

Topic V

Coordination Chemistry: Structures and Isomers of Metal Complexes

V.1 Module 28: Introduction to Coordination Compounds

- 2/12:
- Modern inorganic chemistry is heavily concerned with the transition metals, i.e., the *d*-block elements.
 - Most industrial catalysts utilize transition metal compounds.
 - Transition metals vs. main-group elements:

| Transition-Metal Compounds | Main-Group Elements |
|--|---|
| Multiple oxidation states (e.g., the 11 oxidation states of Mn from -3 to $+7$) | Single oxidation state |
| Brightly colored (thus a gap between HOMO and LUMO of a few electron volts) | Usually colorless |
| Usually have partially occupied valence <i>d</i> -orbitals that are often relatively close in energy | The valence <i>s</i> - or <i>p</i> -orbitals are either fully occupied or empty and are far apart energetically |
| Often paramagnetic | Usually diamagnetic |
| Often interact with small molecules such as CO, C ₂ H ₄ , and H ₂ | Generally do not interact strongly with CO, C ₂ H ₄ , or H ₂ |

- The orbital energy gap matches the bond energies of small molecules pretty well.
 - This is exactly what is needed for activating those chemical bonds, i.e., making catalytic cycles!
- History:
 - Prussian blue ink is the first synthetic blue dye, and one of the first coordination compounds created (used in famous paintings such as *Starry Night*).
 - The structure of coordination complexes was not understood until 1907, however.
 - Blomstrand and Jorgenson tried to determine the structure of $\text{Co}(\text{NH}_3)_4\text{Cl}_3$, but their guess didn't explain isomers.
 - Alfred Werner (late 1800s) was the father of coordination chemistry.
 - He noticed that excess AgNO_3 could only liberate and precipitate as AgCl one chlorine from both the green and violet isomers of $\text{CoCl}_3 \cdot (\text{NH}_3)_4$.
 - However, it could precipitate two chlorines from $\text{CoCl}_3 \cdot (\text{NH}_3)_5$ and three from $\text{CoCl}_3 \cdot (\text{NH}_3)_6$.
 - This observation plus a number of controls led him to **Werner's Conclusions**.

- **Werner's Conclusions:**

1. In this series of compounds, cobalt has a constant **coordination number** of 6.
2. As the NH_3 molecules are removed, they are replaced by Cl^- , which acts as if it is covalently bonded to cobalt.
3. Chloride and ammonia are now called ligands.
4. Ligands are a Lewis base/electron pair donors that can bind to a metal ion.
5. A metal complex is a metal ion combined with ligands.
6. Coordination complexes are neutral and counter ions are not bonded to the central metal ion but balance the charge.

– For example, in $[\text{Co}(\text{NH}_3)_6]^{+3}\text{Cl}_3^{-3}$, the three chloride ions are the counter ions.

- **Coordination number:** The number of groups that can bond directly to the metal.

- Werner also hypothesized an octahedral geometry for all cobalt complexes.

- If it were hexagonal planar or trigonal antiprismatic, there would be three isomers of the coordination sphere for the compound with two chlorines (think ortho, meta, para isomers for the hexagonal planar example).
- However, if it is octahedral, the compound with two chlorines will have two isomers (the chlorines can either be 180° to each other or 90° to each other).
- Octahedral also reduces steric crowding.

- **Coordination compound:** A compound with a metal center, a coordination sphere, and counter ions. *Also known as coordination complex.*

- Werner also resolved hexol into optically active isomers. This was the first optically active chiral *inorganic* compound.

V.2 Module 29: Types and Classes of Ligands

- **Monodentate ligand:** A ligand that binds to a metal ion through a single donor site. *Etymology* one-toothed.

– For example, NH_3 is a monodentate ligand.

- **Bridging ligand:** A ligand that binds to two or more metal ions simultaneously.

– For example, O^{2-} is a bridging ligand.

- **Ambidentate ligand:** A ligand with two kinds of binding sites that can bind through one or the other but not both simultaneously.

