Determining Oxidation State: The Arrow Pushing Method

Created by Jared Pienkos,[1] Lydia Hinchman,[1] Carly Gordon,[2] and Chase Matusek,[1] University of Tennessee at Chattanooga[1] (jared-pienkos@utc.edu) and Auburn University[2] (chg0030@auburn.edu) and posted on VIPEr (www.ionicviper.org (http://www.ionicviper.org/)) on July 28th, 2025,

Learning objectives

1) Students will be able to determine charges on ligands.
2) Students will be able to predict metal oxidation states based on ligand charges.

The **oxidation state (oxidation number)** of a transition metal is the apparent charge on the atom in a compound and indicates how many electrons it has gained or lost when forming bonds with its ligands (what is attached to the metal center). Because transition metals commonly have several different oxidation states, it's important to examine the ligands involved in a complex to determine how they impact the metal center's oxidation state.

We can use the familiar tool of arrow pushing from organic chemistry to determine oxidation states. Curved arrows (e.g., ↷) represent the movement of two electrons. These arrows can help us determine the oxidation state and charge associated with each individual ligand.

1. Consider PMe_3AuCl (**Figure 1**): Starting with the original structure (**a**), this species can be deconstructed by pushing electrons to the ligands (**b**). In the simplest sense, transition metal complexes can be viewed as Lewis-acid Lewis-base interactions between a metal and a ligand.

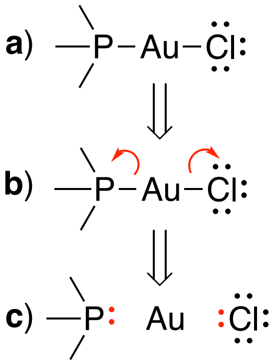


Figure 1: Deconstructing a Transition Metal Complex

Critical thinking questions (see next page for hints):

i. In this species, is the Au acting as a Lewis acid or a Lewis base?
*Note: In Figure 1, going from **b** to **c**, a complex is being deconstructed. For this question, you need to consider the formation of the complex, going from **c** to **b**.*

ii. What is the formal charge (F.C.) of each of the species shown in **Figure 1, c**?

iii. PMe_3 would be classified as a(n) __________ (neutral/ionic) ligand.

iv. Cl would be classified as a(n) __________ (neutral/ionic) ligand.

v. What is the F.C. of the metal (gold, Au) in this complex? How is this calculated? *Note: The formal charge (F.C.) is the same as the oxidation state (O.S.) for this Au metal.*

Recall:

- A **Lewis Acid** accepts a pair of electrons, and a **Lewis Base** donates a pair of electrons.
- F.C. = V – N – B/2; where F.C. = formal charge, V = valence electron count, N = number of non-bonding electrons, and B = number of bonding electrons.

2. In the previous example, the gold (I) species, PMe_3AuCl, was drawn with all the lone pairs indicated on the surrounding ligands. Often, lone pairs are not drawn on transition metal compounds, and, in most cases, ligands can be assumed to have an octet's worth of electrons. For instance, PMe_3AuCl could be drawn with or without the lone pairs on the chloride ligand (**Figure 2**, **a**). Other representative examples are shown with oxoplatin (**Figure 2**, **b**) and tetraplatin (**Figure 2**, **c**), two species commonly used as chemotherapeutics.

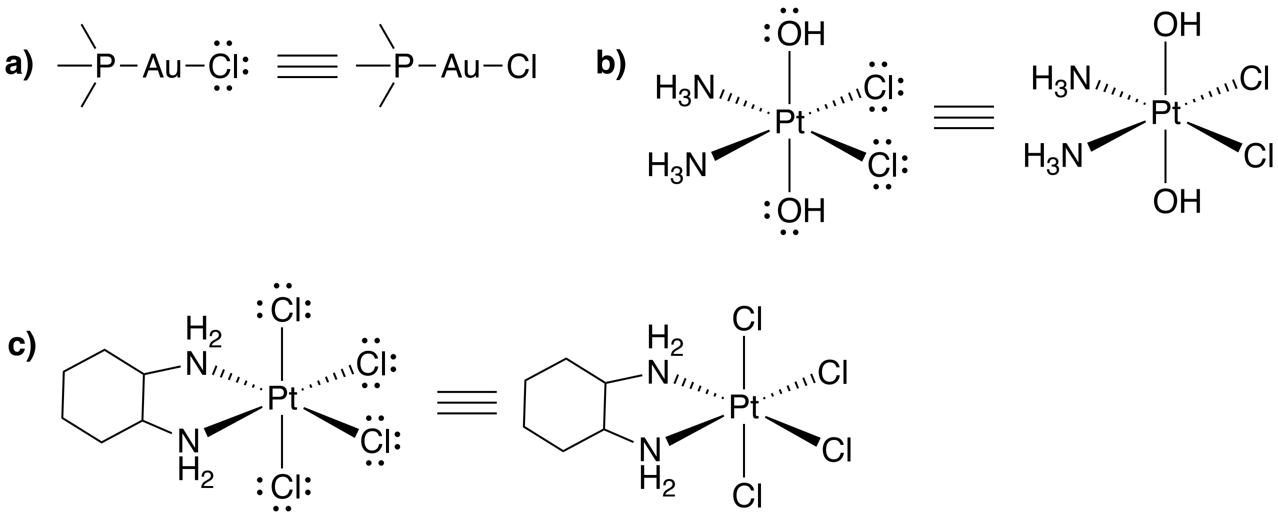
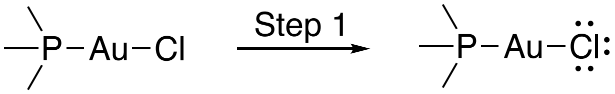


