Chemistry and Spectroscopy of the Transition Metals

- Structure of metal complexes
- Oxidation states of metals
- Color/Spectroscopy
- Magnetic Properties
- Chelate Effects
- Electron Transfer Chemistry

Nobel Prize in Chemistry, 1913

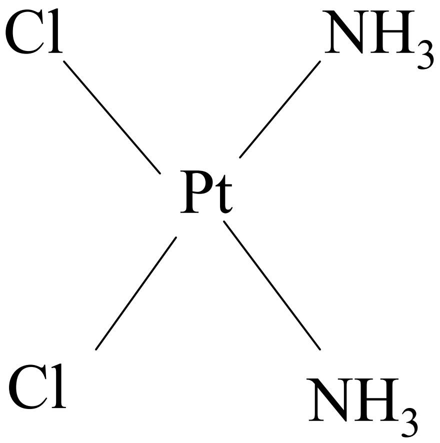
Alfred Werner

"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry”

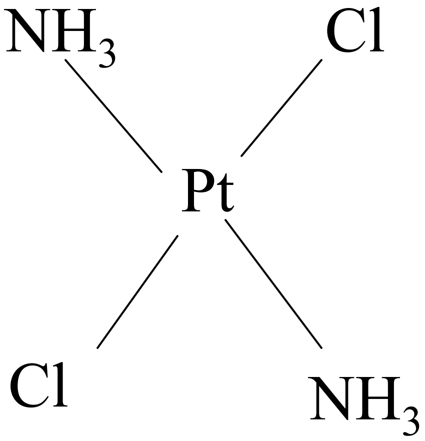
Zurich University

Stereochemistry of Coordination Complexes

$Pt(NH_3)_2Cl_2$



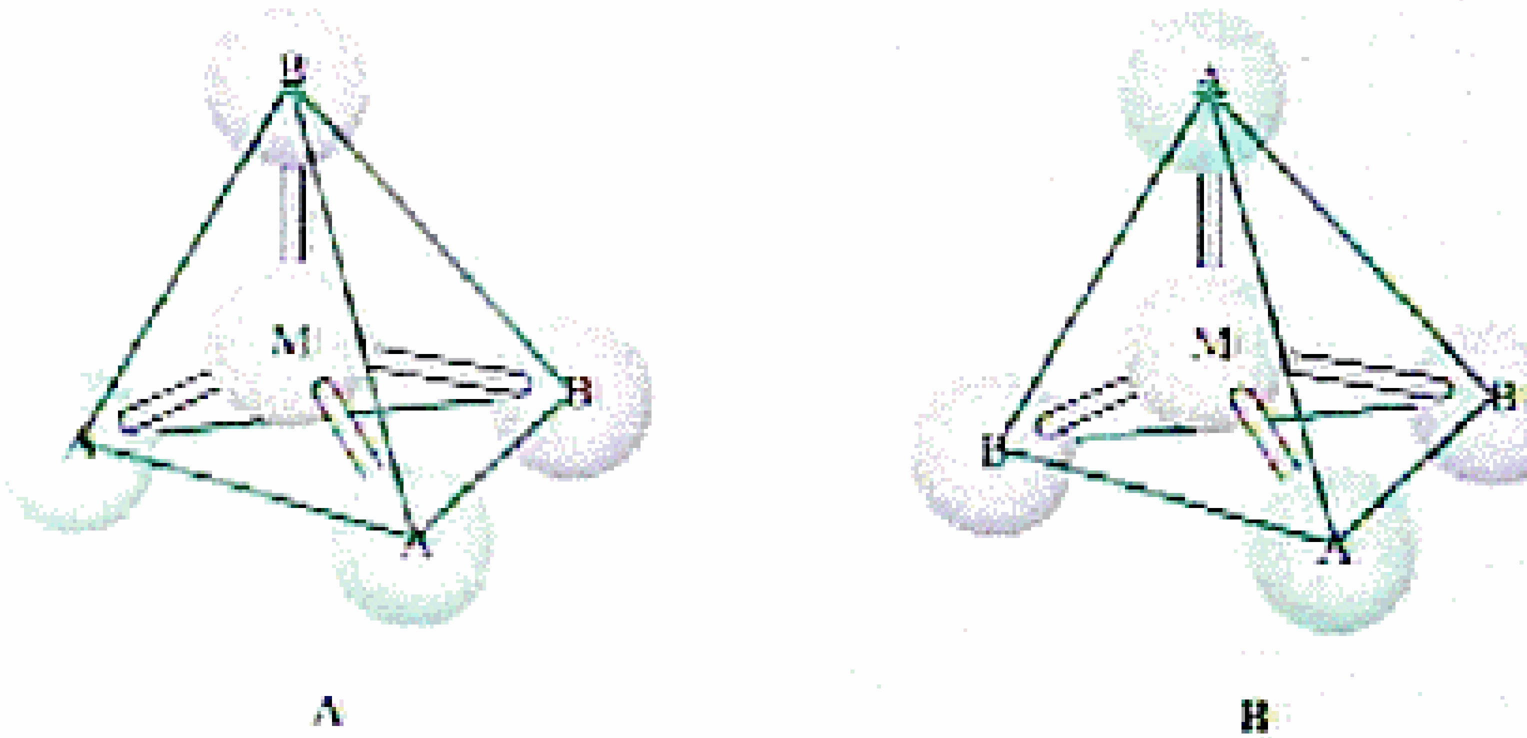
Orange-Yellow
(dipole moment)
(cis-platin)



Pale Yellow
No dipole

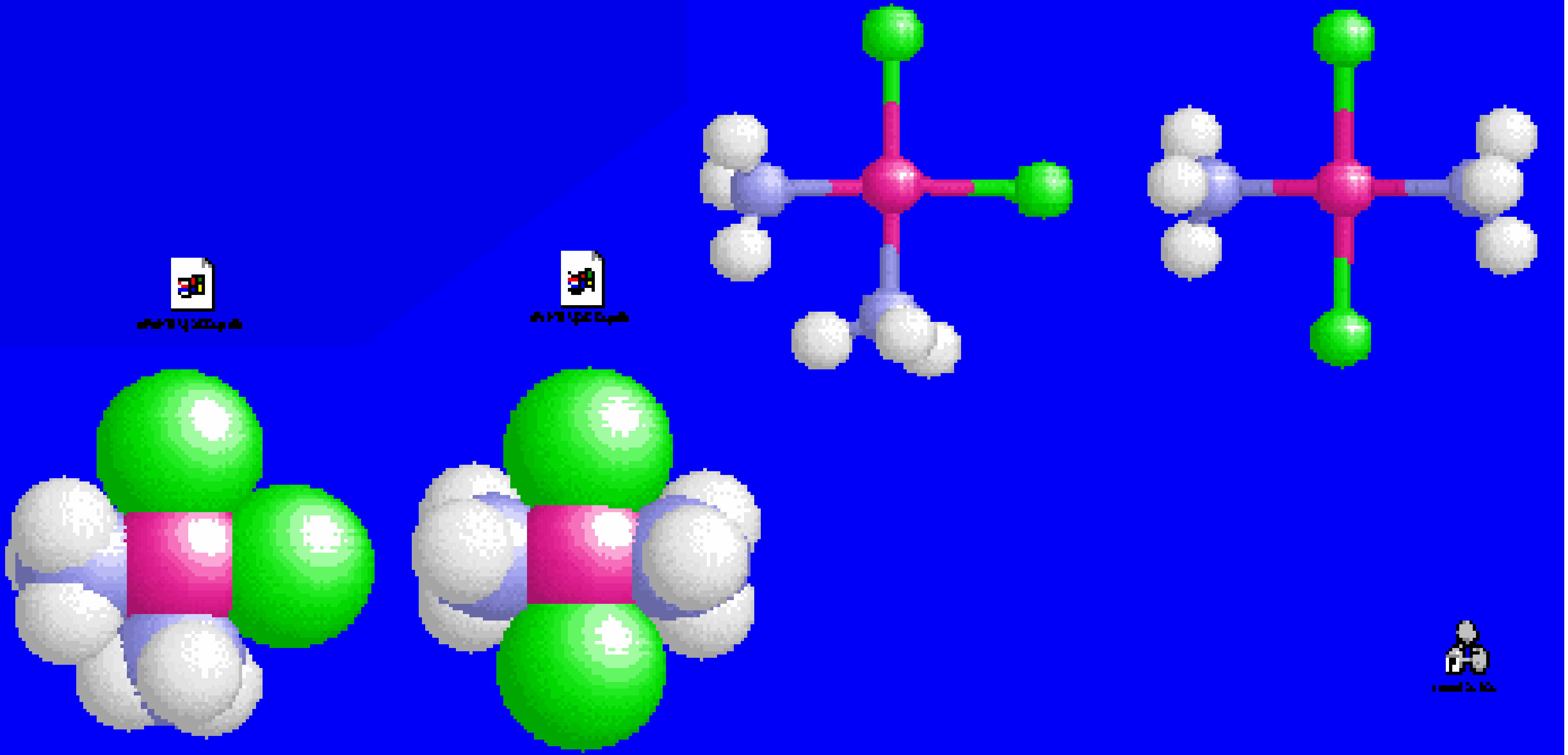
Tetrahedral MA_2B_2

- Does MA_2B_2 have optical isomers?



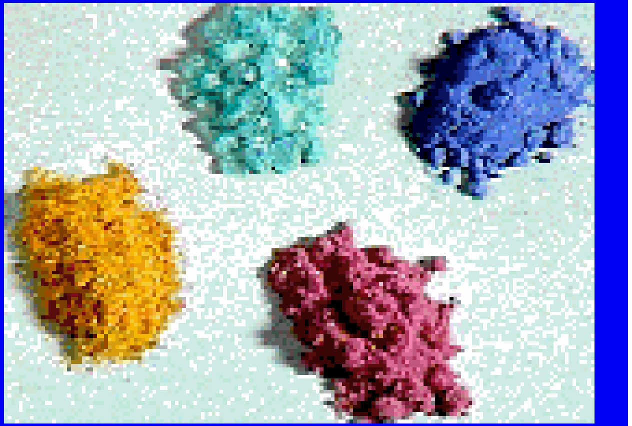
Square Planar Complexes

- $[Pt(NH_3)_2Cl_2]$ exists as cis and trans isomers



Chemistry of Coordination Compounds

- Transition metal compounds (demo samples)
  - variable oxidation number
  - colored
  - unusual composition
  - often contain covalent compounds bonded to the metal
    - hydrates
  - Lewis acid-base adduct
  - coordinate covalent bonds
  - unusual magnetic properties



The Structure of Complexes

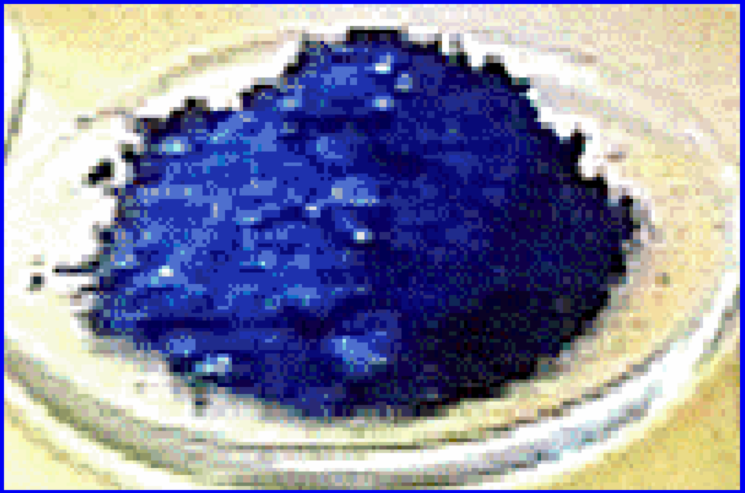
- Contain coordinate covalent bonds
- Unusual composition: Central metal ion or atom + ligands + counter ion (if needed)
- Called complex ion if charged
- $[Cu(NH_3)_4]SO_4{\cdot}H_2O$

hydrate

anion

ligands

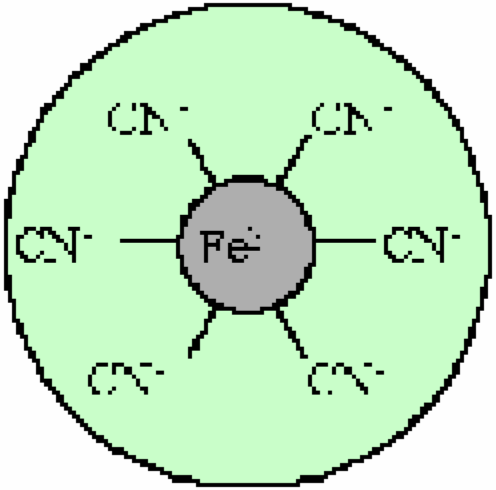
central metal ion



Coordination Sphere

- Nature of coordination compounds is determined by both the oxidation number of the central ion and its coordination number.
- The coordination number is (mostly) constant for a metal with a given oxidation number.
- First coordination sphere: central metal ion and its ligands

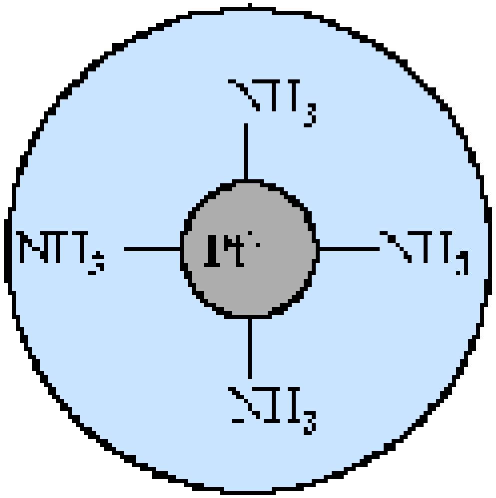
First Coordination Sphere



A. $[Fe(CN)_6]^{3-}$

coordination
number = 6

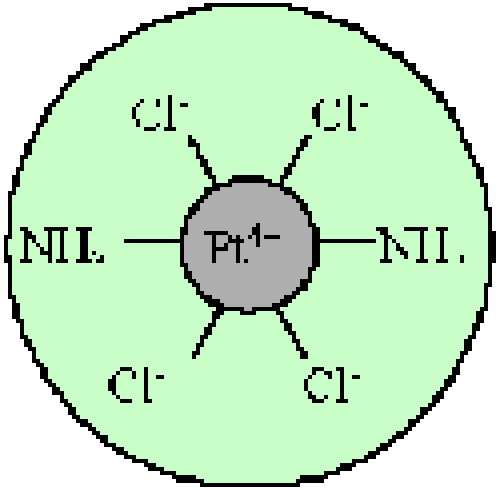
Fe(CN)6-3.pdb



B. $[Pt(NH_3)_4]^{2+}$

coordination
number = 4

Pt4.pdb



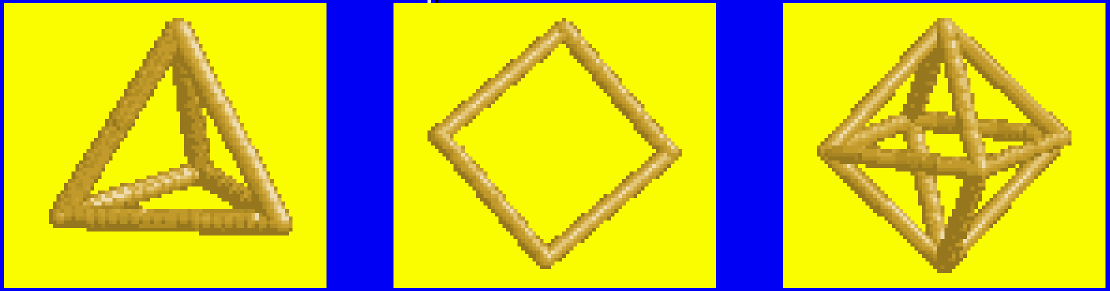
C. $[Pt(NH_3)_2Cl_4]$

coordination
number = 6

Tptcl2.pdb

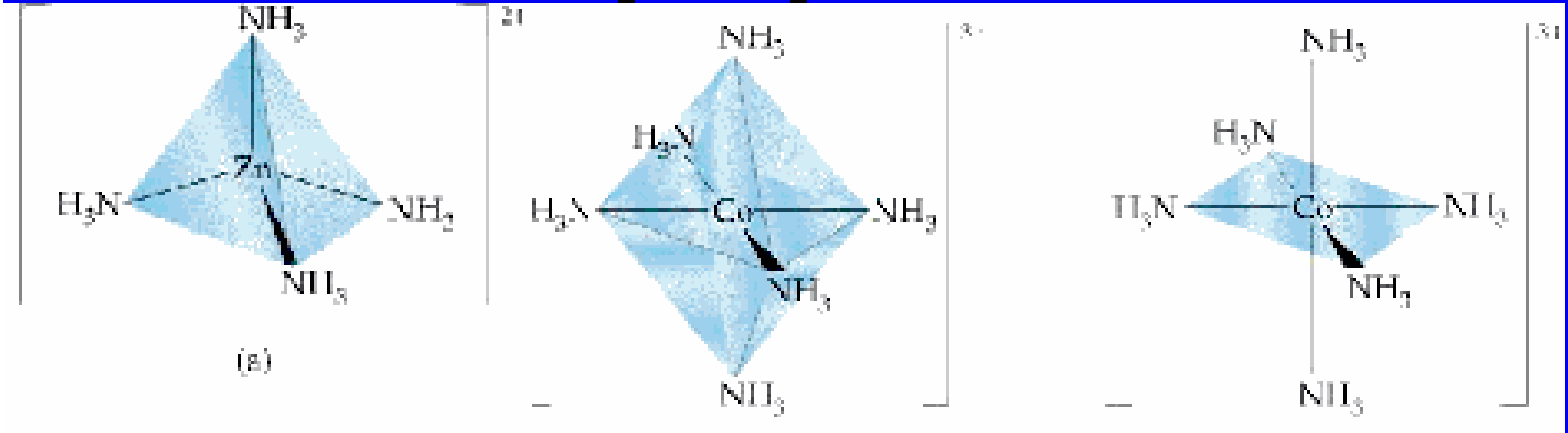
First Coordination Sphere

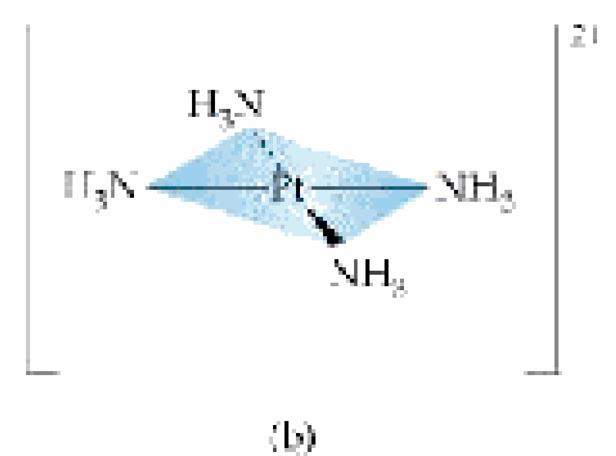
- Coordination number is often 2 x oxidation number (many exceptions)
- Mostly predictable geometry:
  - Coordination number = 2, linear
  - Coordination number = 4, square planar or tetrahedral
  - Coordination number = 6, octahedral



Complex Ion Geometry

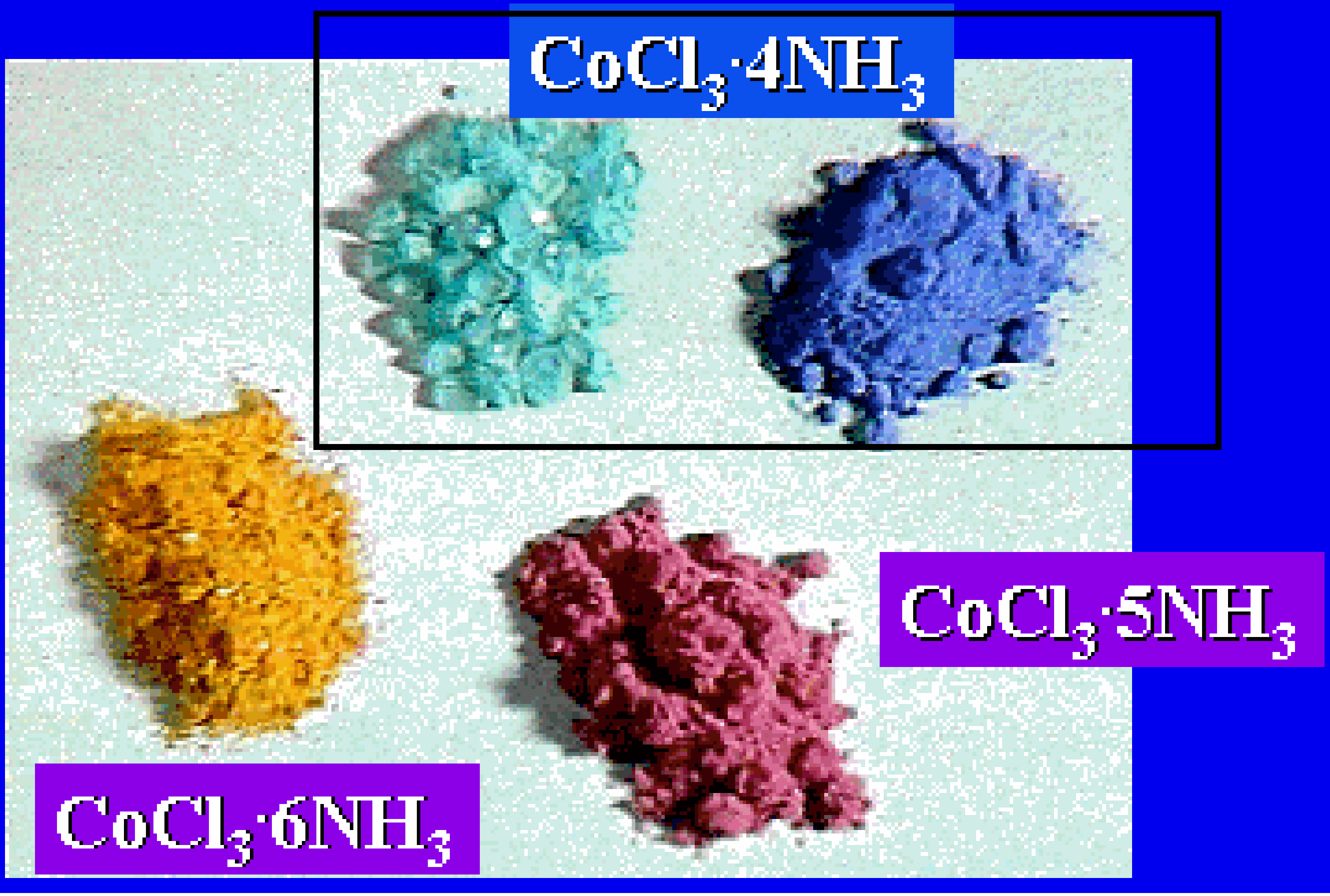
- Tetrahedral, square planar, octahedral





$CoCl_3 \cdot nNH_3$

- Consider $CoCl_3 \cdot nNH_3$, with n = 4, 5, 6



$CoCl_3 \cdot nNH_3$

- How can we have compounds with these various compositions?
- Dissolve in water and add $AgNO_3$. Some Cl^- precipitates as AgCl immediately, some much more slowly. This indicates the relative number of Cl^- that are ionic or covalent.

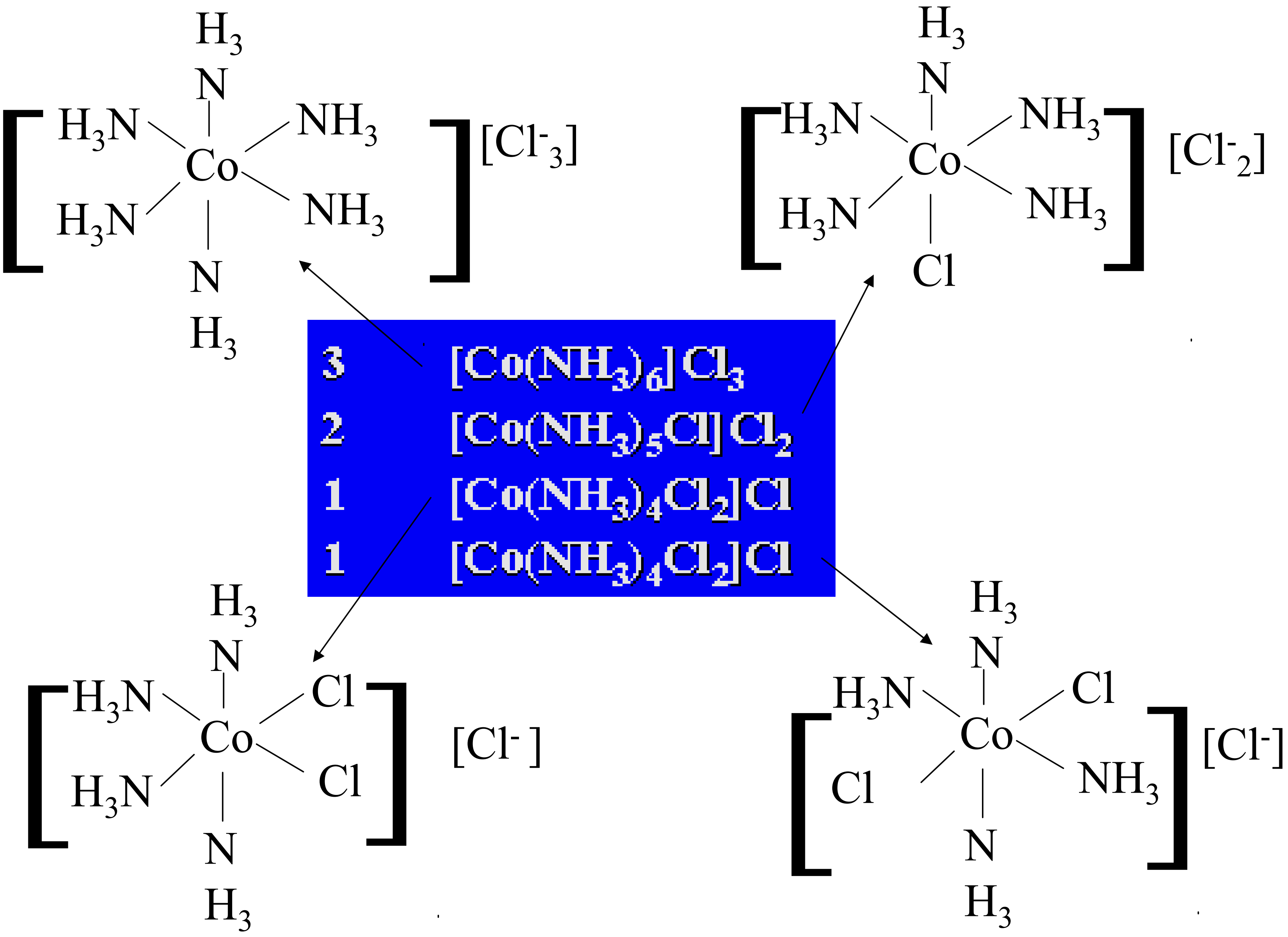
n = 4 n = 5 n = 6

$CoCl_3 \cdot nNH_3$

Composition	Color	No. Cl^- pptd	Formula
$CoCl_3 \cdot 6NH_3$	yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	green	1	$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4NH_3$	violet	1	$[Co(NH_3)_4Cl_2]Cl$

- The green and violet compounds must have some further difference.
- All have 6 ligands (coordination number = 6)

Inner Sphere vs Outer Sphere Coordination



3	$[Co(NH_3)_6]Cl_3$
2	$[Co(NH_3)_5Cl]Cl_2$
1	$[Co(NH_3)_4Cl_2]Cl$
1	$[Co(NH_3)_4Cl_2]Cl$

