Transition Metal Chemistry

Transition metal chemistry
(Coord. Complexes)
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Objectives

- Synthesis of a coordination complex
- Typical reactions of some transition metal complexes

Transition Elements

- Have an incomplete d shell of electrons
- Have a large coordination sphere
- Can have many oxidation states (lots of redox chemistry)
- Form paramagnetic complexes
- Often form colored complexes, in contrast to p-block complexes that are usually colorless.

What is a transition metal complex?

- It is defined as a metal ion bonded (coordinated) to one or more neutral or anionic molecules.

- Shown by using square brackets around the formula: $[Ag(NH_3)_2]^+$

Ligands?

- Metals form cations, the molecules that are attached to them can be neutral or anionic.
- These are called ligands.
- Ligands are Lewis bases, they donate electrons to the metal center.
- Examples of ligands include: H_2O, Cl^-, NH_3, $C{\equiv}N^-$, $C_6H_5^-$

Coordination Sphere

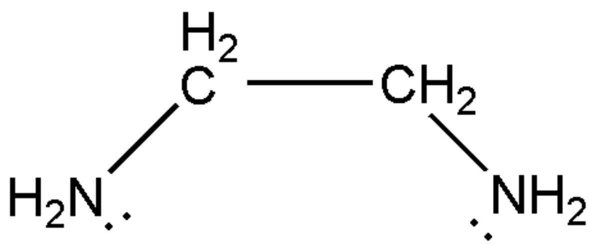
- The number of ligands that are coordinated to the metal center is defined as the coordination sphere
- Transition metals usually have high coordination numbers because of their size and their empty d orbitals that can accommodate lots of ligands

Examples

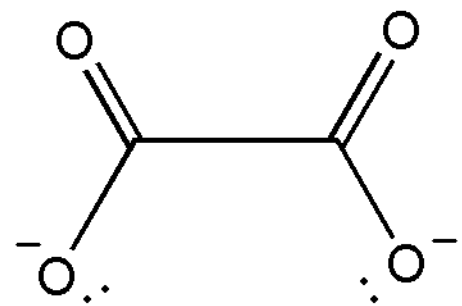
- $[Cu(H_2O)_6]^{2+}$ C.N = 6
- $FeCl_2$ C.N. = 2
- $[FeCl_2(H_2O)_4]$ C.N. = 6
- $K_2\ [Fe(CN)_6]^{2+}$ C.N. = 6
- A coordination number of 6, usually implies octahedral geometry
- A coordination number of 4 is either square planar or tetrahedral geometry

Ligand Types

- Monodentate: one binding site: Cl^-, Br^-, H_2O
- Bidentate: two binding sites
- Tridentate: Three binding sites
- Anything greater than monodentate is called a chelating ligand (Greek for claw)