– For example, thiocyanide can bond through S or N but not both simultaneously.

- **Multidentate chelating ligand:** A ligand bound to a metal through several donor sites. *Etymology* multitooth crab claw (crabs grab their food with two claws in the same way a metal can be attracted to two lone pairs from different groups on the same ligand). *Also known as polydentate chelating ligand.*

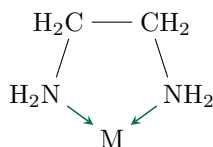


Figure V.1: An example of a bidentate chelating ligand.

- For example, ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; see Figure V.1) can bond to the same metal with both of its nitrogens' lone pairs at the same time.
- Thus, ethylenediamine is bidentate, and it forms a 5-membered chelate ring.
- The chelate effect: For a given metal ion, the thermodynamic stability of a chelated complex involving bidentate or polydentate ligands is greater than that of a complex containing a corresponding number of comparable monodentate ligands.
 - Note that 5-membered rings are more stable than 6, and 4-membered rings (or smaller) are not stable due to angle strain.
 - For example, ethylenediaminetetraacetate (EDTA) is a hexadentate ligand has two nitrogens and four oxygens that wrap entirely around a metal atom and bond very strongly.
 - β -diketones and acetylacetone are also polydentate ligands.
 - Multidentate bonding is incredibly strong.
 - As one last example, hemoglobin and chlorophyll have extra stability because the iron/magnesium ion is attached to four nitrogens.
- Explanations of the chelate effect:
 - Effective concentration: If one bond breaks, the bridge between the two bonding sites in the ligands still holds the other site in close proximity to the metal, making it more likely that the bond will reform than if the metal and ligand were floating entirely independently.
 - Entropy considerations:
 - Imagine you have a coordination complex. If you substitute two monodentate ligands for two other monodentate ligands, you do not change the number of particles.
 - However, if you substitute one polydentate chelating ligand for two monodentate ligands, you increase the number of particles by 1, increasing disorder in the universe and favoring the forward reaction.
 - Looking at the temperature-dependence of equilibrium, we can calculate ΔG° . We can then use this to calculate ΔH and ΔS , and we find that the contributions are very similar. Thus, both explanations of the chelate effect contribute about equally.
- Covalent bond classification (CBC) method:
- **X-type** (ligand): A ligand that donates one electron to the metal and accepts one electron from the metal when using the neutral ligand method of electron counting, or donates two electrons to the metal when using the donor pair method of electron counting.
 - Examples: hydrogen, the halogens, hydroxide, cyanide, carbocation, and nitric oxide.
- **L-type** (ligand): A neutral ligand that donates two electrons to the metal center regardless of the electron counting method being used.
 - Examples: carbon monoxide, PR_3 , ammonia, water, carbenes ($=\text{CRR}'$), and alkenes.
- **Z-type** (ligand): A ligand that accepts two electrons from the metal center as opposed to the donation occurring with the other two types of ligands.
 - Examples: Lewis acids, such as BR_3 .
- LXZ notation:
 - Take the traditional formula and replace the central metal atom with M, each X-type ligand with X, each L-type ligand with L, and each Z-type ligand with Z. Then, if necessary, combine ligands of the same type using subscript arabic numerals, as per usual. Conserve the braces and charge.
 - For example, $[\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{Cl})(\text{NO})]^{2+}$ becomes $[\text{ML}_3\text{X}_2]^{2+}$.