Transition Metal Chemistry

- Multiple Oxidation States
- Coordination Chemistry/Stereochemistry
- Crystal Field Splitting: Optical and Magnetic Properties
- Ligand Field Splitting: Spectrochemical Series
- Distortion to Tetragonal, Square Planar
- Ligand Field Stabilization Energy
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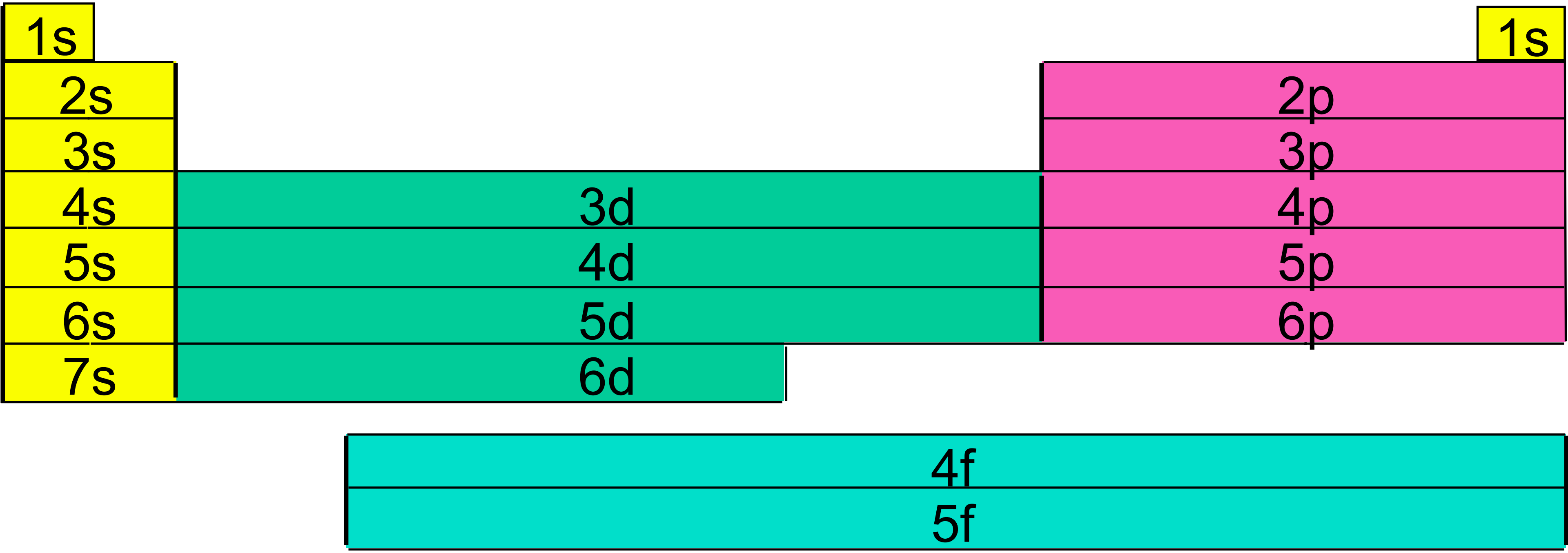
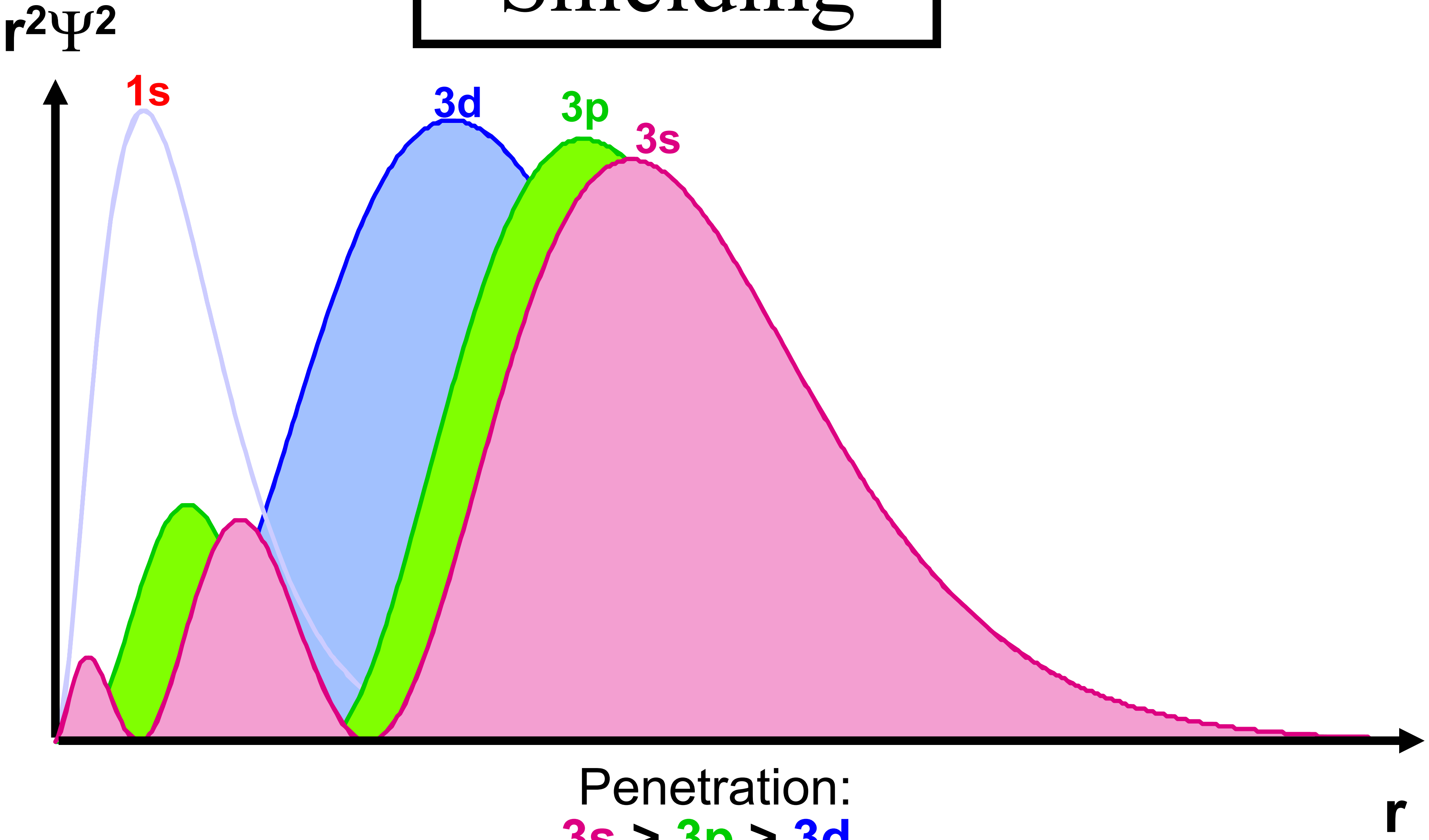
- Water Exchange
- Electron Exchange

Organization of Periodic Chart



1s 1s
2s 2p
3s 3p
4s 3d 4p
5s 4d 5p
6s 5d 6p
7s 6d
4f
5f

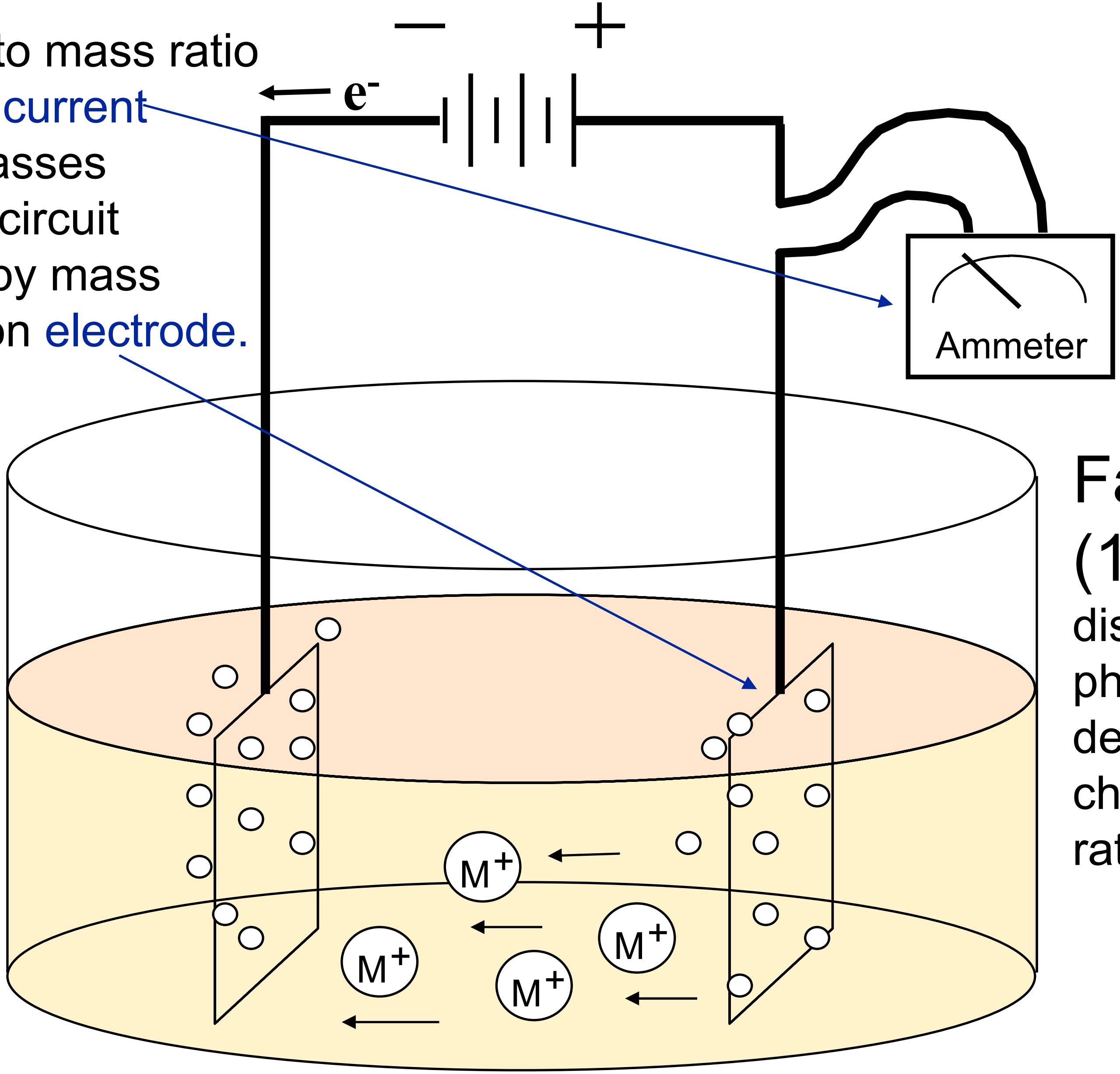
Shielding



Penetration:
3s > 3p > 3d

3d orbitals are shielded and not exposed much;
Outside world won't know as much how many d e^- there are

Transition Metals Are Found in Several Oxidation States

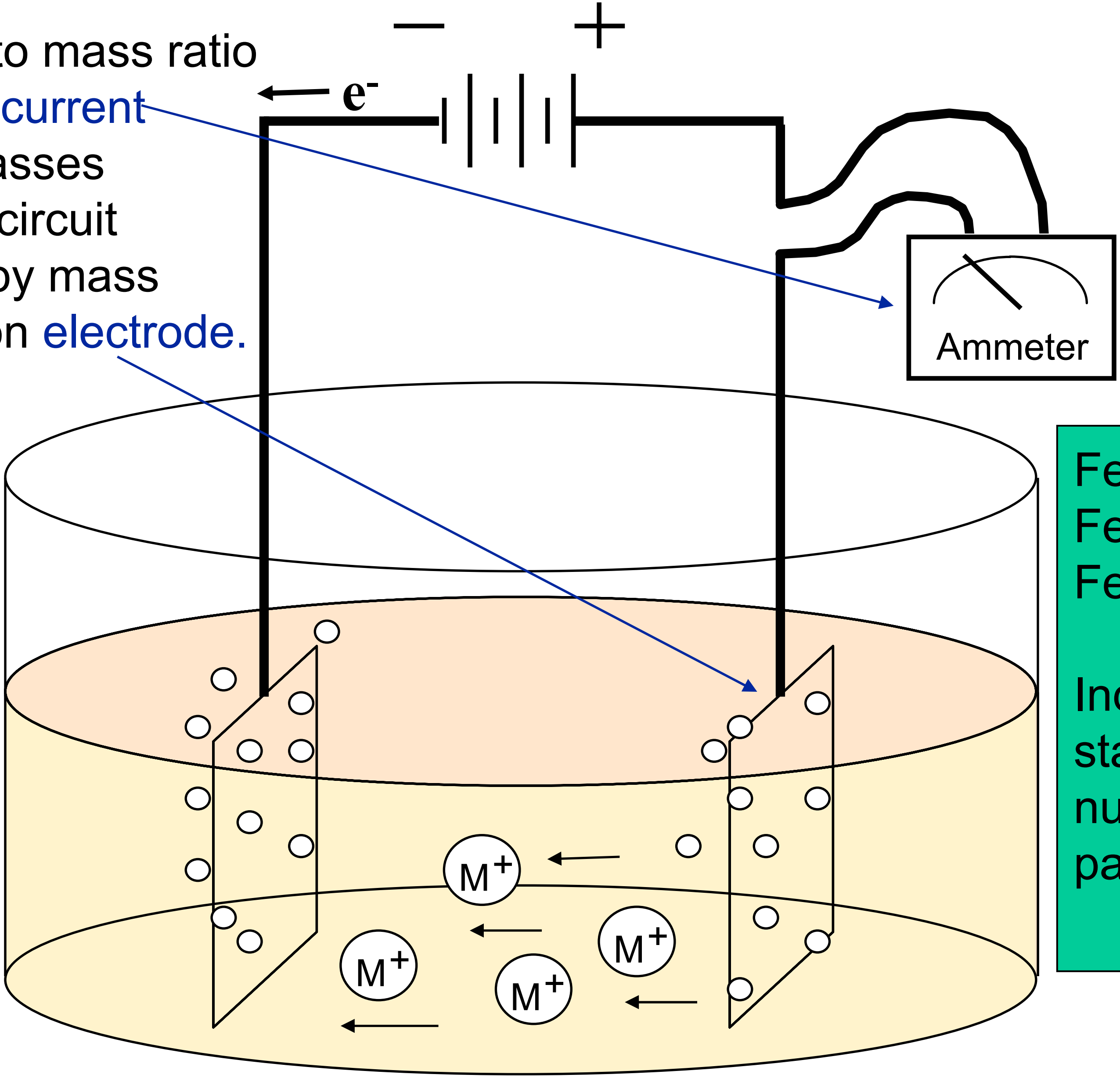


Charge to mass ratio of ions: current which passes through circuit divided by mass gained on electrode.

Faraday (1830):

discovered this phenomenon and determined the charge to mass ratio of ions

Transition Metals Are Found in Several Oxidation States



Charge to mass ratio of ions: current which passes through circuit divided by mass gained on electrode.

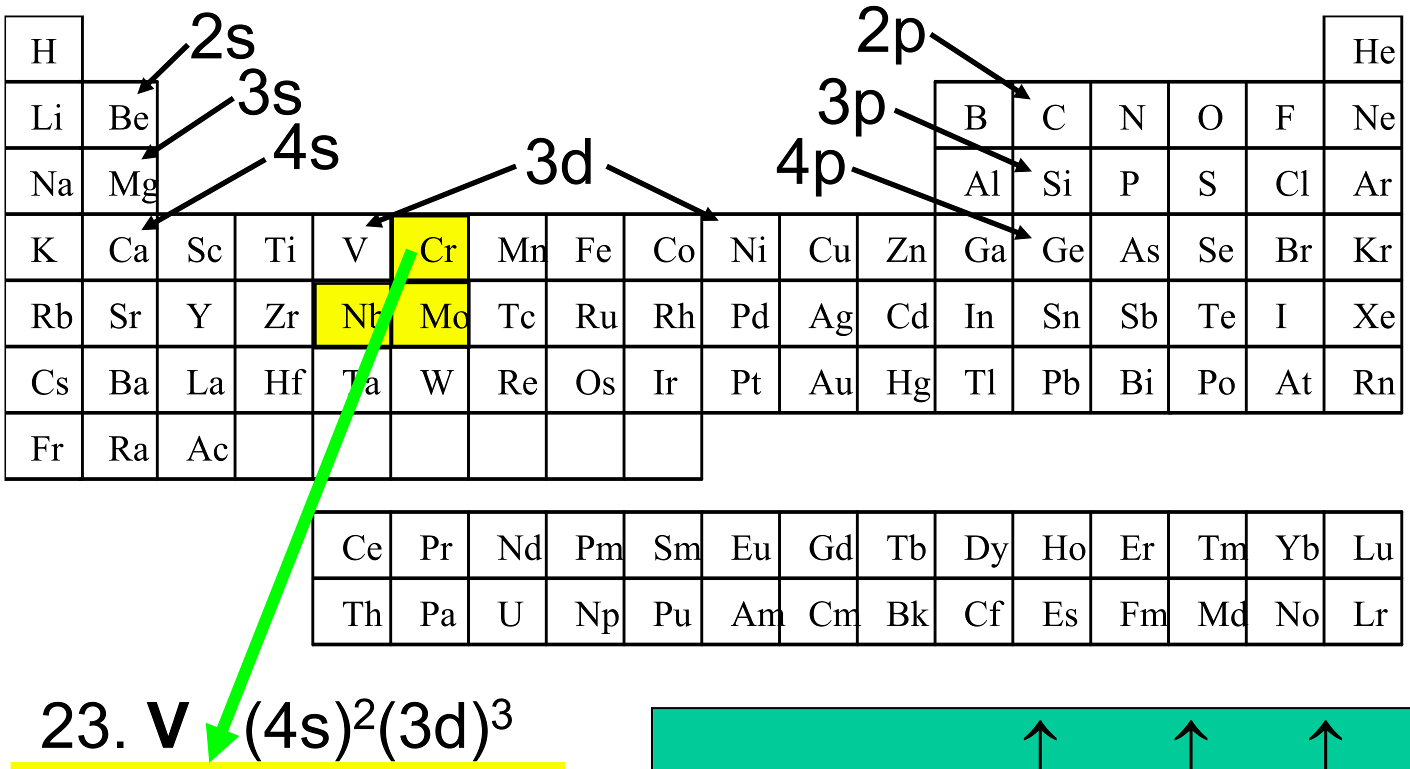
Fe(II)
Fe(III)
Fe(IV)

Indicate oxidation state by Roman numerals in parentheses

Oxidation States of 4th Period Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

Exceptions to Filling Order

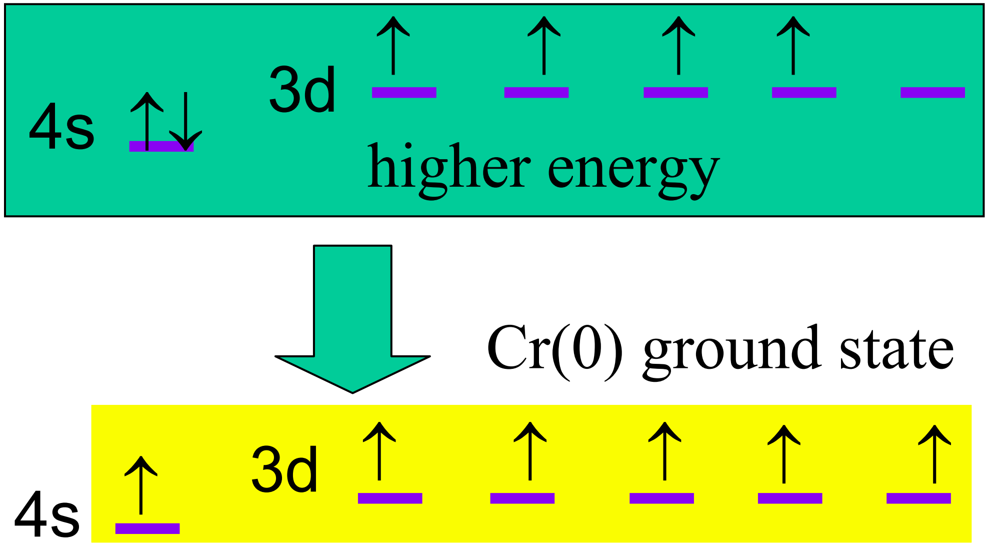


H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

23. **V** $(4s)^2(3d)^3$

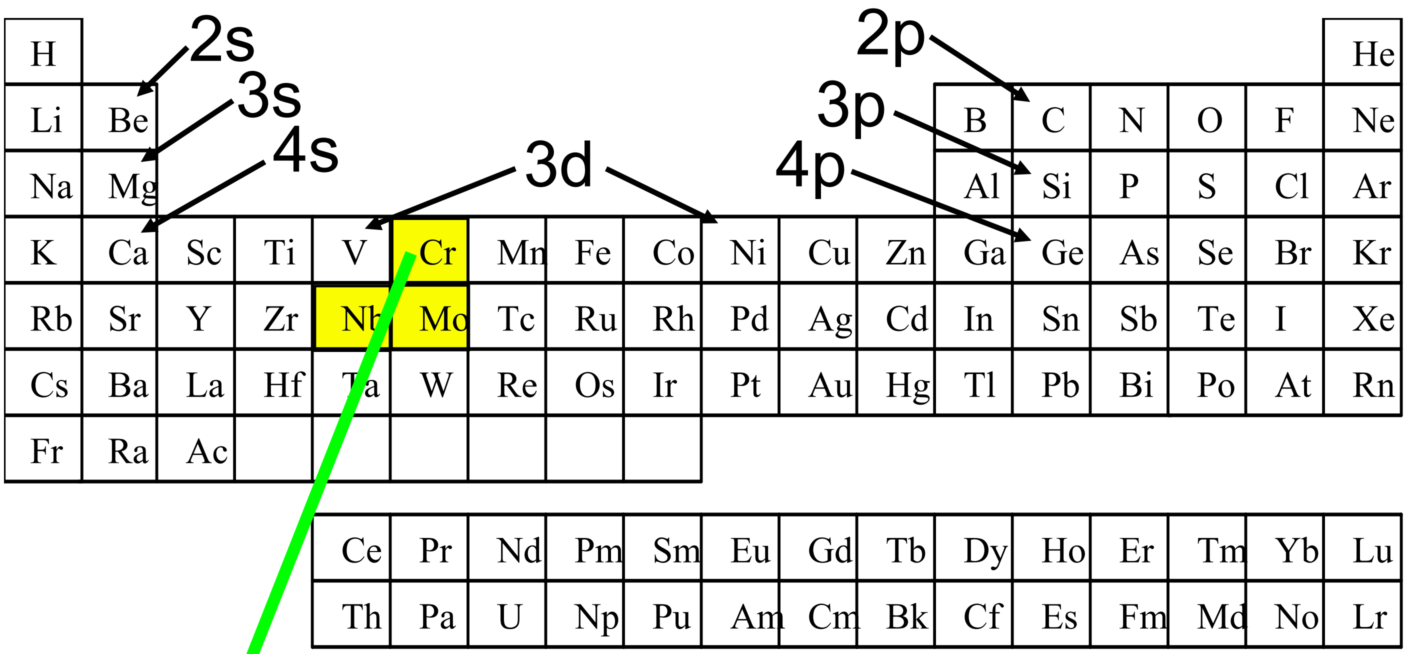
24. **Cr** $(4s)^1(3d)^5$

25. **Mn** $(4s)^2(3d)^5$



Exceptions occur because electrons don’t like to pair up in orbitals; so the highlighted atoms have lower energy.

All Metal Ions Have d^n Configurations



23. **V** $(4s)^2(3d)^3$

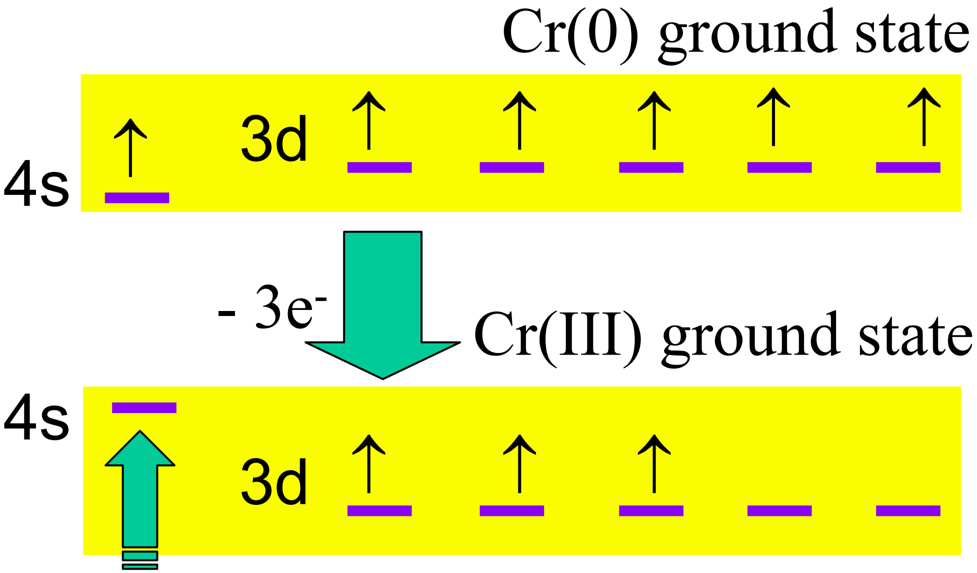
24. **Cr** $(4s)^1(3d)^5$

25. **Mn** $(4s)^2(3d)^5$

Cr(III) $(4s)^1(3d)^2$?