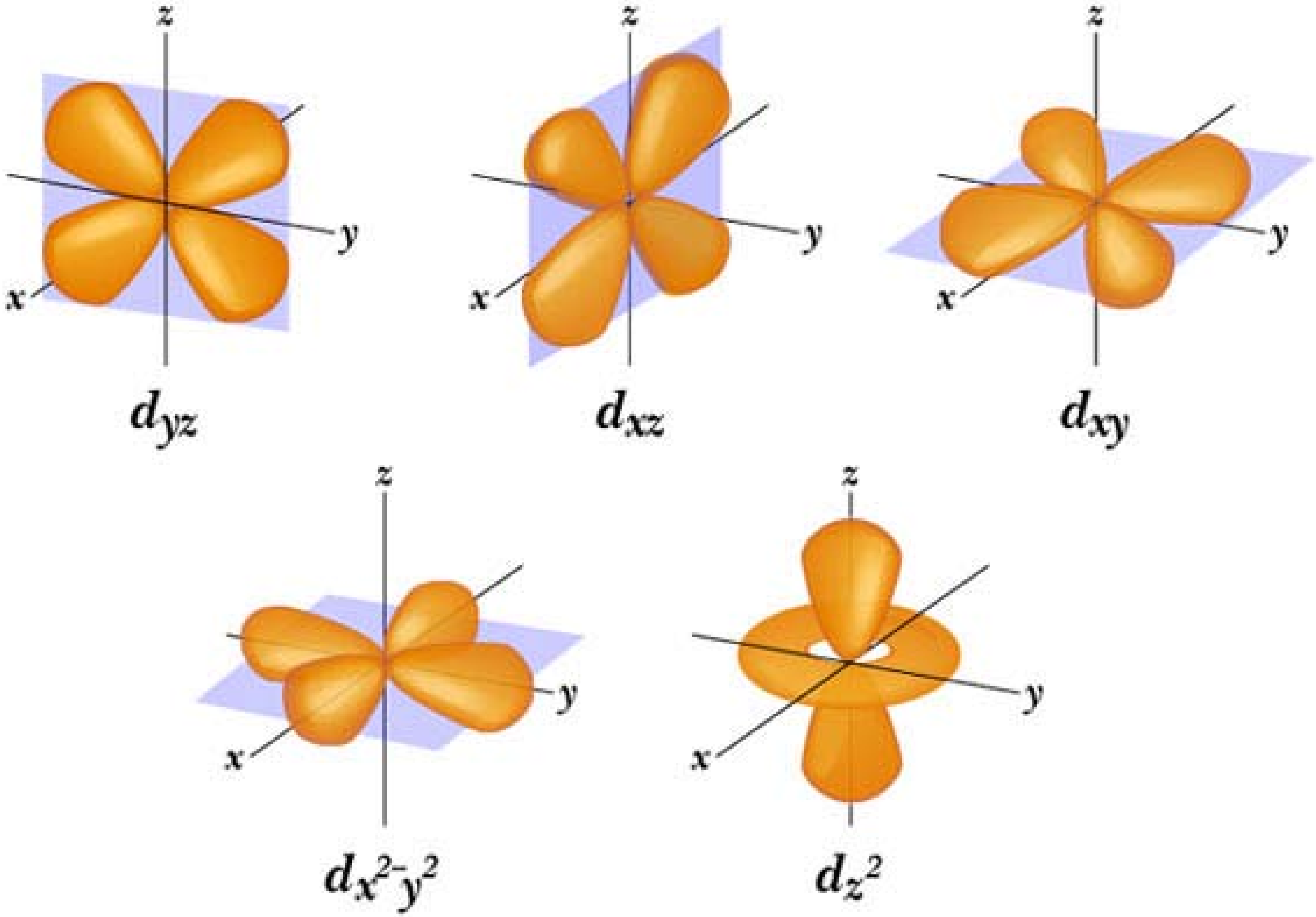
etheylenediamine

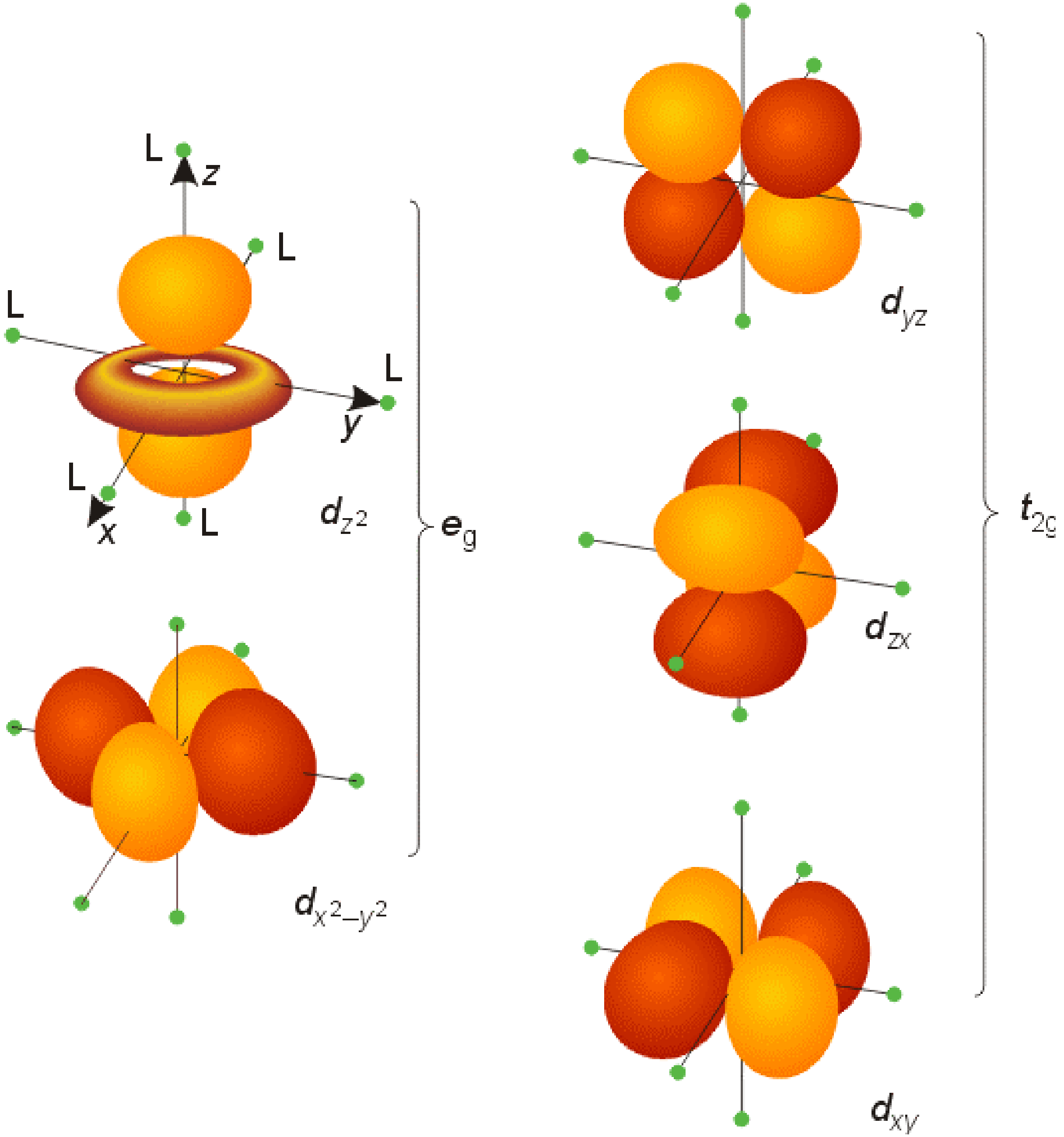


oxalate anion

$H_2\ddot{N}CH_2CH_2\ddot{N}HCH_2CH_2\ddot{N}H_2$ triethyelenediamine

Transition Metal d orbitals





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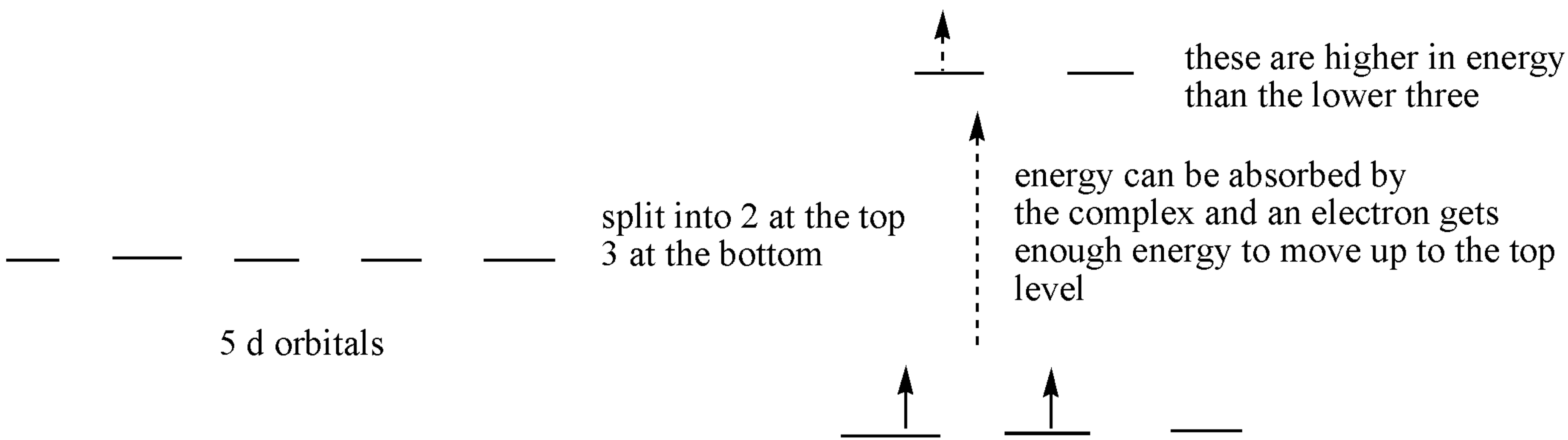

As the excited electron (in the top orbitals), falls back down so light is emitted.

This is why we see colors in transition metal complexes

Ligand Types

- Different ligands have different effects on the energies of the d orbitals of the central ion.
- Some ligands have strong electrical fields which cause a large energy gap when the d orbitals split into two groups. Others have much weaker fields producing much smaller gaps.

- Remember that the size of the gap determines what wavelength of light is going to get absorbed.

- The list shows some common ligands. Those at the top produce the smallest splitting; those at the bottom the largest splitting.

