Topic 6

Coordination Compounds

Coordination Chemistry

- Alfred Werner (Nobel Prize in Inorganic Chemistry 1913):

Compound	Color	+ Ag^+
$CoCl_3 \cdot 6\ NH_3$	Yellow	3 AgCl
$CoCl_3 \cdot 5\ NH_3$	Purple	2 AgCl
$CoCl_3 \cdot 4\ NH_3$	Green/Violet (2 isomers)	1 AgCl

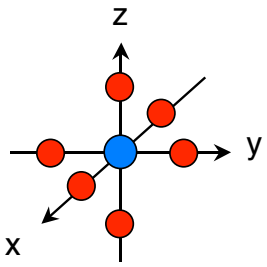
Platinum(II) Complexes

Composition	No. of Ions	Today's formulation
$PtCl_2 \cdot 4\ NH_3$	3	$[Pt(NH_3)_4]Cl_2$
$PtCl_2 \cdot 3\ NH_3$	2	$[Pt(NH_3)_3Cl]Cl$
$PtCl_2 \cdot 2\ NH_3$	0	*cis*-$[Pt(NH_3)_2Cl_2]$
	0	*trans*-$[Pt(NH_3)_2Cl_2]$
$PtCl_2 \cdot NH_3 \cdot KCl$	2	$K[Pt(NH_3)Cl_3]$
$PtCl_2 \cdot 2\ KCl$	3	$K_2[PtCl_4]$

Coordination Chemistry

- **Coordination Compound** (coordination complex, complex): compound containing metal ion and appended groups, which are Lewis bases and may be monoatomic or polyatomic, neutral or anionic.
- **Ligand:** Lewis base bonded (coordinated) to a metal ion in a coordination complex
  Ligands with one point of attachment are monodentate ligands
  Ligands with two (or more) coordinated do not atoms are bidentate (or polydentate) liagnds
- **Coordination number:** Number of ligands coordinated to metal ion
- **Coordination geometry** (octahedral, tetrahedral, square planar): geometrical arrangements of ligands (donor groups) about a metal ion
- **Isomers:**
  Structural isomer: same composition, but different atom connectivity
  Stereo isomer: same atom connectivity, but different spatial arrangement of atoms

Splitting of *d*-Orbital Energy in Octahedral Complexes

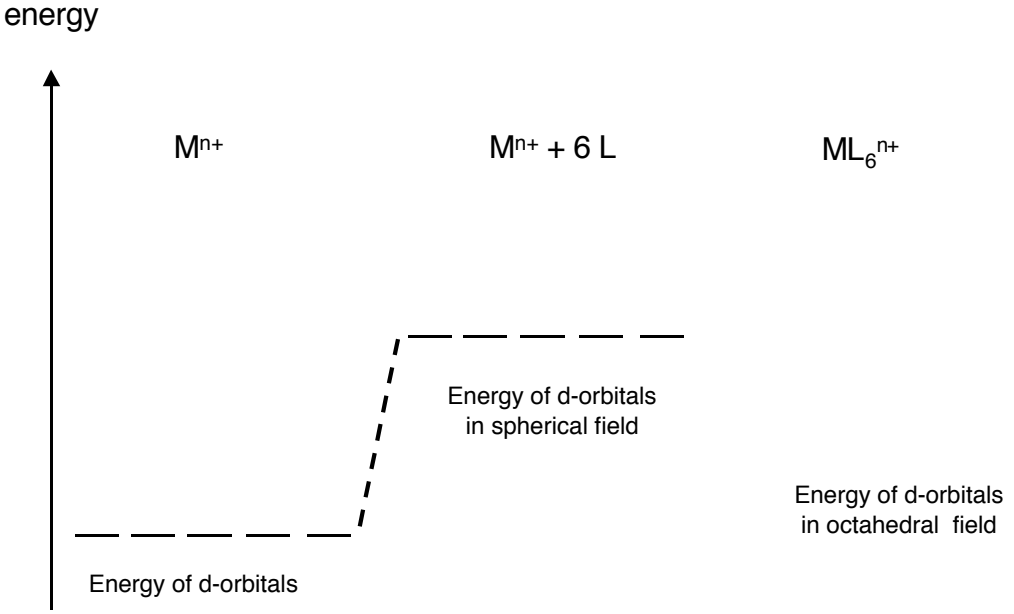


How does the ligand field influence the energy of the five metal d-orbitals?

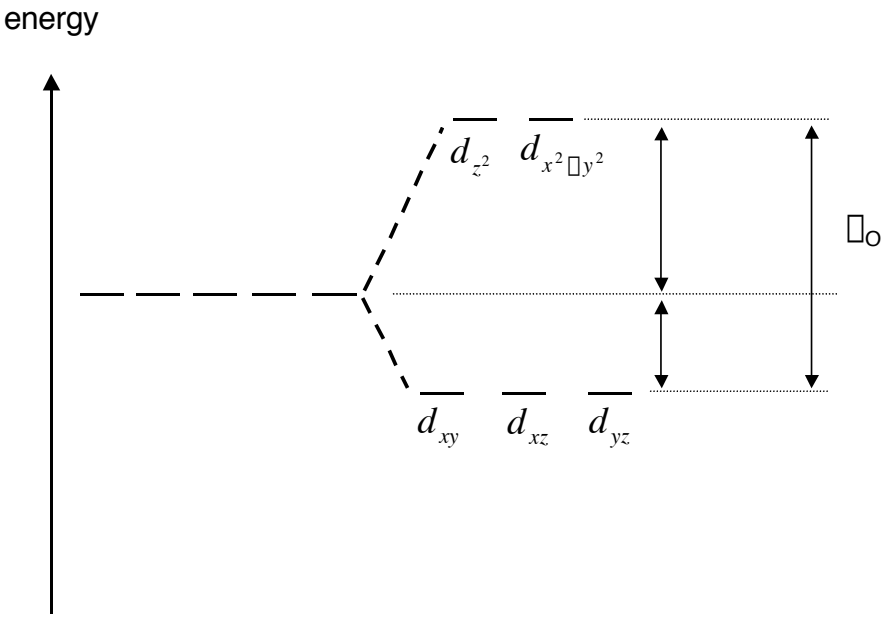
d_{z^2} $d_{x^2-y^2}$ Orientation along ligand-metal bond axis

d_{xy} d_{xz} d_{yz} Orientation between ligand-metal bond axis

Energy Diagram of Octahedral Complexes



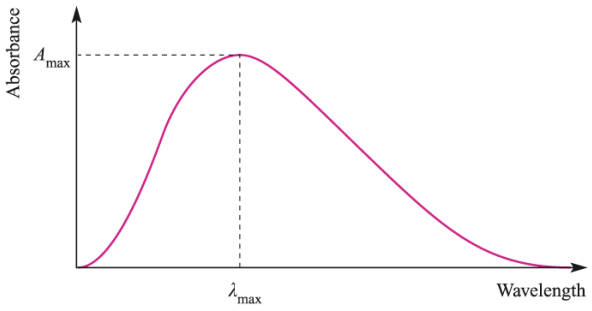
Octahedral Complexes



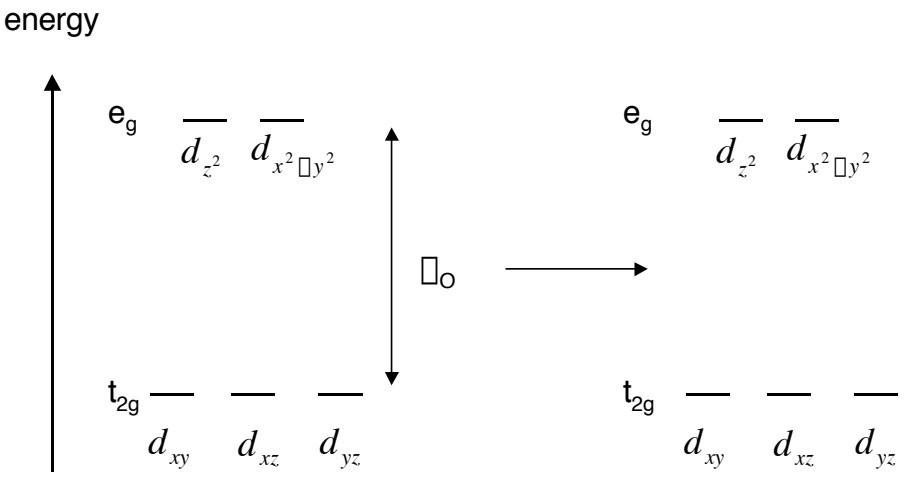
Electronic Spectra

- Studies of electronic spectra of metal complexes provide information about structure and bonding. Absorptions arise from transitions between electronic energy levels:
  - Transitions between metal-centered orbitals possessing d-character = d- d transitions (MC) (weak intensity, Laporte-forbidden)
  - Transitions between metal- and ligand-centered orbitals = metal-to-ligand or liagnd-to-metal charge transfer transitions (MLCT, LMCT) (strong intensity)
- Absorption bands are usually broad due to vibrational and rotational sublevels

$$A_{max} = \varepsilon_{max} \cdot c \cdot l$$



Electronic Absorption Spectroscopy

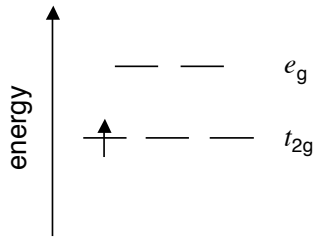


On irradiation with light of frequency ν, which is equal to Δ_O/h, an electrons is transferred to one of the higher energy e_g orbitals.

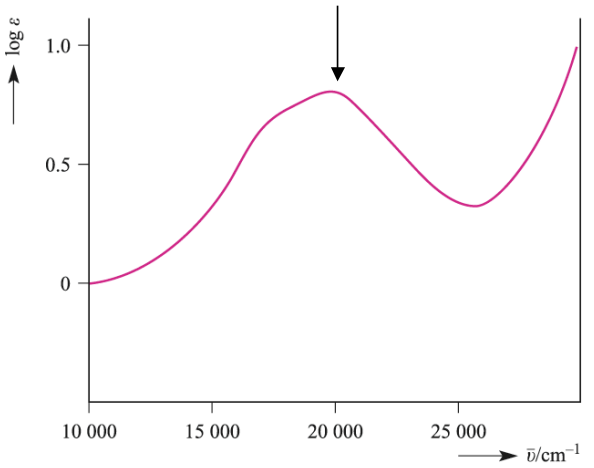
Field Strength

- The splitting energy Δ_{oct} can be determined from spectroscopic data:

Example: $[Ti(H2O)_6]^{3+}$:



Δ_{max} = 20,300 cm^{-1}



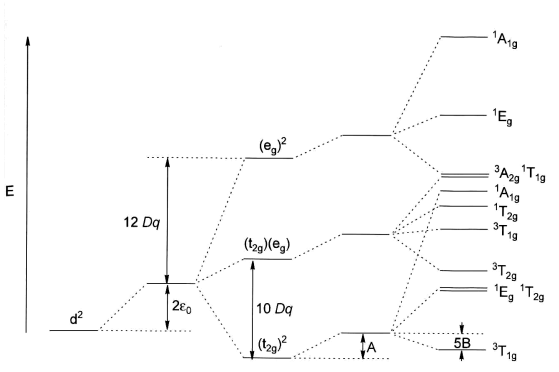
Octahedral Ti(III) Complexes

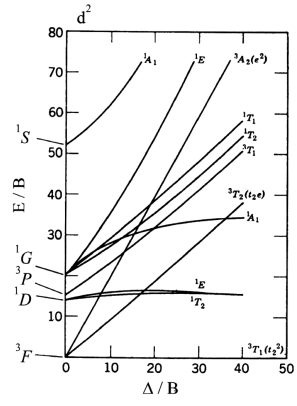
- Ti(III) is a d^1 complex and exhibits ONE absorption in its electronic spectrum due to transition of the electron from the t_{2g} orbitals to the e_g orbitals. The energy of the absorption corresponds to Δ_O.