NO: $(3d)^3\,(4s)^0$

4s becomes higher than 3d in all of the metal ions



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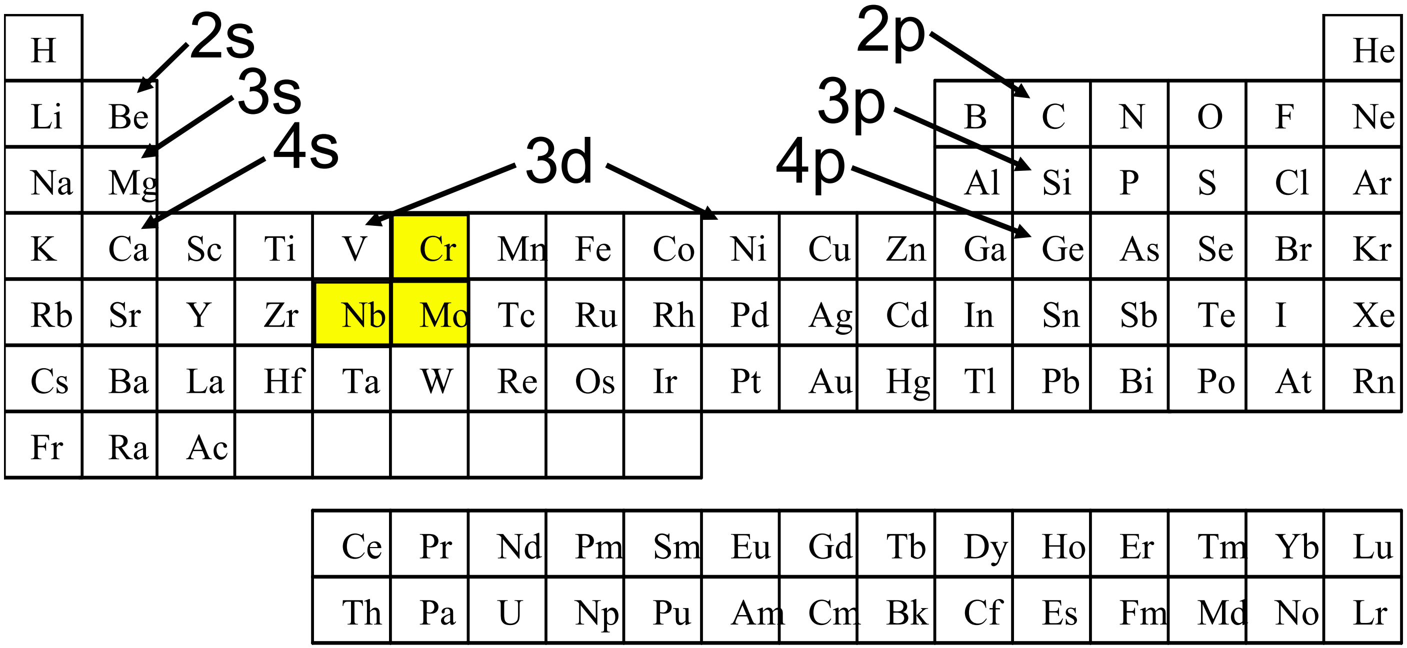
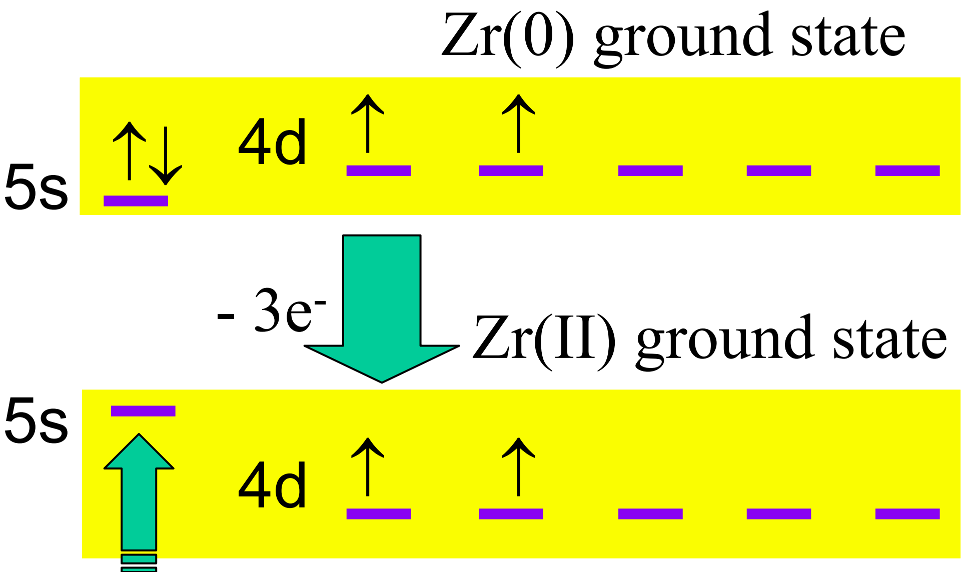


H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

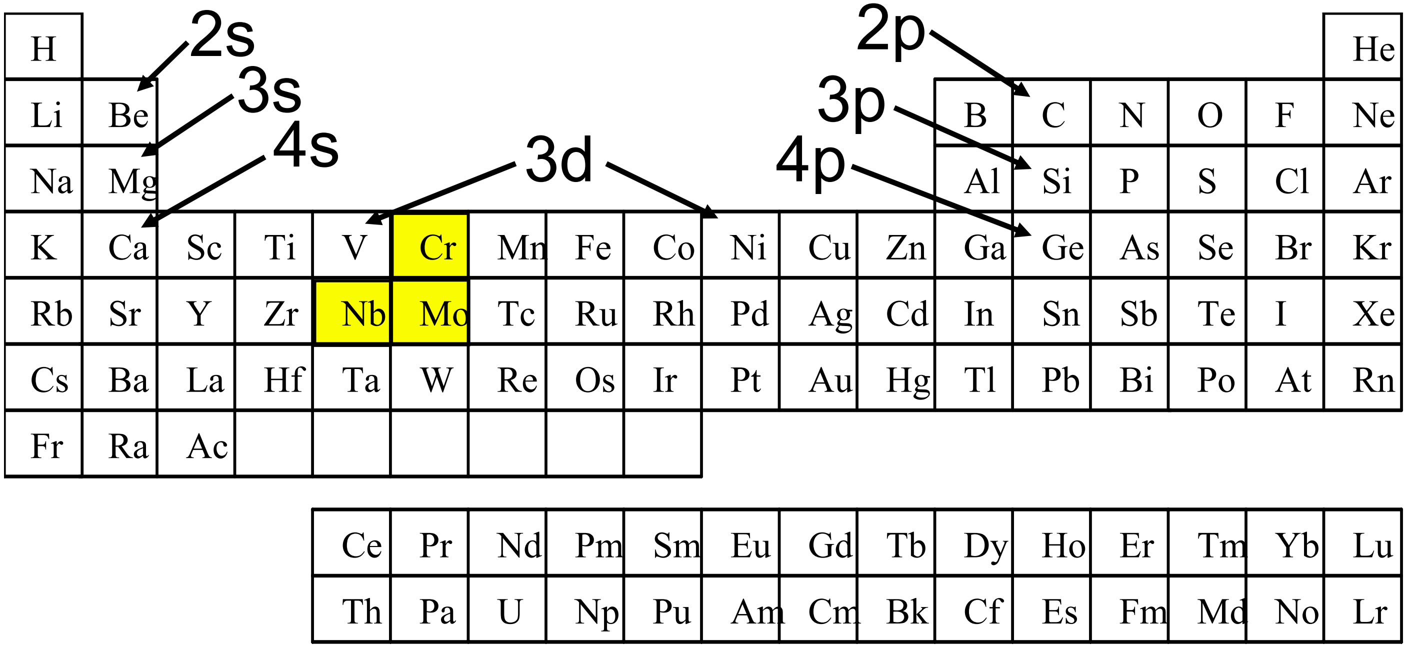
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

40. **Zr** $(5s)^2(4d)^2$
41. **Nb** $(5s)^1(4d)^4$
42. **Mo** $(5s)^1(4d)^5$

Zr(II) $(4d)^2 (5s)^0$



All Metal Ions Have d^n Configurations



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

40. **Zr** $(5s)^2(4d)^2$
41. **Nb** $(5s)^1(4d)^4$
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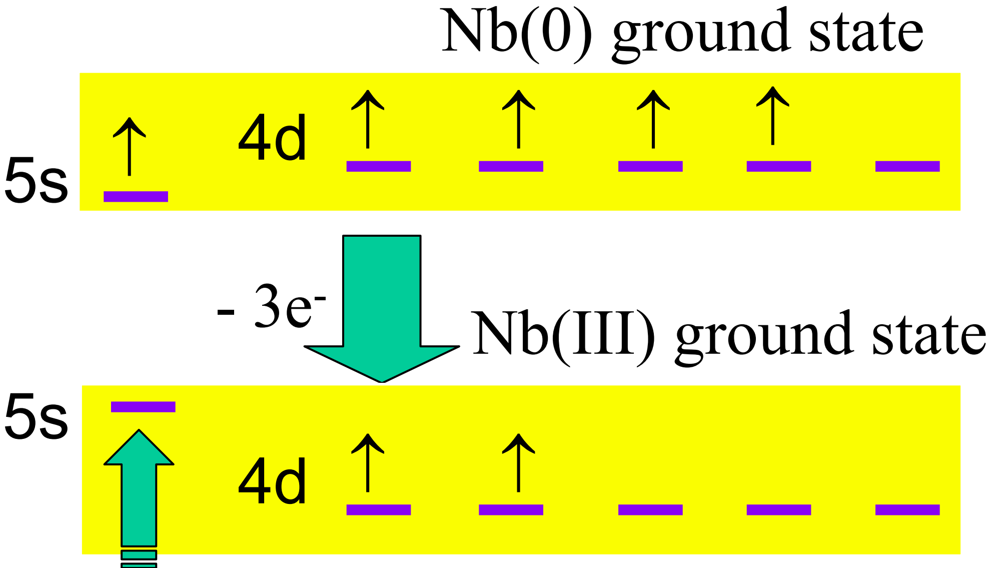
Zr(II) $(4d)^2\,(5s)^0$
Nb(III) $(4d)^2\,(5s)^0$
Mo(IV) $(4d)^2(5s)^0$



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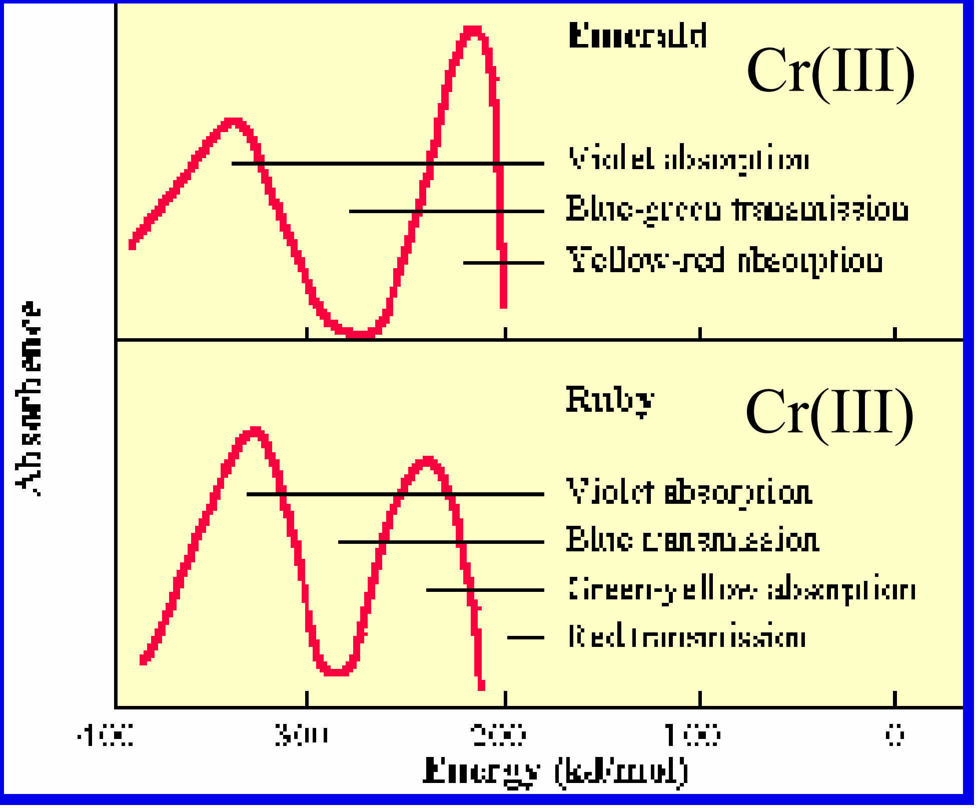
Color

- Differences in color are reflected in differences in electronic spectra



Reactions of Coordination Complexes

$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6\ H_2O$ Ni(II) d^8

Green Blue-violet

$Fe(H_2O)_6^{2+} + 6\ K(CN) \longrightarrow K_4[Fe(CN)_6]^{4-} + 6\ H_2O$ Fe(II) d^6

$Fe(H_2O)_6^{3+} + 6\ K(CN) \longrightarrow K_4[Fe(CN)_6]^{3-} + 6\ H_2O + 2\ K^+$ Fe(III) d^5

$Cu(H_2O)_4^{2+} + 4\ KCl \longrightarrow K_2[CuCl_4]^{2-} + 4\ H_2O + 2\ K^+$ Cu(II) d^9

Oxidation state stays the same
Colors are very different

Color

- A variety of colors is observed for a given metal ion with different ligands.

$[Co(NH_3)_4Cl_2]^+$

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

$[Co(NH_3)_5Cl]^{2+}$

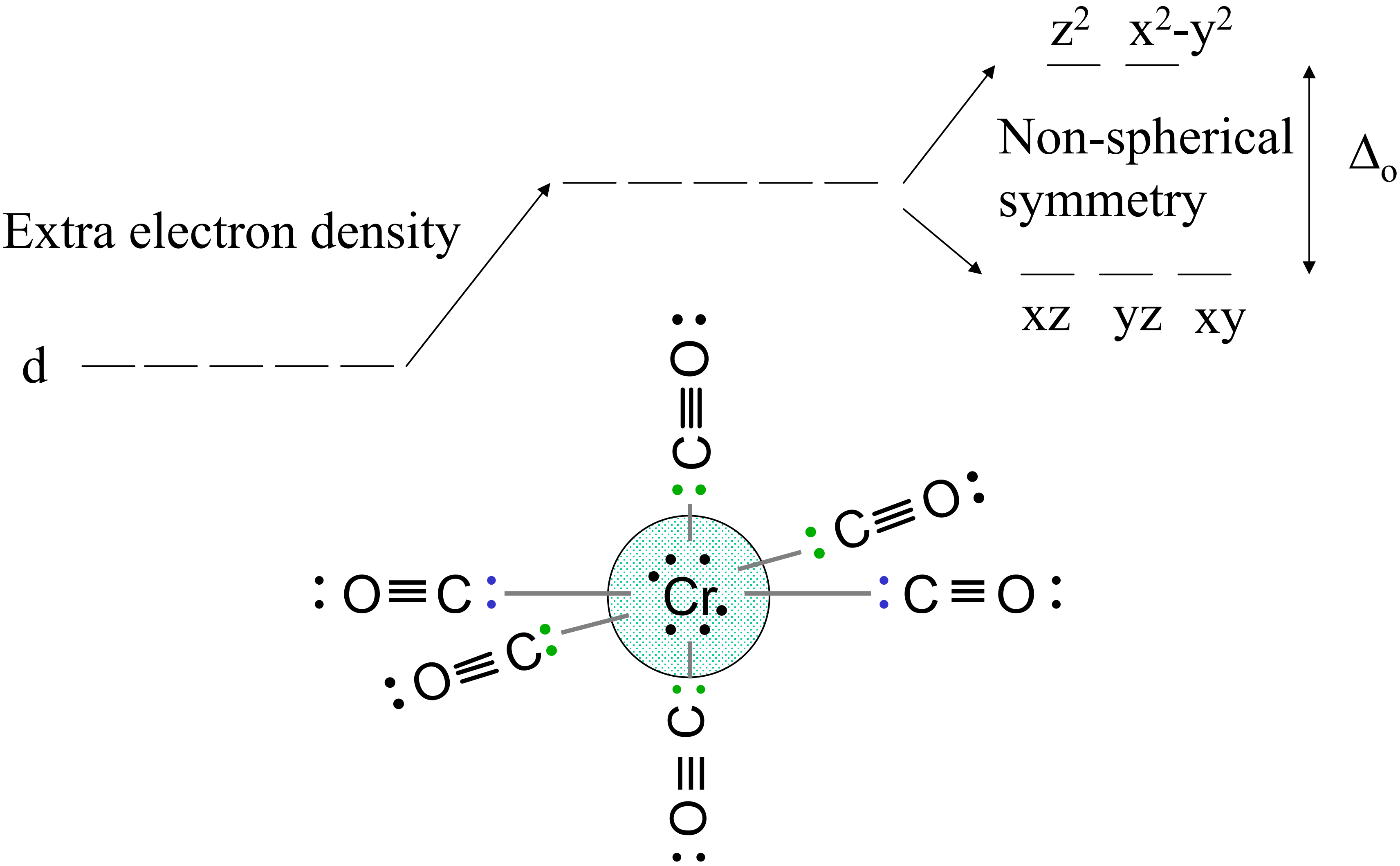
Nobel Prize in Physics, 1966

Hans Bethe, Cornell

Discovery of the C/N cycle that supplies energy to brilliant stars, 1935-1938
Atomic physics and collision theory
Nuclear forces acting on the nucleon
Lamb shift in the H-spectrum; modern quantum electrodynamics
Π mesons and their production by electromagnetic radiation
Crystal Field theory: 1929

Crystal Field Splitting

Octahedral Complexes



Extra electron density

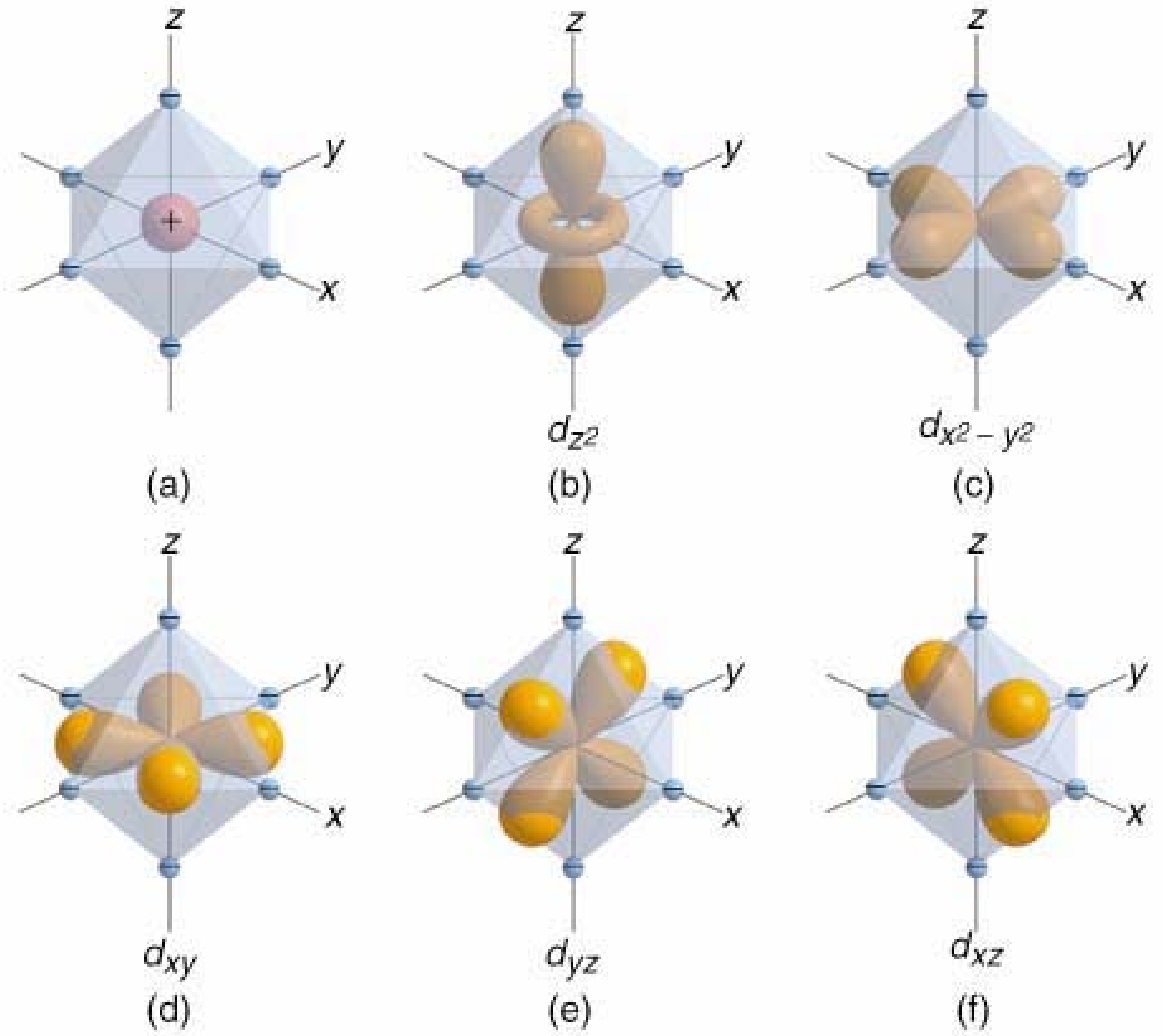
d

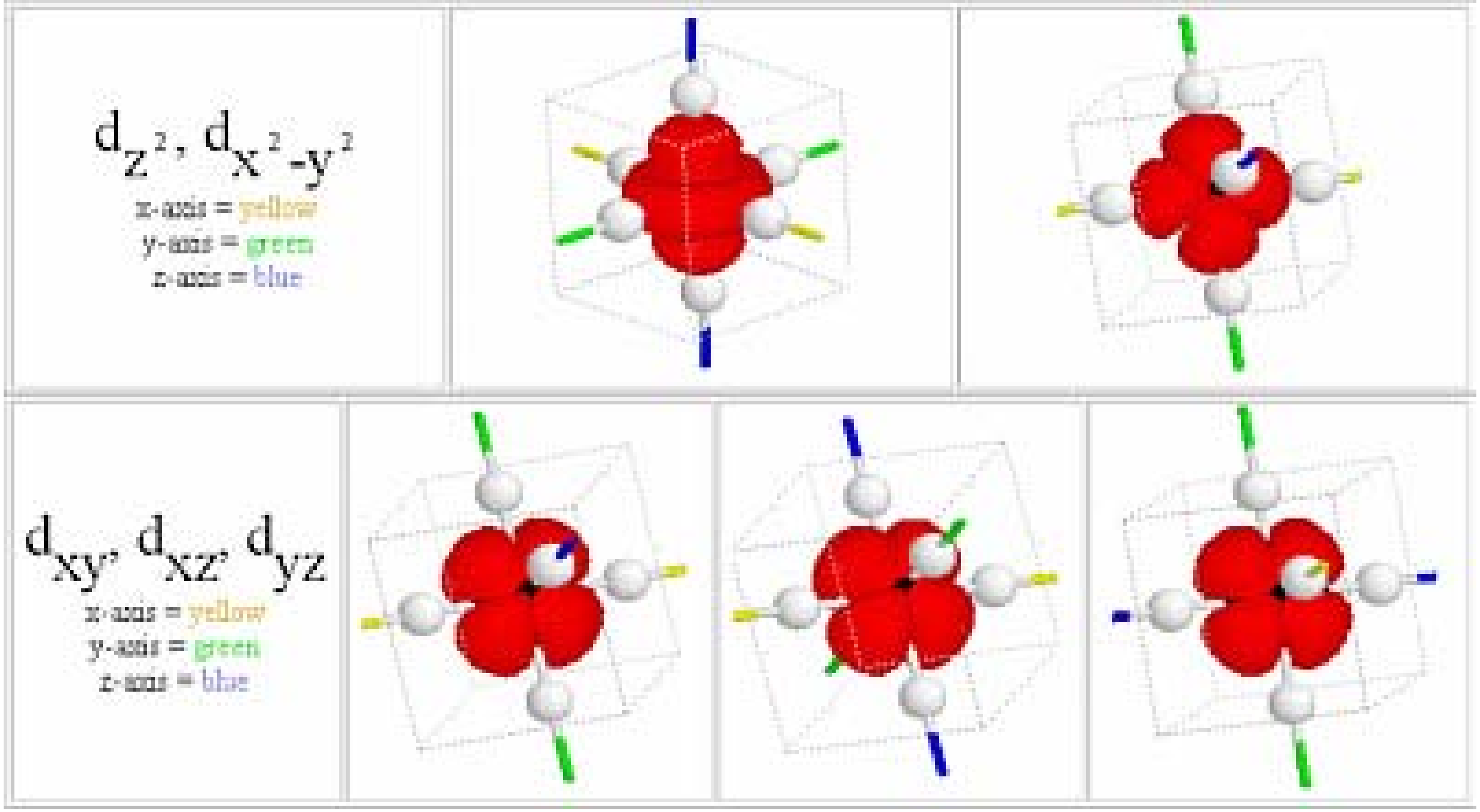
z^2 x^2-y^2

Non-spherical symmetry

Δ_o

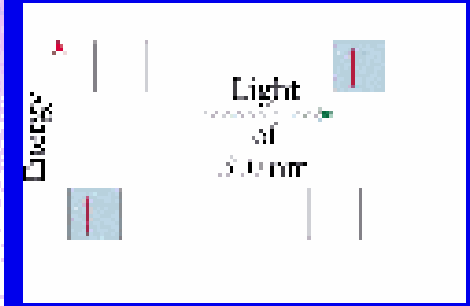
xz yz xy


z
y
x
+
(a)
d_{z^2}
(b)
$d_{x^2-y^2}$
(c)
d_{xy}
(d)
d_{yz}
(e)
d_{xz}
(f)


d_{z^2}, $d_{x^2-y^2}$
x-axis = yellow
y-axis = green
z-axis = blue
d_{xy}, d_{xz}, d_{yz}
x-axis = yellow
y-axis = green
z-axis = blue

Color

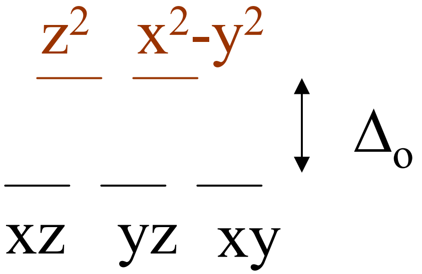
- For many transition metal complex ions, Δ corresponds to wavelengths of visible light, so the complexes are colored.
- We need to have partially filled d orbitals to have any electronic transitions that can give color.
- Ti(III) is violet and Ti(IV) is colorless.

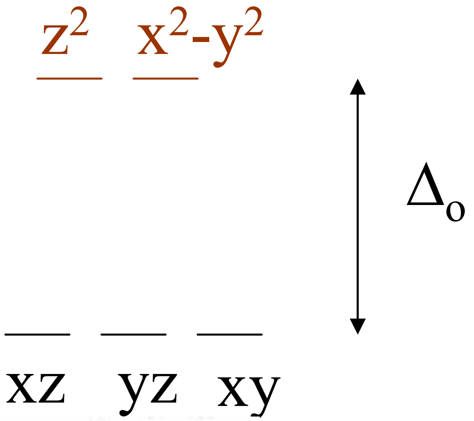


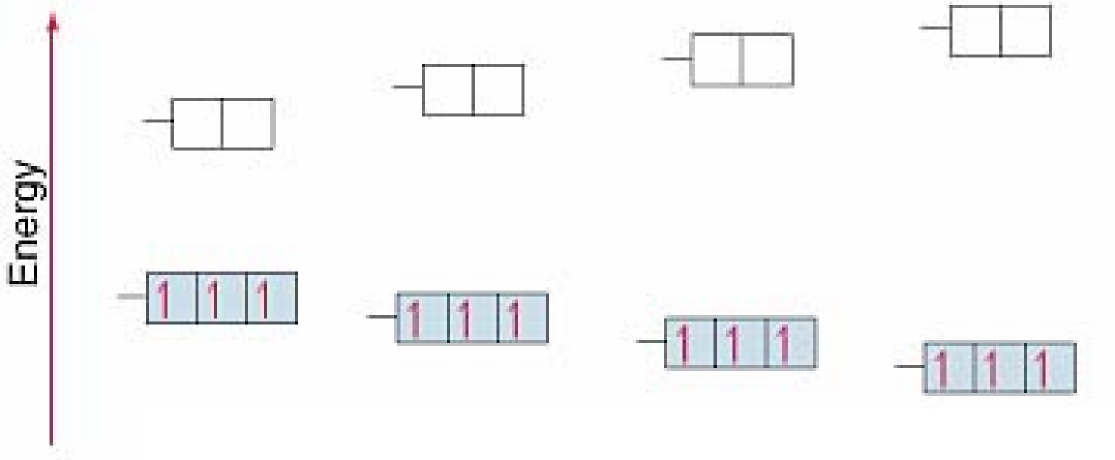
Spectrochemical Series

$I^- < Br^- < Cl^- < F^-$

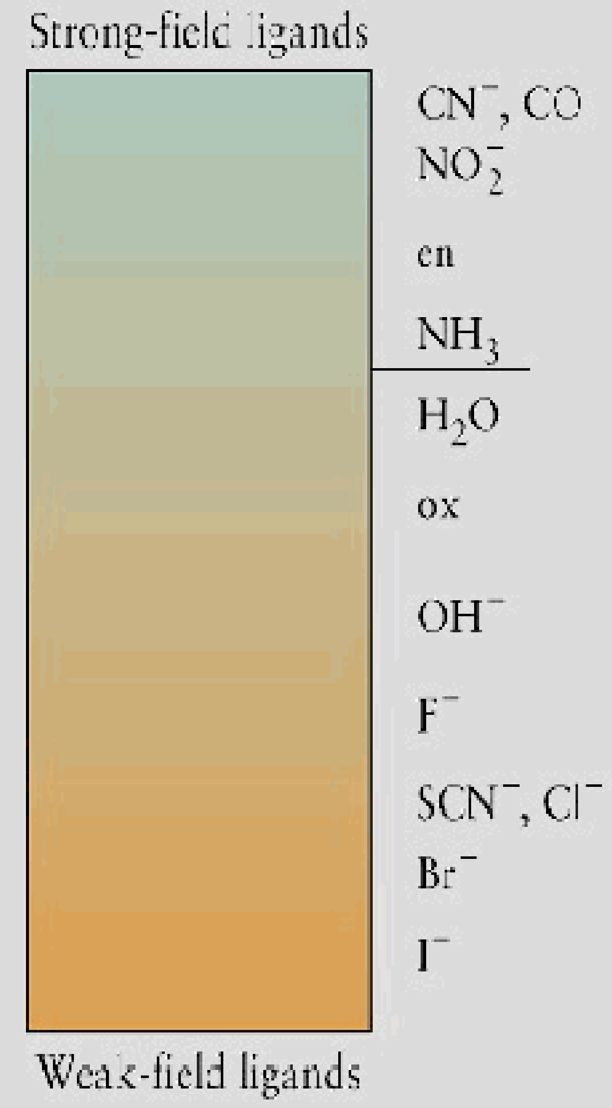
σ Donors







Spectrochemical Series of Ligands



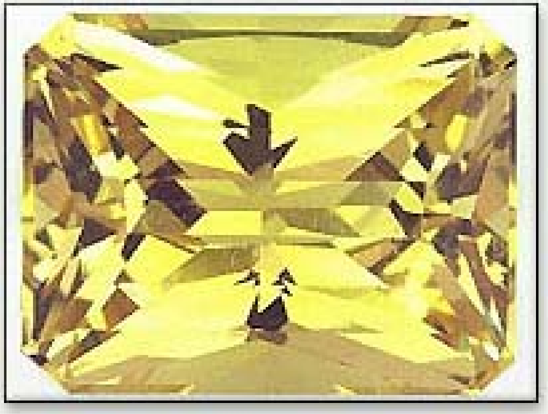
- Ligands can be arranged in a **spectrochemical series** according to the magnitude of the Δ_o they produce, as shown at left.
- H_2O and other ligands below the horizontal line are called **weak-field ligands**.
- NH_3 and others above the line are called **strong-field ligands**.
- Weak-field ligands give smaller Δ_o's than strong-field ligands do.
- Hence the complex absorbs longer wavelength light.

