

Transition Metal and Coordination Chemistry

Transition Metals vs Main Group Elements:

- Natural Abundance vs importance

Variation in Chemistry: What controls properties and reactivity.

Electron Configurations: Trends and exceptions.

TABLE 23.1 Selected Properties of Elements of the First Transition Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electron config. ^a	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁴ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²
Metallic radius, pm	161	145	132	125	124	124	125	125	128	133
Ioniz. energy, kJ mol ⁻¹										
First	631	658	650	653	717	759	758	737	745	906
Second	1235	1310	1414	1592	1509	1561	1646	1753	1958	1733
Third	2389	2653	2828	2987	3248	2957	3232	3393	3554	3833
E°, V ^b	-2.03	-1.63	-1.13	-0.90	-1.18	-0.440	-0.277	-0.257	+0.340	-0.763
Common positive oxidation states ^c	3	2, 3, 4	2, 3, 4, 5	2, 3, 6	2, 3, 4, 7	2, 3, 6	2, 3	2, 3	1, 2	2
mp, °C	1397	1672	1710	1900	1244	1530	1495	1455	1083	420
Density, g cm ⁻³	3.00	4.50	6.11	7.14	7.43	7.87	8.90	8.91	8.95	7.14
Hardness ^d	—	—	—	9.0	5.0	4.5	—	—	2.8	2.5
Electrical conductivity ^e	3	4	6	12	1	16	25	23	93	27

^aEach atom has an argon inner-core configuration.

^bFor the reduction process, M²⁺(aq) + 2e⁻ → M(s) [except for scandium, where the ion is Sc³⁺(aq)].

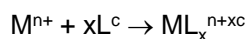
^cThe most important oxidation states are printed in red.

^dHardness values are on the Mohs scale (see Table 22.2).

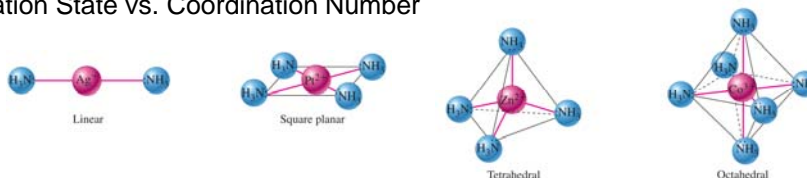
^eElectrical conductivity compared with an arbitrarily assigned value of 100 for silver.

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Coordination Chemistry



Oxidation State vs. Coordination Number



What makes a good ligand?

- Mono- vs polydentate ligands:

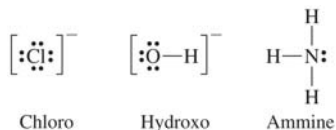


TABLE 24.3 Some Common Polydentate Ligands (Chelating Agents)

Abbreviation	Name	Formula
en	Ethylenediamine	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$
ox ²⁻	Oxalato	$\text{O}=\text{C}-\text{C}(\text{O})=\text{C}(\text{O})-\text{C}(\text{O})=\text{O}$
EDTA ⁴⁻	Ethylenediaminetetraacetato	$\text{N}(\text{CH}_2\text{CO}_2^-)_2$

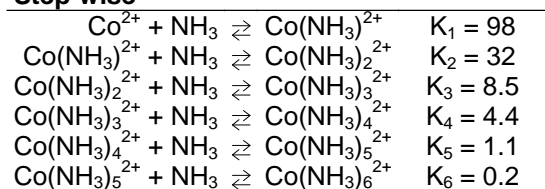
“Stability” of Coord. Compounds:

A Thermodynamic Consideration

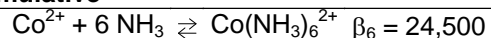
Formation of coordination compounds can be described as equilibrium process.

- Cumulative vs. Step-wise formation constants
 - Impact of large formation constants.