Ligand	Δ_O/cm^{-1}
Br^-	11,400
Cl^-	13,000
$(H_2N)_2C=O$	17,550
NCS^-	18,400
F^-	18,900
H_2O	20,100
CN^-	22,300

Ions with more than one *d*-electron

- The majority of transition metal ions of practical interest have more than one d-electron
  –> an explanation of their electronic structures and absorption spectra in terms of the ligand field theory is considerably more complex, since also forces between the electrons have to be considered
  –> the spectra of such complexes can be interpreted using Tanabe-Sugano diagrams:





Tanabe-Sugano Diagram for d^2 electron configuration

Spectrum of $Mn(H_2O)_6^{2+}$

- Mn(II) has a d^5 high spin electron configuration –> all d-orbitals are occupied with one electron each
  –> none of the possible (d-d) transitions is spin allowed, since for any transition the spin of the electron must be reversed
  (both higher energy e_g orbitals contain already one electron, according to the Pauli principle the spin of the second electron must be reversed)
  Therefore: all possible transitions are very weak, and $Mn(H_2O)_6^{2+}$ is very pale in color

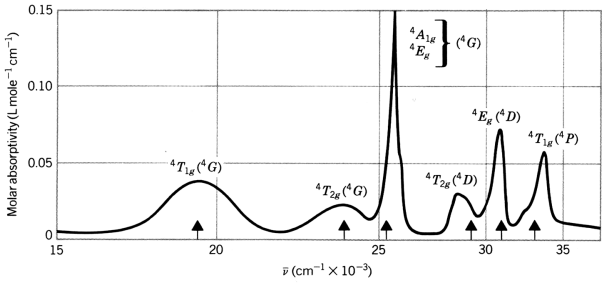
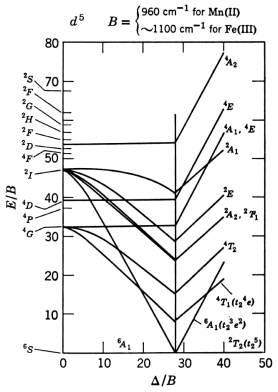


Figure 23-23 The electronic absorption spectrum of $[Mn(H_2O)_6]^{2+}$. Arrows indicate predicted band positions.



Charge Transfer Spectra

- The d-d absorption bands of transition metals involves redistribution of electrons that are localized on the metal
- There are also electronic transitions in which an electron moves from a ligand-based orbital to a metal based orbital, or vice versa
  –> these absorption bands are generally very intense

LMCT: Ligand metal charge transfer band (electron moves from ligand to metal)

Example: $[Fe(SCN)(H_2O)_5]^{2+}$ (red complex)

MLCT: Metal ligand charge transfer band (electron moves from metal to ligand)

Example: $[Cu(phen)_2]^{+}$ (yellow complex)

Magnitude of Splitting Energy (Δ_O)

- **Charge on the metal (oxidation state)**
  For first row transition elements Δ_O varies from about 7,500 cm^{-1} to 12,500 cm^{-1} for divalent ions, and 14,000 cm^{-1} to 25,000 cm^{-1} for trivalent ions.
- **Position in a group**
  values for analogous complexes of metal ions in a group increases by 25% to 50% going from one transition series to the next:
  $[M(NH_3)_6]^{3+}$ with M=Co 23,000cm^{-1}, M=Rh 34,000cm^{-1}, M=Ir 41,000 cm^{-1}
- **Geometry and coordination number**
  For identical (or nearly identical) ligands Δ_t (tetrahedral) is 4/9 of Δ_O. This is a result of the reduced number of ligands and their orientation relative to the d orbitals.
  Note: The energy ordering of the orbitals is reversed in tetrahedral complexes relative to that in octahedral complexes.
- **Identity of ligand**
  The dependence of Δ on the nature of the ligand follows an empirical order, known as the spectrochemical series, for all metals in all oxidation states and geometries.

Spectrochemical Series

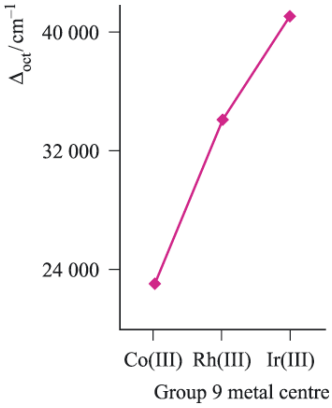
- **Order of ligand field strength with decreasing Dq:**

  $CN^- > phen \sim NO_2^- > en > NH_3 \sim py > H_3O > C_2O_4^{2-} > OH^- > F^- > S^{2-} > Cl^- > Br^- > I^-$

  Note: $H_2O > OH^-$: this cannot be explained in terms of the electrostatic model

- **Order of metals with increasing Dq:**

  Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)



Estimation of Splitting Energies

$$10\ Dq \sim f\ (ligand) \bullet g\ (metal)$$

Ligand	f factor	Metal ion	g factor [1000 cm^{-1}]
Br^-	0.72	Mn(II)	8.0
SCN^-	0.73	Ni(II)	8.7
Cl^-	0.78	Co(II)	9.0
N_3^-	0.83	V(II)	12
F^-	0.90	Fe(III)	14
$C_2O_4^-$	0.99	Cr(III)	17.4
H_2O	1.0	Co(III)	18.2
NCS^-	1.02	Ru(II)	20
gly^-	1.18	Mn(IV)	23
py	1.23	Mo(III)	24.6
NH_3	1.25	Rh(III)	27.0
en	1.28	Tc(IV)	30
bpy	1.33	Ir(III)	32
CN^-	1.70	Pt(IV)	36

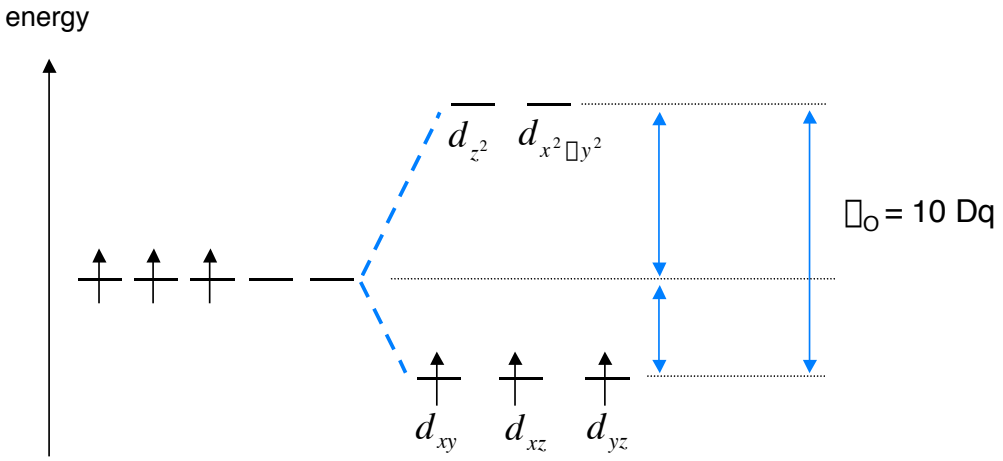
Problem 6-1: Estimate the splitting energy Δ_{oct} for the following octahedral complexes:

a) $[Cr(NH_3)_6]^{3+}$

b) $[Co(en)_2Cl_2]^+$

Ligand Field Stabilization Energy (LFSE)

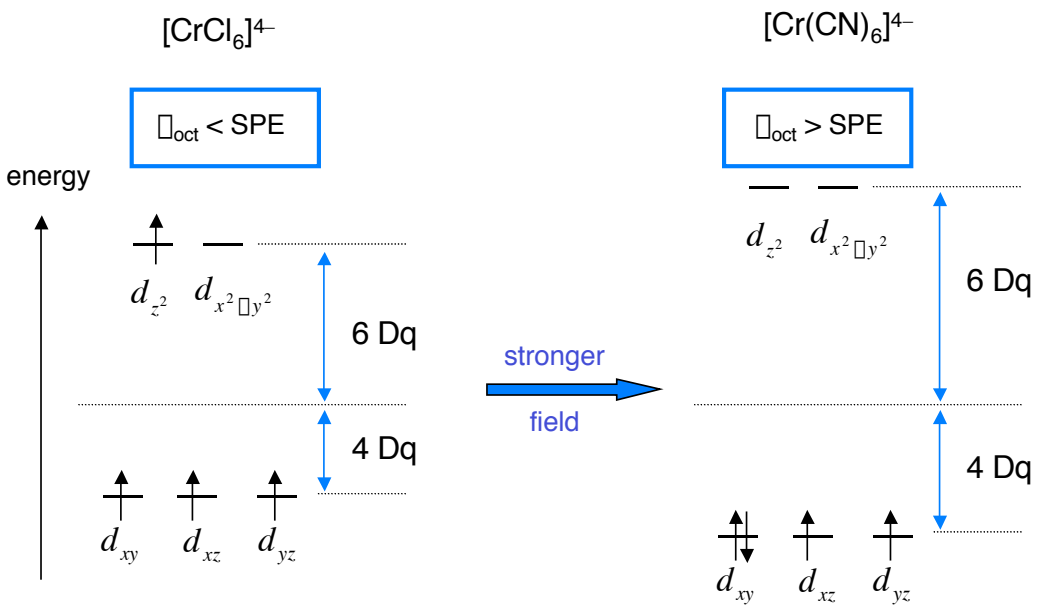
Example: $[Cr(NH_3)_6]^{3+}$ => octahedral complex, d^3 electron configuration



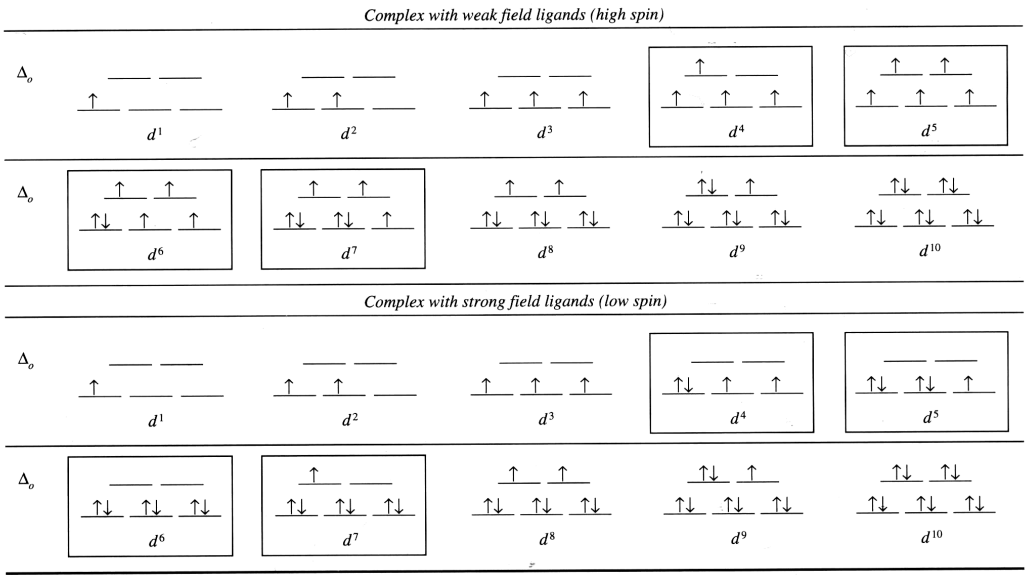
Note: The LFSE for any octahedral complex with d^3 electron configuration is –12 Dq, but the absolute value of Dq varies with ligand and metal!