Aqueous Solutions of Cobalt(III) Complexes with Different Ligands

- Weak-field ligands (left) absorb low-energy red wavelengths and thus appear green.
- Strong-field ligands (right) absorb high-energy violet light and thus have colors near orange and yellow.

Colors of Minerals/Gemstones

Yellow beryl (Heliodor) is colored by the presence of F3+ ions. Beryl includes emerald , aquamarine, and lesser known varieties: goshenite (colorless), morganite (pink), Heliodor (yellow), and bixbite (red).



beryllium
aluminum silicate
$Be_2Al_2Si_6O_{18}$

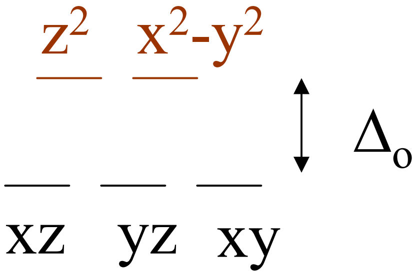
Red ruby. The name ruby comes from the Latin "Rubrum" meaning red. The ruby is in the Corundum group, along with the sapphire. The brightest red and thus most valuable rubies are usually from Burma. Violet

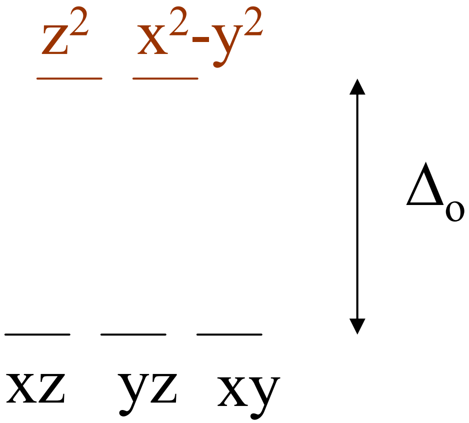
Cr(III) in Al_2O_3

Green emerald. The mineral is transparent emerald, the green variety of Beryl on calcite matrix. 2.5 x 2.5 cm. Coscuez, Boyacá, Colombia

Cr(III) in $Be_2Al_2Si_6O_{18}$

Spectrochemical Series





Δ_o: $Mn^{2+} < Ni^{2+} < Rh^{3+} < Co^{2+} < Fe^{2+} < Fe^{3+} < Cr^{3+}$
$< Co^{3+} < Ir^{3+} < Pt^{4+}$

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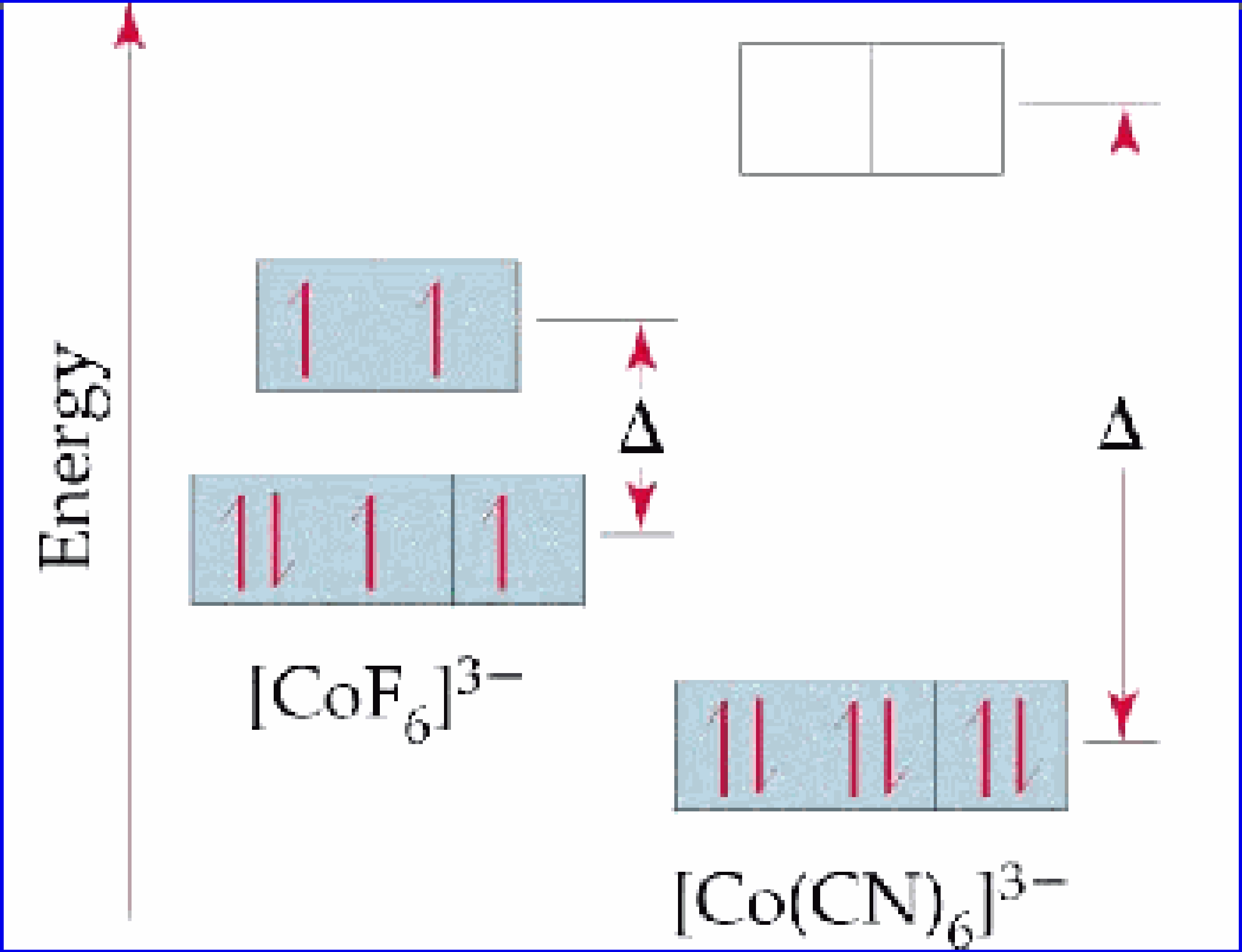
Magnetism

Magnetism

- Many transition metal complexes are paramagnetic (i.e. they have unpaired electrons).
- There are some interesting observations. Consider a d^6 metal ion:
  - $[Co(NH_3)_6]^{3+}$ has no unpaired electrons, but $[CoF_6]^{3-}$ has four unpaired electrons per ion.
- We need to develop a bonding theory to account for both color and magnetism in transition metal complexes.

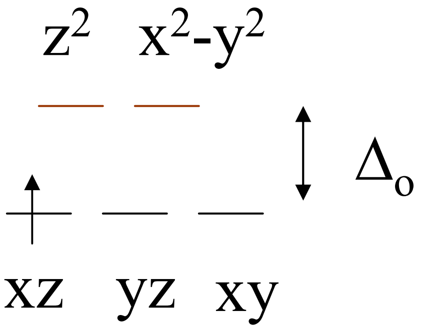
Low Spin and High Spin Complexes



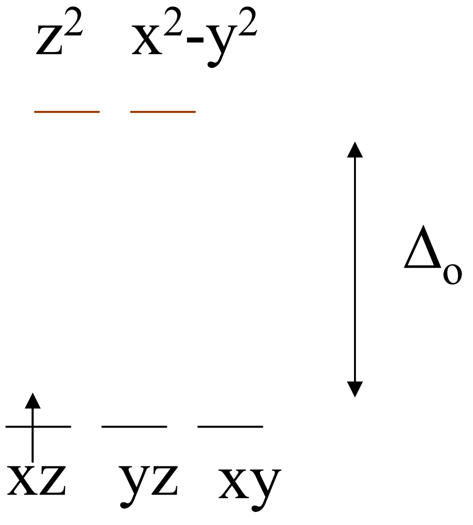
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^1



High Spin

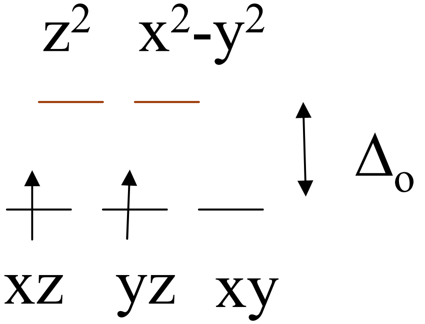


Low Spin

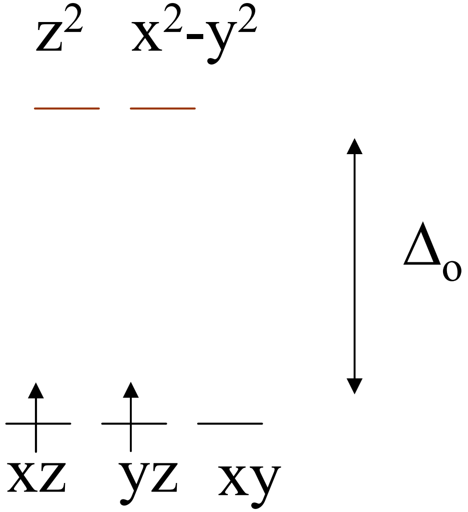
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^2



High Spin

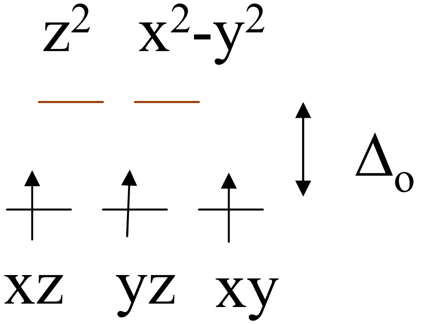


Low Spin

Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^3

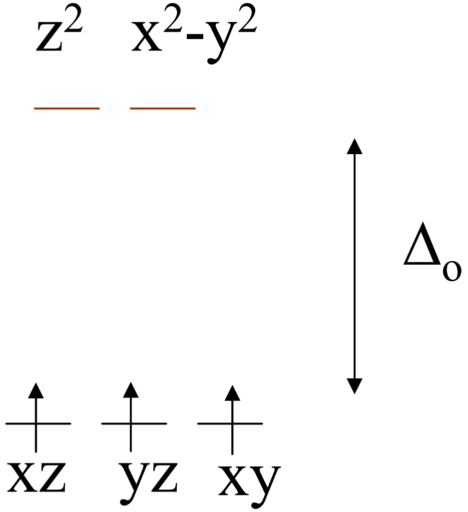


z^2 x^2-y^2

Δ_o

xz yz xy

High Spin



z^2 x^2-y^2

Δ_o

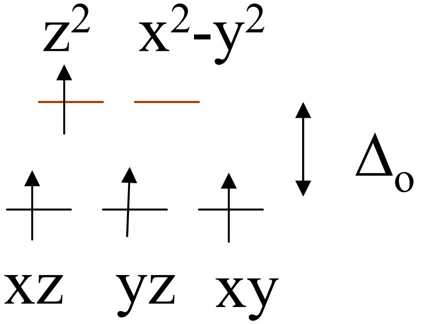
xz yz xy

Low Spin

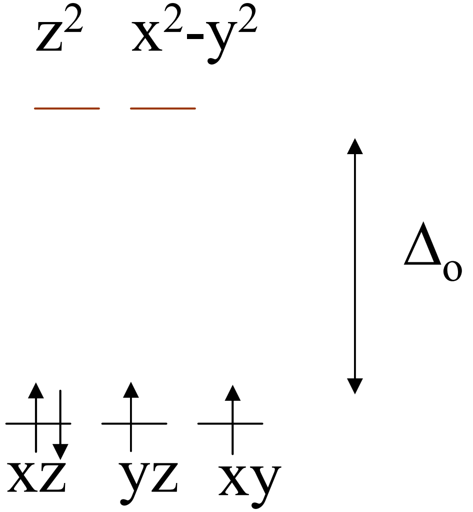
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^4



High Spin

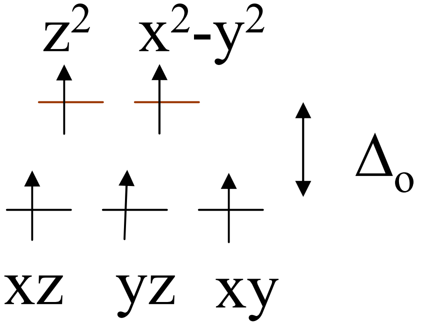


Low Spin

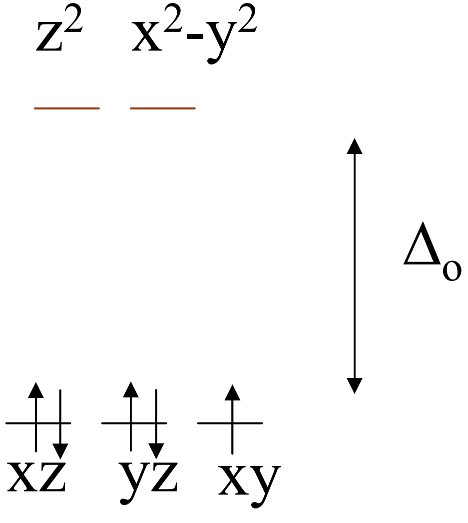
Magnetic Properties of Octahedral Complexes

$\mathrm{I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO}$

d^5



High Spin

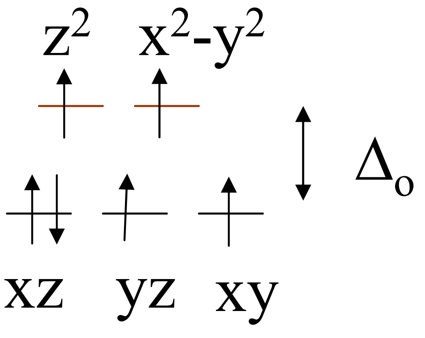


Low Spin

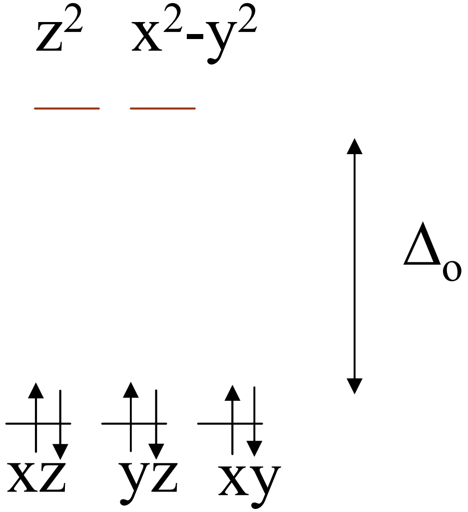
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^6



High Spin

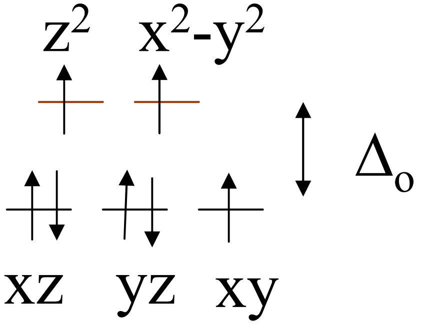


Low Spin

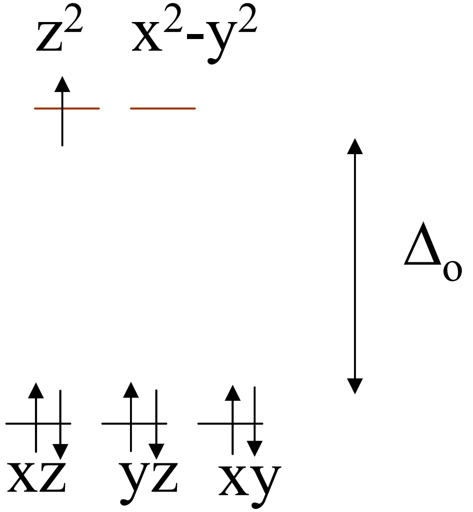
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^7



High Spin

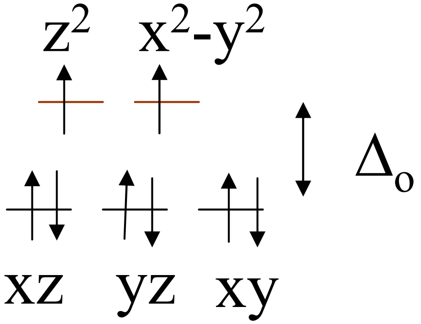


Low Spin

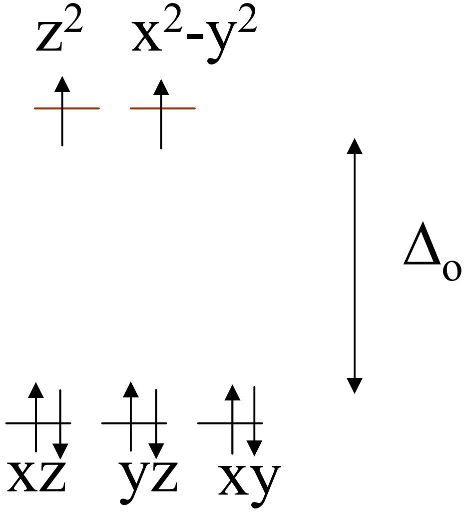
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^8



High Spin

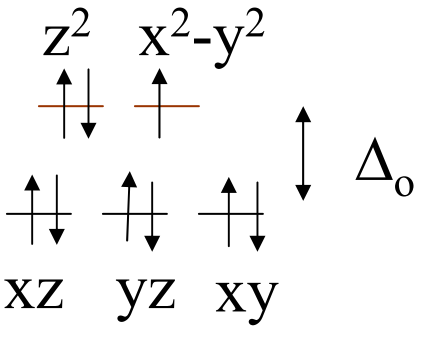


Low Spin

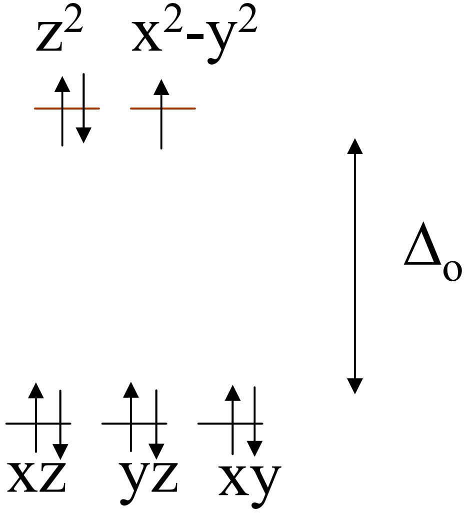
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^9



High Spin

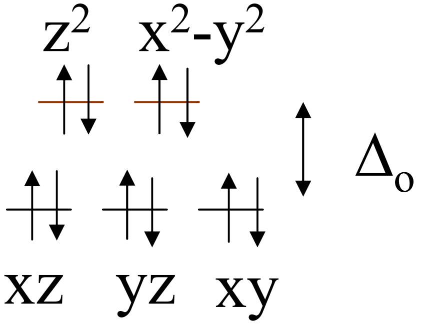


Low Spin

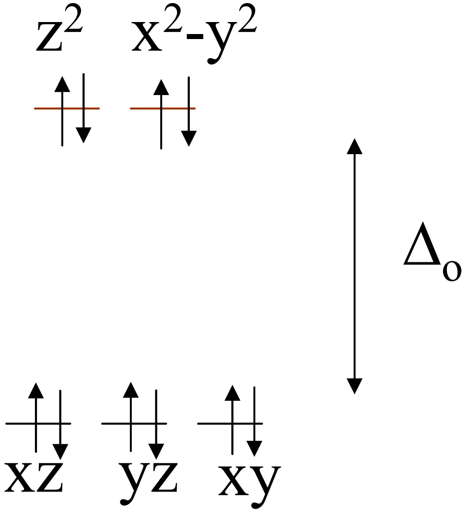
Magnetic Properties of Octahedral Complexes