Figure 2: Representative ways to draw transition metal compounds with and without lone pairs.

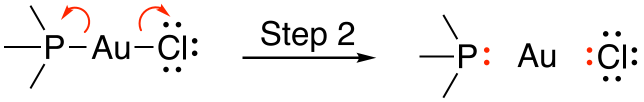
Critical thinking questions:

i. Write out a procedure for calculating the oxidation state of a transition metal compound, where the lone pairs are not explicitly drawn. *Hint: When doing so, consider the first example where we calculated the oxidation state of Au in PMe_3AuCl. Structures have been provided to assist with defining the steps.*

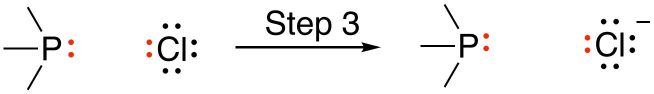
Step 1:



Step 2:



Step 3:



Step 4:

Charge of complex = F.C. (complex) = F.C. (PMe_3) + F.C. (Cl) + F.C. (Au)

Note: The oxidation state of the metal is the same as the formal charge (F.C.) of this transition metal.

ii. What is the oxidation state of the platinum metal in oxoplatin (**Figure 2, b**) and in tetraplatin (**Figure 2, c**)?

iii. Tetraplatin (**Figure 2, c**) contains a bidentate ligand (coordinated on two sites). Draw out the structure of this bidentate ligand separate from the metal center. What is the charge, if any, on this ligand?

3. Calculating the oxidation state of iron (Fe) compounds

i. Calculate the oxidation state (O.S.) on the following iron (Fe) metal center (**Figure 3**). Steps are as follows: 1) Add lone pairs to the ligands so each atom has an octet. 2) Push electrons from the metal center to the ligands. 3) Calculate the formal charges (F.C.s) of the ligands (*Hint: You must consider the overall charge of each ligand, i.e., if a ligand has two or more formal charges, the charge of that ligand is the sum of all the formal charges for that species*). 4) Calculate F.C. of the metal based on F.C. of the ligands and charge of the complex. Use the F.C. of the metal to calculate the O.S. of the metal.

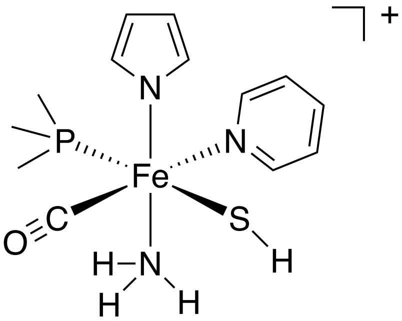


Figure 3: Iron compound containing various ligands.

ii. The ligands attached to the metal are part of the inner coordination sphere of the transition metal complex. We can look at an analogous species where there is a chloride (Cl^-) anion as part of the outer sphere of this complex.

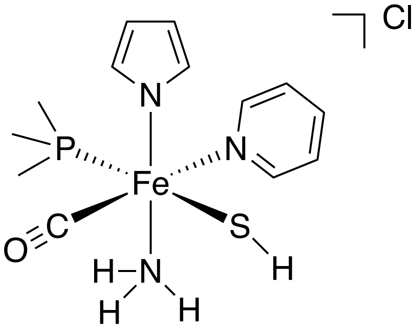


Figure 4: Iron complex with outer sphere chloride.

iii. Is the O.S. of the Fe metal center changed when comparing the species in **Figure 3** and **Figure 4**? Explain.

Created by Jared Pienkos,[1] Lydia Hinchman,[1] Carly Gordon,[2] and Chase Matusek,[1] University of Tennessee at Chattanooga[1] (jared-pienkos@utc.edu) and Auburn University[2] (chg0030@auburn.edu) and posted on VIPEr (www.ionicviper.org (http://www.ionicviper.org/)) on July 28th, 2025,

4. Challenging problem. Consider the following species with bridging chlorides. A chloride (Cl^-) has a F.C. of -1. How do these bridging chlorides affect the O.S. of each dysprosium (Dy) metal? *Hint: For this, calculate the oxidation state of each of the following Dy atoms separately. Note the symmetry in this complex.*