Problem 6-2: Calculate the crystal field stabilization energy (in cm^{-1}) for $[Co(NH_3)_6]^{2+}$. (Δ_{oct} = 10,200 cm^{-1})

Influence of Splitting Energy



Spin State and Ligand Field Strength



Ligand Field Stabilization Energies

Number of d electrons	*Weak-field arrangement*					
	t_{2g}			e_g		$LFSE(\Delta_o)$
1	↑					−2/5
2	↑	↑				−4/5
3	↑	↑	↑			−6/5
4	↑	↑	↑	↑		−3/5
5	↑	↑	↑	↑	↑	0
6	↑↓	↑	↑	↑	↑	−2/5
7	↑↓	↑↓	↑	↑	↑	−4/5
8	↑↓	↑↓	↑↓	↑	↑	−6/5
9	↑↓	↑↓	↑↓	↑↓	↑	−3/5
10	↑↓	↑↓	↑↓	↑↓	↑↓	0

Number of d electrons	*Strong-field arrangement*					
	t_{2g}			e_g		$LFSE(\Delta_o)$
1	↑					−2/5
2	↑	↑				−4/5
3	↑	↑	↑			−6/5
4	↑↓	↑	↑			−8/5
5	↑↓	↑↓	↑			−10/5
6	↑↓	↑↓	↑↓			−12/5
7	↑↓	↑↓	↑↓	↑		−9/5
8	↑↓	↑↓	↑↓	↑	↑	−6/5
9	↑↓	↑↓	↑↓	↑↓	↑	−3/5
10	↑↓	↑↓	↑↓	↑↓	↑↓	0

Hydration Enthalpies of M^{2+} Ions

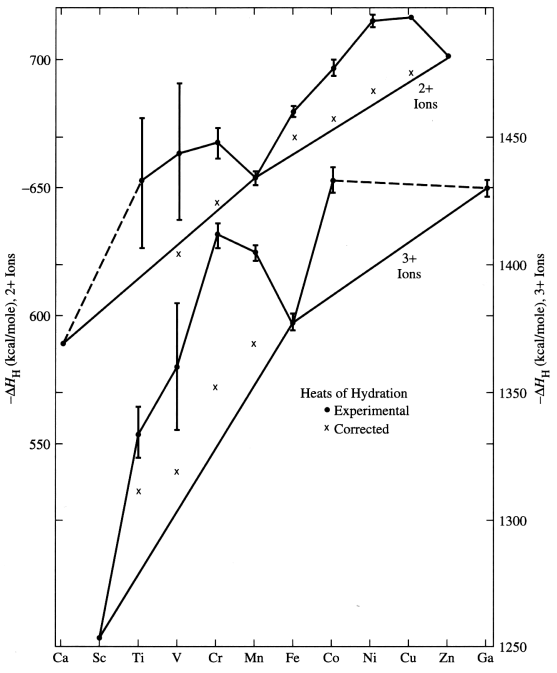


FIGURE 10-7 Enthalpies of Hydration of Transition Metal Ions. Values of ΔH derived from spectroscopic Δ_o's are subtracted from each value of $-\Delta H_H$ and form the "corrected" curve. The straight lines Ca-Mn-Zn or Sc-Fe-Ga are also shown. (Reproduced from P. George and D. S. McClure, *Prog. Inorg. Chem.*, **1959,** *1*, 418. Copyright © 1959, John Wiley & Sons Inc. Reprinted by permission of John Wiley & Sons Inc.)

Splitting Energies for Aqueous Complexes

	Ion	Δ_o	Π	*Ion*	Δ_o	Π
d^1				Ti^{3+}	20,300	
d^2				V^{3+}	18,000	
d^3	V^{2+}	11,800		Cr^{3+}	17,600	
d^4	Cr^{2+}	14,000	23,500	Mn^{3+}	21,000	28,000
d^5	Mn^{2+}	7,500	25,500	Fe^{3+}	14,000	30,000
d^6	Fe^{2+}	10,000	17,600	Co^{3+}	17,000-19,000	21,000
d^7	Co^{2+}	9,700	22,500	Ni^{3+}		27,000
d^8	Ni^{2+}	8,600				
d^9	Cu^{2+}	13,000				
d^{10}	Zn^{2+}	0				

SOURCE: Data from D. S. McClure, "The Effects of Inner-orbitals on Thermodynamic Properties," in *Some Aspects of Crystal Field Theory,* T. M. Dunn, D. S. McClure, and R. G. Pearson, Harper & Row, New York, 1965, p. 82. The value of Δ_o for Co^{3+} is from J. S. Griffith and L. E. Orgel, *Quart. Revs.,* **1957,** *XI,* 381.

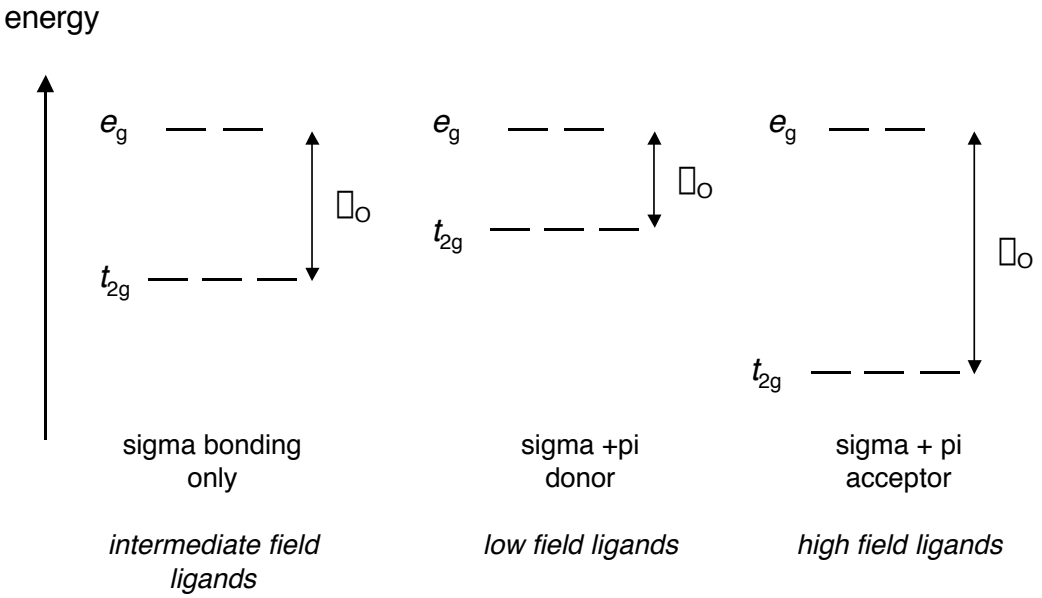
□ = Spin pairing energy

Note: Only Co^{3+} has a splitting energy similar to the spin pairing energy
–> It is the only *low-spin* aqua complex of the listed examples!

Low-Spin vs. High-Spin Complexes

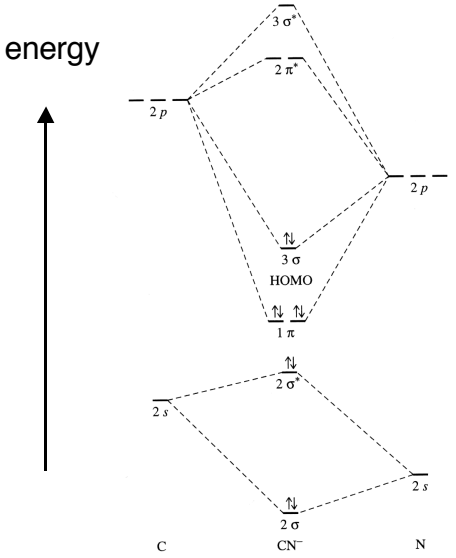
- **Strong-field ligands = low-spin complexes**
  Strong field ligands have pi-acceptor orbitals or low-lying *d*-orbitals:
  □* as in CO or CN^-, □* as in CH_2=CH_2, low lying *d* as in PR_3, PF_3
- **Weak field ligands = high-spin complexes**
  Weak field ligands have pi-donor orbitals:
  Usually multiple *p*-orbitals as in X^-
- **Intermediate field ligands = usually high-spin for +2 ions, low-spin for +3 ions**
  Intermediate field ligands have few, or no pi-donor or acceptor orbitals, or there is a poor match in energy of available pi-orbitals: NH_3, H_2O, pyridine
- Note:
  Complex stability and reactivity do not necessarily correlate with ligand field strength
  –> Thermodynamic stability refers to the energetics of a given reaction
  –> Kinetic stability (=reactivity) refers to the rate with which a given reaction occurs (activation energy)

Effect of pi-donor/acceptor interactions

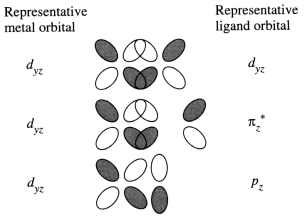


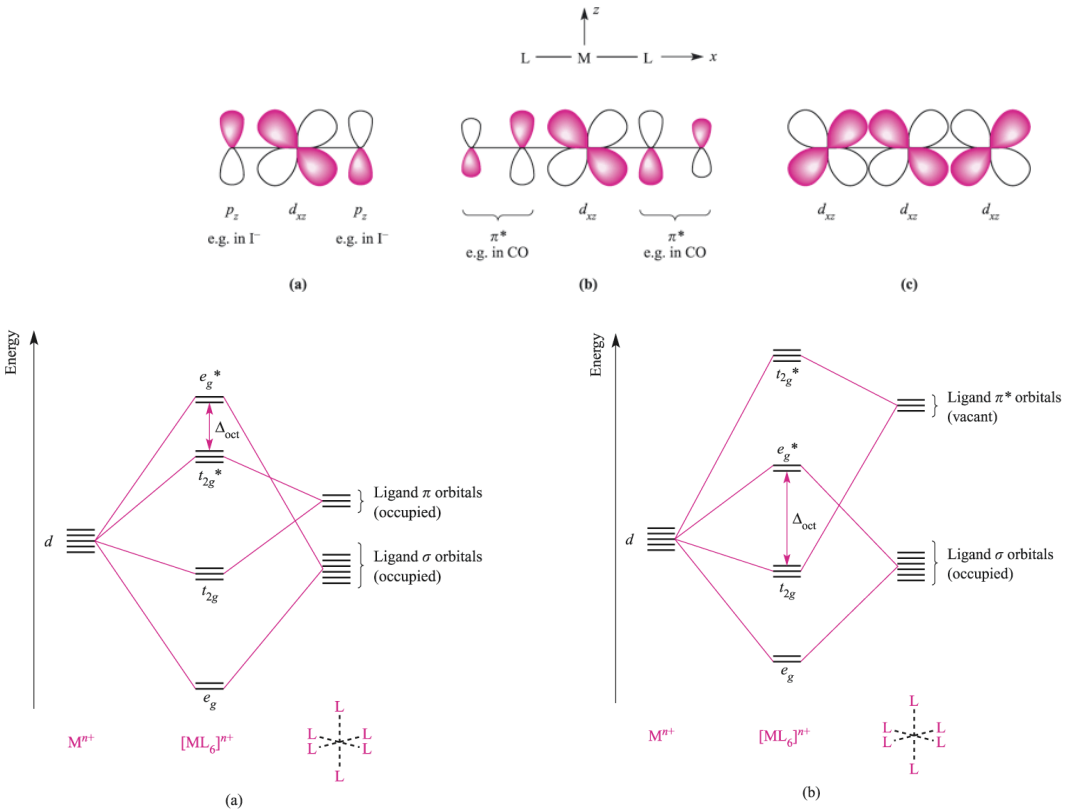
Cyanide is a Pi-Acceptor

MO-Diagram of CN^-



Overlap of *d*, π*, and *p*-orbitals with metal d orbitals:
–>Overlap is good with ligand *d* and p π*-orbitals, poorer with ligand *p*-orbitals

