Some Important Features of Metal Ions

Electronic configuration
- Oxidation State/Charge.
- Size.
- Coordination number.
- Coordination geometry.
- “Soft vs. Hard”.
- Lability.
- Electrochemistry.
- Ligand environment.
**Oxidation State/Charge**

- The oxidation state describes the charge on the metal center and number of valence electrons.
- Group - Oxidation Number = d electron count.

**Size**

- Size of the metal ions follows periodic trends.
- Higher positive charge generally means a smaller ion.
- Higher on the periodic table means a smaller ion.
- Ions of the same charge decrease in radius going across a row, e.g. Ca$^{2+}$>Mn$^{2+}$>Zn$^{2+}$.
- Of course, ion size will effect coordination number.
Coordination Number

- Coordination Number = the number of donor atoms bound to the metal center.
- The coordination number may or may not be equal to the number of ligands bound to the metal.
- Different metal ions, depending on oxidation state prefer different coordination numbers.
- Ligand size and electronic structure can also effect coordination number.

Common Coordination Numbers

- Low coordination numbers (n = 2, 3) are fairly rare, in biological systems a few examples are Cu(I) metallochaperones and Hg(II) metalloregulatory proteins.
- Four-coordinate is fairly common in complexes of Cu(I/II), Zn(II), Co(II), as well as in biologically less relevant metal ions such as Pd(II) and Pt(II).
- Five-coordinate is also fairly common, particularly for Fe(II).
- Six-coordinate is the most common and important coordination number for most transition metal ions.
- Higher coordination numbers are found in some 2nd and 3rd row transition metals, larger alkali metals, and lanthanides and actinides.
Coordination Geometry

- Metals can dictate the coordination geometry, but usually ligands play a larger role, especially in biological systems.

Standard Coordination Geometries, CN=2, 3

- Linear
- Trigonal
- Pyramidal
- T-Shaped
Standard Coordination Geometries, CN=4

Square planar

Tetrahedral

Standard Coordination Geometries, CN=5, 6

Trigonal bipyramidal

Square pyramidal

Octahedral
Higher Coordination Numbers, CN=7, 8, 9

- CN=6, Octahedral or Trigonal Prism
- CN=7, Pentagonal Bipyramidal or Monocapped Trigonal Prism
- CN=8, Square Antiprism
- CN=9, Tricapped Trigonal Prism

Axial versus Equatorial

- Ligands will behave differently depending on whether they are in the axial or equatorial positions of the coordination sphere.
Facial versus Meridional

- Octahedral coordination describes an OCTAHEDRON (duh?).
- Arrangements of certain ligands can be described as facial (fac-isomer) or meridional (mer-isomer).

Stereochemistry

- Some metal centers can be chiral.
- An easy example would be a tetrahedral metal center with four different ligands - just like a chiral carbon center, but this is not particularly common . . .
Seeing the Octahedron

- Seeing the chirality in an octahedral environment can be a little tricky.

- We need to visualize the coordination sphere from a facial perspective.

Octahedral Stereochemistry

- Octahedral metal ions can have an inherit “propeller twist” depending on the nature of the ligands.

- The two enantiomers are called Δ and Λ isomers and are optically active.
Stereochemistry Challenge

Soft vs. Hard Acids

- Introduced by R.G Pearson as a renaming of Ahrland, Chatt, and Davies ‘class A’ and ‘class B’ acids and bases.
- Formal definition of hardness is “the difference between the ionization energy of the neutral atom and its anion”, $\eta$

$$\eta = \frac{1}{2}(I - A_e)$$

- Soft = low charge, large ionic radius, bonding electrons are polarizable, bonds are more covalent, low ionization energies and electron affinities (Hg$^{2+}$, Cd$^{2+}$, Cu$^+$).
- Hard = high charge, small ionic radius, bonding electrons are not polarizable, bonds are more ionic, high ionization energies and low electron affinities (Fe$^{3+}$, Al$^{3+}$, K$^+$).
- Rule of thumb “Soft prefers soft, hard prefers hard”.
- Therefore, this helps define the ligands (bases) that will interact with a given metal ion (R$_3$P, R$_2$S for soft, F$^-$, HO$^-$ for hard).
Periodic Hard vs. Soft

- Ultimate Hard Interactions = NaCl, totally ionic.
- Hardness effects distribution in nature (Al, Ca versus Ni, Zn, Cu).

Lability

- Metal complexes that rapidly exchange ligands (ns or μs) are called labile, those that exchange ligands slowly are called inert.
- Most group I/II and first row transition metals are labile with some exceptions.
- Second and third row transition metals are generally inert and this is one reason why they are not widely found in Nature - lability is required for good reactivity!
- So how does one get lability and stability at the same time?
Macrocyclic Effects

• Ligands that are comprised of multiple donor atoms linked together in a ring benefit from the “macrocyclic effect”.
• The macrocyclic effect is just an extreme version of the “chelate effect”.

