

Coordination Complexes Lectures

what is coordination complex?

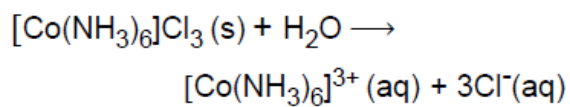
a central metal atom or ion to which ligands are bound by coordinate covalent bonds

more

- coordinate covalent bond:
covalent bond where one atom contributes both electrons (in olden times called 'dative' bond)
- ligand:
ion or molecule which binds to central atom, contributing both electrons to a covalent bond
- coordination number:
how many coordinate covalent bonds around central atom/ion

simple example (figure on p. 936)

$[\text{Co}(\text{NH}_3)_6] \text{Cl}_3 (\text{s})$ salt of complex ion



$[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ion denoted by []'s

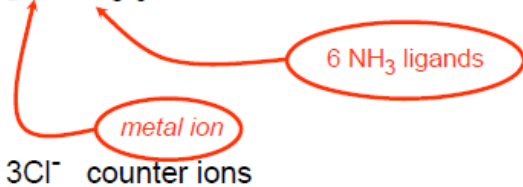
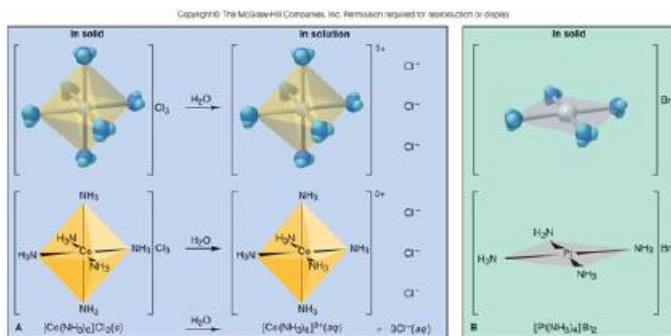


figure 23.9 (Silberberg)

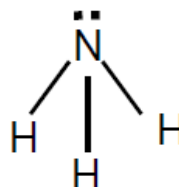
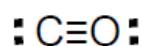
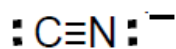
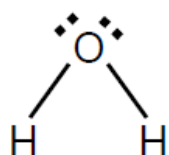
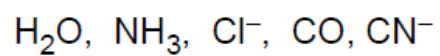


octahedral



square planar

examples of common 'simple' ligands



Coordinate covalent bond: Lewis acid-Lewis base *CHEM 1A nr*

Lewis acid

Lewis base

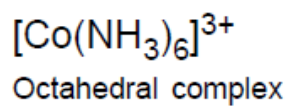
ligand

metal

L:

M^{+n}

coordinate covalent bonding



coordination number = 6

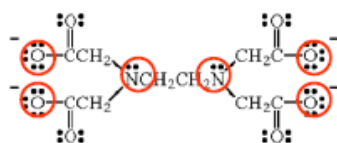
possible geometries of coordination complexes
(table 23.6 Silberberg) [see figure 19.6 Zumdahl]

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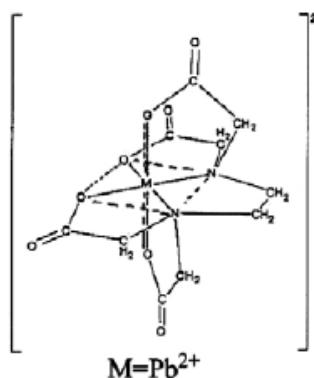
Table 23.6 Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape	Examples
2	Linear	$[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$
4	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PtCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral	$[\text{Cu}(\text{CN})_4]^{2-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
6	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Cr}(\text{NH}_3)_6\text{Cl}_2]^+$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$

EDTA a chelate (claw!!)



hexadentate



determining: num ligands charge oxidation state d-electrons

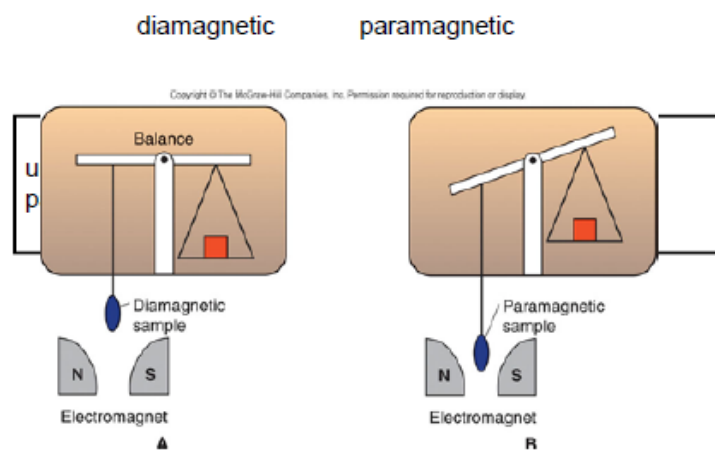
given $[\text{Co}(\text{NH}_3)_n] \text{Cl}_3$ is salt of octahedral complex