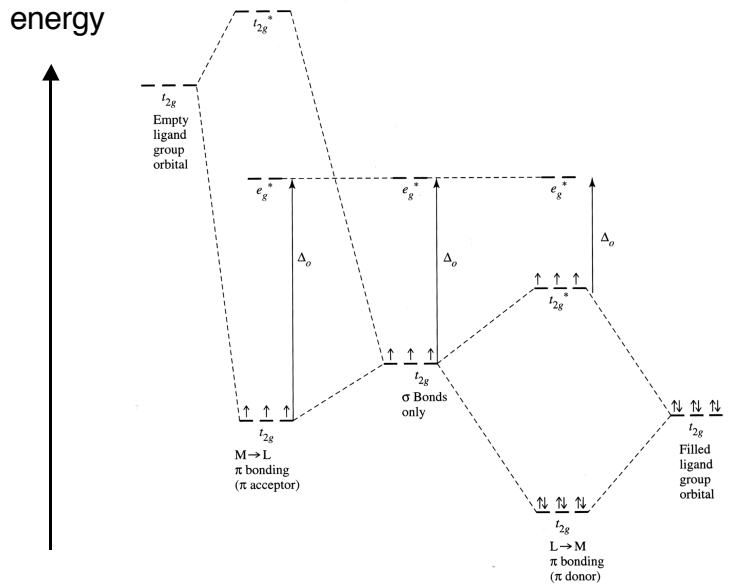




π-donor ligands

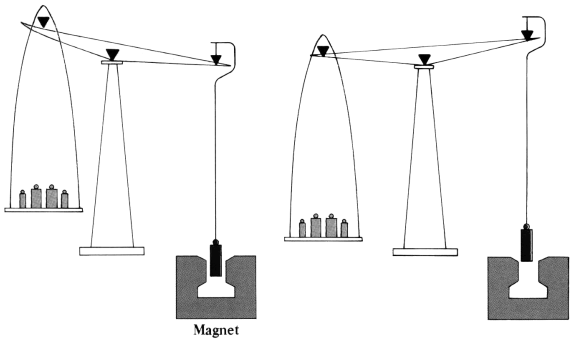
π-acceptor ligands

Effect of pi-Bonding



Magnetic Susceptibility

- As for diatomic molecules, the magnetic properties of a coordination compound can give direct evidence of the orbital energy levels
  –> Hund's rule requires the maximal number of unpaired electrons in energy levels with equal (or nearly equal) energies
- A compound with unpaired electrons is paramagnetic and is attracted into a magnetic field
  –> the measure of this magnetism is called **magnetic susceptibility**



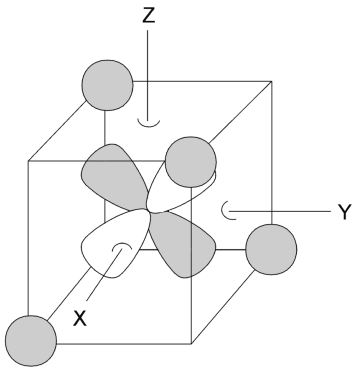
Gouy Magnetic Susceptibility Apparatus

Total Electron Spin and Multiplicity

- Paramagnetism arises because electrons behave as tiny magnets.
- Although there is no direct evidence for a spinning movement by electrons, a charged particle spinning would generate **a spin magnetic moment**
- The total spin magnetic moment is characterized by the spin quantum number S, which is equal the to the maximum total spin (sum of the m_s values of all electrons)
  –> molecules with S≠0 are paramagnetic, molecules with S=0 are diamagnetic
- The number of unpaired electrons is often expressed in form of the spin multiplicity: a = 2S+1 (related to the number of lines observed in a spectrum)

Problem 6-3: What is the total spin and multiplicity of $Cr(H_2O)_6^{3+}$?

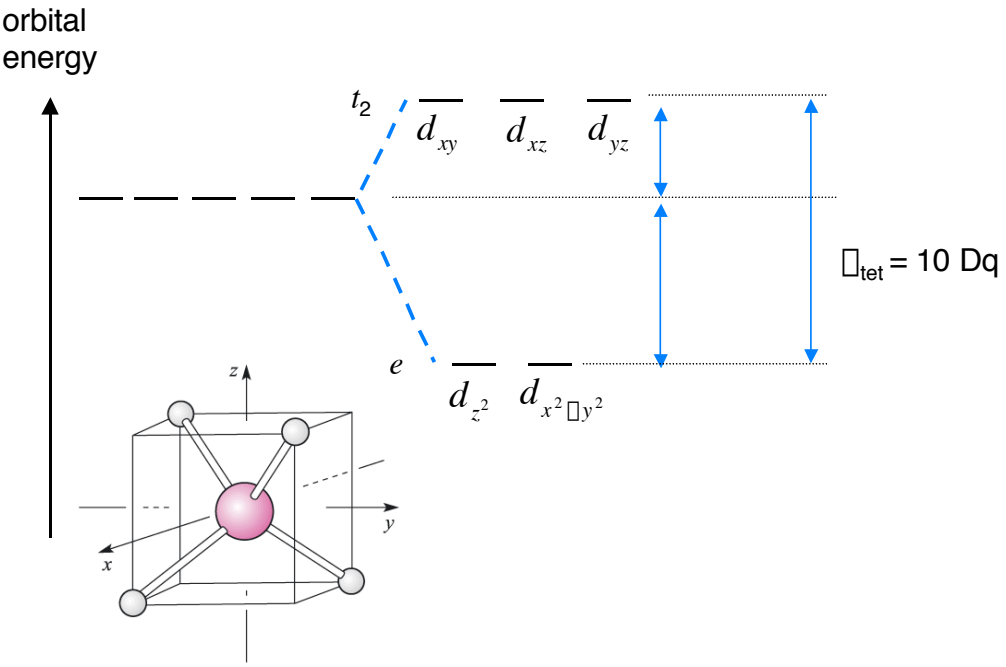
Tetrahedral Complexes



Tetrahedral arrangement of four ligands showing their orientation relative to the Cartesian axes and the d_{xz} orbital (the orientation with respect to the other two t_2 orbitals d_{yz} and d_{xy} is identical)

The interaction of the four ligands with the t_2 orbitals (d_{xy}, d_{xy} and d_{yz}) is considerably greater than with the e type oritals (d_{z2} and d_{x2-y2})
–> the e orbitals are therefore lower in energy

Tetrahedral Complexes



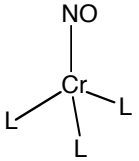
Tetrahedral Complexes

- least ligand-ligand repulsion
- Small ligand field splitting energy (only four ligands, and they are not aligned along the orbital axis)
  –> the ligand field splitting energy is in most cases too small to overcome the spin pairing energy, therefore tetrahedral low spin complexes are very rare!
- Ideal geometry for metal cations with no LFSE (d^0, d^5 and d^{10}), or only little LFSE (d^2, d^7)

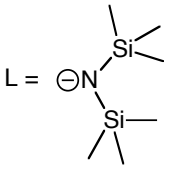
Examples: MnO_4^- (d^0), FeO_4^{2-} (d^2), $FeCl_4^-$ (d^5, high spin)

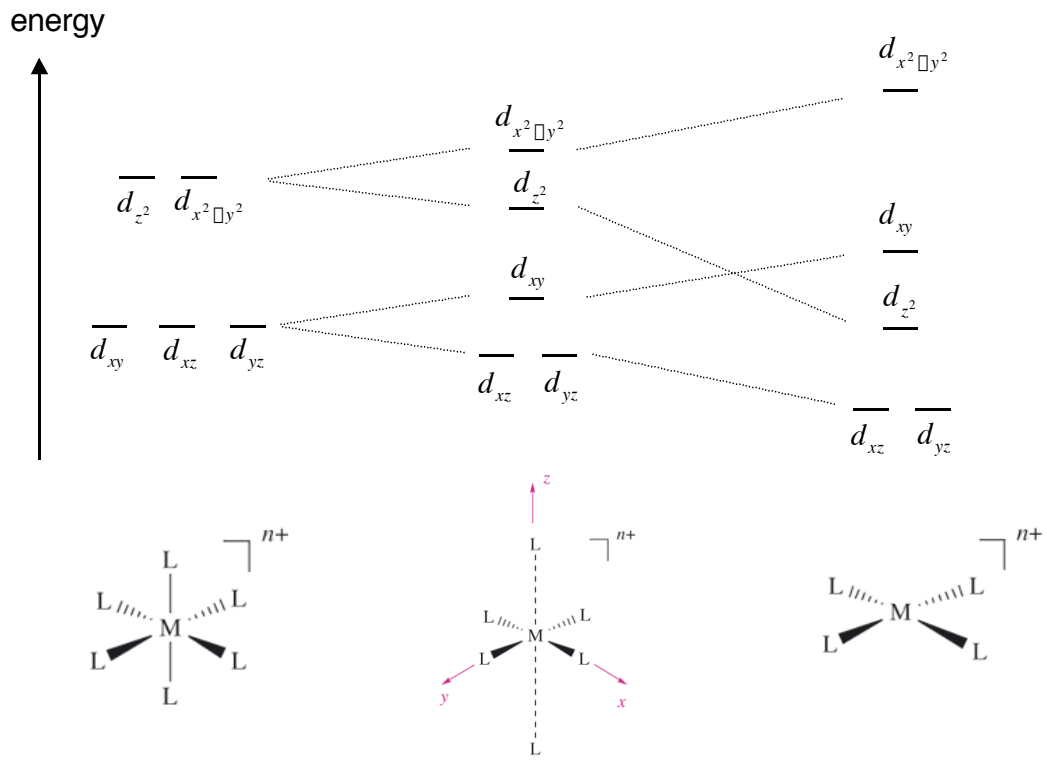
$CoCl_4^{2-}$ (d^7, high spin), $ZnCl_4^{2-}$ (d^{10})

$Cr[N(SiMe_3)_2]_3NO$



A rare example for a low spin complex with tetrahedral coordination geometry

L = 



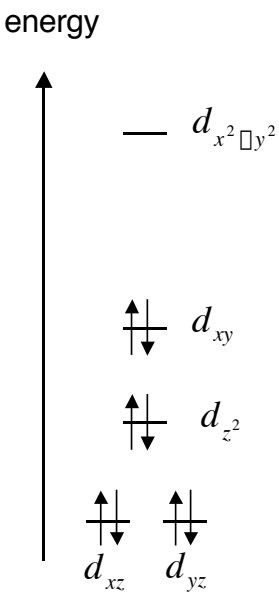
Square Planar Complexes

- Square planar complexes are expected for all metal cations with d^8 electron configuration
  –> this geometry offers the greatest stabilization according to the ligand field theory, since the highest energy orbital d_{x2-y2} remains unoccupied

  Examples: Ni(II), Pt(II), Pd(II), Au(III)

- Square planar complexes with d^8 configuration are always diamagnetic

  Examples: $Ni(H_2O)_6^{2+}$: octahedral –> paramagnetic
  $Ni(CN)_4^{2-}$: square planar –> diamagnetic
  $Ni(Cl)_4^{2-}$: tetrahedral –> paramagnetic



Problem 6-4:

a) The anion $[Ni(SPh)_4]^{2-}$ is tetrahedral. Explain why this complex is paramagnetic.

b) The complexes $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic and diamagnetic. What does this tell you about their structures?