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

d^{10}



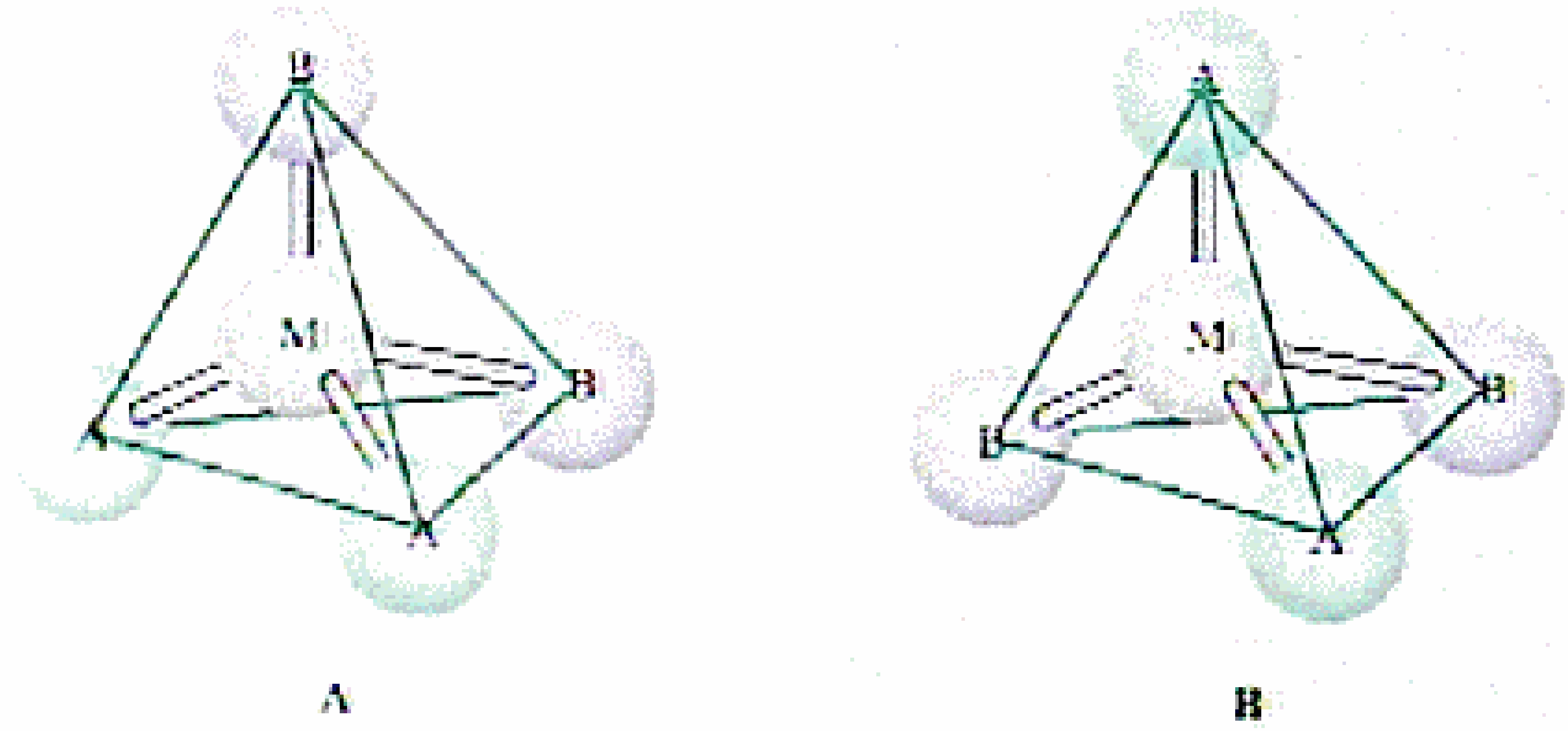
High Spin



Low Spin

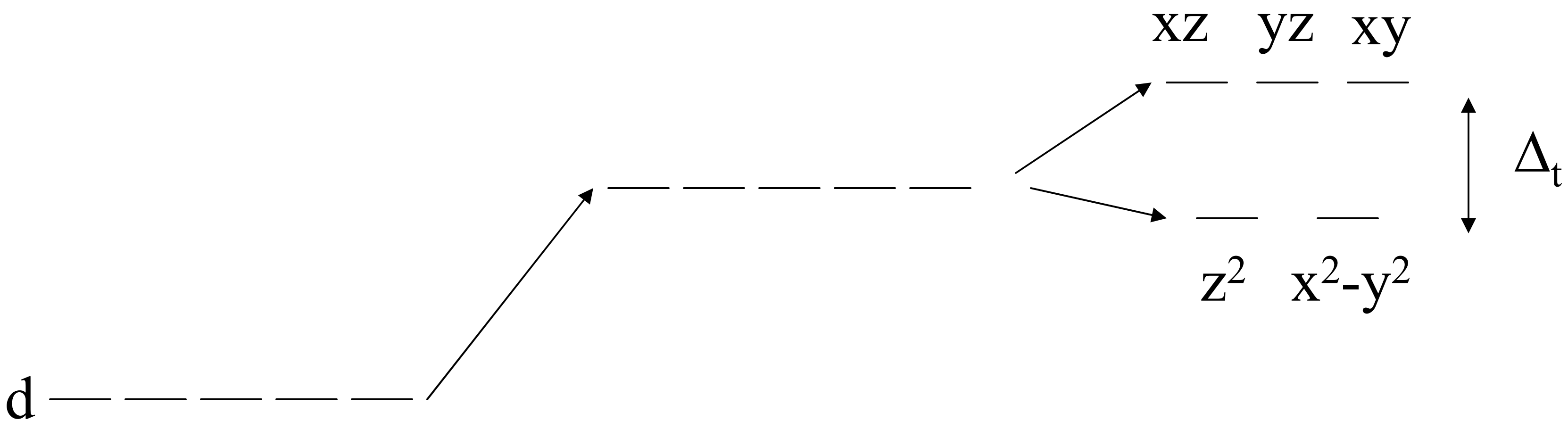
Tetrahedral MA_2B_2

Crystal Field Theory For Tetrahedral Complexes



Crystal Field Splitting

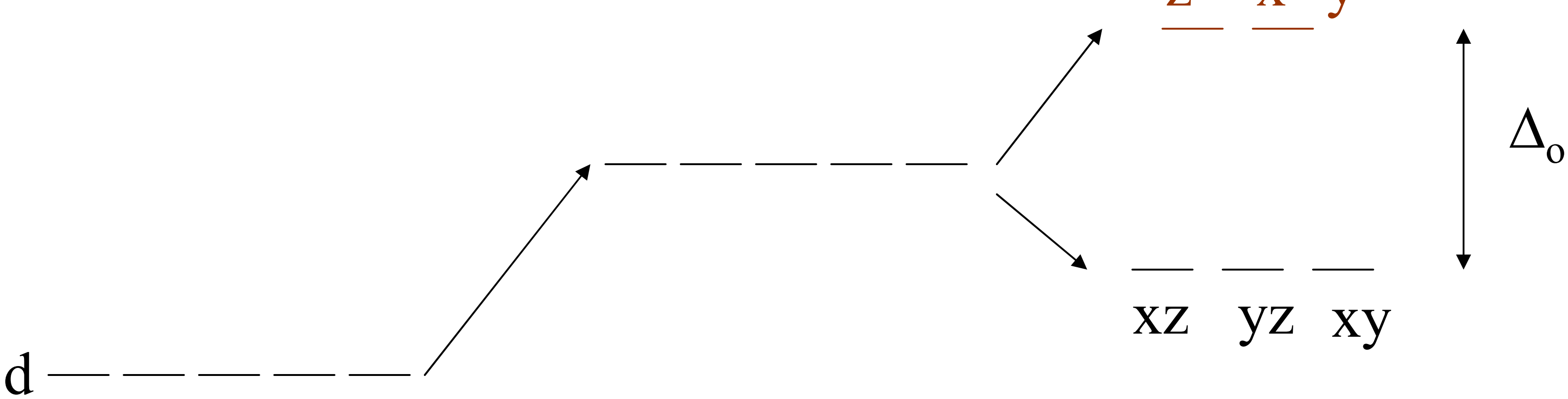
Tetrahedral Complexes



$\Delta_t = -4/9\ \Delta_o$

Crystal Field Splitting

Octahedral Complexes

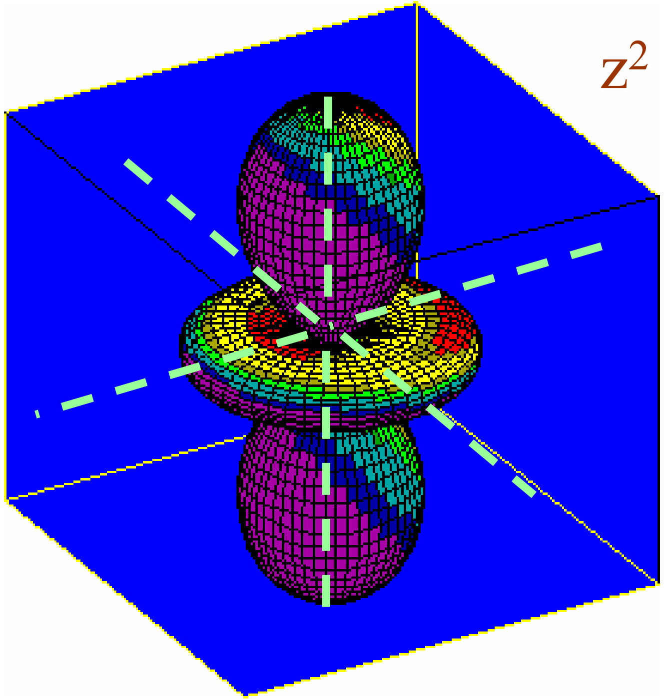


z^2 $x^2\text{-}y^2$

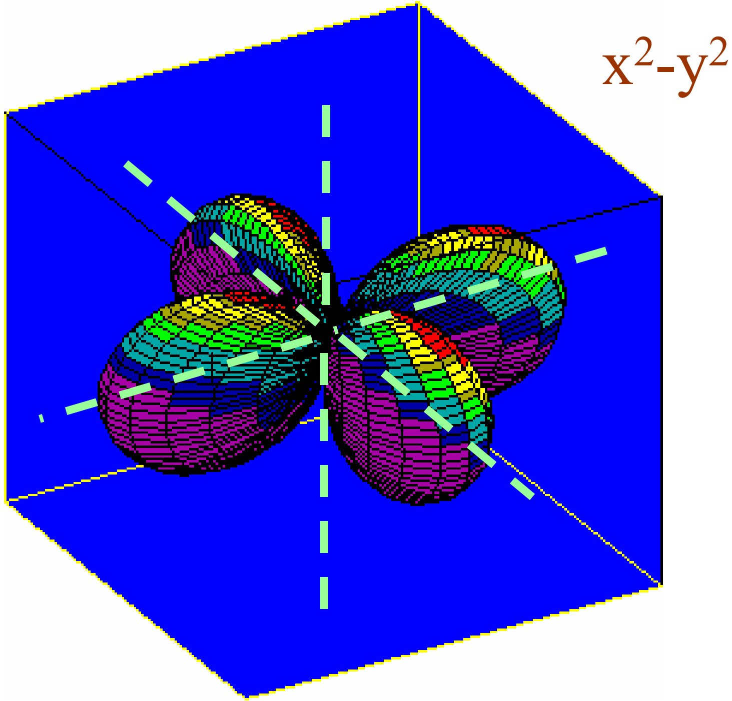
Δ_o

d

xz yz xy



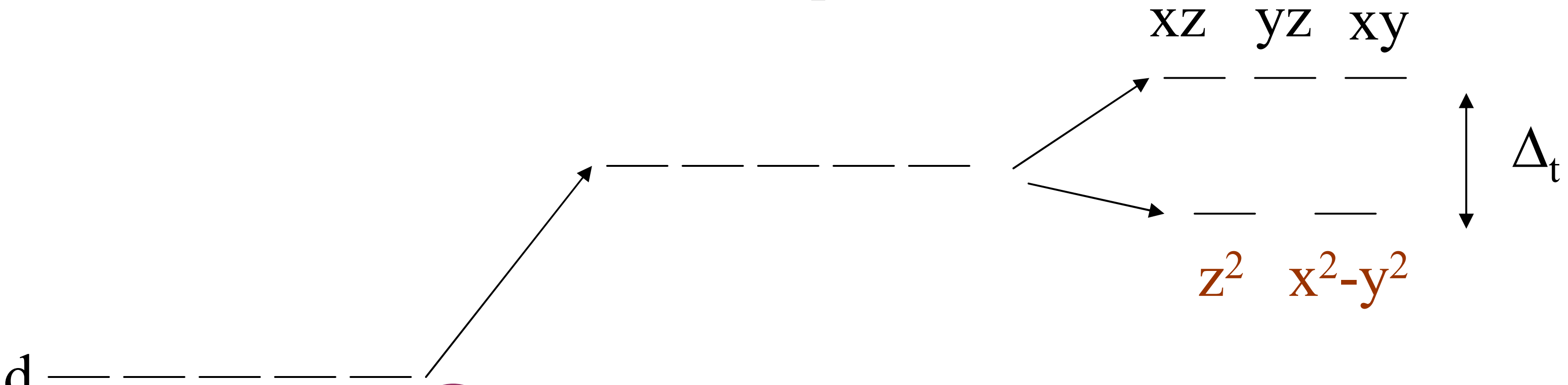
z^2



$x^2\text{-}y^2$

Crystal Field Splitting

Octahedral Complexes

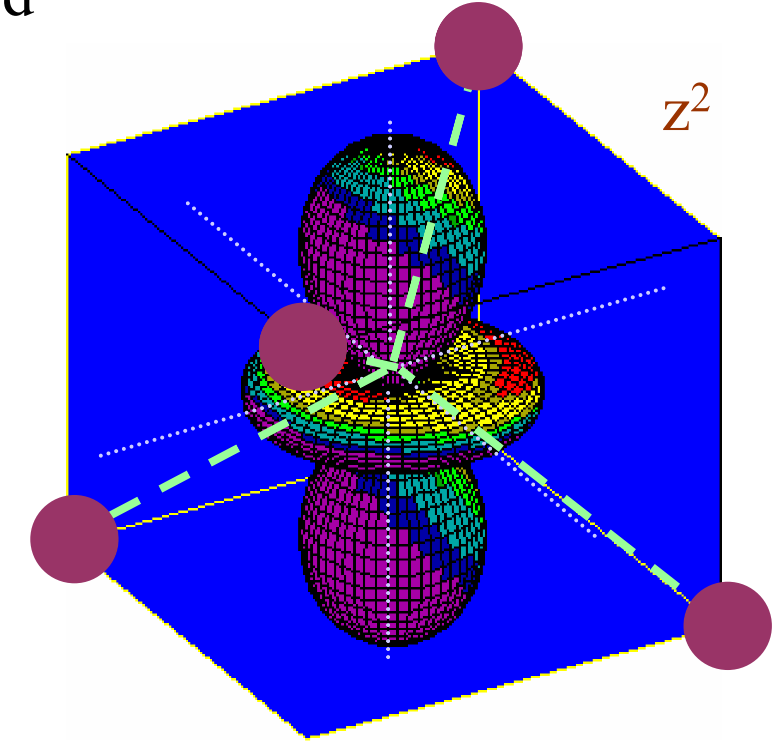


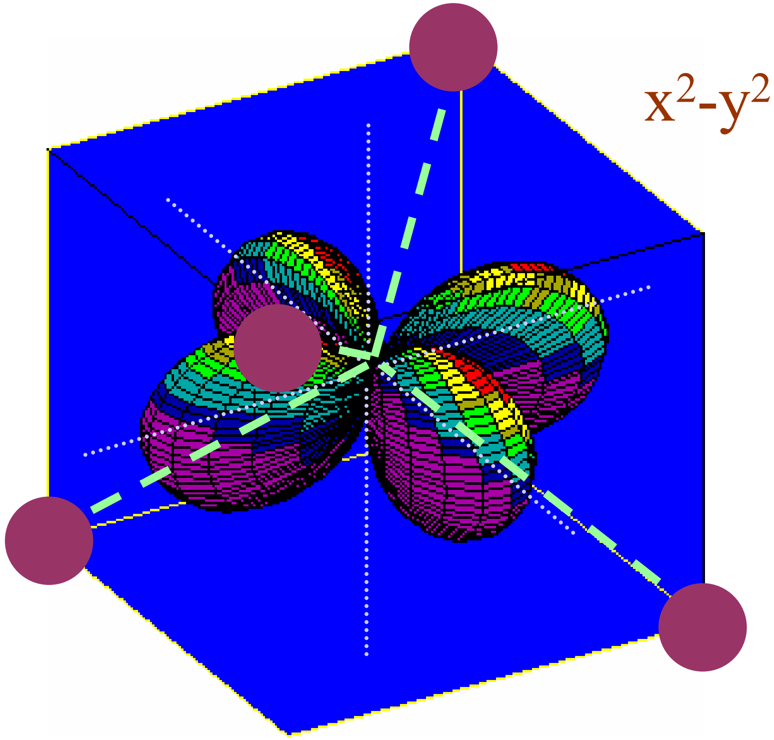
xz yz xy

Δ_t

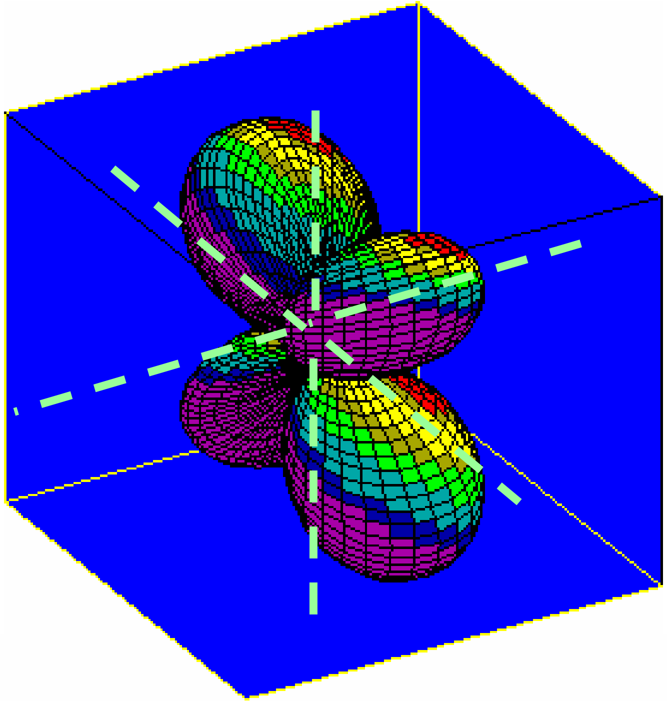
z^2 x^2-y^2

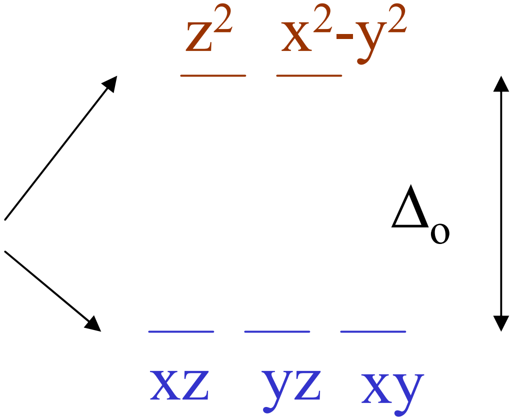
d





xz



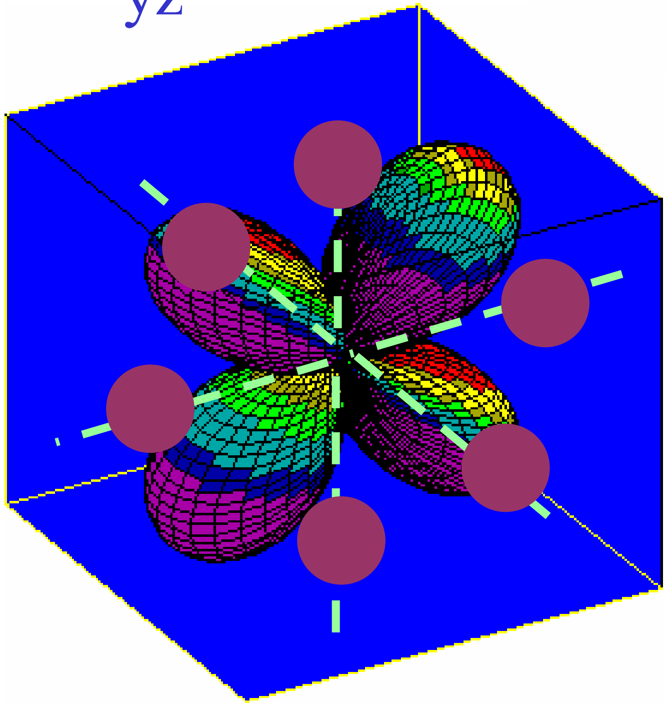


z^2 x^2-y^2

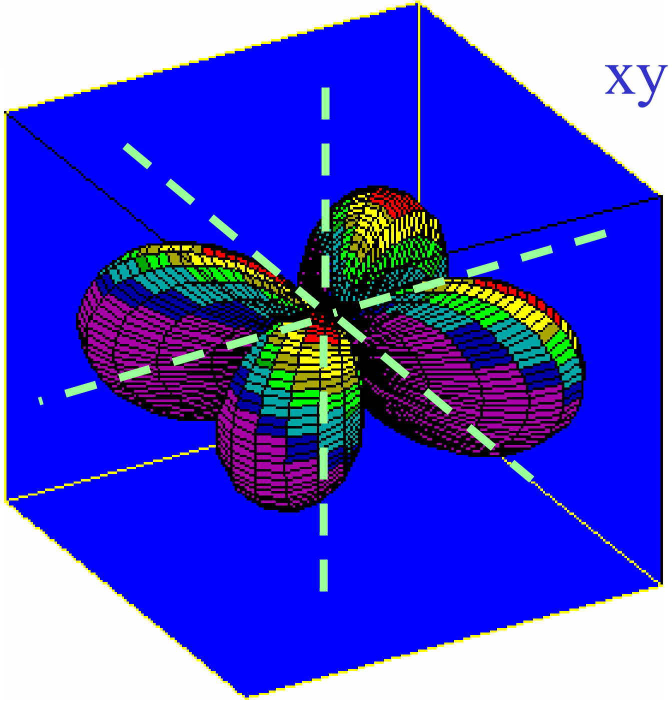
Δ_o

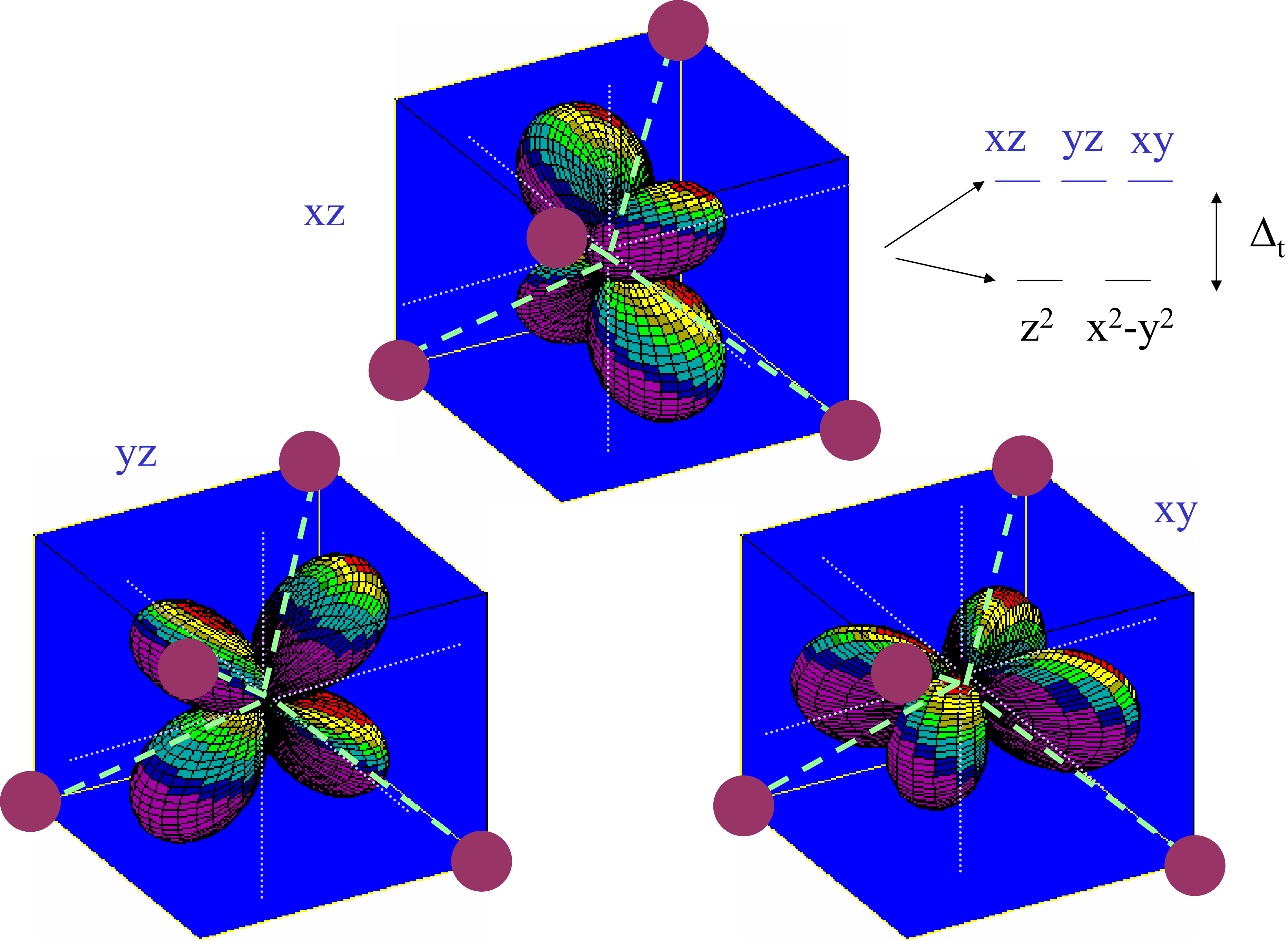
xz yz xy

yz



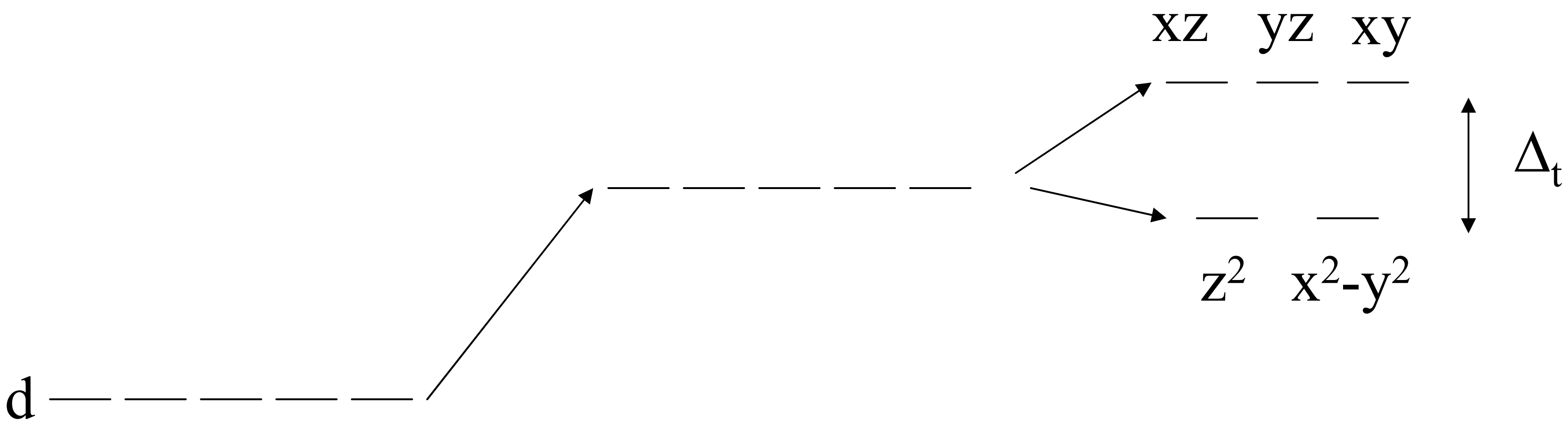
xy




xz
xz yz xy
Δ_t
z^2 x^2-y^2
yz
xy

Crystal Field Splitting

Tetrahedral Complexes



$\Delta_t = -4/9\ \Delta_o$

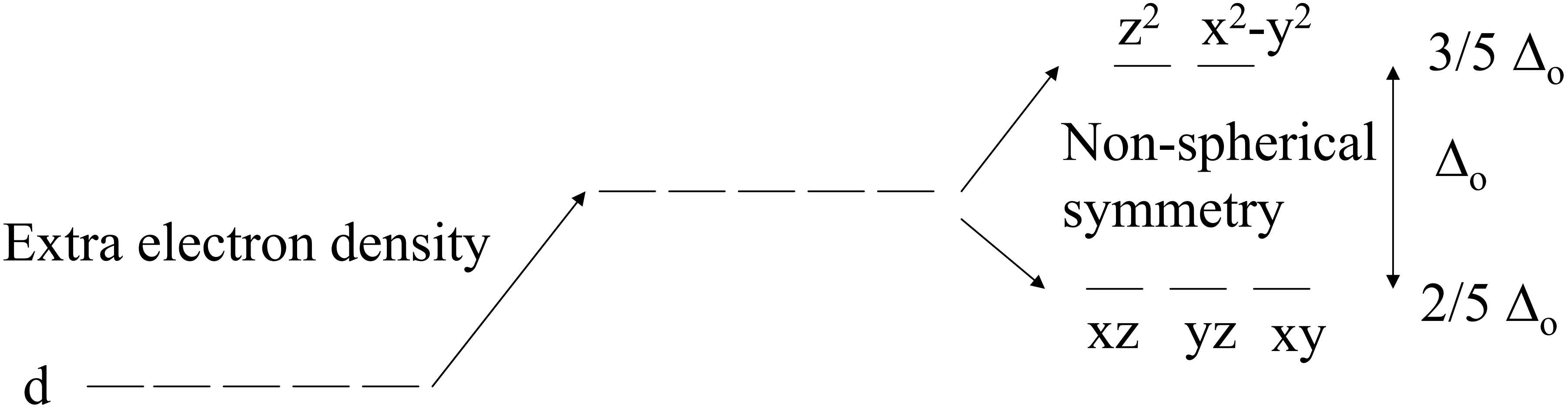
No low spin tetrahedral complexes

Transition Metal Chemistry

- Multiple Oxidation States
- Coordination Chemistry/Stereochemistry
- Crystal Field Splitting: Optical and Magnetic Properties
- Ligand Field Splitting: Spectrochemical Series
- Ligand Field Stabilization Energy
- Chelate Effect
- Stereochemical Control of Binding Affinity
- Electron Exchange

