

# Chemistry 1000 Lecture 25: Introduction to transition metal chemistry

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# The transition metals

- d block of periodic table

Sc [Ar]3d <sup>1</sup> 4s <sup>2</sup>	Ti [Ar]3d <sup>2</sup> 4s <sup>2</sup>	V [Ar]3d <sup>3</sup> 4s <sup>2</sup>	Cr [Ar]3d <sup>5</sup> 4s <sup>1</sup>	Mn [Ar]3d <sup>5</sup> 4s <sup>2</sup>	Fe [Ar]3d <sup>6</sup> 4s <sup>2</sup>	Co [Ar]3d <sup>7</sup> 4s <sup>2</sup>	Ni [Ar]3d <sup>8</sup> 4s <sup>2</sup>	Cu [Ar]3d <sup>10</sup> 4s <sup>1</sup>	Zn [Ar]3d <sup>10</sup> 4s <sup>2</sup>
Y [Kr]4d <sup>1</sup> 5s <sup>2</sup>	Zr [Kr]4d <sup>2</sup> 5s <sup>2</sup>	Nb [Kr]4d <sup>4</sup> 5s <sup>1</sup>	Mo [Kr]4d <sup>5</sup> 5s <sup>1</sup>	Tc [Kr]4d <sup>5</sup> 5s <sup>2</sup>	Ru [Kr]4d <sup>7</sup> 5s <sup>1</sup>	Rh [Kr]4d <sup>8</sup> 5s <sup>1</sup>	Pd [Kr]4d <sup>10</sup>	Ag [Kr]4d <sup>10</sup> 5s <sup>1</sup>	Cd [Kr]4d <sup>10</sup> 5s <sup>2</sup>
La [Xe]5d <sup>1</sup> 6s <sup>2</sup>	Hf [Xe]4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	Ta [Xe]4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	W [Xe]4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	Re [Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	Os [Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	Ir [Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	Pt [Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	Au [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	Hg [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>

# Chemistry of the transition metals

- Electronegativities range from 1.1 (La) to 2.4 (W, Au)
- Many transition metal (TM) compounds are essentially covalent
- TM atoms/ions typically act as Lewis acids
- Rough rule: TMs form ionic compounds in lower oxidation states, covalent compounds in higher oxidation states

- Common and less common oxidation states:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+1			Blue	Blue	Blue	Blue	Blue	Blue	Red	
+2		Blue	Blue	Blue	Red	Red	Red	Red	Red	Red
+3	Red	Red	Red	Red	Red	Red	Red	Blue	Blue	
+4		Red	Red	Blue	Blue	Blue	Blue	Blue		
+5			Red	Blue	Blue		Blue			
+6				Red	Blue	Blue				
+7					Red					
	[Ar]3d <sup>1</sup> 4s <sup>2</sup>	[Ar]3d <sup>2</sup> 4s <sup>2</sup>	[Ar]3d <sup>3</sup> 4s <sup>2</sup>	[Ar]3d <sup>5</sup> 4s <sup>1</sup>	[Ar]3d <sup>5</sup> 4s <sup>2</sup>	[Ar]3d <sup>6</sup> 4s <sup>2</sup>	[Ar]3d <sup>7</sup> 4s <sup>2</sup>	[Ar]3d <sup>8</sup> 4s <sup>2</sup>	[Ar]3d <sup>10</sup> 4s <sup>1</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup>

# Complexes and ligands

- Coordinate bond:** bond made between a metal ion and a Lewis base  
This can almost always be considered to be an ordinary polar covalent bond. The special name only serves to emphasize that coordinate bonds are typically easier to rearrange than other covalent bonds.
- Coordination complex:** complex molecule or ion consisting of a central metal atom or ion acting as a Lewis acid with coordinate bonds to one or (usually) several Lewis bases
- Ligand:** one of the Lewis bases in a coordination complex

# Complexes and ligands (continued)

**Coordination number:** number of coordinate bonds formed by a metal centre

A given metal ion in a given oxidation state typically has a preferred coordination number found in most of its compounds.

- Coordination complexes do not obey the VSEPR rules. Rather, the shape is connected to the coordination number.
  - Coordination number 6 gives octahedral complexes.
  - Coordination number 4 gives either tetrahedral or square planar complexes.

## Example: Chloro-anions

- Many metal ions form complex anions with chloride ions.
- Some examples:

Complex	Metal oxidation state
$[\text{CdCl}_4]^{2-}$	2
$[\text{HgCl}_4]^{2-}$	2
$[\text{PtCl}_4]^{2-}$	2
$[\text{PbCl}_3]^{-}$	2
$[\text{AgCl}_2]^{-}$	1
$[\text{CuCl}_3]^{2-}$	1

## Example: Ammine-cations

- Many metal ions form complex cations with ammonia.
- Some examples:

Complex	Metal oxidation state
$[\text{Co}(\text{NH}_3)_6]^{3+}$	3
$[\text{Co}(\text{NH}_3)_6]^{2+}$	2
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2
$[\text{Cd}(\text{NH}_3)_4]^{2+}$	2
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2



# Square bracket notation

- In the preceding examples, you may have noticed that coordination complexes are shown in square brackets.
- This is important since it makes the connectivity clear: The metal atom/ion and its ligands are shown in square brackets together.