Energy Diagram Overview

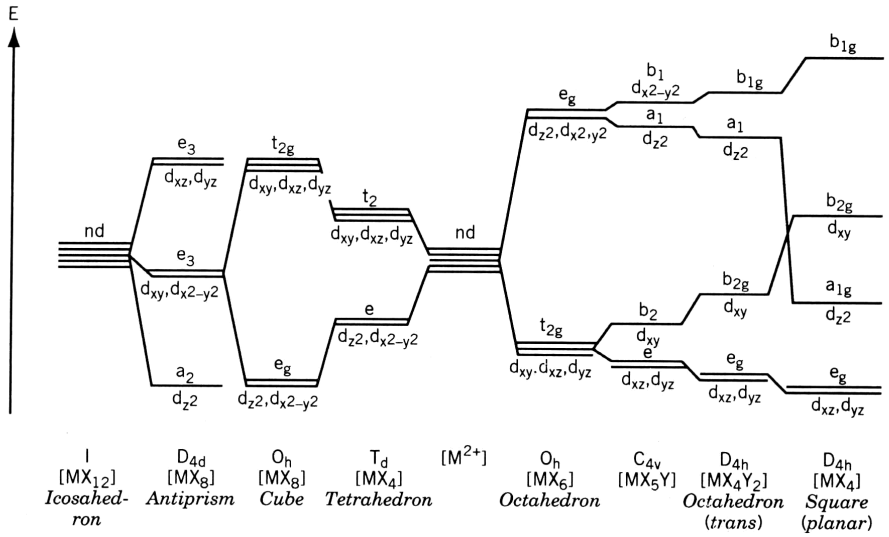


Figure 4.5. Splitting of *d*-orbital energy levels in ligand fields of different symmetries. In MX_5Y and MX_4Y_2 complexes the splitting of the T_{2g} and E_g terms can be inverted depending on the ratio of field strengths X/Y. (After [4.12].)

Structures of Coordination Compounds

- The number of d-electrons significantly influences the structure and geometry of transition metal complexes:

Electron configuration	Factors influencing geometry
d^0, d^5 (high spin), d^{10}	Coordination geometry determined mostly by steric demand of the ligands
All other configurations:	Coordination geometry significantly influenced by ligand field stabilization energy (as well as steric demand)

Coordination Number Two

- Relatively rare
- Occurs mainly with the +1 cations of Cu, Ag, Au and Hg^{2+} (all d^{10} electron configuration)

Examples: $Cu(NH_3)_2^+$ $Ag(NH_3)_2^+$ $Au(CN)_2^-$ $Hg(CN)_2$

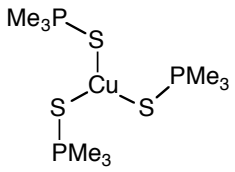
Note: Such complexes are typically unstable towards addition of further ligands:

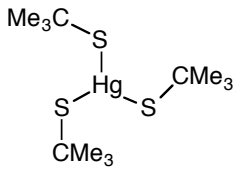
Coordination Number Three

- Very rare, usually trigonal planar geometry:

Examples:

$[Cu(SPMe_3)_3]ClO_4$ $[Hg(SCMe_3)_3]^-$





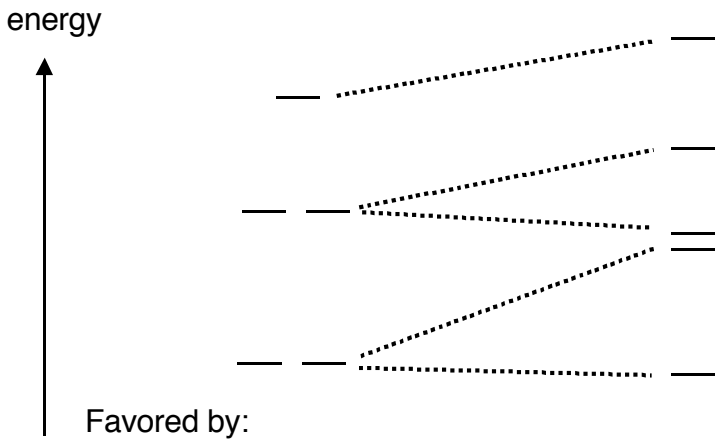
Coordination Number Four

- Tetrahedral Complexes:
  - favored by steric requirements
  - small splitting energy results small LFSE –> favored in complexes with large ligands and metals with noble gas configuration (d^0, d^{10}) or low LFSE (e.g. Co(II) d^7)

- Square Planar Complexes:
  - small ligands
  - favored by metals with d^8 electron configuration (Ni^{2+}, Pd^{2+}, Pt^{2+}, Au^{3+}), and Cu^{2+} (d9), otherwise octahedral geometry preferred
  - cis/trans isomerism

Coordination Number Five

- Less common than C.N.=6, but still important
- Trigonal bibyramid, and square pyramid are the most important structures:



Favored by:
d^1, d^2, d^3, d^4, d^8, d^9

Favored by:
d^6 low spin

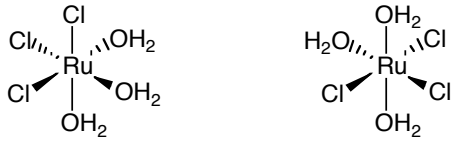
Note: The energy difference between the two geometries is small, and many complexes adopt intermediate structures .

Coordination Number Six

- Most common coordination number
- Octahedral complexes show two different types of geometrical isomers:

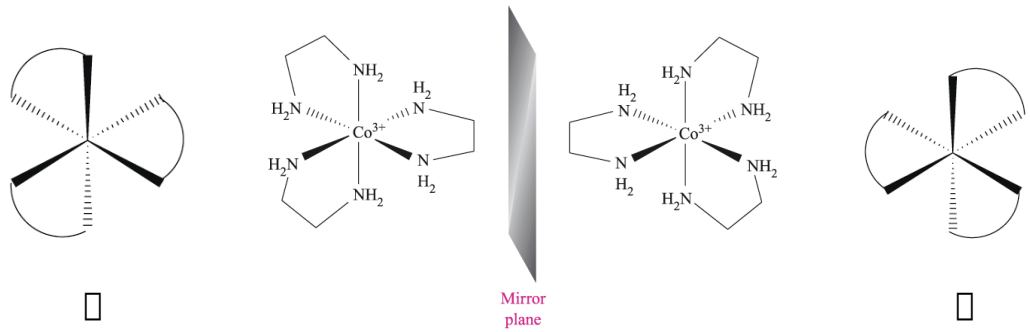
Typ MA_2B_4:

Typ MA_3B_3:



Optical Isomerism

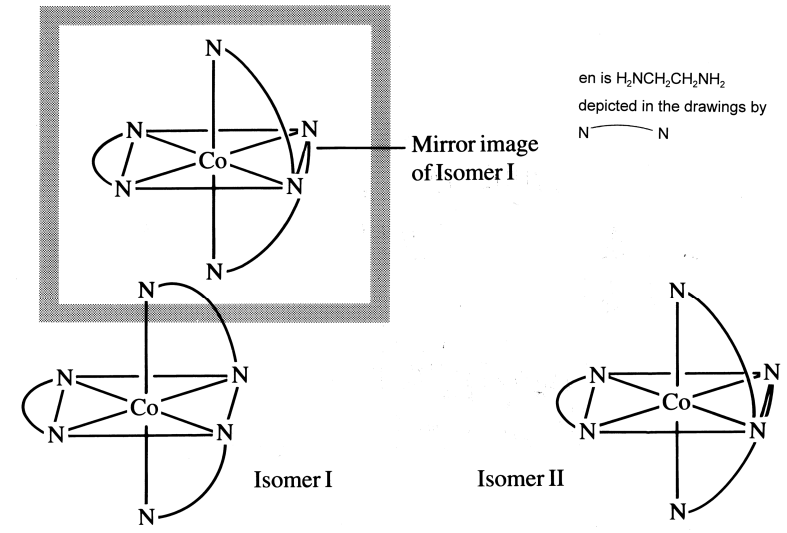
- Simplest case: metal cation surrounded by three identical bidentate ligands, e.g. $[Co(en)_3]^{3+}$:



–> the two isomers are non-superimposable images of each other and therefore chiral molecules

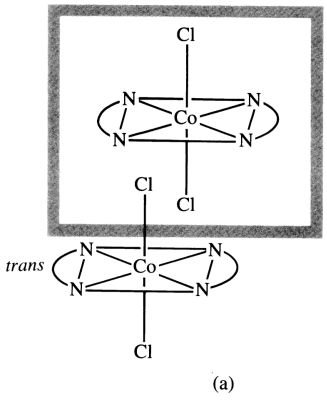
Δ and Λ prefixes: labels to identify the two enantiomers.
The octahedron is viewed down a 3-fold axis, and the chelate defines then a right (Δ) or left (Λ) handed helix.

Optical Isomers of $[Co(en)_3]^{3+}$



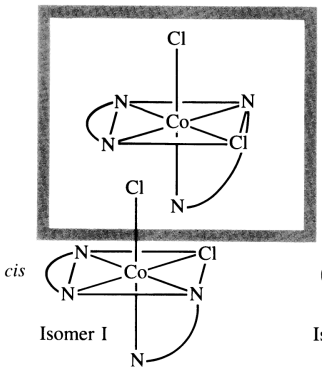
Isomers of $[Co(en)_3]^{3+}$ are nonsuperimposable mirror images

Cis/trans-Isomers of $[CoCl_2(en)_2]^+$

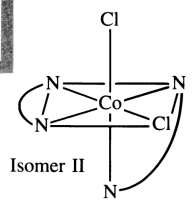


(a)

The *trans* isomer and its mirror image are identical. They are not isomers of each other.



Isomer II cannot be superimposed exactly on isomer I. They are not identical structures.