Ligand Splitting

Cl^- — smallest splitting

F^-

OH^-

H_2O

NH_3

CN^- — largest splitting

How does splitting affect color?

- The ligands that cause a big splitting usually give the more intensely colored complexes.
- Smaller splitting ligands (halides) are usually less strongly colored

Stability (Reactivity) of ligands and complexes

- The stability of a complex will be determined by introducing an anion that if combined with the metal cation will form a precipitate.

For example:

- $NiCl_2$ in solution, dissolves and we have Ni^{2+} and $2Cl^-$ as ions.

- If OH^- is introduced (as NaOH) then the Ni^{2+} can bond with either the Cl^- or the OH^-.

- $Ni(OH)_2$ is insoluble, if this forms, a precipitate will be observed and we can postulate that the Ni^{2+} has preference for the OH^- over the Cl^-

Ligand Displacement

$$[ML_x] + L' \rightarrow [ML'_x] + L$$

For example:

$$[Cu(H_2O)_4]SO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$

- The NH_3 is said to ‘displace’ the H_2O from the metal.
- This means that the NH_3 is a more reactive ligand and that the metal-NH_3 bond is stronger than the H_2O bond

Procedure

- A variety of oxalate coordination complexes are to be prepared.
- YOU choose which one you would like to prepare: Cr, Cu, Fe or Al.
- Try and do a different metal from your neighbor so you can compare the different properties.

Naming your product

- Example: $K_4[Fe(CN)_6]$ is potassium hexacyano ferrate
- The cation outside the square bracket is named first
- The hexa cyano is because there are six CN- ligands.

Ligand Names

- The ending changes when the ligand is *inside* the square bracket
- CN^- = cyano
- NH_3 = ammine
- H_2O = aqua
- $C_2O_4^{2-}$ = oxalato

Naming complexes

·H_2O indicates a hydrated complex.

·$3H_2O$ = tri hydrate

Isolate your product

- Collect the dried crystalline product.
- Record the weight, and calculate your theoretical and percent yield.