*The porphyrin ring is the most important example of a macrocyclic ligand in biological systems.*

Macrocyclic Effects

• The ‘macrocyclic effect’ is much like an enhanced chelate effect.
• Thermodynamic stabilization comes from enthalpic contributions (less well solvated donor atoms than acyclic compounds) and entropic contributions (reduced flexibility of macrocycle).
• Kinetic stabilization is achieved through large number of fixed donor atoms (e.g. iron porphyrins).
Ligand Exchange Reactions

**Associative Mechanism**

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{M} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{M} & \quad \text{X} & \quad \text{Y} & \quad \text{H}_3\text{N} & \quad \text{M} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{M} & \quad \text{X} & \quad \text{Y} & \quad \text{H}_3\text{N} & \quad \text{M} & \quad \text{NH}_3 \\
\end{align*}
\]

**Dissociative Mechanism**

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{M} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{M} & \quad \text{X} & \quad \text{Y} & \quad \text{H}_3\text{N} & \quad \text{M} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{M} & \quad \text{X} & \quad \text{Y} & \quad \text{H}_3\text{N} & \quad \text{M} & \quad \text{NH}_3 \\
\end{align*}
\]

**Electrochemistry**

- Dictated by the metal, but strongly tuned by the ligand field.
- Mn, Fe, and Cu most redox active in nature. Zn(II) and Group I/II redox inactive due to closed-shell electron configuration.
- Organic groups such as quinones, chlorophylls, etc. also play electron transfer roles in biological systems.
“Blue” Cu Redox Proteins

As described earlier, ‘blue’ copper proteins are an electron transfer motif in bioinorganic chemistry. Cu(II) prefers a square planar. Tetrahedral geometry facilitates reduction to Cu(I). Combination of soft sulfur donors and medium nitrogen donors tunes redox potential.

Summary of Effects

Without considering the ligand environment itself, these factors can describe a metals behavior fairly well. At the right is an example summary for zinc(II).

Table 2 Properties of ZnII that are pertinent to its role in enzymes (Information taken from refs. 2 and 3)

| Redox properties | The divalent Zn• ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to Mn, Fe, and Cu. |
| Coordination geometries | The d0 configuration of ZnII indicates that these complexes are not subject to ligand field stabilization effects and so coordination number and geometry is only dictated by ligand size and charge. In enzymes, zinc shows a strong preference for tetrahedral coordination which enhances both the Lewis acidity of a zinc atom and the inherent stability of a coordinated water molecule. Only CuII is a better Lewis acid. |
| Ligand binding properties | Zinc is an element of borderline hardness, so that nitrogen, oxygen, and sulfur ligands can all be accommodated, in contrast to magnesium and calcium which favor binding to oxygen. Therefore, zinc binds strongly to many proteins. |
| Ligand exchange | The flexibility in coordination geometry makes ligand exchange more facile than for Ni or Mg and enhances for ability of zinc to effect a catalytic cycle. |
| Ligand nucleophility | Anions such as OH-, OR-, and SR- retain nucleophilic character when coordinated to zinc. Only CoII, FeIII, and CuII are better in this regard. |
Atomic Orbitals of the Transition Metal

- s- and p-Orbitals

Harvey & Porter “Introduction to Physical Inorganic Chemistry” Addison-Wesley 1963

Atomic Orbitals of the Transition Metal

- d-Orbitals
Symmetry Adapted Ligand $\sigma$-Orbitals

- Combinations of the $\sigma$-orbitals for ligands in an octahedral environment.
- These are combined with the metal orbitals to give the overall MO diagram.

Interaction of Metal and Ligand Orbitals

- $\sigma$-symmetric interactions of metals and ligands.
- These represent the six primary bonding and antibonding orbitals in an octahedral complex.
Combining Metal and Ligand Orbitals

- The orbitals combine in a predictable fashion.

Octahedral Complexes

- Therefore, for an octahedral complex you get . . .
The Nonbonding Orbitals

• So what are these nonbonding orbitals? . . only the famous $t_{2g}$ orbitals!
• Because they don’t point directly at the ligands, they are nonbonding.

Overall Octahedral Orbitals

• This gives the classic orbital picture for an octahedral metal center.
d-Orbital Splitting

- The d-orbital splitting dictates various properties of the metal center.

\[ \Delta \]

\[ \Delta_0 \]

\[ \frac{3}{5}\Delta_0 \]

\[ \frac{2}{5}\Delta_0 \]

\[ \text{LFSE} = (-0.4x + 0.6y) \Delta_0 \]

Low spin Fe\(^{2+}\)
Large \(\Delta_0\)

High spin Fe\(^{2+}\)
Small \(\Delta_0\)

\[ \pi \]-Interactions are Important

- \(\sigma\)-orbitals don’t interact with \(d_{xy}\), \(d_{xz}\), or \(d_{yz}\) in octahedral symmetry, but \(\pi\)-symmetry orbitals can!
Types of $\pi$-Bonding