Isomer II has the same structure as the mirror image of isomer I

(b)

Problem 6-5: State the types of isomerism that may be exhibited by the following complexes, and draw structures of the isomers.

a) $[Co(en)_2(ox)]^+$

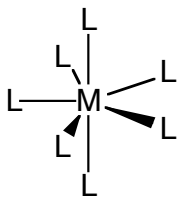
b) $[Co(en)(NH_3)_2Cl_2]^{2+}$

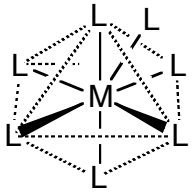
Higher Coordination Numbers

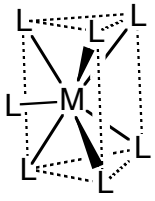
- Coordination numbers of seven, eight and nine are not frequently found

- Reason:
  Addition of ligand to octahedral complex leads to increased ligand-ligand repulsion and weaker bonds

Structural arrangements for 7 coordinate complexes:





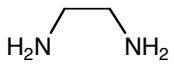


Types of Ligands

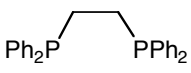
- The majority of ligands are anions or neutral molecules that function as electron-pair donors (Lewis base)
  Ligands that bind with a single donor atom to the metal are called monodentate (“one-toothed” ligands):

  F^-, Cl^-, Br^-, CN^-, NH_3, H_2O

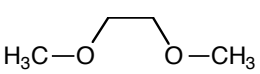
  Ligands with two or more heteroatoms are called bidentate or polydentate:



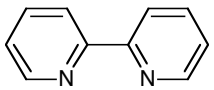
ethylenediamine



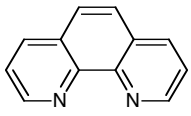
Bis(diphenylphosphino)ethane (=diphos or dppe)



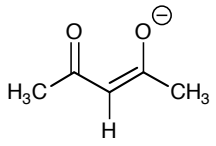
glyme



2,2’-bipyridine (bpy)



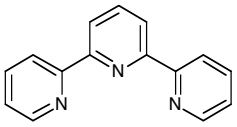
1,10-Phenanthroline (phen)



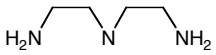
acetylacetonate (acac)

Types of Ligands

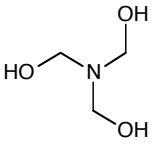
- Examples for polydentate ligands:



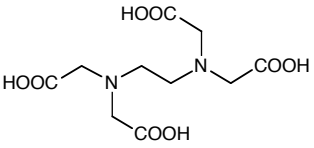
Terpyridine (trpy)



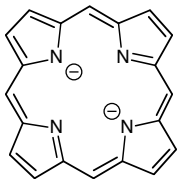
Diethylene triamine (dien)



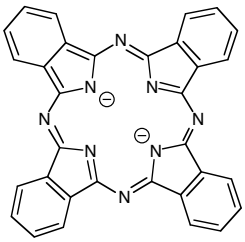
Tris(hydroxymethyl)amine (tris)



Ethylene diamine tetraacetic acid (EDTA)



porphyrine



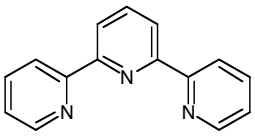
phthalocyanine

Problem 6-6: Comment on the possibility of isomer formation for each of the following complexes:

a) $[Ru(py)_3Cl_3]$

b) $[Ru(bipy)_2Cl_2]^+$

c) $[Ru(tpy)Cl_3]$



tpy

MRI Contrast Agents: Probing the Change in Coordination Environment

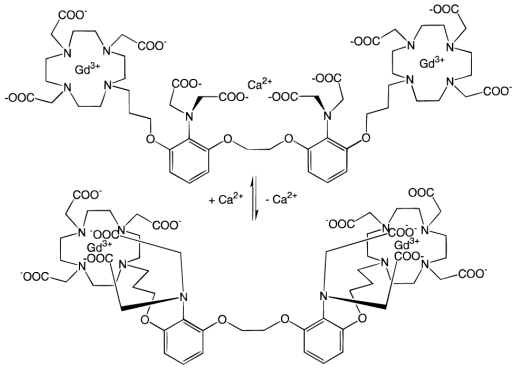


Figure 1. Schematic of DOPTA−Gd representing the proposed conformational dependence of the structure in the presence and absence of Ca^{2+}.

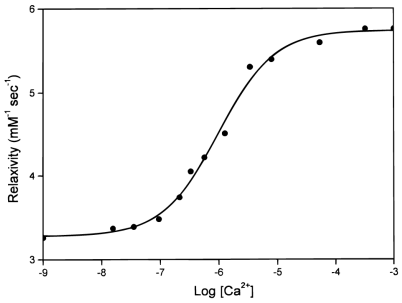
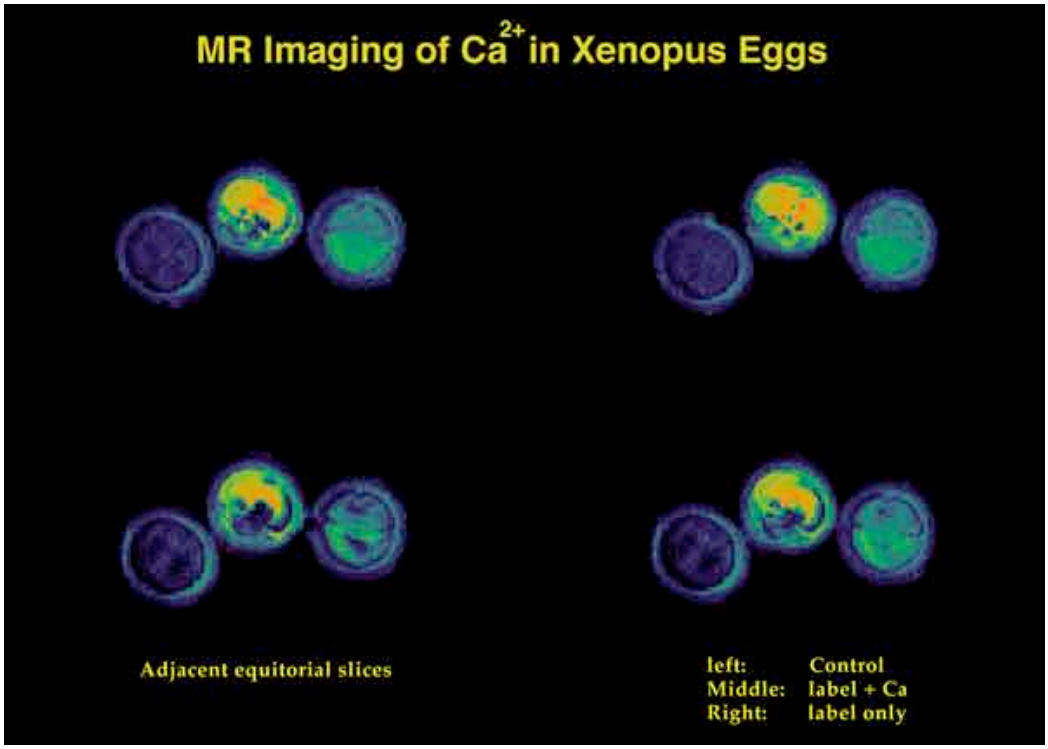


Figure 3. Relaxivity measurement of DOPTA−Gd as a function of free $[Ca^{2+}]$.[11] The fitted curve corresponds to the apparent dissociation constant = 0.96 μM and Hill coefficient = 0.92.

Calcium binding causes an increase in relaxivity, due to the additional coordinated water (which replaces the carboxylate ligands)



Nomenclature for Coordination Compounds

- Names are written according to IUPAC rules (International Union of Pure and Applied Chemistry)

  1) The name of the coordination compound begins with the name of the ligand(s), the metal is listed next, followed by the oxidation state in parentheses

  2) When more than one of a given ligand is bound to the same metal, the number is designated by the following prefixes:
  2 di, 3 tri, 4 tetra, 5 penta, 6 hexa, 7 hepta, 8 octa
  Note: when the name of the ligand contains already such prefix, the following prefixes are used:
  2 bis, 3 tris, 4 tetrakis, 5 pentakis, 6 hexakis, 7 heptakis, 8 octakis

  3) Neutral ligands are given the same name as the uncoordinated molecule
  Exceptions: NH_3 = ammine, H_2O aqua, NO = nitrosyl,
  CO = carbonyl

Nomenclature for Coordination Compounds

4) Anionic ligands are given the same name that end in the letter “o”.

Exceptions: with ending ate => ato, ide => ido, ite => ito

Special names:
CN^- = cyano, F^- = fluoro, Cl^- = chloro, Br^- = bromo, I^- = iodo
O^{2-} = oxo, O_2^{2-} = peroxo, OH^- = hydroxo, H^- = hydrido
CH_3 = methyl, C_2H_5 = ethyl

5) When the coordination entity is either neutral or cationic, the usual metal name is used (oxidation state in parentheses). When the coordination entity is an anion, the name of the metal is altered to end in “ate”:

Chromium => chromate, rhodium => rhodate, manganese => manganate
Tungsten => tungstate, cobalt => cobaltate

Special names (derived from Latin): iron => ferrate, copper => cuprate, silver => argenate
Gold => aurate

Problem 6-7: Assign a systematic name for the following compounds:

a) $K_2[Zn(CN)_4]$

b) $Cs[VOF_4]$

c) $[Fe(CO)_5]$

Stability of Coordination Compounds

- The stability of coordination compounds (metal complexes) is given by two different variables:
  - **Thermodynamic stability:**
    refers to the change in energy going from reactants to products

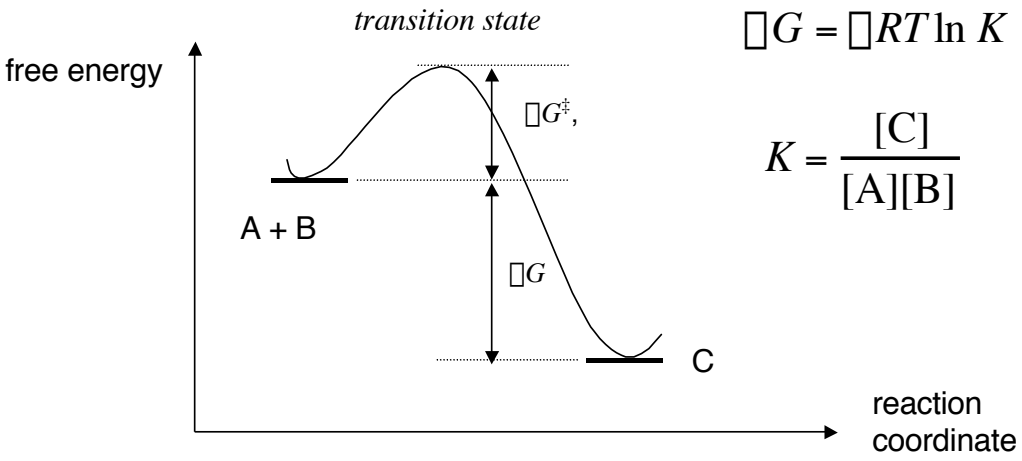
  - **Kinetic stability:**
    refers to the reactivity, generally ligand substitution

    –> Complexes which undergo fast ligand substitution reactions are called *kinetically labile*, those which undergo only very slow substitution reactions are called *kinetically inert*