Step-wise



Cumulative



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Naming Coordination Compounds

1. Cation first, anion second
2. Ligands before the metal
 - Mono vs polyatomic ligands
 - Multiple ligands
 - Alphabetical order
3. Oxidation state of metal
4. Charged complexes

Examples:

- $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2$
- $\text{Na}_3[\text{Co}(\text{CN})_6]$

TABLE 24.2 Some Common Monodentate Ligands

Formula	Name as Ligand	Formula	Name as Ligand	Formula	Name as Ligand
Neutral molecules		Anions		Anions	
H ₂ O	Aqua	F ⁻	Fluoro	SO ₄ ²⁻	Sulfato
NH ₃	Ammine	Cl ⁻	Chloro	S ₂ O ₃ ²⁻	Thiosulfato
CO	Carbonyl	Br ⁻	Bromo	NO ₂ ⁻	Nitrito-N ^a
NO	Nitrosyl	I ⁻	Iodo	ONO ⁻	Nitrito-O ^a
CH ₃ NH ₂	Methylamine	O ²⁻	Oxo	SCN ⁻	Thiocyanato-S ^b
C ₅ H ₅ N	Pyridine	OH ⁻	Hydroxo	NCS ⁻	Thiocyanato-N ^b
		CN ⁻	Cyano		

^aIf the nitrite ion is attached through the N atom (—NO₂), the designation *nitrito-N* is used; if attached through an O atom (—ONO), *nitrito-O*.

^bIf the thiocyanate ion is attached through the S atom (—SCN), the name *thiocyanato-S* is used; if attachment is through the N atom (—NCS), *thiocyanato-N*.

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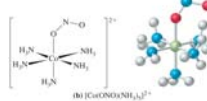
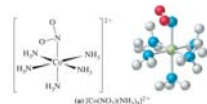
Isomerism: Structural vs. Stereoisomers

Structural Isomerism:

Ionization:

Coordination:

Linkage:

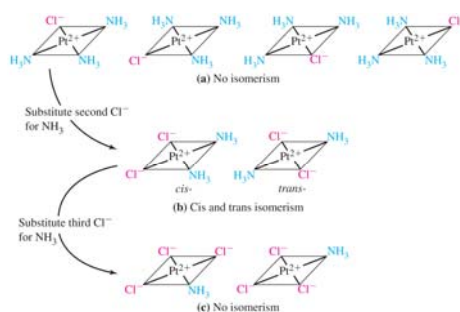


Stereoisomerism:

Geometric Isomerism:

Options depend on coordination number

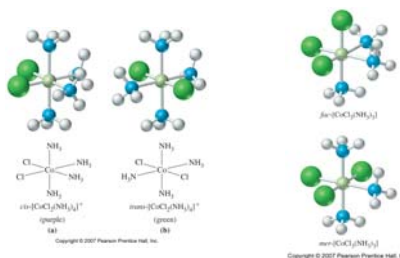
Optical isomerism (chirality):



Isomerism: Structural vs. Stereoisomers

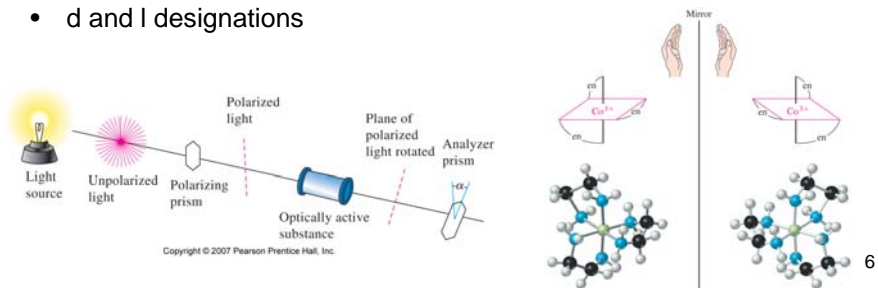
More geometric isomers:

- Naming changes as number of equivalent substituents change



Optical isomers:

- Enantiomers and chirality
- d and l designations



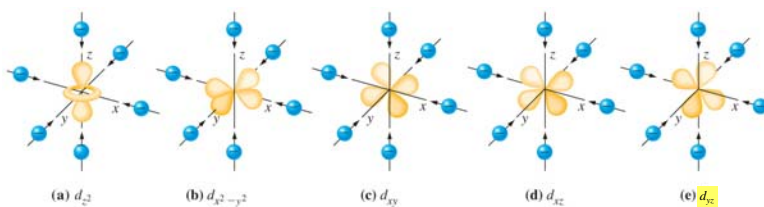
Bonding Models for Coord. Chemistry

Valence bond doesn't work for transition metals!