V.3 Module 30: Nomenclature and Isomers of Metal Complexes

2/15:

- Midterm 1:
 - Average: 67.0.
 - Standard deviation: 14.8.
 - Max: 93.
 - 80+ scores: 10.
- Midterm 2 will cover modules 13-31 (with concepts from modules 1-12).
- Suggested reading: Miessler et al. (2014) Section 9.2.
- Naming metal complexes:
 1. For complex ions, write the cation first and anion last.
 - For example, $\text{K}_2[\text{PtCl}_4]$ is potassium tetrachloroplatinate.
 - Note that you do not use the prefix mono, di, tri, etc. here to indicate the number of cations.
 2. Name the ligands first in alphabetical order, the metals last.
 3. Prefixes to indicate numbers (di, tri, tetra, ...) for all monoatomic ligands, polyatomic ligands with short names and neutral ligands with special names.
 4. Prefixes bis-, tris-, tetrakis-, pentakis-, hexakis- for ligands whose names contain a prefix of the first type, neutral ligands without special names, and ionic ligands with particularly long names.
 5. If the anion is complex, add the suffix -ate to the name of the metal. If the symbol comes from Latin/Greek, then we go back to the Latin/Greek for the name of the anion.
 6. Put the oxidation state in Roman numerals in parentheses after the name of the central metal ion of the ligand.
- Examples:
 - $[\text{CoCl}_4]^{2-}$ is the tetrachlorocobaltate (II) ion.
 - $[\text{Fe}(\text{CN})_6]^{4-}$ is the hexacyanoferrate (II) ion.
 - Notice the use of “ferr” for iron (this is going back to the Latin/Greek name of the central metal ion as in Step 5).
 - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ is the tetraaquadichlorochromium (III) ion.
 - No use of -ate because this is a cation (not an anion).
 - $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$ is the tris(ethylenediamine)chromium (III) ion.
 - Note that ammine with two m’s is correct — an **amine** is a functional group from ammonia, while an **ammine** is a group of coordination compounds where ammonia is a ligand.
- Neutral ligands have the same name as the molecule with 4 exceptions:
 - NH_3 is ammine.
 - H_2O is aqua.
 - Aquo or aqua?
 - CO is carbonyl.
 - NO is nitrosyl.
- Anionic ligands require replacing -ide in the ionic name (if present) with -o. For example:
 - Cl^- becomes chloro.
 - OH^- becomes hydroxo.

- SO_4^{2-} is still sulfate?
- Bridging ligands:

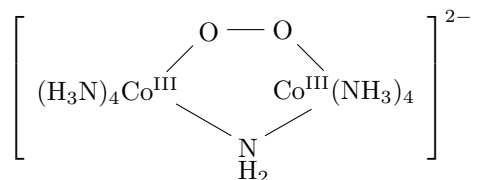


Figure V.2: A coordination compound with bridging ligands.

- Use μ to indicate a bridge.
- If there are more than one of a given bridging ligand, the prefix indicating the number of ligands is placed after the μ .
- If there are more than one different bridging ligands, they are given in alphabetical order.
- For example, the compound in Figure V.2 is the tetraaminecobaltate(III)- μ -amido- μ -peroxo-tetraaminecobaltate(III) ion.

| Common Name | IUPAC Name | Formula |
|--------------|-----------------------|--------------------------------|
| nitrido | nitrido | N^{3-} |
| azido | azido | N_3^- |
| oxo | oxido | O^{2-} |
| thiocyano | thiocyanato-S | SCN^- |
| isothiocyano | thiocyanato-N | NCS^- |
| thiocarbonyl | thiocarbonyl | CS |
| nitro | nitrito-N | NO_2^- |
| nitrito | nitrito-O | ONO^- |
| phosphine | phosphane | PR_3 |
| pyridine | pyridine (abbrev. py) | $\text{C}_5\text{H}_5\text{N}$ |
| amido | azanido | NH_2^- |
| imido | azanediido | NH^{2-} |

Table V.1: Irregular and unfamiliar monodentate ligands.

- Table V.1 lists some more common but irregular or unfamiliar ligands.
 - Note that when listed in Table V.1, ambidentate ligands bind through the atom listed most to the left in the formula.
 - Note also that the slides list a number of common bidentate and polydentate ligands.
- Suggested reading: Miessler et al. (2014) Section 9.3.
- Coordination complex isomers are divided into:
 - Structural isomers (different bonds).
 - Coordination isomerism.
 - Linkage isomerism.
 - Stereoisomers (same bonds, different spatial arrangements).