Ligand Field Stabilization Energy

High Spin Octahedral Complexes



z^2 x^2-y^2

$3/5\ \Delta_o$

Non-spherical symmetry

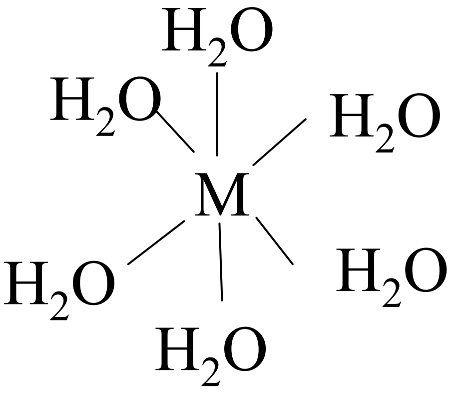
Δ_o

Extra electron density

$2/5\ \Delta_o$

xz yz xy

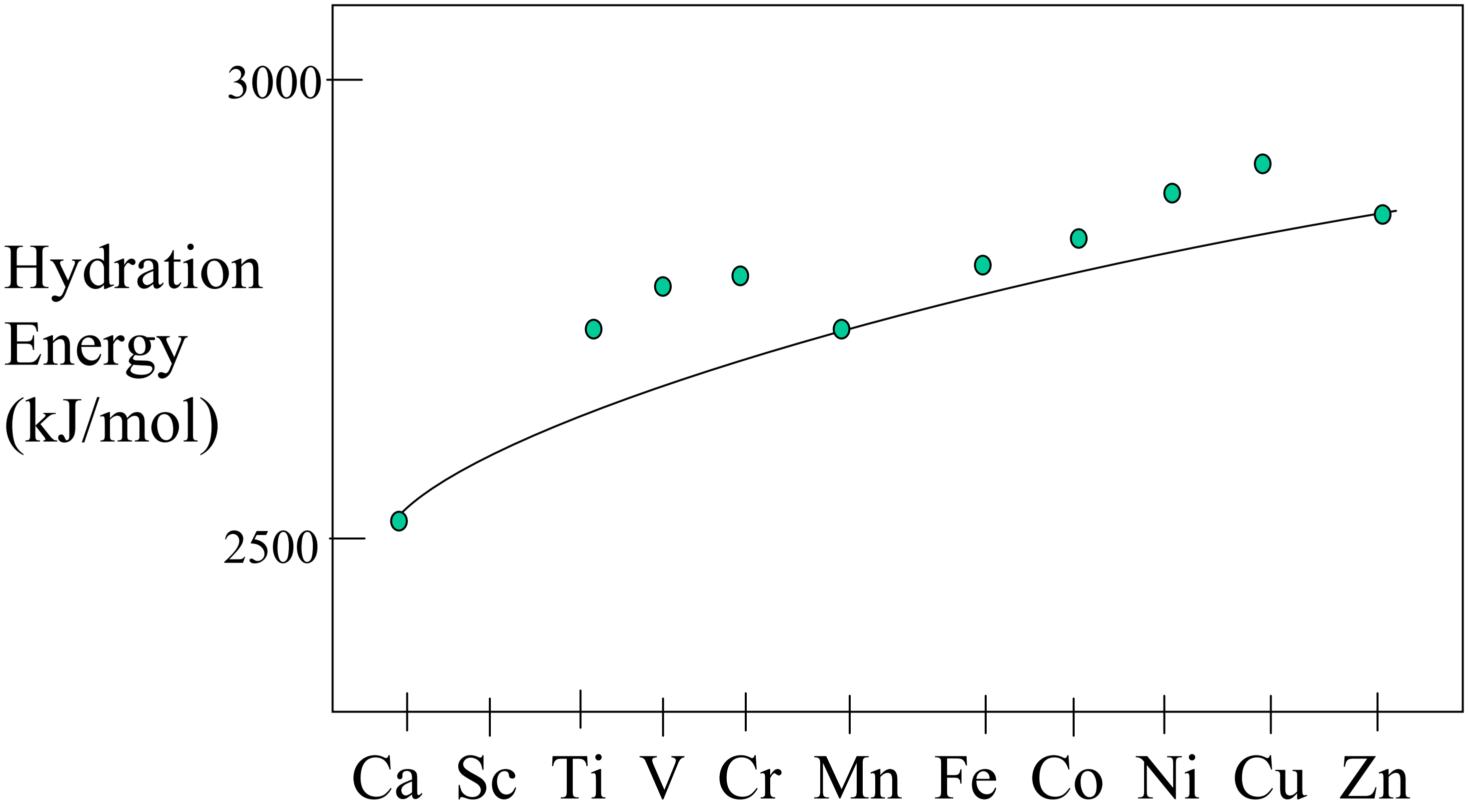
d



d^n	Δ_o
d^1, d^6	2/5
d^2, d^7	4/5
d^3, d^8	6/5
d^4, d^9	3/5
d^0, d^5, d^{10}	0

Ligand Field Stabilization Energy

$$M^{2+}(g) \;+\; \infty\, H_2O \longrightarrow [M(H_2O)_6]^{2+}$$



- Energy of hydration always favorable
- Energy increases as ionic radius decreases (to right)
- Additional stabilization due to crystal field energy

Transition Metal Chemistry

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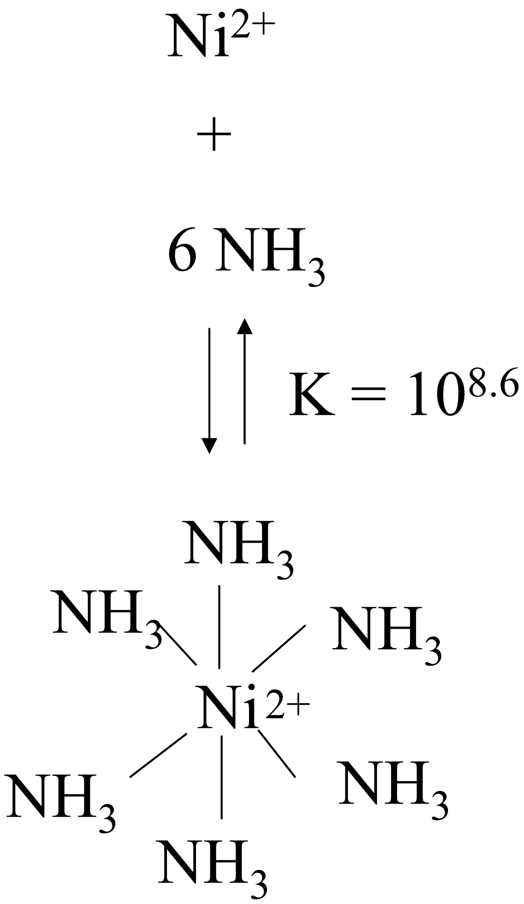
Binding Constants for Multiple Ligands

				K
Cd^{2+}	$+ NH_3$	$\rightleftharpoons$	$[Cd(NH_3)]^{2+}$	$10^{2.05}$
$[Cd(NH_3)]^{2+}$	$+ NH_3$	$\rightleftharpoons$	$[Cd(NH_3)_2]^{2+}$	$10^{2.10}$
$[Cd(NH_3)_2]^{2+}$	$+ NH_3$	$\rightleftharpoons$	$[Cd(NH_3)_3]^{2+}$	$10^{1.44}$
$[Cd(NH_3)_3]^{2+}$	$+ NH_3$	$\rightleftharpoons$	$[Cd(NH_3)_4]^{2+}$	$10^{0.93}$
Cd^{2+}	$+ 4\ NH_3$	$\rightleftharpoons$	$[Cd(NH_3)_4]^{2+}$	$10^{7.12}$

Decrease mostly statistical: as ligand count increases more changes to lose L as opposed to gaining L

Chelate Effect

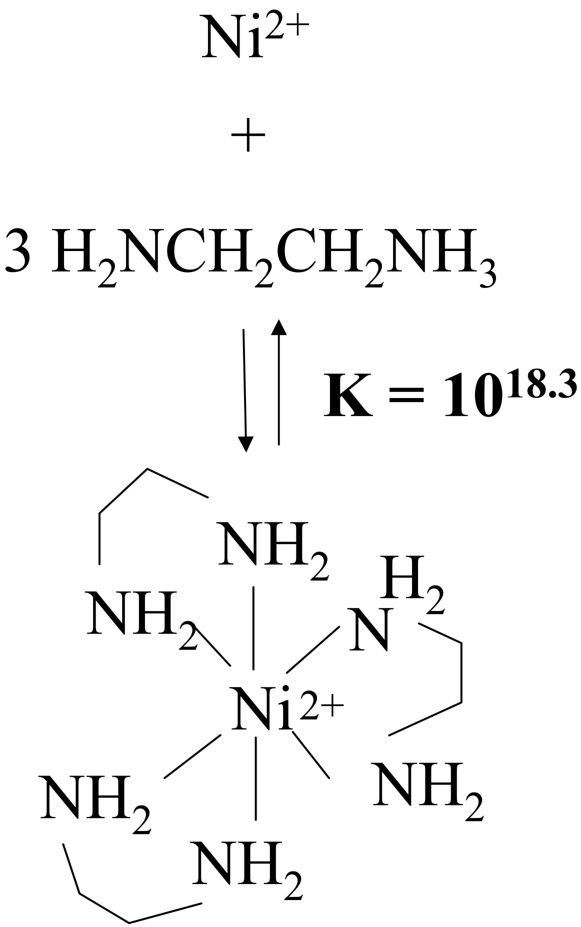


Ni^{2+}

$+$

$6\ NH_3$

$\rightleftharpoons$ $K = 10^{8.6}$



Ni^{2+}

$+$

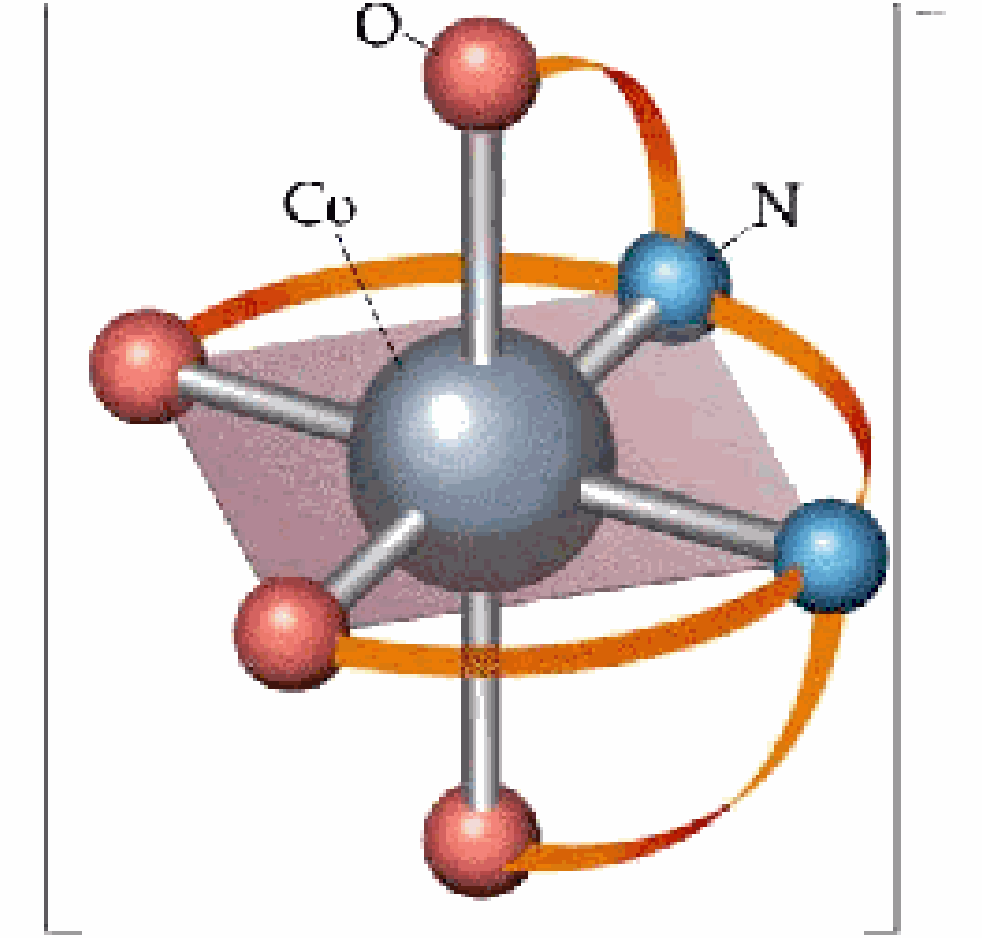
$3\ H_2NCH_2CH_2NH_3$

$\rightleftharpoons$ $\mathbf{K = 10^{18.3}}$

Chelating Ligands

- One very important chelating agent is ethylenediaminetetraacetate ($EDTA^{4-}$).
- EDTA is used
  - to tie up Ca^{2+} in bathroom cleaners, shower sprays
  - to prevent blood clots
  - to remove heavy metals from the body when poisoned
  - to solubilize iron in plant fertilizer
  - to remove the iron taste from mayonnaise (arising from its preparation in iron vats)

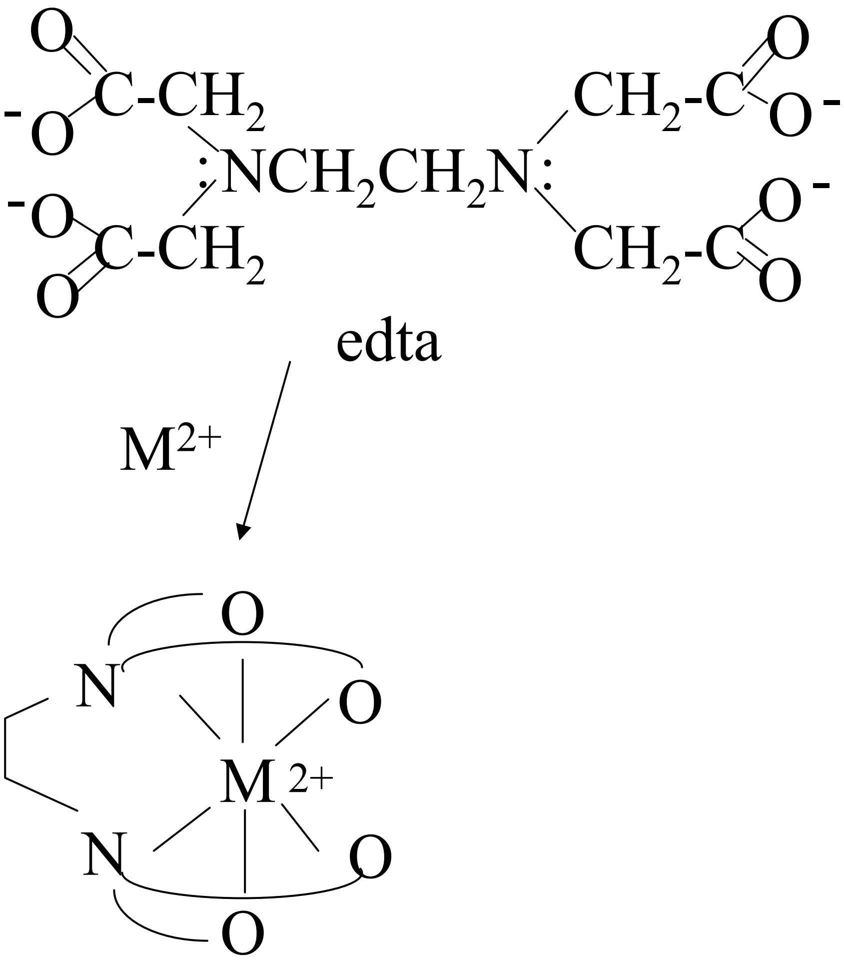
$[Co(EDTA)]^{-}$



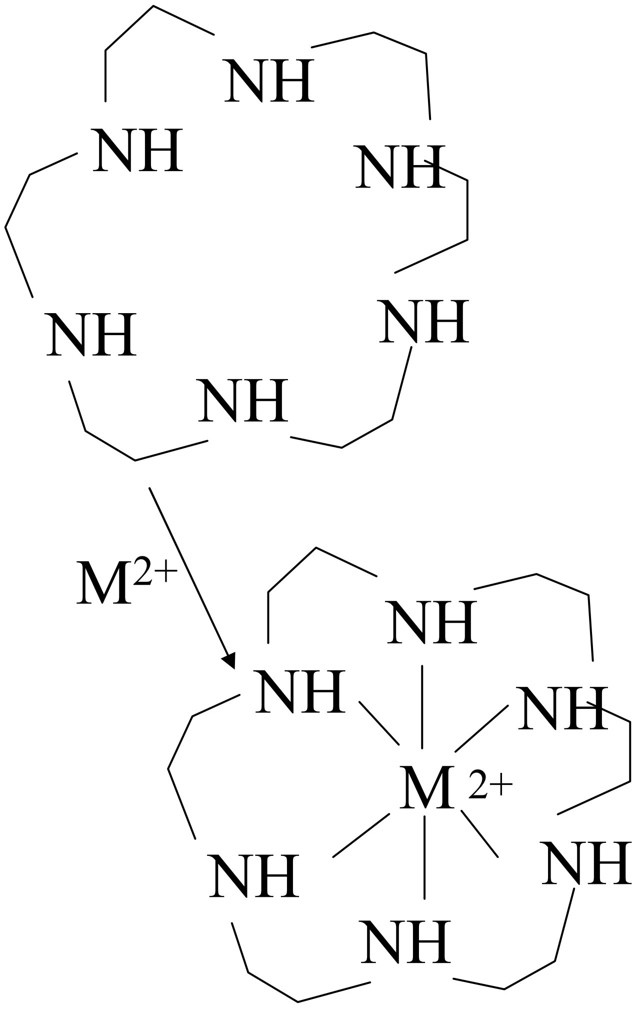
CoEDTA

Chelate Effect

Useful chelating ligands: en, sepulchrate, edta,

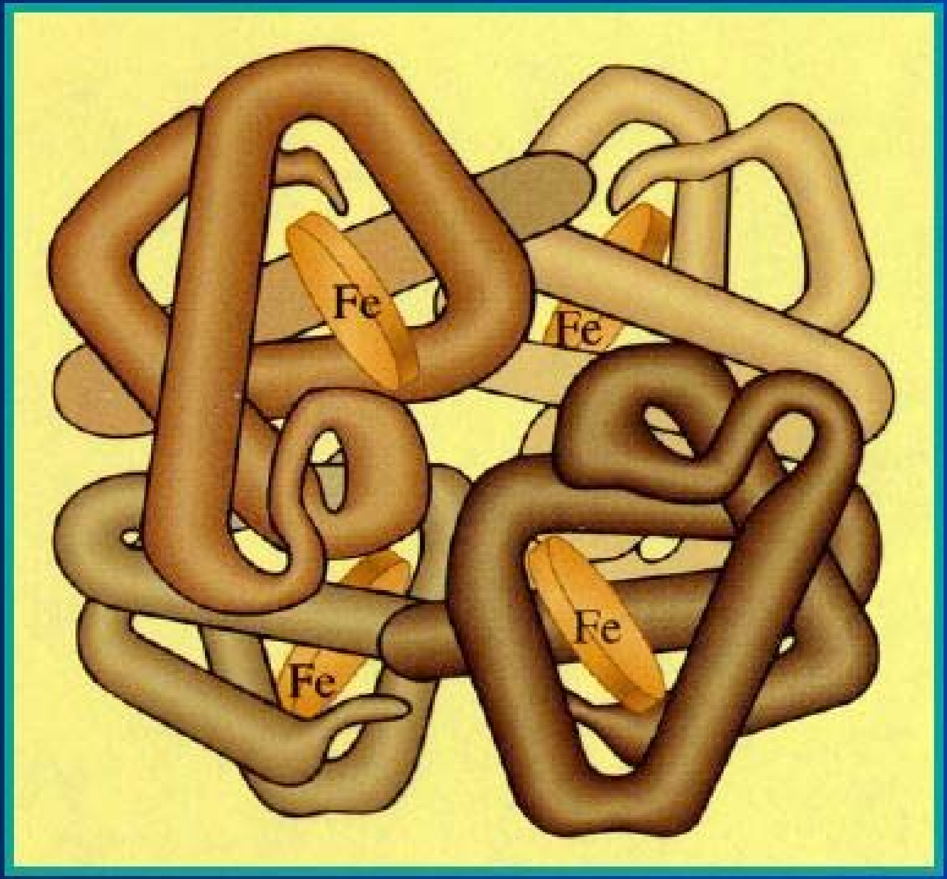


M(edta)$^{2-}$



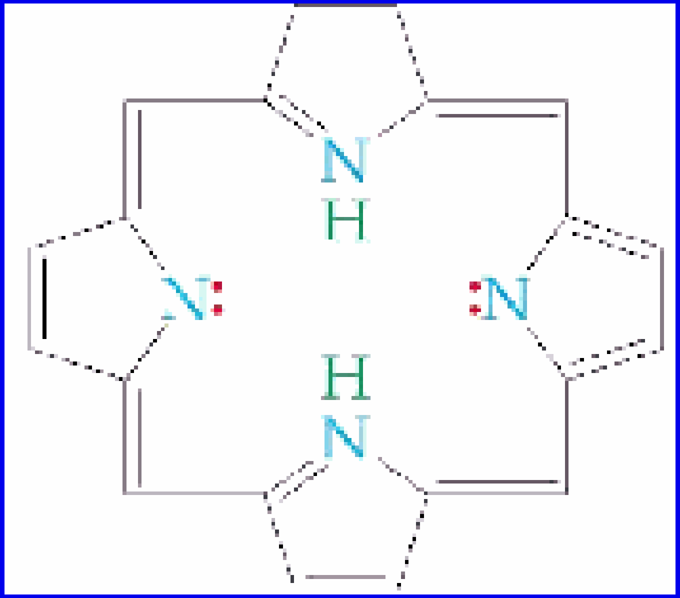
M(sep)$^{2+}$

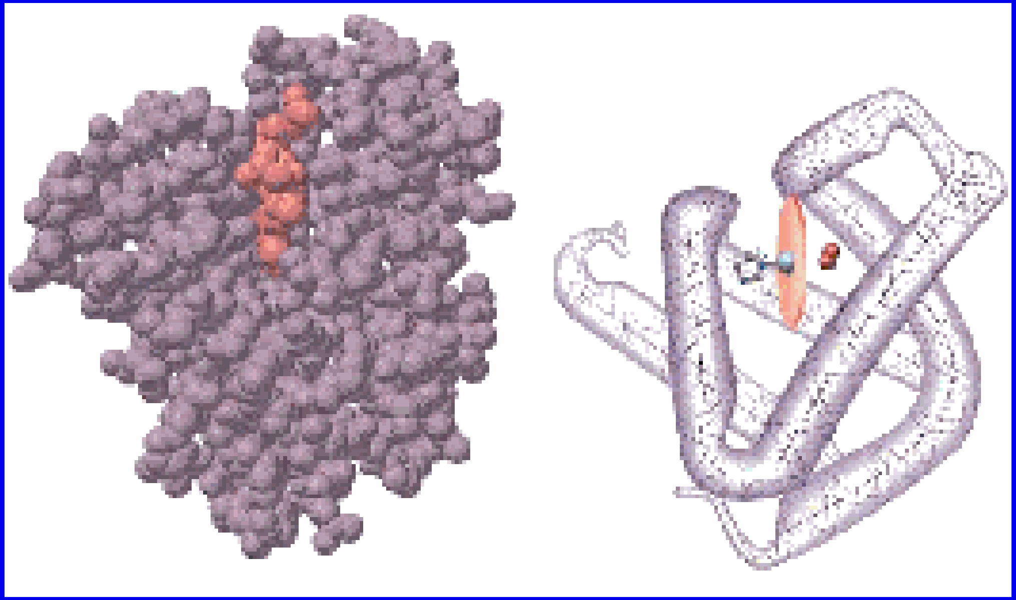
Hemoglobin



Metals and Chelates in Living Systems

- The heme unit in hemoglobin involves a rigid chelating ligand. H_2O or O_2 or CO can be the 6th ligand.

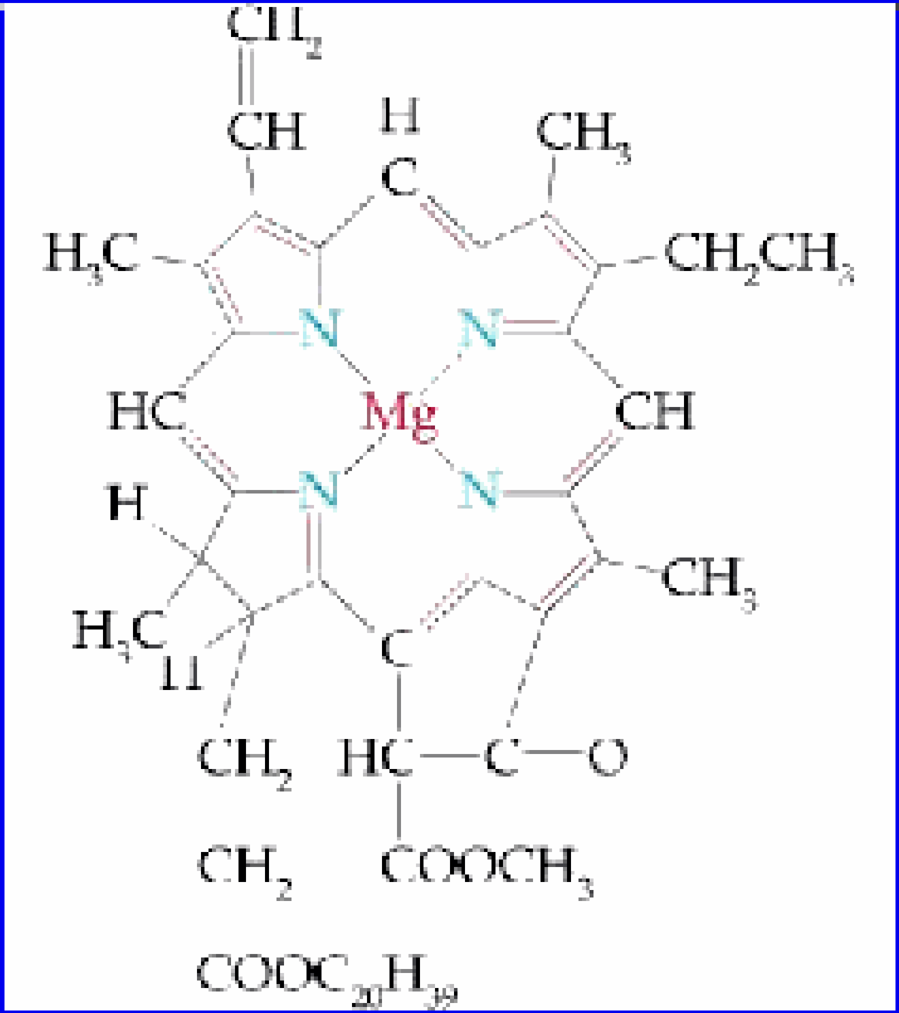




Metals and Chelates in Living Systems

- Chlorophyll, involved in photosynthesis, is a complex ion of magnesium(II) ion.

chlorophyll.pdb



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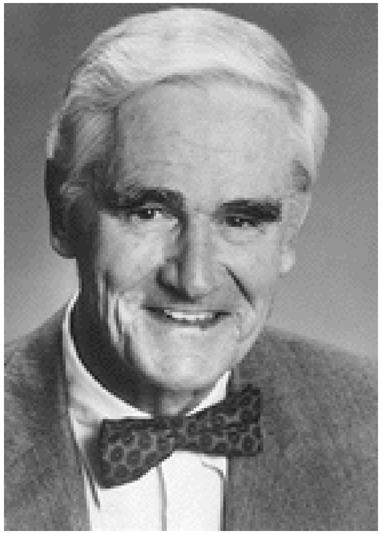
Ionic Radii and Charge Densities for the Alkali Metal Cations

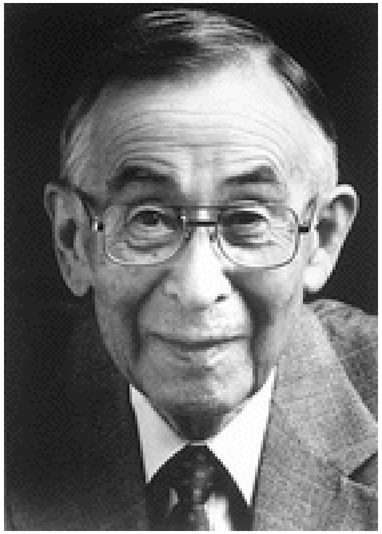
Ion	Ionic radius/Å	Charge Density/C Å^{-3}
Li^+	0.66	12.1×10^{-20}
Na^+	0.95	4.46×10^{-20}
K^+	1.33	1.62×10^{-20}
Rb^+	1.48	1.18×10^{-20}
Cs^+	1.69	0.79×10^{-20}

So how do we get ligands to preferentially bind Na^+ or K^+ vs Li^+?