  Note: High thermodynamic stability does not imply slow reactivity

Stability of Coordination Compounds

- The kinetic stability depends on the activation energy ($\Delta G^{\ddagger}$) of the ligand substitution reaction, the thermodynamic stability is given by the free energy change:



$$\Delta G = \Delta RT \ln K$$

$$K = \frac{[C]}{[A][B]}$$

Thermodynamic Stability

- The thermodynamic stability of a coordination compound is often expressed by the equilibrium constant for the reaction of the aquated metal ion with the corresponding ligand (other than water):

$$[Cu(OH_2)_4]^{2+} + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4\ H_2O$$

- The overall equilibrium expression for this reaction, generally referred to as β_n (here n=4) is defined as:

Note: The overall equilibrium β_n constant is obtained as the product of the stepwise equilibrium constants K_n

Formation (Stability) Constants

$$[Cu(OH_2)_4]^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(OH_2)_3(NH_3)]^{2+} + H_2O \qquad \log K_1$$

$$[Cu(OH_2)_3(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(OH_2)_2(NH_3)_2]^{2+} + H_2O \qquad \log K_2$$

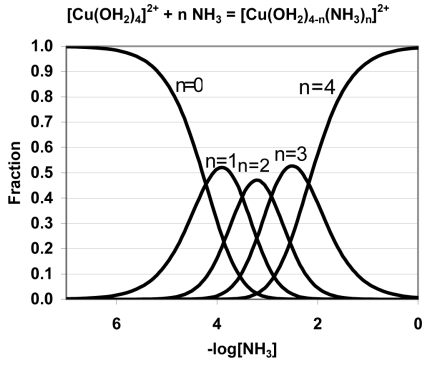
$$[Cu(OH_2)_2(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(OH_2)(NH_3)_3]^{2+} + H_2O \qquad \log K_3$$

$$[Cu(OH_2)(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} + H_2O \qquad \log K_4$$

$$\log \beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4 = 12.82$$

Thermodynamic Stability

- The decrease in successive step-wise constants is invariably observed and is due to several factors:
  - Statistics (number of replaceable positions)
  - Increased steric interaction
  - Charge neutralization (in case of anionic ligands)
- The fractional concentrations of each complex depends on the overall ammonia concentration and can be plotted in a species distribution diagram:



Chelate Effect

- The stability of the complex of a metal ion with a bidentate ligand such as ethylenediamine (en) is significantly greater than the complex of the same ion with two monodentate ligands of comparable donor ability (e.g. two ammonia molecules):

$$[Cu(OH_2)_4]^{2+} + en \overset{K_{en}}{\rightleftharpoons} [Cu(OH_2)_2(en)]^{2+} + 2\,H_2O \qquad \log K_{en} = 10.6$$

$$\Delta H = -54\ kJmol^{-1},\ \Delta S = 23\ JK^{-1}mol^{-1}$$

$$[Cu(OH_2)_4]^{2+} + 2\,NH_3 \overset{K_{NH3}}{\rightleftharpoons} [Cu(OH_2)_2(NH_3)_2]^{2+} + 2\,H_2O \qquad \log \beta_2 = 7.7$$

$$\Delta H = -46\ kJmol^{-1},\ \Delta S = -8.4\ JK^{-1}mol^{-1}$$

- This greater stability for complexes of chelate complexes is termed chelate effect
  –> it's origin is primary the difference in entropy between chelate and non-chelate complex reactions (the substitution with a chelate ligand results in a greater disorder due to the formation of a large number of free particles in the products)

Effect of Ring Size

Ligand:	Ni(II)	Cu(II)
NH_3, β_2	5.0	7.6
en, K_1	7.5	10.7
pn, K_1	6.5	10.0

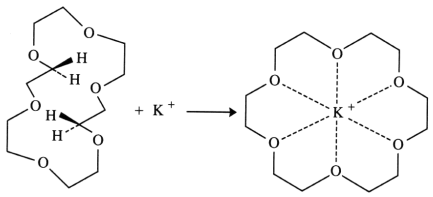
- The stability of pn (=propylendiamine) complexes is smaller compared to en complexes with the same metal

Thermodynamic Data for EDTA Complexes

(20°C, kJmol^{-1})

Metal:	ΔG	ΔH	$T\Delta S$	C.N.
Mg^{2+}	–48.5	+14.6	63.1	
Ca^{2+}	–59.8	–27.2	32.6	10
Mn^{2+}	–77.4	–19.2	58.2	7
Co^{2+}	–91.2	–17.6	73.6	6
Ni^{2+}	–104.6	–31.4	73.2	6
Cu^{2+}	–105.4	–33.9	71.5	6
Zn^{2+}	–92.5	–20.1	72.4	6

Macrocyclic Complexes



		Na^+	K^+	Ba^{2+}
log K_1	18-crown-6	4.36	6.06	7.04
	pentaglyme	1.44	2.1	2.3
	log K difference	2.92	3.96	4.74
ΔH	18-crown-6	−35.1	−56.0	−43.5
	pentaglyme	−16.7	−36.4	−23.8
	ΔH difference	−18.4	−19.6	−19.7
ΔS	18-crown-6	−33	−71	−13
	pentaglyme	−29	−84	−33
	ΔS difference	−4	13	20

[a] Modified from Hancock, R. D.; Martell, A. E. *Comments Inorg. Chem.* **1988**, *6*, 237–284. Free energy and enthalpy changes are expressed in kJ mol^{-1}. Entropy changes are expressed in J mol^{-1} K^{-1}.

Irving-Williams Series

- The stability for many transition metal complexes follows the following order:

$$Mn < Fe < Co < Ni < Cu > Zn$$

- Based on the increasing electron affinity (increasing effective nuclear charge!) an increase of log K (or ΔH) would be naturally expected

  But: The complex stability is also influenced by d-electron-electron repulsion
  –> complexes with greater ligand field stabilization energy are expected to be thermodynamically more stable
  –> therefore, copper(II) is expected to form the most stable (high-spin) complexes

Effect of LFSE

$$[M(OH_2)_6]^{2+} + 3\ en \rightleftharpoons [M(en)_3]^{2+} + 6\ H_2O$$

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
log β_3	5.6	9.7	13.9	18.4	20.0, β_2	12.9
ΔH	–46	–67	–93	–120	–105	–87
ΔLFSE	0	4.8	19	44		0

Macrocycles in Biology

- Various antibiotics are macrocycles:
  Valinomycin binds potassium ions with high selectivity and transports up to 10^4 K^+ ions/sec across a membrane
- In a bacteria cell, the intracellular and extracellular concentration of potassium ion is very different, and this transmembrane concentration gradient is vital to normal cell metabolism
  –> the ionophore equilibrates the potassium ion gradient which results in a breakdown of the cell metabolism and leads ultimately to cell death

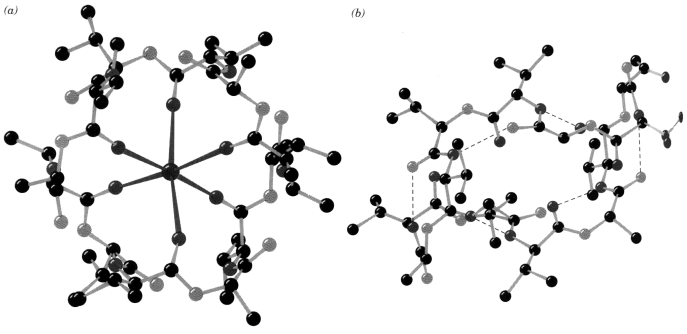
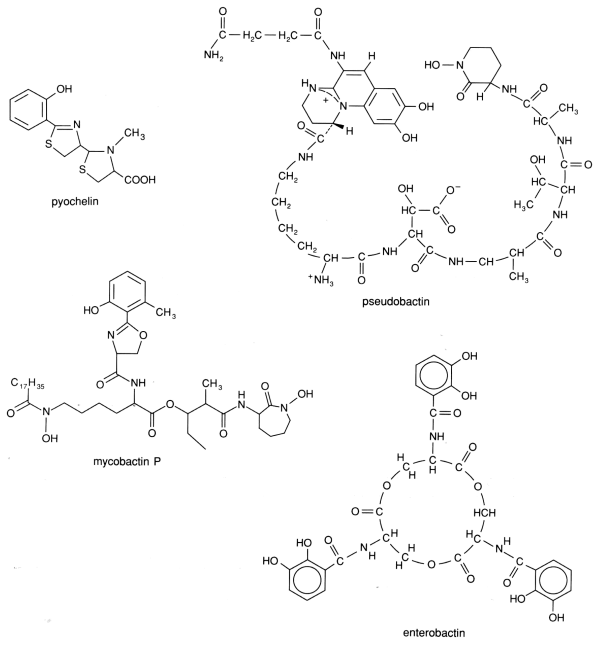


FIGURE 18-8. Valinomycin X-ray structures. (*a*) The K^+ complex. The six oxygen atoms that octahedrally complex the K^+ ion are darker red than the other oxygen atoms. [After Neupert-Laves, K. and Dobler, M., *Helv. Chim. Acta* **58,** 439 (1975).] (*b*) Uncomplexed valinomycin. [After Smith, G.D., Duax, W.L., Langs, D.A., DeTitta, G.T., Edmonds, R.C., Rohrer, D.C., and Weeks, C M., *J. Am. Chem. Soc.* **97,** 7242 (1975).] Hydrogen atoms are not shown.

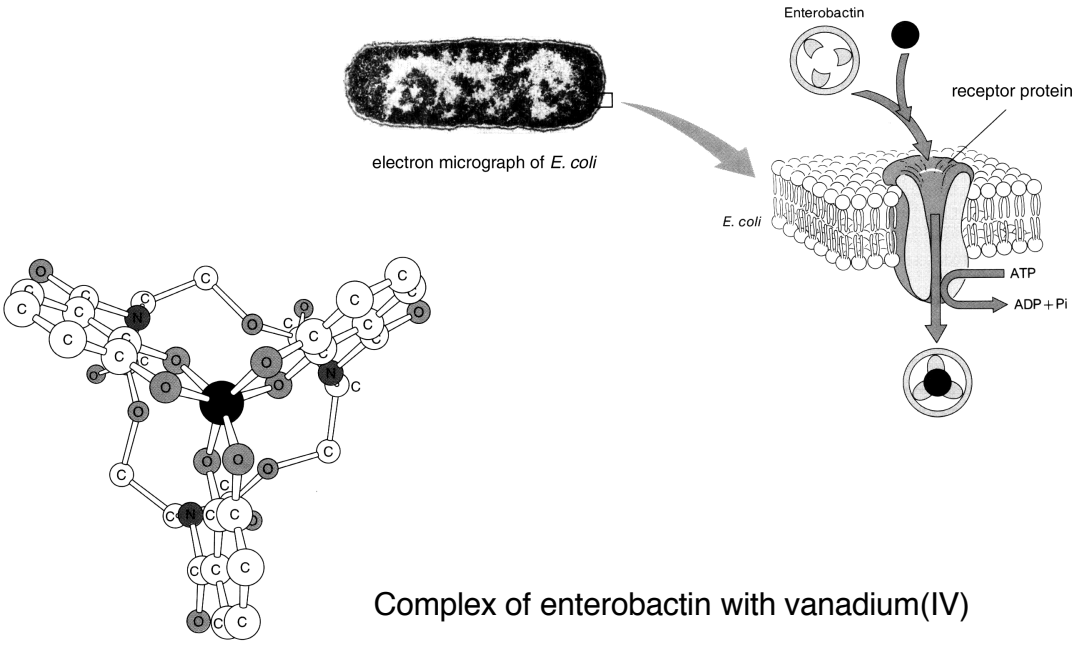
Iron-Siderophores

- Siderophores are polydentate iron-sequestering ligands, which are produced by micro-organisms (bacteria)

  Enterobactin forms with Fe(III) a complex with log $K = 52$!