- Geometric isomerism (*cis-trans*).
- Optical isomerism.
- **Ionization isomers:** Ligands inside the coordination sphere exchange places with ligands outside the coordination sphere.
 - So named because these give different ions when dissolved in water.
 - Werner's four isomers of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are ionization isomers.
- **Linkage isomers:** Variations in at which site an ambidentate ligand bonds.
- **Geometric isomers:** Found in square planar and octahedral complexes — *cis*- vs. *trans*-isomers.

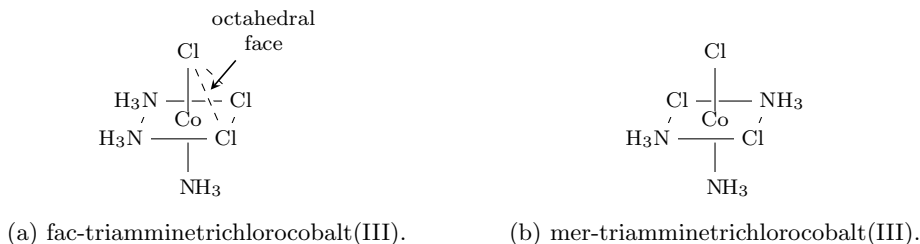


Figure V.3: Facial and meridional geometric isomers.

- Be aware of **facial** (fac) vs. **meridional** (mer) geometric isomers.
- In Figure V.3a, all three $\text{Cl}-\text{Co}-\text{Cl}$ bond angles are 90° .
- In Figure V.3b, two $\text{Cl}-\text{Co}-\text{Cl}$ bond angles are 90° , and the other is 180° .
- Note that there are several different ways to represent an octahedrally coordinated metal ion.



Figure V.4: Methods of sketching octahedral complexes.

- Which way you choose depends on what you are trying to show.
- **Optical isomers:** Two compounds with non-superimposable mirror images (two chiral molecules).
 - C_1 , C_n , D_n , T , O , and I point groups are chiral.
 - Usually associated with tetrahedral/octahedral geometries.
- Octahedral complexes have special chirality.
 - Octahedral complexes with two bidentate ligands:

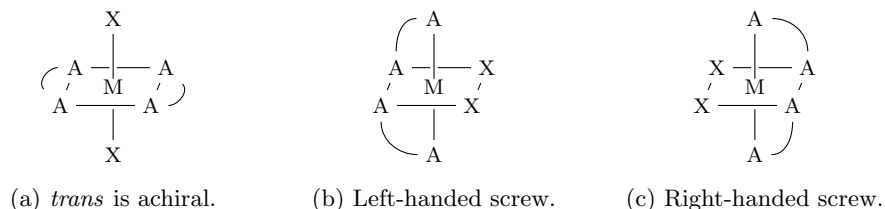


Figure V.5: Chirality of octahedral complexes with two bidentate ligands.

- As we can see in Figure V.5, *trans*-M(A–A)₂X₂ is not chiral, but *cis*-M(A–A)₂X₂ is chiral with two specially named forms.
- Octahedral complexes with three bidentate ligands:
 - Also known as **propellor chirality**.
 - Left-handed helices are Λ form, while right-handed helices are Δ form.

V.4 Chapter 9: Coordination Chemistry I (Structures and Isomers)

From Miessler et al. (2014).