Crystal Field Theory – based on electrostatic interactions

- Primary goal is to rationalize observable properties (like any theory).
- nd atomic orbitals (in free atoms) have similar energies, but the properties of coordination compounds imply things are different when atoms interact with ligands.

Example: octahedral geometry

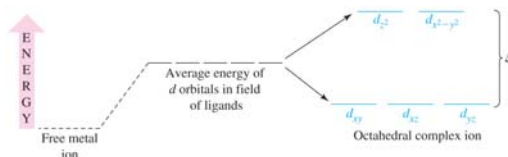


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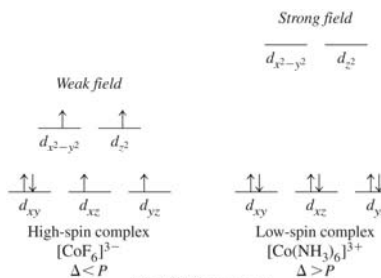
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Bonding Models for Coord. Chemistry

- Crystal Field Splitting
 - Orbital energies “split” – “Crystal Field Splitting”
 - WHY?



- Crystal field splitting (size) determines MO filling
 - Strong Field (low spin) versus Weak Field (high spin)
 - “Spectrochemical Series” (large Δ) $\text{CN}^- > \text{NO}_2^- > \text{NH}_3 > \text{EDTA} > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ (small Δ)

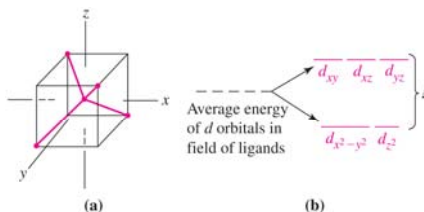


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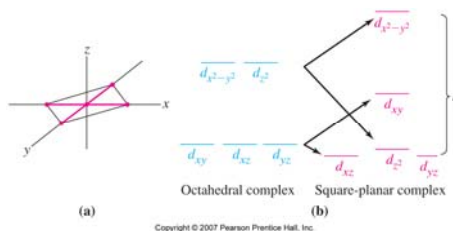
Bonding Models for Coord. Chemistry

- Crystal field splitting and other geometries

Tetrahedral



Square Planar



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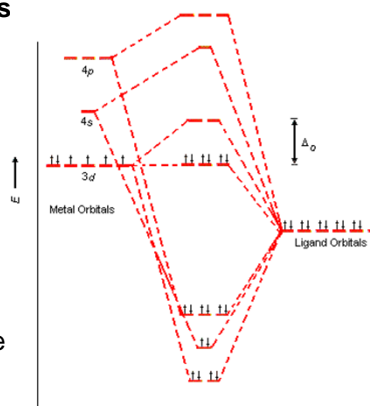
Bonding Models for Coord. Chemistry

MO Theory and Coordination Compounds

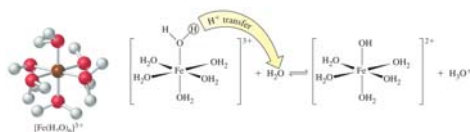
- Remember the basics of MO theory
 - Build “new” molecular orbitals
- Relative energies of metal and ligand orbitals are key!
 - Ligand-Field Theory – based on “covalent” interactions**

Odds and Ends

- Labile vs inert - Rates of ligand exchange
- Acidity of aqua complexes



<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/ligand.php>



$$K_a \sim 10^{-4}$$

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