Iron Uptake with Siderophores



Complex of enterobactin with vanadium(IV)

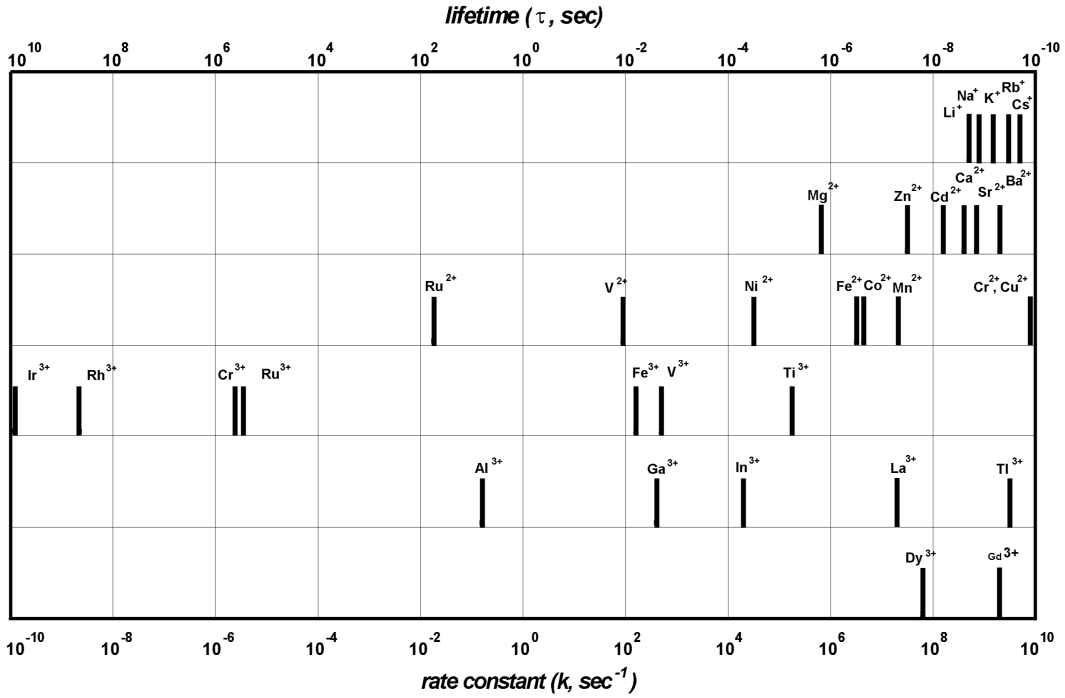
Kinetic Stability of Coordination Compounds

- Ligand exchange reactions offer a good way to examine the kinetic stability of coordination compounds
- Water exchange rates have been determined for a wide range of metal ions (Table):

$$[M(OH_2)_y]^{z+} + n\,H_2{}^{17}O \rightleftharpoons [M(^{17}OH_2)_y]^{z+} + n\,H_2O$$

- Although the absolute rate of exchange will differ for other ligands these values can be used to gauge the relative reactivity of two metal ions or two different oxidation states of the same metal

Water Exchange Rate Constants



Kinetics of Water Exchange

- It is convenient to classify metal ions in four categories based on the measured exchange rates:

Class I: Very fast (diffusion controlled); $k > 10^8\ s^{-1}$
alkali, larger earth alkaline metals: Cd^{2+}, Hg^{2+}, Cr^{2+}, Cu^{2+}

Class II: Rate between $10^4 – 10^8\ s^{-1}$
divalent first-row transition metals (except V^{2+}, Cr^{2+}, Cu^{2+}), Ti^{3+}, Mg^{2+}, trivalent lanthanides

Class III: Rate between $1 – 10^4\ s^{-1}$
Be^{2+}, V^{2+}, Al^{3+}, Ga^{3+}

Class IV: Kinetically inert; rate between $10^{-6} – 10^{-2}\ s^{-1}$
Cr^{3+}, Co^{3+}, Rh^{3+}, Ru^{2+}, Ir^{3+}, Pt^{2+}

Factors Influencing Exchange Rates

- Charge density (Z^2/r) of metal cation: an increase in oxidation state for the metal reduces the rate of exchange (with exceptions)
  e.g. $k(Fe^{2+}) > k(Fe^{3+})$ (both high-spin)

- d-electron configuration:
  e.g. Cr^{2+}, Cu^{2+}: rapid exchange (due to Jahn-Teller distortion)

  Kinetically inert complexes have large ligand field stabilization energy
  e.g. Cr^{3+} (d^3), low-spin Ru^{3+} (d^5), and Rh^{3+}, Ir^{3+}, Ru^{2+} (d^6)

  Reasons:
  a) the ligand substiution requires dissociation or association of a ligand, which results in a large loss of the ligand field stabilization energy
  b) the absence of electrons in the e_g type d-orbitals (aligned with ligand-metal bond axis) strengthens the metal-ligand interactions (in the molecular orbital model the e_g orbitals are antibonding with respect to the metal-ligand interaction!)

Ligand Field Effects

- Change in ligand field stabilization energy upon changing a six-coordinate complex to a five-coordinate or seven coordinate species:

	High spin		Low spin	
System	C.N. = 5	C.N. = 7	C.N. = 5	C.N. = 7
d^0	0	0	0	0
d^1	+0.57	+1.28	+0.57	+1.28
d^2	+1.14	+2.56	+1.14	+2.56
d^3	−2.00	−4.26	−2.00	−4.26
d^4	+3.14	−1.07	−1.43	−2.98
d^5	0	0	−0.86	−1.70
d^6	+0.57	+1.28	−4.00	−8.52
d^7	+1.14	+2.56	+1.14	−5.34
d^8	−2.00	−4.26	−2.00	−4.26
d^9	+3.14	−1.07	+3.14	−1.07
d^{10}	0	0	0	0

[a] Units are Dq or $\Delta/10$. Negative quantities refer to *loss* of LFSE and destabilization of the complex.

[b] Modified from Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967.

Problem 6-8: Which of the following complexes do you expect to be kinetically inert?

a) $Co(NH_3)_4^{2+}$ b) $Zn(CN)_4^{2-}$ c) $Fe(CN)_6^{4-}$ d) $Ti(H_2O)_6^{3+}$

Problem 6-9: The aquation rate (substitution with water) of Ru(III) chloro complexes vary enormously: The complex $[RuCl_6]^{3-}$ has a half lifetime of a few seconds, whereas the half lifetime of $[RuCl(H_2O)_5]^{2+}$ was measured to be about one year. How do you explain this observation? Which mechanism does the reaction presumably follow?

Mechanisms for Substitution Reactions

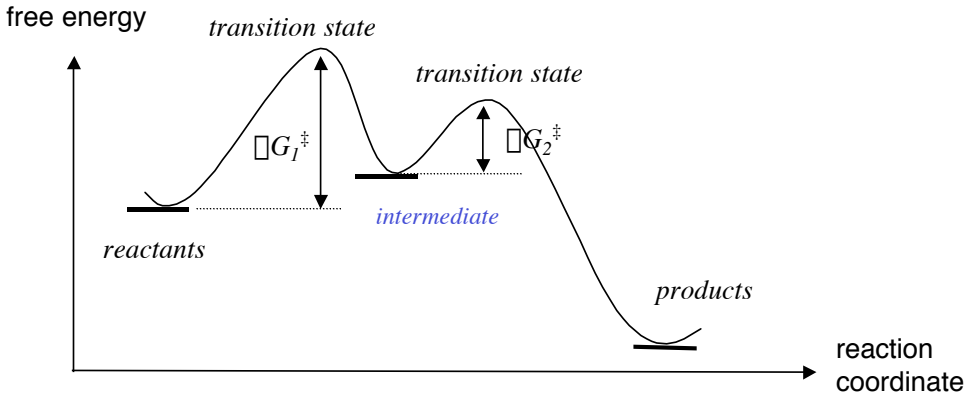
If rate determining step is:

a) breaking bond of leaving group –> dissociative mechanism (D)
(this mechanism corresponds to the S_N1 reaction in organic chemistry)

b) making bond of entering group –> associative mechanism (A)
(this mechanism corresponds to the S_N2 reaction in organic chemistry)

Note: A and D mechanisms are the two limiting cases, reactions often show a mechanism which is somewhere in between

- Both, dissociative and associative reaction mechanisms involve two-step pathways and an intermediate:



Dissociative Mechanism (D):

$ML_5X \longrightarrow ML_5 + X$

intermediate

$ML_5 + Y \longrightarrow ML_5Y$

Associative Mechanism (A):

$ML_5X + Y \longrightarrow ML_5XY$

intermediate

$ML_5XY \longrightarrow ML_5Y + X$

Dissociative Mechanism

$[Co(NH_3)_5(H_2O)]^{3+} + X^-$

X^-	$k(M^{-1}s^{-1})$
NCS^-	1.3×10^{-6}
$H_2PO_4^-$	2.0×10^{-6}
Cl^-	2.1×10^{-6}
NO_3^-	2.3×10^{-6}
SO_4^{2-}	1.5×10^{-5}

There is only little dependence of reaction rates on the nature of the incoming ligand (if bond making were of significant importance, the opposite would be expected!)

$[Co(NH_3)_5X]^{m+} + H_2O$

X^-	$k(M^{-1}s^{-1})$
NCS^-	5.0×10^{-10}
$H_2PO_4^-$	2.6×10^{-7}
Cl^-	1.7×10^{-6}
NO_3^-	2.7×10^{-5}
SO_4^{2-}	1.2×10^{-6}

Since bond breaking is of importance, the reaction rates depend on the nature of the M–X bond being broken

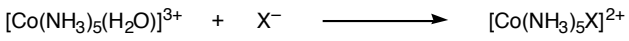
Associative Mechanism

$[Ti(H_2O)_6]^{3+} + Y^- \longrightarrow Ti(H_2O)_5Y]^{2+} + H_2O$

Y^-	$k(M^{-1}s^{-1})$
NCS^-	8.3×10^3
$ClCH_2CO_2^-$	2.1×10^5
$CH_3CO_2^-$	1.8×10^6

In order for the entering ligand to bond to the metal there must be a vacant (preferably) or partially vacant orbital that is accessible to the entering ligand
–> in an octahedral complex, only the t_{2g} orbitals are accessible (the e_g orbitals and the n+1 s and p orbitals are blocked by the presence of the already coordinated six ligands)
–> associative processes are more likely for larger metal ions (2nd and 3rd row TM, and more important for metals early in the transition series)

Problem 6-10: Consider the following substitution reaction:



X^-	k $[M^{-1}s^{-1}]$
NCS^-	$1.3 \cdot 10^{-6}$
$H_2PO_4^-$	$2.0 \cdot 10^{-6}$
Cl^-	$2.1 \cdot 10^{-6}$
NO_3^-	$2.3 \cdot 10^{-6}$

a) Assign a mechanism (associative/dissociative) based on the measured rate constants and briefly justify your choice.

b) Would you expect an increase or decrease of the rate constants for the analogous substitution reactions with $[Co(NH_3)_5(H_2O)]^{2+}$?