- 3/8:
- Coordination compounds are examples of acid-base adducts.
 - Modern formulas write the coordination sphere in brackets.
 - **Stock system:** A method for designating charge or oxidation number that uses the oxidation number of the metal.
 - **Ewing-Bassett system:** A method for designating charge or oxidation number that uses the charge on the coordination sphere.
 - An example of complicated bridging nomenclature:

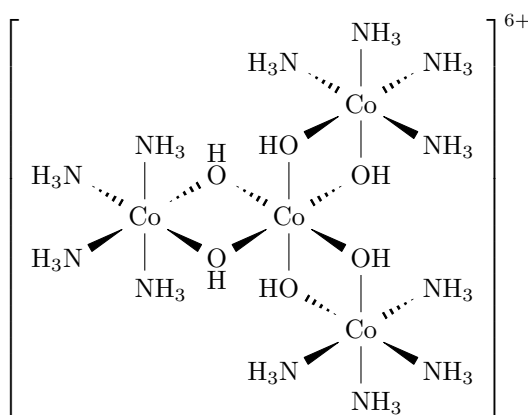


Figure V.6: The tris(tetraammine- μ -dihydroxocobalt)cobalt(6+) ion, $[\text{Co}(\text{Co}(\text{NH}_3)_4(\text{OH})_2)_3]^{6+}$

- When a complex is negatively charged, the names for these metals are derived from the source of their symbols:

| Metal | Name |
|-------------|-----------|
| iron (Fe) | ferrate |
| silver (Ag) | argentate |
| lead (Pb) | plumbate |
| tin (Sn) | stannate |
| gold (Au) | aurate |

Table V.2: Latin/Greek anion names.

- We will not discuss isomerism where the ligands themselves are isomers.

- Some large bidentate chelating ligands can span *trans* positions; however, as ligand length increases, so does the probability of the ligand bonding to multiple metal centers in a bridging fashion instead of just one.
- Molecules that lack S_n axes are chiral:
 - “Because $S_1 \equiv \sigma$ and $S_2 \equiv i$, locating a mirror plane or inversion center in a structure indicates that it is not chiral. A structure may be achiral by virtue of an S_n axis where $n > 2$ even without the presence of a mirror plane or inversion center as symmetry elements” (Miessler et al., 2014, p. 323).
 - Thus, chiral molecules either have no symmetry elements (are C_1) or have only axes of proper rotation (are C_n).
- **Facial** (isomer of a $ML_3L'_3$ complex): An isomer with three identical ligands on one triangular face.
- **Meridional** (isomer of a $ML_3L'_3$ complex): An isomer with three identical ligands in a plane bisecting the molecule.
- Facial and meridional isomers are possible with monodentate and tridentate ligands.
- Linear tetradentate ligands (e.g., triethylenetetramine or trien):
 - Three forms: “ α , with all three chelate rings in different planes; β , with two of the rings coplanar; and *trans*, with all three rings coplanar” (Miessler et al., 2014, pp. 323–24).
- Common numbering of octahedral ligands: We have “positions 1 and 6 in axial positions and 2 through 5 in counterclockwise order as viewed from the 1 position” (Miessler et al., 2014, p. 325).
- Pólya used group theory to calculate the number of certain types of isomers.
 - Miessler et al. (2014) explores this at depth.
- **Left-handed** (propeller): One such that rotating it counterclockwise would move it away from the observer.
- **Right-handed** (propeller): One such that rotating it clockwise would move it away from the observer.
 - This is why rotating right-handed (screws) tightens them (moves them away from the observer).
- A molecule with more than one pair of rings may require more than one label: Determine the handedness of each pair of skew rings, and then include all the designations in the final description.
- Ligand ring conformation:
 - Ligand rings (such as en) can also have their own conformations.
 - Construct a line between the two atoms bonded to the metal, and a second line connecting the other two atoms (in en).
 - If, when viewed through the lines looking at the metal, the second line is rotated counterclockwise compared to the first, the ring is in the λ conformation. Otherwise, it is in the δ conformation.
- Different conformations have varying stabilities.
- **Hydrate isomerism**: Water as a ligand vs. as an additional occupant (or solvate) within the crystal structure.
 - For example, $[Cr(H_2O)_6]Cl_3$, $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$, and $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ are hydrate isomers.
- **Solvent isomerism**: Hydrate isomerism with ammonia or other ligands.

- **Coordination isomerism:** With two or more metal centers, the ligand:metal ratio remains the same, but the ligands attached to a specific metal ion change.
- Covers methods of separating isomers.

