖} exhibits no changes in oxidation state, d count, or type.

Fe – B will be our base Lewis structure of this type. This is not any type of ligand as no bond is present.

Fe – B[⊖] exhibits no changes in oxidation state or d count. This is a Z-type ligand.

Fe = B^{2⊖} exhibits no changes in oxidation state, d count, or type (still Z-type). \square

¹As per Sophie's explanation in office hours, there are not actually more electrons in the M–C double bond in this resonance structure; rather, it simply shows up spectroscopically as shorter, so we denote this still 2-electron bond as having bond order 2. We have a similar case for the other resonance structures.

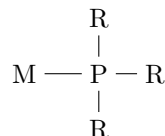
- c) How might the valence of the species differ from the oxidation state in the resonance structure depicted in the chem draw above?

Answer. For the reason discussed in Footnote 1, the valence would not change in any of the Fe–N resonance structures. However, depending on the nature and extent of the Fe–B bonding, it could well increase when bonding first occurs (although, again, it will not likely change within the bonded resonance structures). \square

4. For the following ligands, draw all possible resonance structures with formal charges, indicate the number of electrons donated to a generic metal complex, and assign the ligand to its appropriate “L/X/Z” formulation.

- a) PR_3 .

Answer. Structure:

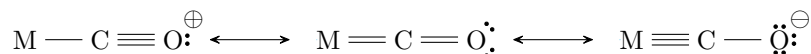


2-electron donor.

L-type ligand. \square

- b) CO.

Answer. Resonance structures:

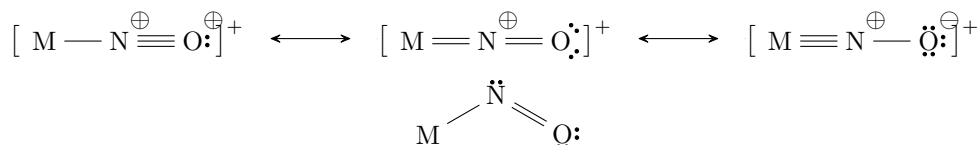


2-electron donor.

L-type ligand. \square

- c) NO.

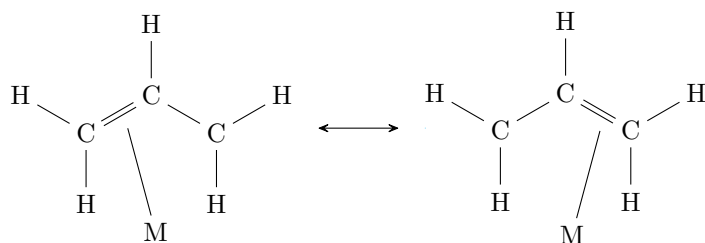
Answer. Resonance structures:



The top set of resonance structures are 3-electron-donating L-type ligands. The bottom structure is a 1-electron-donating X-type ligand. \square

- d) C_3H_5 .

Answer. Resonance structures:

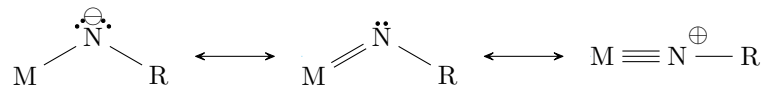


3-electron donor.

LX-type ligand. \square

e) "NR."

Answer. Resonance structures:



2-electron donor.

X₂-type ligand.

□

5. Predict the spin state, μ_{eff} , and χT values for the following ions in the indicated geometry.

a) Tetrahedral Mn(II).

Answer. High spin d^5 (tetrahedral has small orbital splitting). Thus,

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{\frac{5}{2}\left(\frac{5}{2} + 1\right)} & \chi T &= \frac{2^2}{8}\left(\frac{5}{2}\left(\frac{5}{2} + 1\right)\right) \\ &= \sqrt{35} & &= \frac{35}{8} \end{aligned}$$

□

b) Octahedral Ir(III).

Answer. Low spin d^6 (high oxidation state implies large Δ , so low spin). Thus,

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{0(0 + 1)} & \chi T &= \frac{2^2}{8}(0(0 + 1)) \\ &= 0 & &= 0 \end{aligned}$$

□

c) Octahedral Ru(III).

Answer. Low spin d^5 (high oxidation state implies large Δ , so low spin). Thus,

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)} & \chi T &= \frac{2^2}{8}\left(\frac{1}{2}\left(\frac{1}{2} + 1\right)\right) \\ &= \sqrt{3} & &= \frac{3}{8} \end{aligned}$$

□

d) Square planar Co(II).

Answer. Low spin d^7 (square planar has large orbital splitting). Thus,

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)} & \chi T &= \frac{2^2}{8}\left(\frac{1}{2}\left(\frac{1}{2} + 1\right)\right) \\ &= \sqrt{3} & &= \frac{3}{8} \end{aligned}$$

□

- e) Square planar Pt(II).

Answer. Low spin d^8 (square planar has large orbital splitting). Thus,

$$\begin{aligned}\mu_{\text{eff}} &= 2\sqrt{0(0+1)} & \chi T &= \frac{2^2}{8}(0(0+1)) \\ &= 0 & &= 0\end{aligned}$$

□

- f) Octahedral Ni(II).

Answer. High spin d^8 (low oxidation state implies small Δ , so high spin). Thus,

$$\begin{aligned}\mu_{\text{eff}} &= 2\sqrt{1(1+1)} & \chi T &= \frac{2^2}{8}(1(1+1)) \\ &= 2\sqrt{2} & &= 1\end{aligned}$$

□

- g) Tetrahedral Cr(II).