# Complex salts

A **complex ion** is a coordination complex with a net charge.

A **complex salt** is a compound in which at least one of the ions is a complex ion.

**Examples** with simple counterions:

- $\text{Na}_2[\text{CdCl}_4]$
- $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

**Note** that we list the cation first, then the anion.

The following **pairs of compounds** are different:

- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ .

# Monodentate ligands

**Monodentate:** literally, having one 'tooth'

- These are ligands that coordinate only once to a metal.
- Examples of monodentate ligands:  
 $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OH^-$ ,  $H_2O$ ,  $NH_3$ ,  $CO$
- Note that these are all Lewis bases, but not necessarily Brønsted bases.

For example,  $Cl^-$  is a Lewis base, but it is **not** a Brønsted base.  
How do we know that  $Cl^-$  is not a Brønsted base?




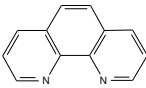
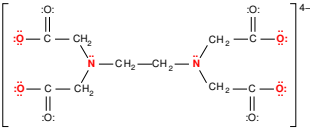
# Polydentate ligands

**Bidentate:** coordinates twice to a metal, i.e. can donate lone pairs from two **different** atoms

**Polydentate:** coordinates more than once to a metal

**Denticity:** number of donor atoms in a ligand through which it coordinates

## Polydentate ligands (continued)

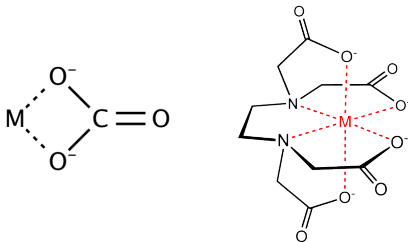
Structure	Denticity	Abbreviation
	1 or 2	$\text{CO}_3^{2-}$
	2	$\text{ox}^{2-}$
	2	en
	2	phen
	6	$\text{EDTA}^{4-}$

# Chelates

**Chelate:** a complex in which a bidentate or polydentate ligand forms a closed ring with a metal atom by forming two or more coordinate bonds

**Chelating agent:** a ligand that can form chelates

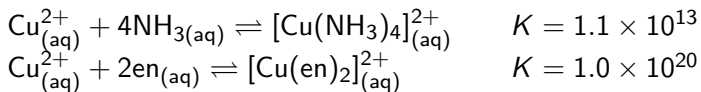
Examples of chelates:



# Chelate effect

- Chelates tend to be much more stable than similar complexes containing monodentate ligands (chelate effect).

Example:



These equilibrium constants are such that  $\text{Cu}^{2+}$  will preferentially bind en at any reasonably comparable concentrations of en and ammonia.

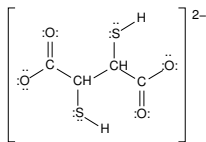
- Chelation makes ions unavailable in solution.

### Applications:

Added to **detergents** to reduce water hardness (EDTA)

**Food additive** to prevent catalysis of oxidation by metal ions  
(EDTA)

**Chelation therapy** for metal poisoning, esp. hypercalcemia,  
mercury or lead poisoning  
(dimercaptosuccinate)





# Isomerism

**Isomers** are compounds with the same chemical formula (same atoms), but arranged differently.

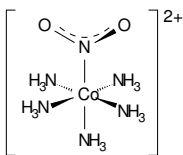
**Structural isomers** differ in what is bonded or coordinated to what.

**Stereoisomers** have identical chemical bonds, but are arranged differently in space.

# Linkage isomerism: an example of structural isomerism

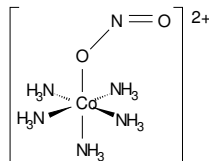
Linkage isomers contain a ligand coordinated to the metal centre through different donor atoms.

Example:



yellow-orange

and



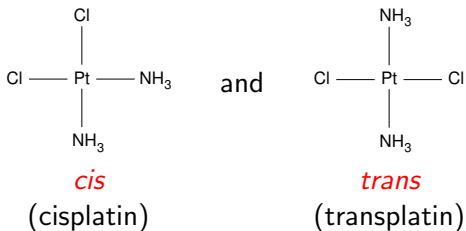
red-orange

# Some types of stereoisomerism

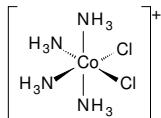
**Geometrical isomers** have identical bonds, but the distances between some nonbonded atoms are different due to a different arrangement of the bonds in space.

- In square planar complexes with chemical formula  $\text{MX}_2\text{Y}_2$  or in octahedral complexes with formula  $\text{MX}_2\text{Y}_4$ , the two X ligands can be adjacent (*cis*) or opposed (*trans*).

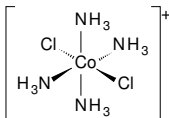
Example:



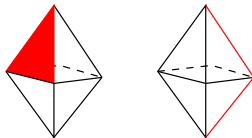
Example:

*cis*

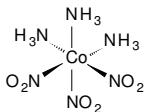
and

*trans*

- In octahedral complexes with formula  $\text{MX}_3\text{Y}_3$ , the three X ligands can be in the same face of the octahedron (*fac*) or along a meridian (*mer*):

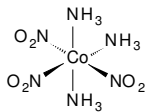


Example:



*fac*

and



*mer*