1987 Nobel Prize in Chemistry



Donald Cram



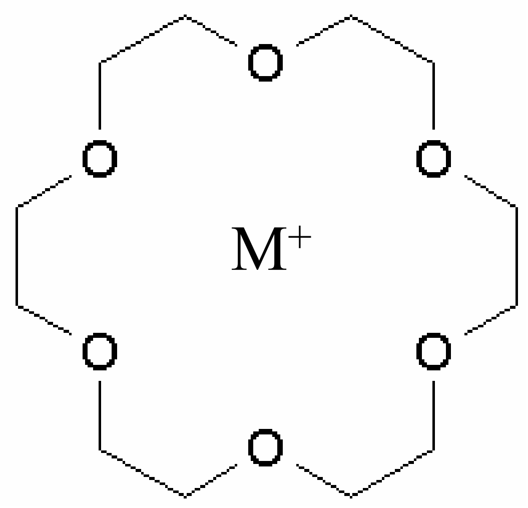
Charles J. Pedersen

Jean-Marie Lehn

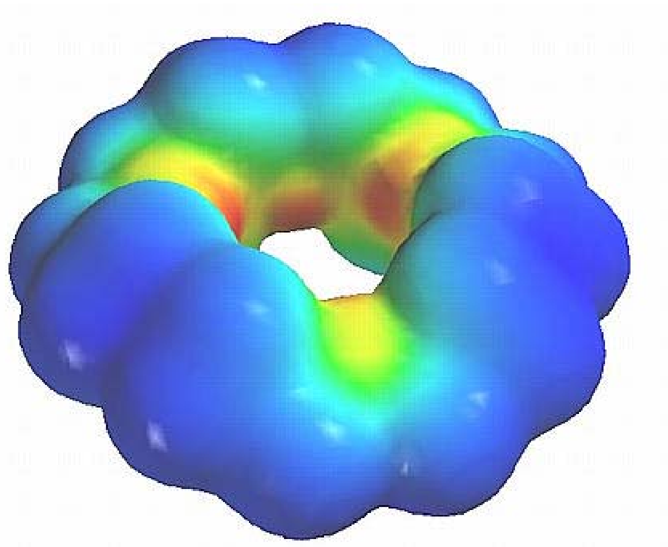
"for their development and use of molecules with structure-specific interactions of high selectivity"

Chelate Effect

Useful chelates: crown ethers (host/guest chemistry)

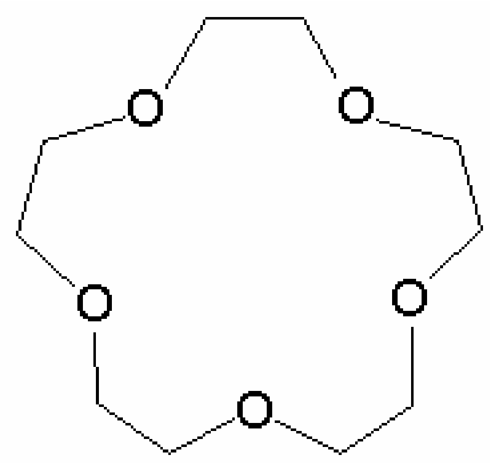


18-crown 6



Fits Cs^+ nicely (used to separate Cs in radioactive waste)

Crown Ethers

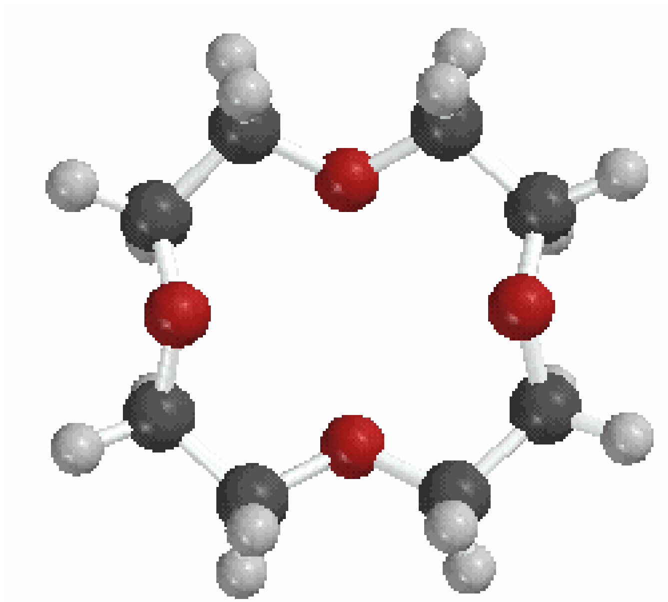


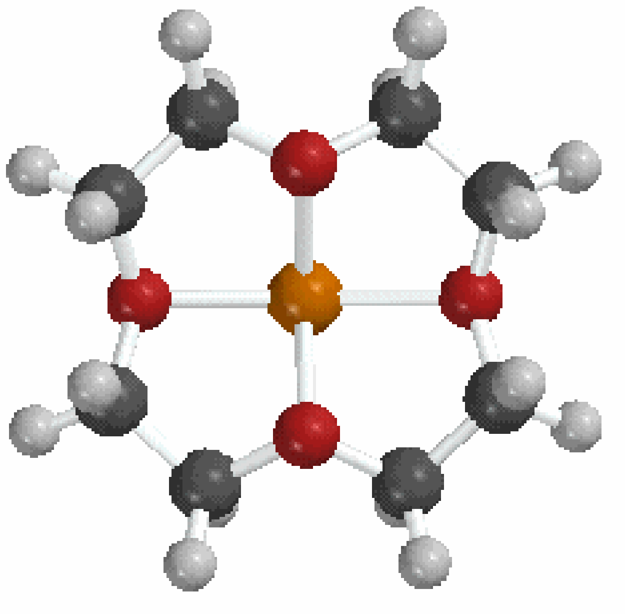
Fits Na^+ and K^+ nicely

15-crown 5

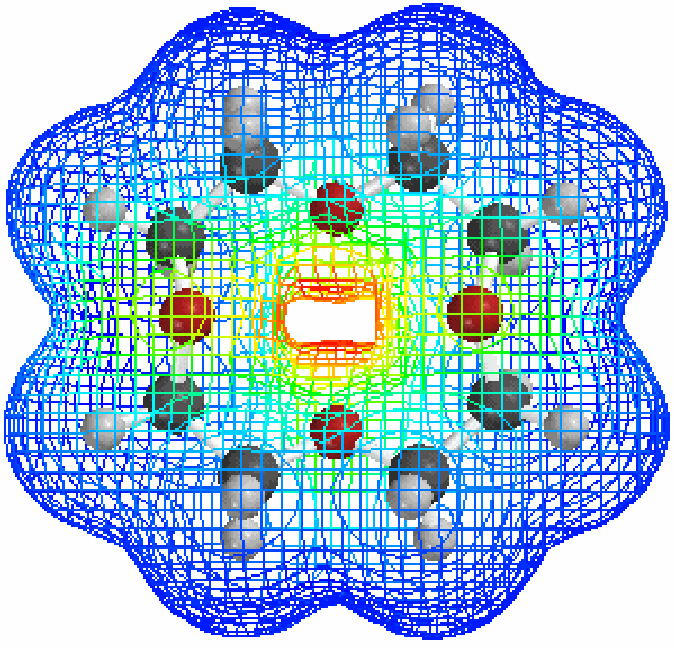
($C_{10}H_{20}O_5$)

Crown Ethers



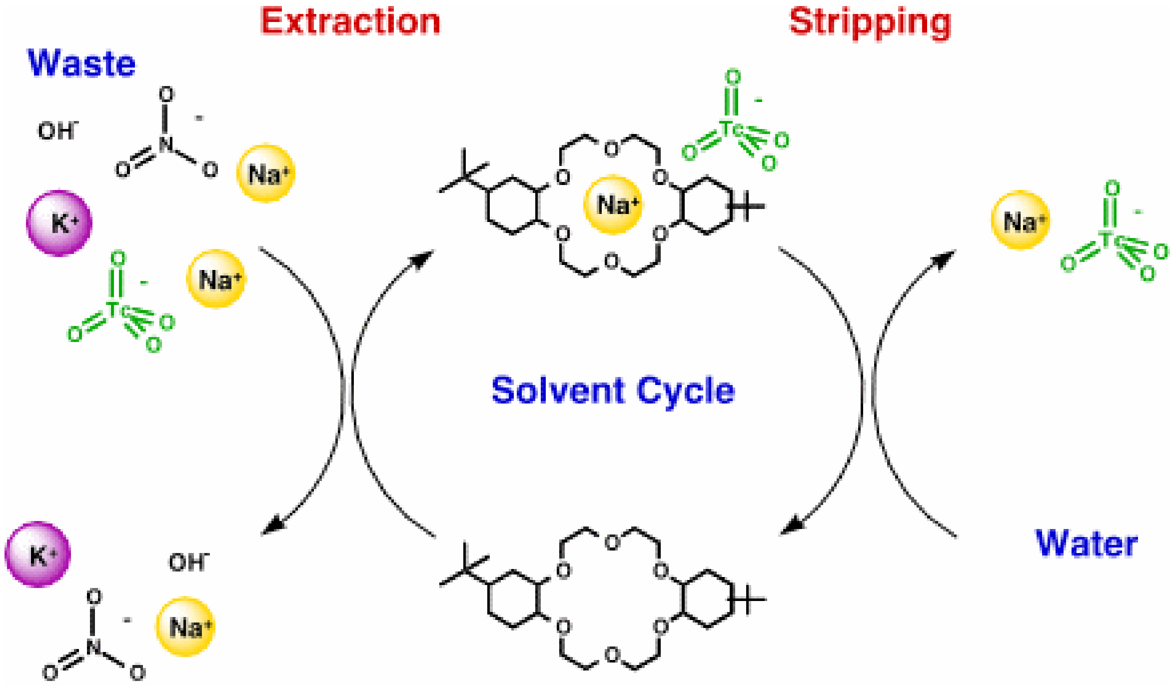


12-crown 4 + Li^+



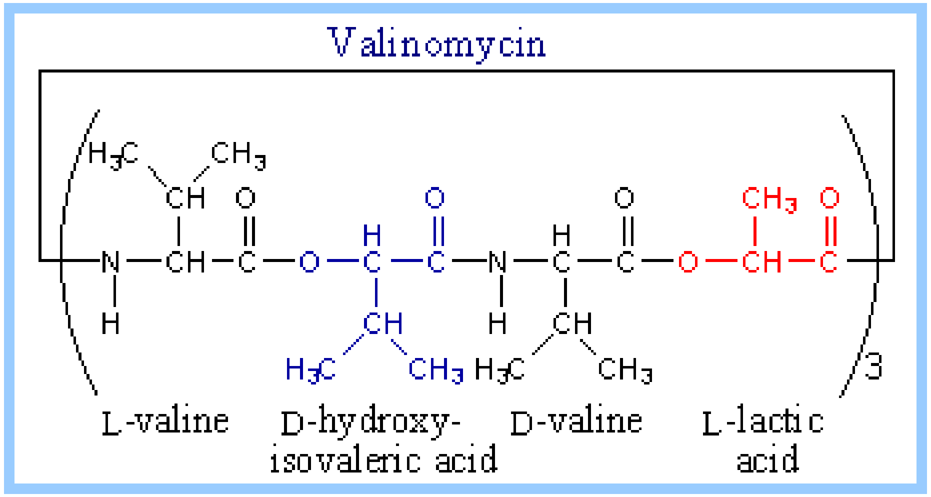
Crown Ethers

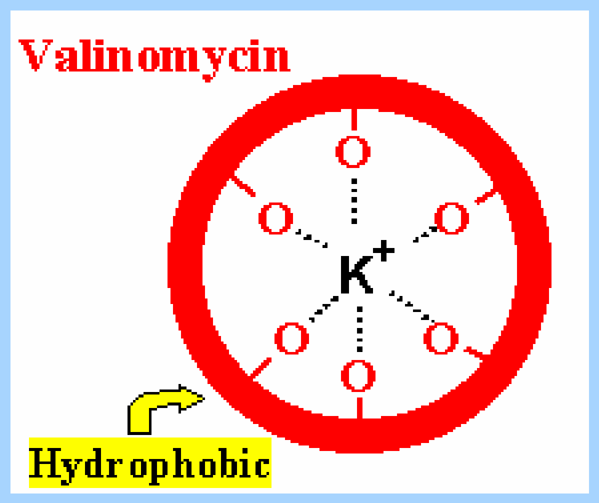
Useful chelates: crown ethers (host/guest chemistry)



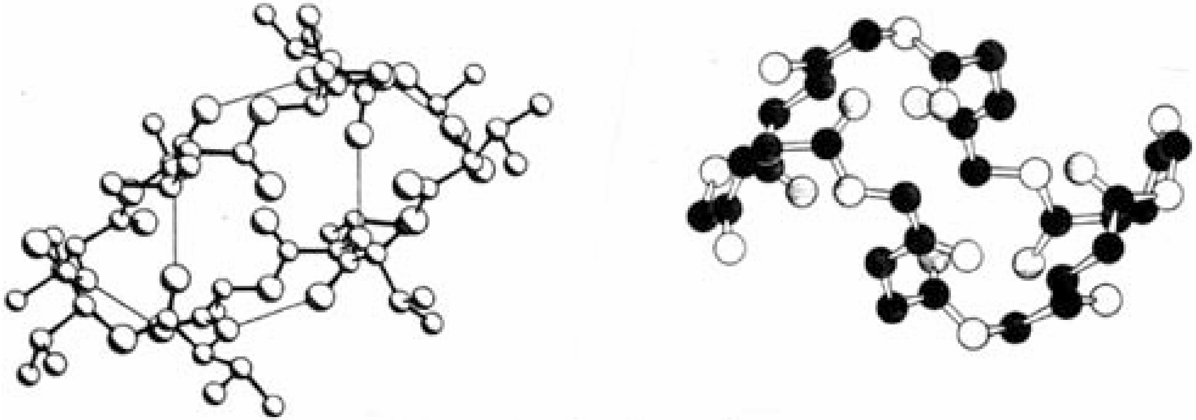
Also used to “bring along” pertechnetate anion into non-aqueous solvents

Biological Host-Guest Complexes

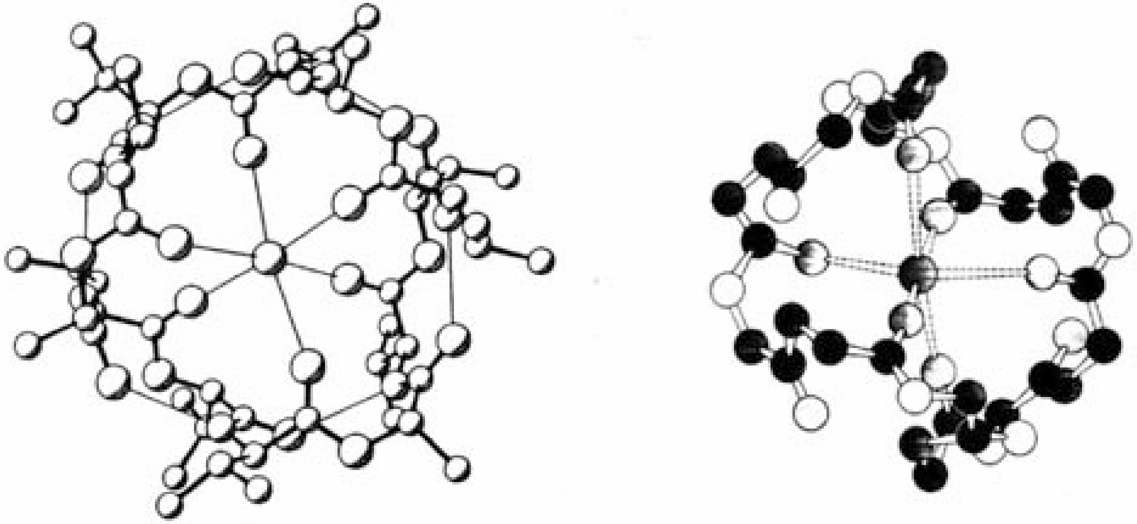




Transports K$^+$ through lipid membranes

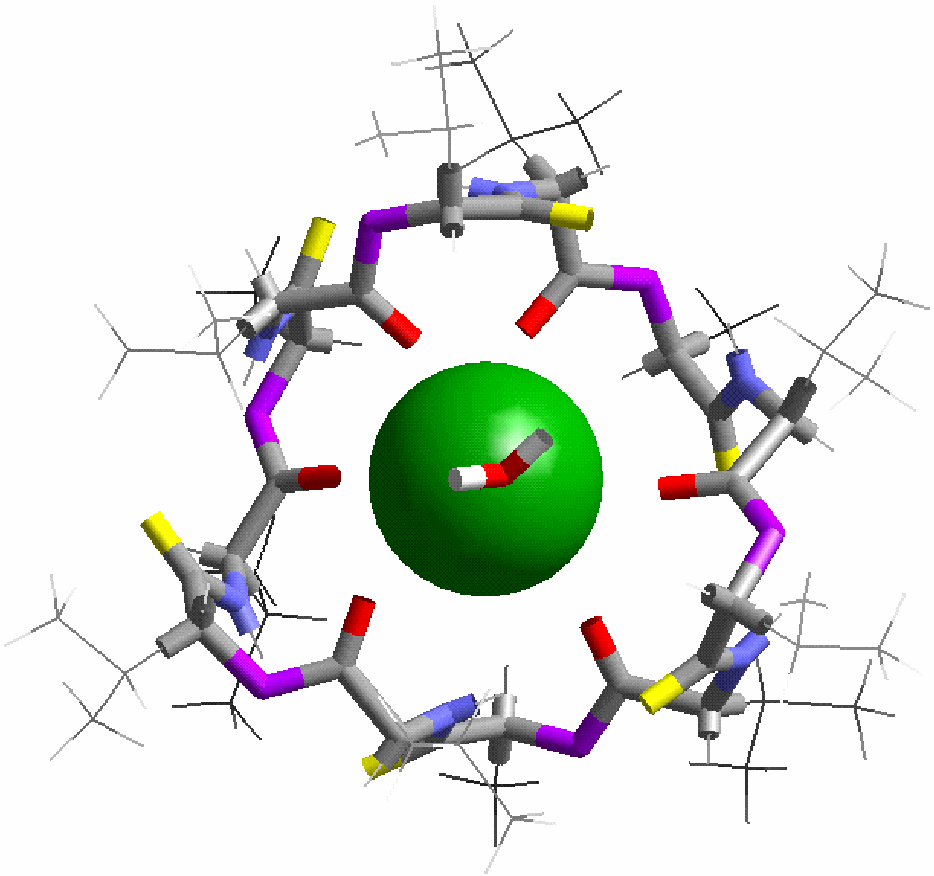


Uncomplexed valinomycin.

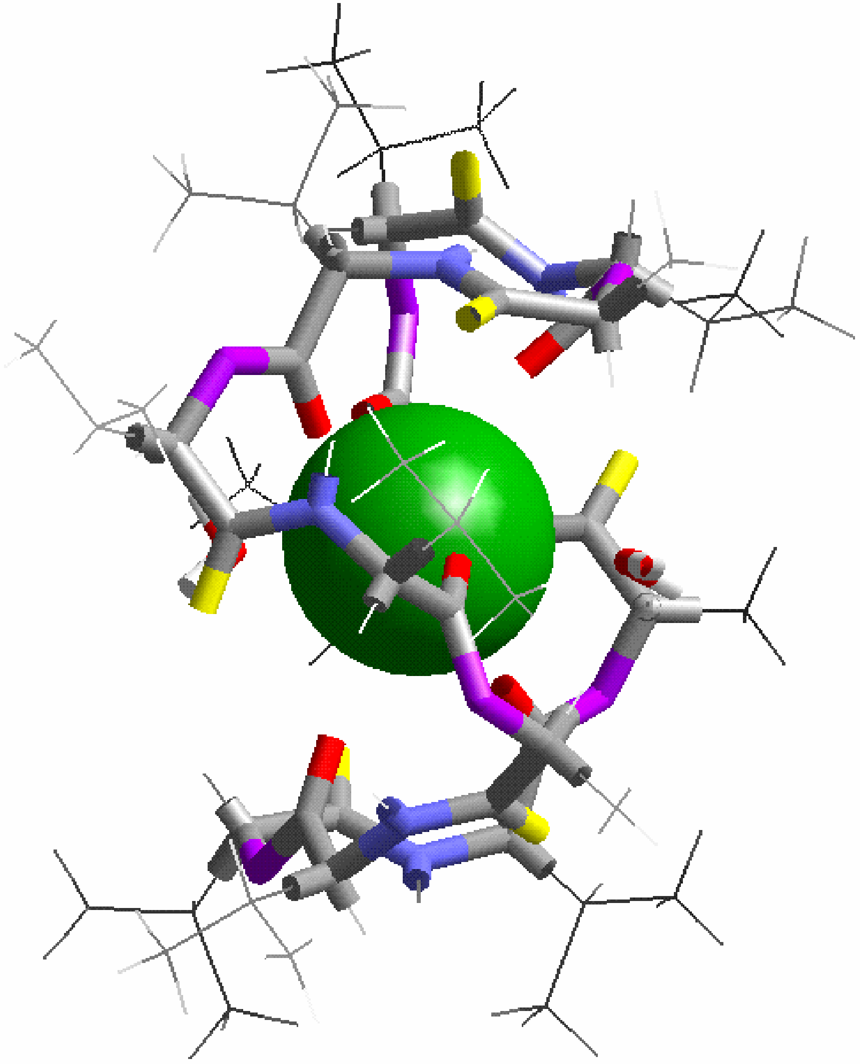


K$^+$ complex of valinomycin.

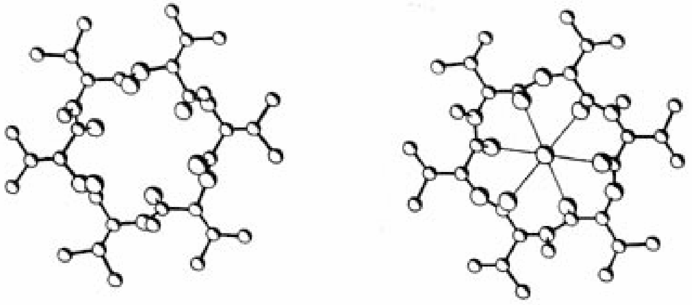
K^+-Valinomycin Complex



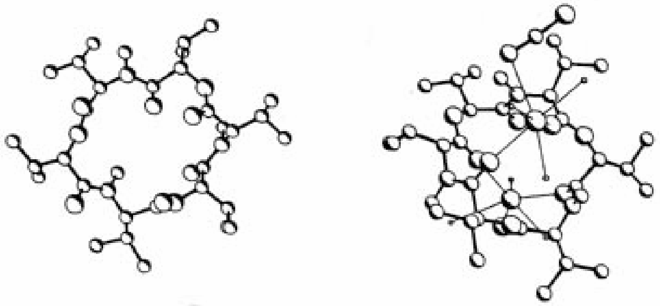
Top View



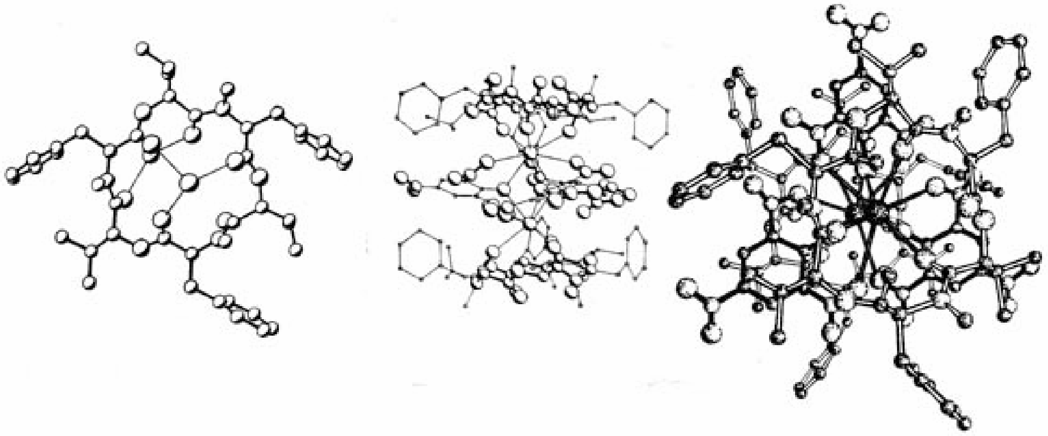
Side View



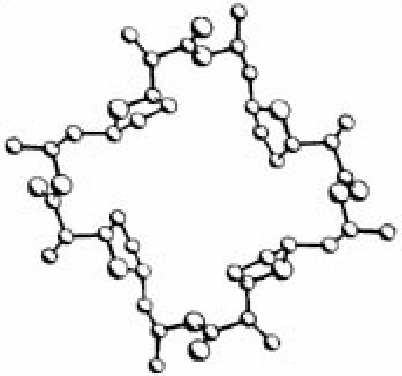
Enniatin B and its potassium ion complex



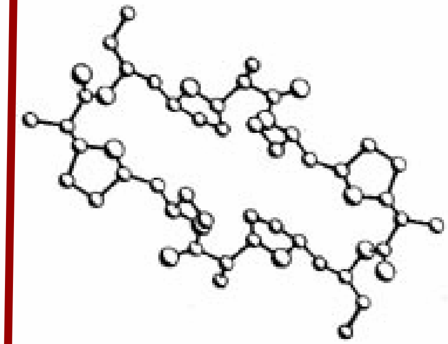
A stereoisomer of enniatin B and its rubidium ion complex (coordinated NCS^- also shown)



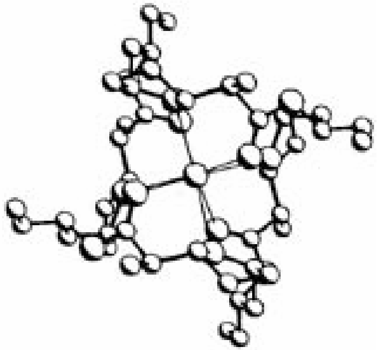
Beauvericin hydrate and the “triple decker”complex formed between barium picrate and beauvericin (Bv-Ba-(pic)$_3$-Ba-Bv)



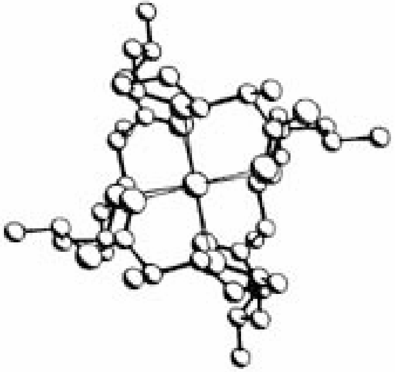
Free nonactin



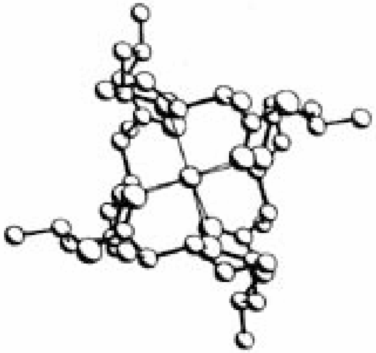
Free tetranactin



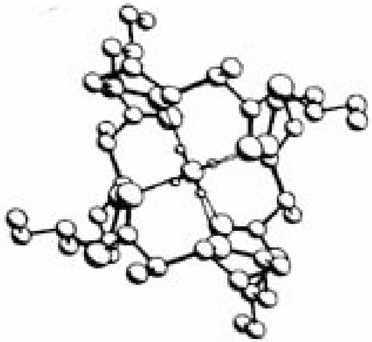
K(tetranactin)$^+$



K(nonactin)$^+$

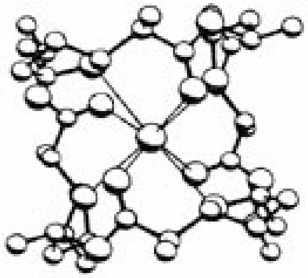


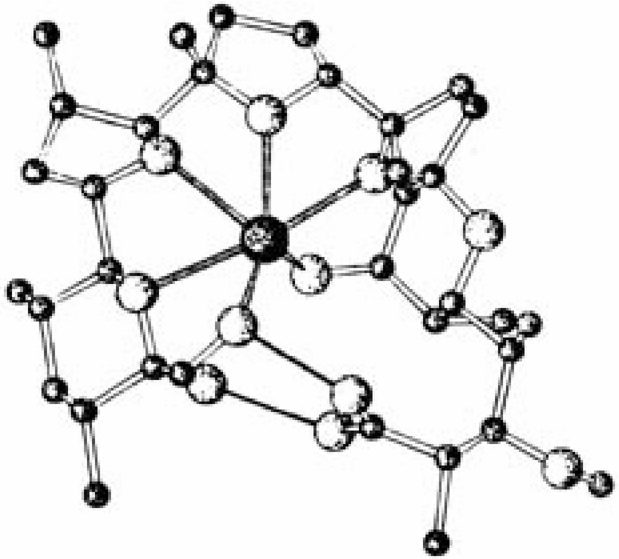
Na(nonactin)$^+$



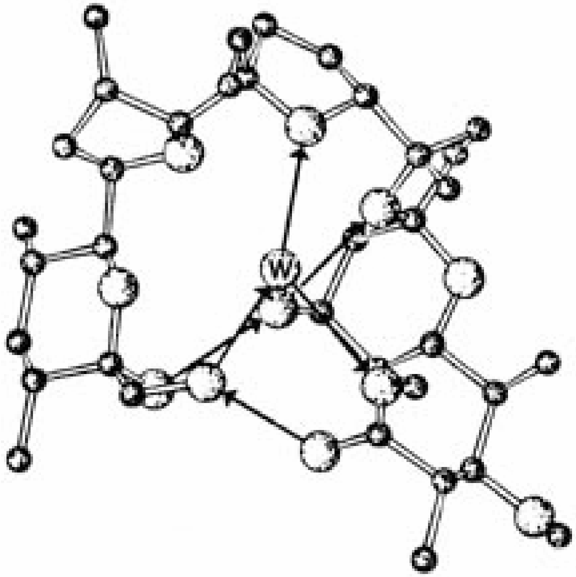
NH$_4$(tetranactin)$^+$

Cs(nonactin)$^+$

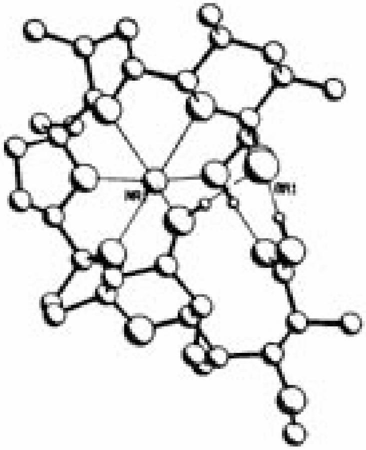




Spatial structure of the Ag^+ complex of monensin. Note the two head to tail hydrogen bonds (full narrow lines) in the lower part of the figure.