Answer. High spin d^4 (tetrahedral has small orbital splitting). Thus,

$$\begin{aligned}\mu_{\text{eff}} &= 2\sqrt{2(2+1)} & \chi T &= \frac{2^2}{8}(2(2+1)) \\ &= 2\sqrt{6} & &= 3\end{aligned}$$

□

6. Predict the relative radii between the two ions listed (i.e., same, larger, or smaller) assuming an octahedral field, and rationalize your choice.

- a) Low spin Fe(II) or high spin Fe(II).

Answer. High spin Fe(II) has a larger radius than low spin Fe(II) because the e_g orbitals are antibonding, so having more antibonding electrons both pushes the bounds of the atom (increasing the atomic radius) and weakens bonds (increasing the covalent radius). □

- b) Mn(II) or Mn(III).

Answer. Mn(II) has a larger radius than Mn(III) because having more electrons means more intra-orbital repulsions, all of which push the bounds of the atom. □

- c) Low spin Ti(II) or high spin Ti(II).

Answer. The radius is the same (low spin equals high spin for d^2 complexes). □

- d) Zr(IV) or Zr(III).

Answer. Zr(III) has a larger radius than Zr(IV) for the same reasons listed in part (b). □

7. The isolobal analogy is frequently used to help relate seemingly disparate fragments. Utilize this analogy to compare the bonding in terminal nitride (N) and alkylidyne (CR) complexes.

Answer. Since we have $\text{M} = \text{N} \cdot$ and $\text{M} = \ddot{\text{C}} - \text{R}$ for how the two ligands bond, we can assume based on the fact that the two ligands are isoelectronic and isolobal (simply replace a lone pair in the nitride with the bond in the alkylidyne, or vice versa) that they have similar bonding, stability, and chemical properties. □

8. Read Green (1995). Based on this paper, answer the following questions.

- a) In your own words, explain the reasons why the author considers a different form of bond classification necessary.

Answer. The ionic method relies heavily on the calculation of the metal center's oxidation state and coordination number. However, while these two quantities suitably treated the known inorganic compounds of the early twentieth century (i.e., ones that were easily described as ionic), they play less nicely with the oft covalently bonded complexes of today. As such, Green (1995) created the covalent bond classification method to solve issues arising from these two quantities. In brief, the problems with the oxidation state stem from the fact that calculations of it are debatable for some bonds, and they flat-out neglect homopolar bonds. The problems with coordination number mainly surround the fact that it can treat very similar compounds quite differently (for example, $\text{Mo}(\text{CO})_6$, $\text{Mo}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3$, and $\text{Mo}(\eta\text{-C}_6\text{H}_6)_2$ have coordination numbers of 6, 9, and 12, respectively). \square

- b) Is it more common to have a MoL_2X_4 compound or MoL_4X_2 compound?

Answer. It is more common to have a MoL_2X_4 compound than a MoL_4X_2 compound, as can be read from Figure 1 on Green (1995, p. 128). \square

- c) What are the differences in the ligand bonding orbitals for L-, X-, and Z-type ligands?

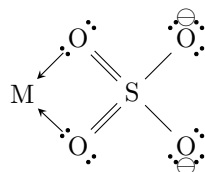
Answer. L-type: Two electrons are donated from a ligand-based orbital to an empty orbital on the metal center via the formation of a single dative bond.

X-type: One electron is donated from a singly occupied ligand-based orbital to the metal center via the formation of a single covalent bond that also requires one electron from the metal center.

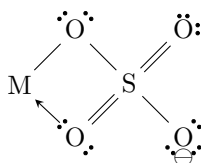
Z-type: An empty ligand orbital accepts an electron pair from the metal via the formation of a single bond. \square

- d) Draw L_2 , LX , and X_2 forms of a sulfate ion bound to a generic metal M.

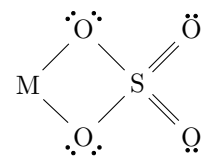
Answer.



(a) L_2 form.



(b) LX form.



(c) X_2 form.

Figure 1: Different ways sulfate can bind to a metal center.

\square

- e) What does valency/valence number mean and how does that differ from oxidation state? What type of complex has a different valence number and oxidation state? Similarly, what does ligand bond number mean and how does this differ from coordination number? Give an example of a ligand where coordination number and ligand bond number differ.

Answer. **Valency:** The number of X-functions on the ligands, where an X-function is a singly occupied orbital on the ligand which requires one electron from the metal center to form a two-electron covalent bond. *Also known as valence number, V.N.*

Oxidation state: The number of electrons that the metal center gains or loses when all bonds are homolytically and ionically cleaved. *Also known as O.S.*

Unlike the O.S., the V.N. includes homopolar (e.g., M-M) bonds and cannot, by definition, be negative.

Ligand bond number: The sum of the number of X-functions and the number of L-functions on the ligands, where an X-function is defined as above and an L-function is a single ligand orbital occupied by two electrons, both of which are donated to an empty orbital on the metal center during bonding. *Also known as L.B.N.*

Coordination number: The number of other atoms bonded to the metal center. *Also known as C.N.*

The L.B.N. and C.N. differ when the metal ligand bonding is more complex. For example, one place where the two differ is in any coordination complex with a double bonded ligand (that's two X-functions but only one ligand). □

- f) What does two ligands being in the same ligand domain mean? How does this relate to the isolobal analogy from question 7?

Answer. It means that they have similar steric and electronic properties. Although ligands in the same domain may not be isolobal (or isoelectronic) and have *that* kind of close similarity, they do share more than a passing resemblance. □