- **Optical rotatory dispersion:** With respect to optically active isomers, the optical rotation, as caused by a difference in the refractive indices of the right and left circularly polarized light according to the equation

$$\alpha = \frac{\eta_l - \eta_r}{\lambda}$$

where η_l and η_r are the refractive indices for left and right circularly polarized light, and λ is the wavelength of the light. *Also known as* **ORD**.

- **Cotton effect:** The variance of plane-polarized light absorption with wavelength.
 - This quantity is positive when the rotation is positive (right-handed) at low energy, and negative when it is positive at high energy.
- **Circular dichroism:** A spectral phenomenon caused by the difference in the absorption of right- and left-circularly polarized light, defined by the equation $\varepsilon_l - \varepsilon_r$ where ε_l and ε_r are the molar absorption coefficients for left- and right-circularly polarized light. *Also known as* **CD**.
 - Observed in the vicinity of an absorption band.
 - CD is more selective than ORD.
- When describing molecular geometries, we assume that the metal d electrons are stereochemically inactive.
- The structure of a coordination compound is the result of four interdependent factors of shifting relative importance:
 1. VSEPR considerations.
 2. Occupancy of d orbitals.
 3. Steric interference.
 4. Crystal packing effects.
 - Sizes of ions and shapes of coordination complexes when packed into a crystalline lattice.
- 1-coordinate complexes don't exist in solution; however, there are a few organometallic examples.
- There are some linear and a number of nonlinear 2-coordinate complexes.
- Low-coordinate compounds' **coordinative unsaturation** provides opportunities for small molecule **activation** and unique magnetic properties.
 - Small molecules are favored for activation because bulky ligands are used to stabilize low-coordinate structures, meaning that only a small molecule will be able to access the coordination center.
- **Activation:** Enabling molecules to react which are otherwise unreactive under a set of conditions.
- 4-coordinate species:
 - Tetrahedral and see-saw geometries are both fairly common.
 - The Jahn-Teller effect may distort some tetra-coordinated complexes from tetrahedral geometry.
 - Square-planar geometry is also fairly common, especially with d^8 ions.
- 5-coordinate species:
 - Trigonal-bipyramidal, square-pyramidal, and pentagonal-planar geometries (the latter being exceedingly rare) predominate.

- Molecules sometimes alternate rapidly between the former two due to their typically small energy difference.
- 6-coordinate species:
 - The most common coordination number.
 - Octahedral complexes predominate, but trigonal prismatic structures are also known.
 - Trigonal prismatic structures exist in eclipsed, staggered, and in between conformations.
- 7-coordinate species:
 - Pentagonal-bipyramidal, capped trigonal prism, and capped octahedron geometries are possible.
 - “In the capped shapes, the seventh ligand is simply added to a face of the core structure, with necessary adjustments to the other angles to accommodate the additional ligand” (Miessler et al., 2014, p. 343).
 - Preference for one structure over another is driven by the ligands.
- 8-coordinate species:
 - Square antiprismatic and dodecahedral geometries.
 - Less common with first-row transition metals because a relatively larger atomic/ionic radius better accommodates the many ligands.
- Coordination numbers are known up to 16.
 - 9-coordinate lanthanides and actinides are not uncommon.
 - Tricapped trigonal prismatic geometry: A triangular prism with a cap through each rectangular face.
 - Capped square antiprismatic.
 - One newly synthesized compound appears to have a 12-coordinate sd^5 -hybridized Mo center, and a cluster with Zn–Zn bonding.
- **Coordination polymer:** A solid in which coordination complexes are linked through ligands in “infinite” arrays.
- **Metal-organic framework:** A three-dimensional extended structure in which metal ions or clusters are linked through organic molecules that have two or more sites through which links can be formed. *Also known as MOF.*
- There is a detailed classification system for networks by three-letter codes, e.g., bcc for body-centered cubic.
- **Metalloligand:** A coordination complex with an attached donor group on its ligand.