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Ligand examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_\pi-d_\pi$</td>
<td>Donation of electrons from filled $p$-orbitals of ligand to empty $d$-orbitals of metal</td>
<td>RO, RS, F, Cl, R$_2$N$^-$.</td>
</tr>
<tr>
<td>$d_\pi-d_\pi$</td>
<td>Donation of electrons from filled $d$-orbitals of metal to empty $d$-orbitals of ligand</td>
<td>R$_2$S (R$_3$P, R$_3$As).</td>
</tr>
<tr>
<td>$d_\pi-\pi^*$</td>
<td>Donation of electrons from filled $d$-orbitals of metal to empty $\pi^*$ (antibonding)-orbitals of ligand</td>
<td>CO, RNC, pyridine, CN$^-$, N$_2$, NO$_2^-$, ethylene.</td>
</tr>
<tr>
<td>$d_\pi-\sigma^*$</td>
<td>Donation of electrons from filled $d$-orbitals of metal to empty $\sigma^*$-orbitals of ligand</td>
<td>H$_2$, alkanes.</td>
</tr>
</tbody>
</table>

$\pi$-Acids and Bases

- d-Orbital splitting is strongly affected by the ligand environment.

\[ \Delta_0 \] \[ \Delta_0 \text{ known as "weak field"} \] ligands, e.g. Cl$^-$, H$_2$O.
\( \pi \)-Acids and Bases

• Will they stay or will they go?

\( \pi \)-acids raise \( \Delta_O \) - known as “strong field” ligands, e.g. CO, bipy

CO Ligand

• CO is a classic \( \pi \)-acid ligand.
• Looking at the MO diagram for this diatomic molecule, the HOMO has \( \sigma \) symmetry and the LUMO has \( \pi \) symmetry.
• The LUMO can act as an electron acceptor (e.g. \( \pi \)-acid), but this is an antibonding orbital (can you draw it?) for the CO - what is the effect?
CO Stretching Frequency

- When CO acts as a $\pi$ acid, the B.O. of the C-O bond is reduced.
- Therefore, the bond length increases - this increase is most easily observed as a reduction in the IR stretching frequency of CO ligand in metal complexes (2143 versus 2000 cm$^{-1}$ in Cr(CO)$_6$).

Both interactions strengthen the metal-ligand bond, but the $\pi$ bond also weakens the C-O interaction.

Examples

- Examples of strong and weak field.
- Heavier metals (2nd and 3rd row transition metals) have better overlap with ligands and therefore are almost always strong field.

\[
\begin{align*}
\text{Examples:} & \quad \text{[Cr(H$_2$O)$_6$]}^{2+} \quad \text{[Cr(CN)$_6$]}^{3-} \quad \text{[Ru(Cl)$_6$]}^{2+} \\
\end{align*}
\]
The Spectrochemical Series

- The spectrochemical series defines ligands from weak to strong field.
- I⁻<Br⁻<S²⁻<SCN⁻<Cl⁻<NO₃⁻<F⁻<C₂O₄²⁻<H₂O<NCS<CH₃CN<NH₃<en<bipy<p hen<NO₂⁻<PPh₃<CN<CO.
- Can be summarized as: π bases<weak π bases<no π effect<π acids.

The Metal Effect

- The nature of the metal ion also affects the ligand field splitting.
- The splitting gets larger with both oxidation number and down a group.
- Mn²⁺<V²⁺<Co²⁺<Fe²⁺<Ni²⁺<Fe³⁺<Co³⁺<Mn⁴⁺<Mo³⁺<Rh³⁺<Ru³⁺<Pd⁴⁺<Ir³⁺<Pt⁴⁺.
Tetrahedral Complexes

- In tetrahedral symmetry things change a bit.

Tetrahedral Orbitals

- In the tetrahedral environment the t and e orbitals are reversed.
- The energy $\Delta_T$ is usually much smaller than $\Delta_O$ and so most tetrahedral complexes are high spin.
Distortions from Octahedral

- Distortion from perfect symmetry leads to changes in d-orbital splitting and electronic configuration.
- Example at right is for a d⁹ metal such as Cu(II).
- Where did the orbitals come from (t₂g or e_g)?

Distortions from Tetrahedral

- Tetrahedral distortions are also possible and change orbital configuration.
- Can you visualize square planar from octahedral?
Interrelation

octahedral $O_h$

axially elongated octahedral $D_{4h}, C_{4v}$

square planar $D_{4h}$

distorted tetrahedral $D_{2d}$

tetrahedral $T_d$

$x^2-y^2$

$\Delta O_h$

$\Delta T_d$

$e$

More Distortions

octahedral $D_{4h}$

square pyramidal $C_{4v}$

trigonal planar $D_{3h}$

tetrahedral $T_d$

square-planar $D_{2d}$

$E_{g}$

$z^2$

$E_{u}$

$x^2-y^2$

$xy$

$(x^2-y^2, xy)$

$(xz, yz)$

$x^2$