Uncomplexed monensin in a similar orientation as for the Ag^+ complex. A water molecule (W) occupies the central cavity. Arrows mark the direction of the H-bonds from donor to acceptor.



Na(monensin)Br

Biological Ionophores

	Li^+	Na^+	K^+	Rb^+	Cs^+
Valinomycin	<0.7	0.67	4.90	5.26	4.42
Monactin	<0.3	2.60	4.38	4.38	3.30
Enniatin B	1.28	2.42	2.92	2.74	2.34
Nigericin	-	4.7	5.6	5.0	-
Monensin	3.6	6.5	5.0	4.3	3.6

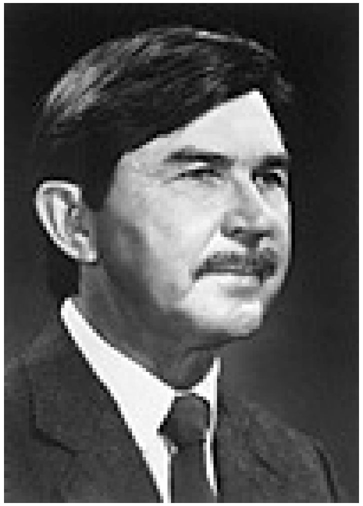
Transition Metal Chemistry

- Multiple Oxidation States
- Coordination Chemistry/Stereochemistry
- Crystal Field Splitting: Optical and Magnetic Properties
- Ligand Field Splitting: Spectrochemical Series
- Ligand Field Stabilization Energy
- Chelate Effect
- Stereochemical Control of Binding Affinity
- Electron Exchange

Nobel Prizes in Chemistry

(and “nice guys finish first”)

1983



Henry Taube

"for his work on the mechanisms of
electron transfer reactions,
especially in metal complexes"

1992

Rudy Marcus

"for his contributions to the theory
of electron transfer
reactions in chemical systems"

“Nuclei do all the work, then the electrons move”

Electron Exchange

Simplest chemical reaction, yet enormous rate differences

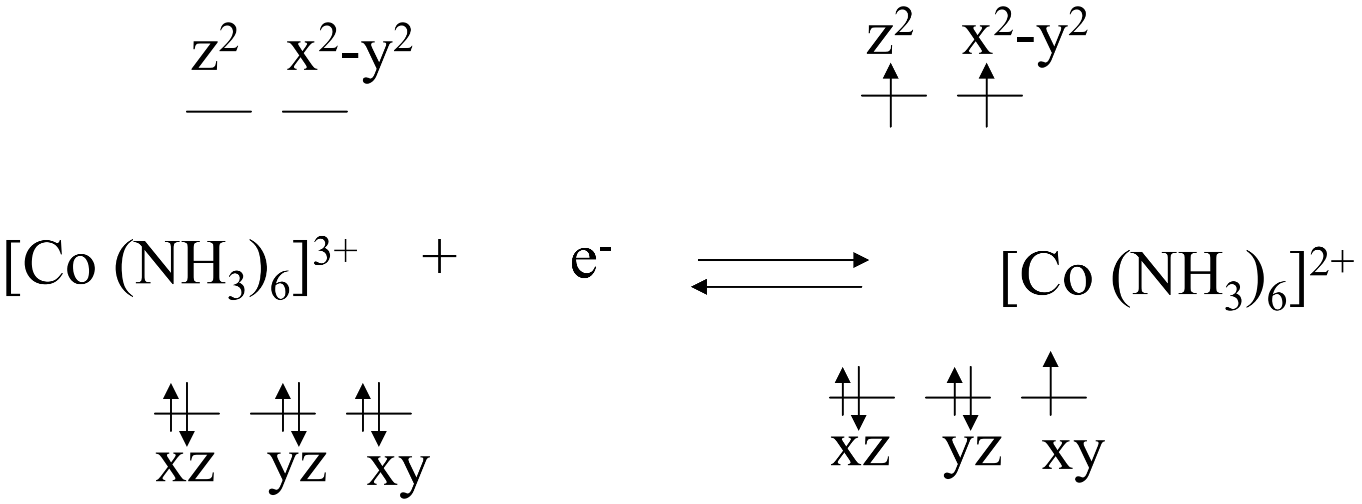
$$[Co\ (NH_3)_6]^{3+} \quad + \quad e^- \quad \rightleftharpoons \quad [Co\ (NH_3)_6]^{2+}$$

$k = 10^{-6}\ M^{-1}\ s^{-1}$

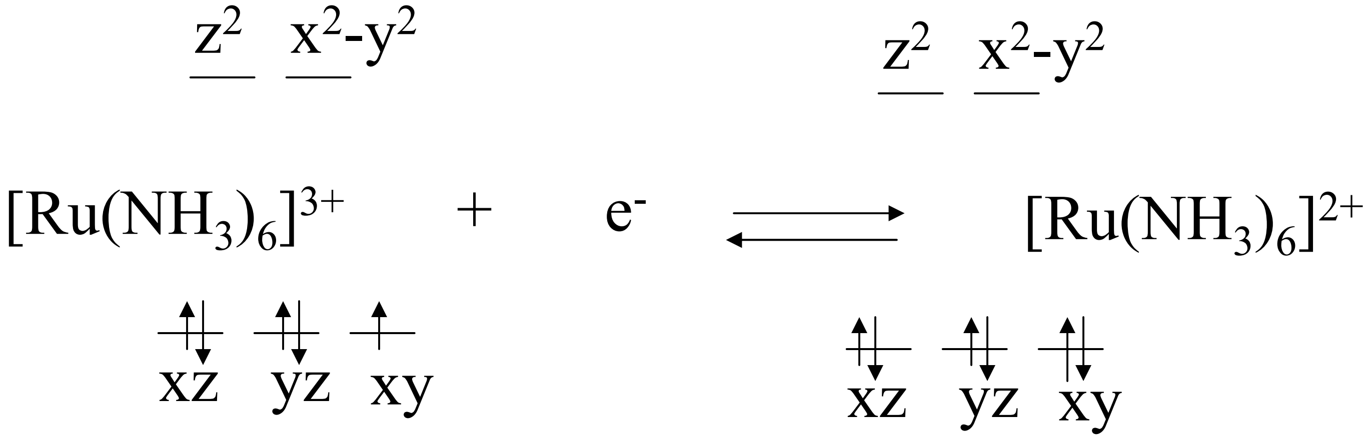
$$[Ru(NH_3)_6]^{3+} \quad + \quad e^- \quad \rightleftharpoons \quad [Ru(NH_3)_6]^{2+}$$

$k = 10^{4}\ M^{-1}\ s^{-1}$

Electron Exchange

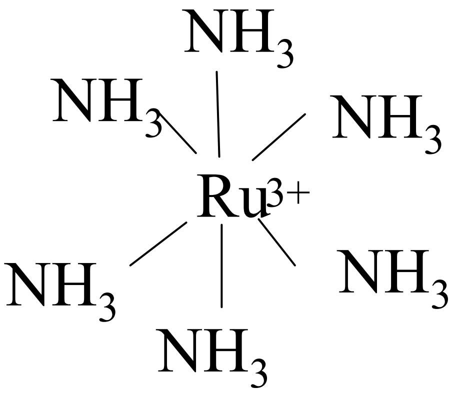


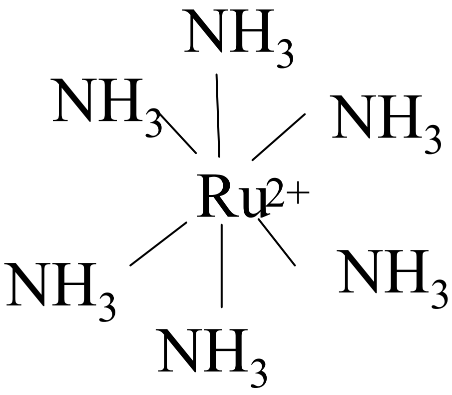
$$[\mathrm{Co}\,(\mathrm{NH_3})_6]^{3+} + e^- \rightleftharpoons [\mathrm{Co}\,(\mathrm{NH_3})_6]^{2+}$$

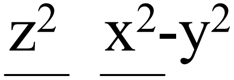


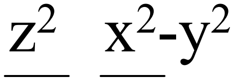
$$[\mathrm{Ru}(\mathrm{NH_3})_6]^{3+} + e^- \rightleftharpoons [\mathrm{Ru}(\mathrm{NH_3})_6]^{2+}$$

Electron Exchange

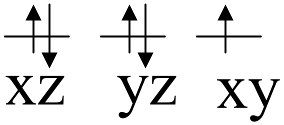


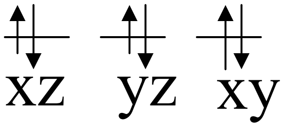




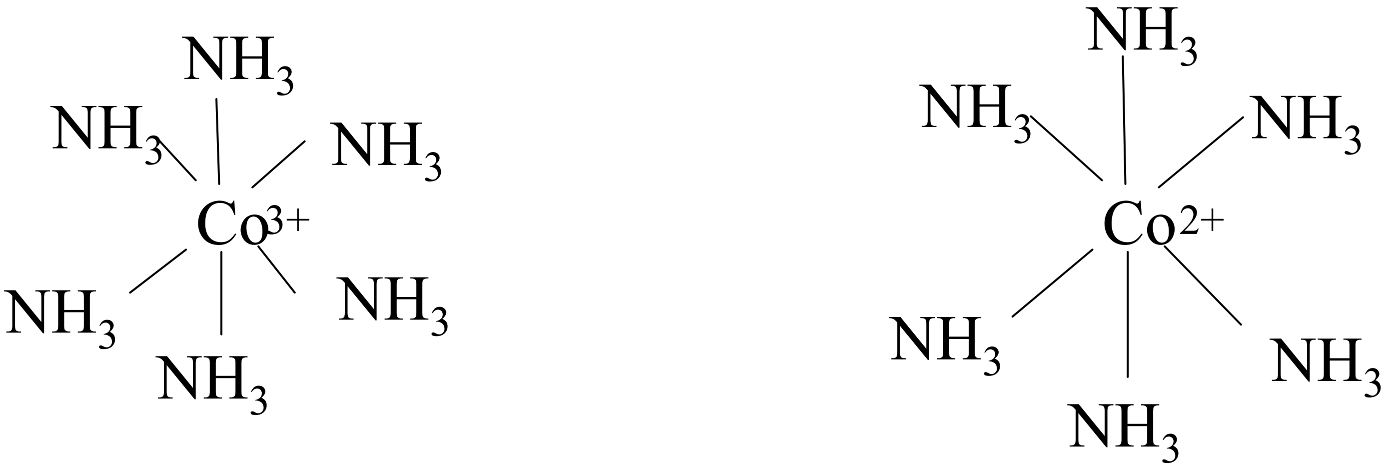


$$[Ru(NH_3)_6]^{3+} \quad + \quad e^- \quad \rightleftarrows \quad [Ru(NH_3)_6]^{2+}$$



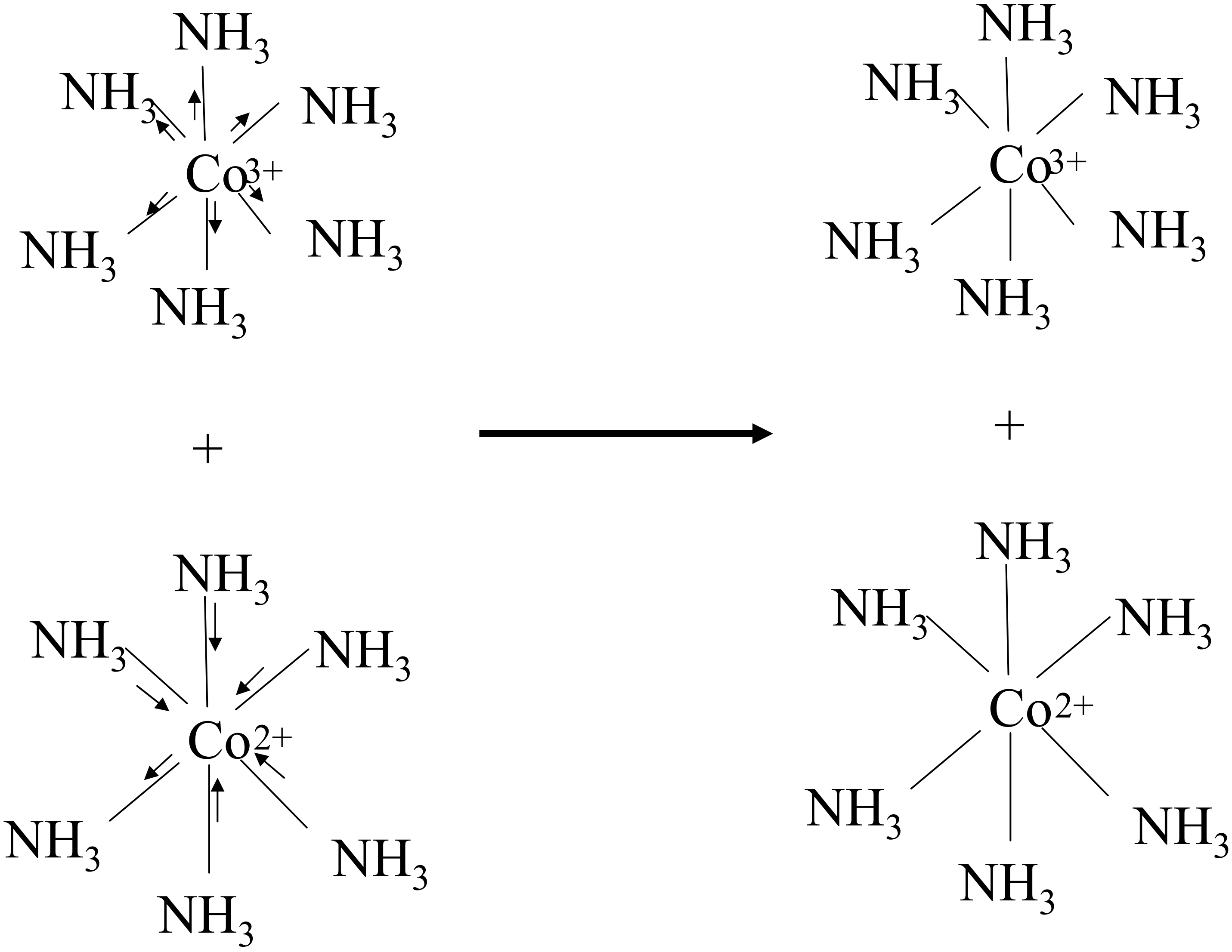


Electron Exchange

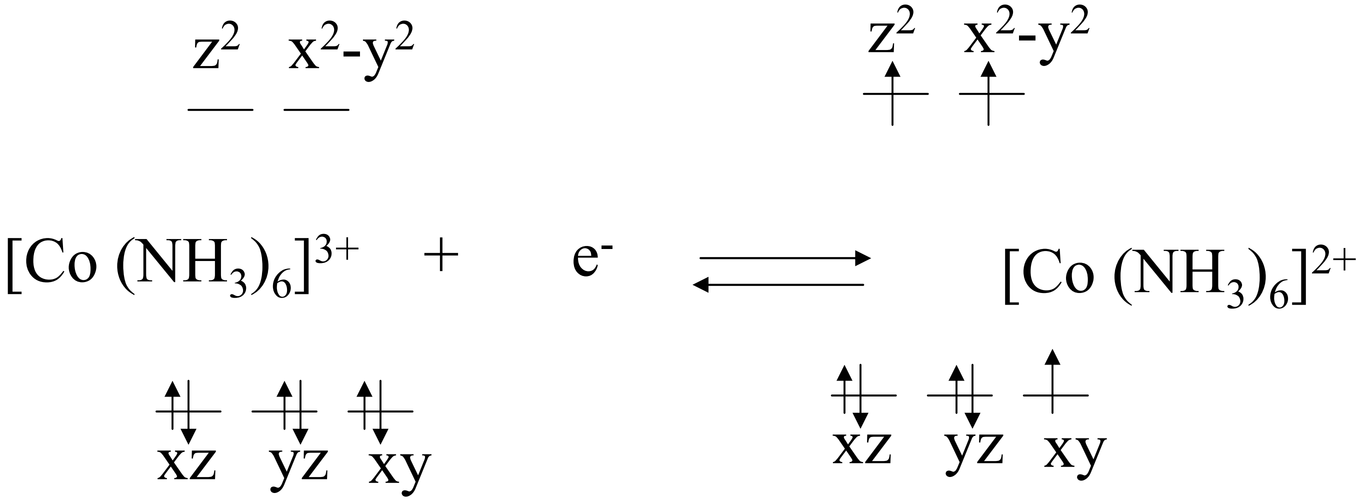


$[Co\ (NH_3)_6]^{3+}$ + e^- $\rightleftharpoons$ $[Co\ (NH_3)_6]^{2+}$

Electron Exchange

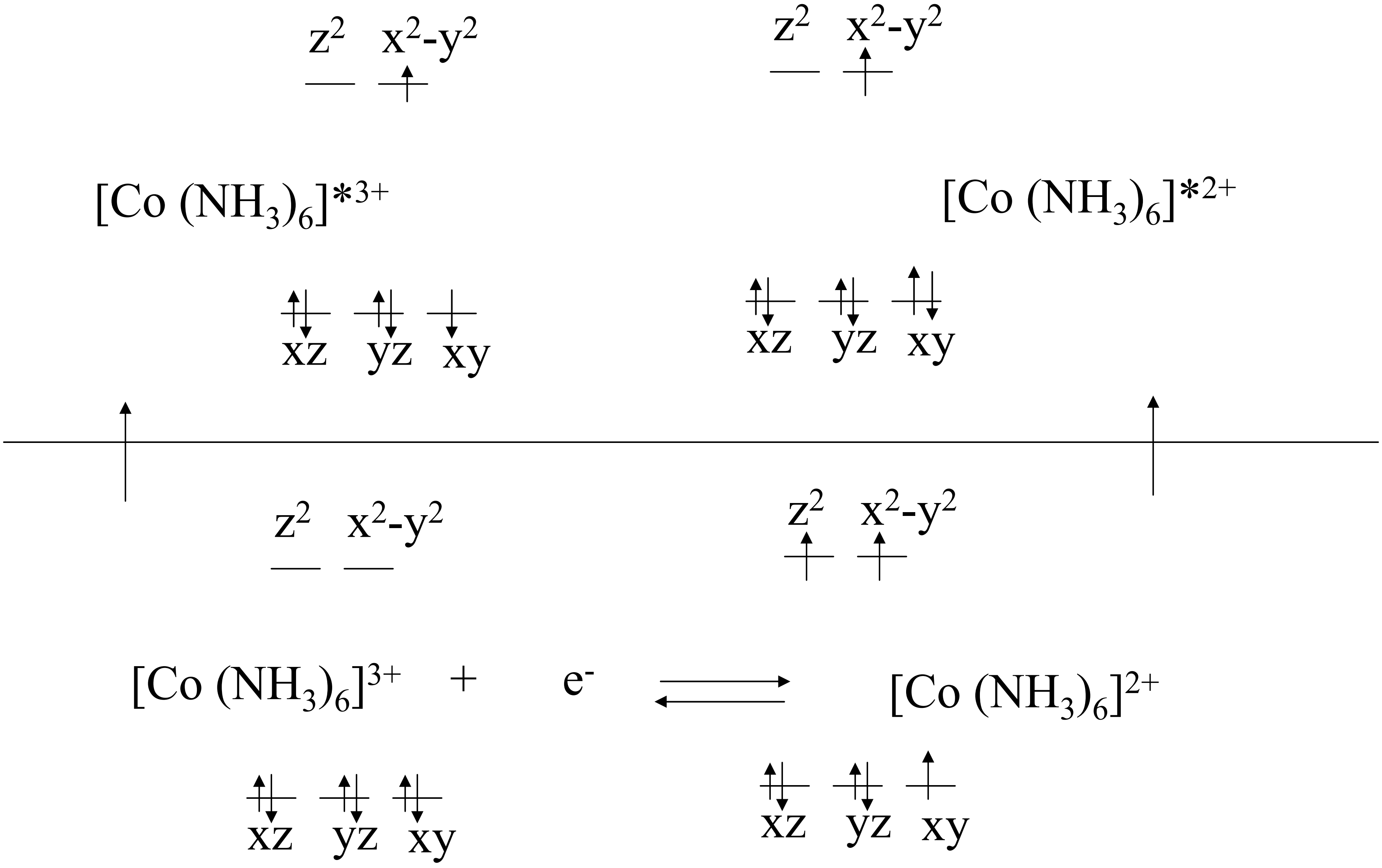


Electron Exchange



$$[\mathrm{Co}\ (\mathrm{NH_3})_6]^{3+} \quad + \quad e^- \rightleftharpoons [\mathrm{Co}\ (\mathrm{NH_3})_6]^{2+}$$

Electron Exchange



z^2 x^2-y^2

z^2 x^2-y^2

$[Co(NH_3)_6]^{*3+}$

$[Co(NH_3)_6]^{*2+}$

xz yz xy

xz yz xy

z^2 x^2-y^2

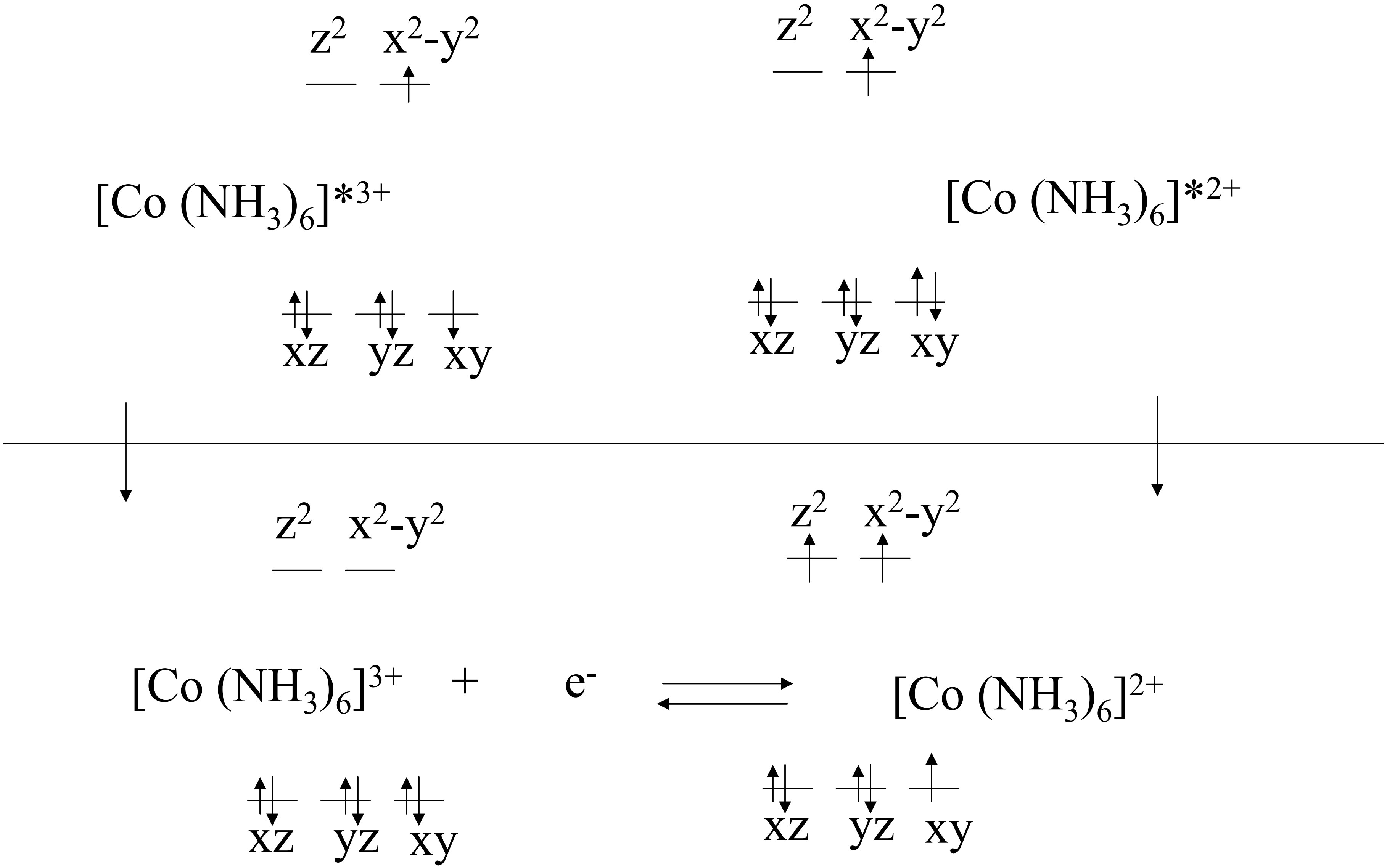
z^2 x^2-y^2

$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$

xz yz xy

xz yz xy

Electron Exchange



$$[Co\ (NH_3)_6]^{3+} + e^- \rightleftharpoons [Co\ (NH_3)_6]^{2+}$$

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- Multiple Oxidation States
- Coordination Chemistry/Stereochemistry
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- Ligand Field Splitting: Spectrochemical Series
- Ligand Field Stabilization Energy
- Chelate Effect
- Stereochemical Control of Binding Affinity
- Electron Exchange

The Nature of the Chemical Bond in Chem 1a

- Atomic Structure
- Explain Atomic Line Spectra, Galaxies, etc.
- Shapes of Orbitals in Atoms for Bonding
- Ionization Energies and Trends in Chemical Reactivity (e.g., Li^+ vs Li)
- Which Molecules are Likely to Exist and Their Shapes and Reactivities (Ozone, Glo. Warm.)
- Covalent Bonding Properties of Organic Molecules
- Special Properties of Resonance Stabilization
- Directionality of Covalent Chemical Bonds
- Bonding in Solids
- Bonding of the Transition Metals (Optical and Magnetic Properties, Electron Transfer Reactions)