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Coordination Chemistry: "Atomic Machinery in Action!"

The amazing power of chemistry is hidden in its coordination chemistry. Coordination chemistry is all about a metal ion center, capable of accepting lone pairs of electrons from other atoms, usually nonmetals which serve as electron-pair donors. Therefore, a special covalent bond is created which is called a **coordinate covalent bond**. The central metal cation has special vacant orbitals and when combined with the net positive ion charge, it can attract the lone pairs of the nonmetals into their vacant orbitals to create stable bonds. A simple diagram showing the bonding process of the metal cation with two non-metals is shown below. Here, the vacant orbitals of the metal cation (M^{n+}) are shown as boxes and lone pairs of the nonmetal (NM) are shown as tear drop shaped gray orbitals each carrying 2 electrons (shown as dots), thus a pair of **coordinate covalent bonds** are formed.

In this case only two coordinate bonds are shown. Metal cations typically form 2,4 or 6 bonds referred to as **coordination number** (CN). An important aspect of this amazing bond is that it can serve as a bridge holding nonmetals to a specific shape. Biology is the direct beneficiary of such bonding as many important proteins and enzymes have metal ion centers which directly influence properties of proteins. For example, hemoglobin, an iron-containing, oxygen-transport metalloprotein is a complex protein formed from 4 protein subunits capable of selectively bonding with diatomic oxygen. Life in its complex vertebrate form depended on hemoglobin to evolve so that oxygen could reach and nourish the furthest cells away from our lungs.

The central metal ion exhibits 2 distinct "nano" level properties, *oxidation state* (OS) and *coordination number* (CN). As stated earlier, coordination number is the number of coordinate covalent bonds with the nonmetal. For example, the above hypothetical example shows a coordination number of 2. Oxidation state is the local charge on the metal ion. We refer to the nonmetal as a **ligand**. Ligands are either neutral or negatively charged (anion).

Let's put it all together in a formula. When ligand(s) bond with the metal cation, we get a charged specie called a **complex ion**. Complex ions are either cation or anion. There is a net charge we place over the entire complex ion which is obtained by totaling the charges of ligands with the charge of the central metal ion. This charge resides over the complex ion and often shown outside of a bracket. Sometimes, the bracket is omitted for simplicity. For example consider 4 chloride ions which bond to a cobalt (+2) metal ion. Let's write it as a reaction:

$$4 \text{ Cl}^- + \text{Co}^{2+} \rightarrow [\text{CoCl}_4]^{2-}$$





CoCl₄²⁻

This is a tetrahedral complex ion with coordination number of 4 as the models show. Oxidation state of cobalt is +2 and you should be able to determine the OS given the complex ion formula only. As shown to the right of the model, when we refer to the complex ion only we often omit the bracket for simplicity. Complex ions can be isolated as a pure compound and they are accompanied by counter ions. For example, the sodium salt of the above compound would have the following formula. Two sodium ions are necessary to balance out the -2 charge of complex ion. This is now called a **coordination compound**. This compound is called sodium tetrachlorocobaltate(II).

Na₂[CoCl₄]

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Below are examples of complex ion structures, hybridization and geometry classification. **Determine the charge** (OS) of each metal ion and place it over the metal in the formula shown.

CN	Geometry		Hybridization	Example
2	Linear	-	sp	[Ag(NH ₃) ₂] ⁺
4	Tetrahedral	+	sp^3	[Cd(NH ₃) ₄] ²⁺
4	square planar		$ m sp^2d$	[Cu(OH ₂) ₄] ²⁺
5	trigonal bipyramid	•	$ m sp^3d$	Fe(CO) ₅
5	Square pyramidal		$ m sp^2d^2$	[Mn(Cl) ₅] ³⁻
6	Octahedral	: E.	$ m sp^3d^2$	[Fe(CN) ₆] ⁴⁻

Moving up on the complexity ladder, ligands can get complex in their structure and 1 ligand can bond in more than one place onto the metal ion. The structure to the right is an example of two such ligands (phenanthroline or abbreviated as "phen") bonded to an octahedral rhodium metal ion. Examine the structure to the right



and circle the bonding points on the ligand shown to the left. The complex ion structure shown to the right also includes 2 chloride ion ligands (called chloro groups). Below is the formula of

this complex ion. The "phen" ligand is a **bidentate** ligand which uses both of its nitrogen atoms on the conjugated ring to bond with the complex ion.

cis-[Rh(phen)₂Cl₂]⁺

What is oxidation state (OS) of rhodium metal in this complex ion? _____ CN?____