- **coordination number=6** since octahedral
- **n=6** since NH_3 is monodentate ligand
- **3+** charge on complex from counterion: 3Cl^-
- **Co^{3+}** oxidation state of metal from charge on complex and zero charge on NH_3 ligands
- **d^6** d-electrons from aufbau principle FOR CATIONS



- How are the magnetic properties of transition metal complexes related to the shape of d-orbitals?
- Why are transition metal complexes colored?

paramagnetism vs diamagnetism (Gouy balance)



strength of paramagnetism depends on
number of unpaired electrons

not now



crystal field theory and color

- most electronic excitations in UV
(H 1s \rightarrow H 2p $\lambda=121 \times 10^{-9}$ m)
- $\text{Co}^{3+} [\text{Ar}]3d^6 \rightarrow \text{Co}^{3+} [\text{Ar}]3d^5 4s^1$ ($\lambda=75.3 \times 10^{-9}$ m) **UV**
 $\text{NH}_3 \rightarrow \text{NH}_3^*$ (excited state) ($\lambda=216 \times 10^{-9}$ m) **UV**

Co^{3+} and NH_3 are colorless !!!

but in coordination complex

- $[\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow$ excited state* ($\lambda=430 \times 10^{-9}$ m,
absorbs 'indigo')

$[\text{Co}(\text{NH}_3)_6]^{3+}$ appears yellow !!

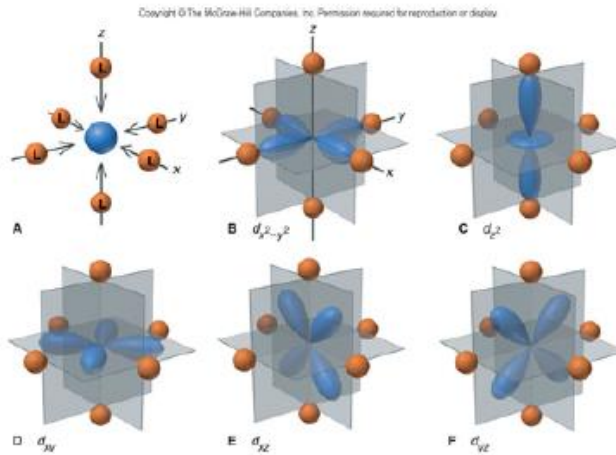
crystal field theory and magnetic properties

$[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic

but

$[\text{Co}(\text{F})_6]^{3-}$ is paramagnetic

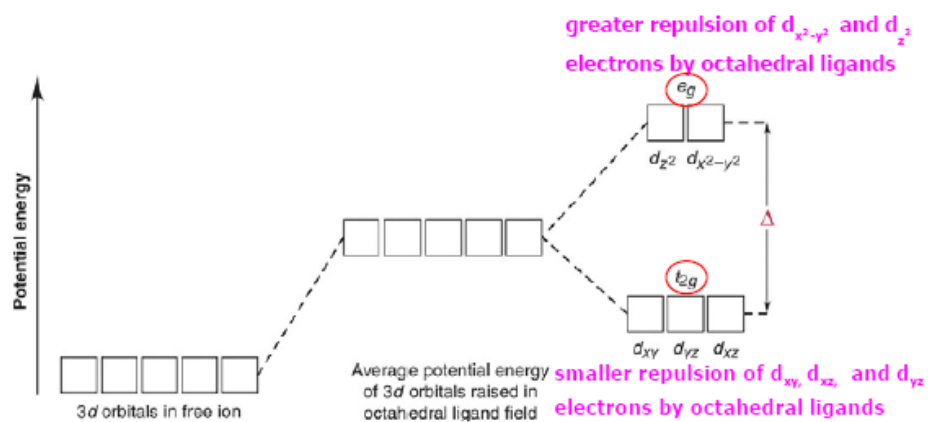
metal ion *d*-orbitals in **octahedral** complex
(Silberberg fig. 23.17; Zumdahl fig. 19.21)



http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/lmo/CrystalField/CFT_OrbsOctahedral.html



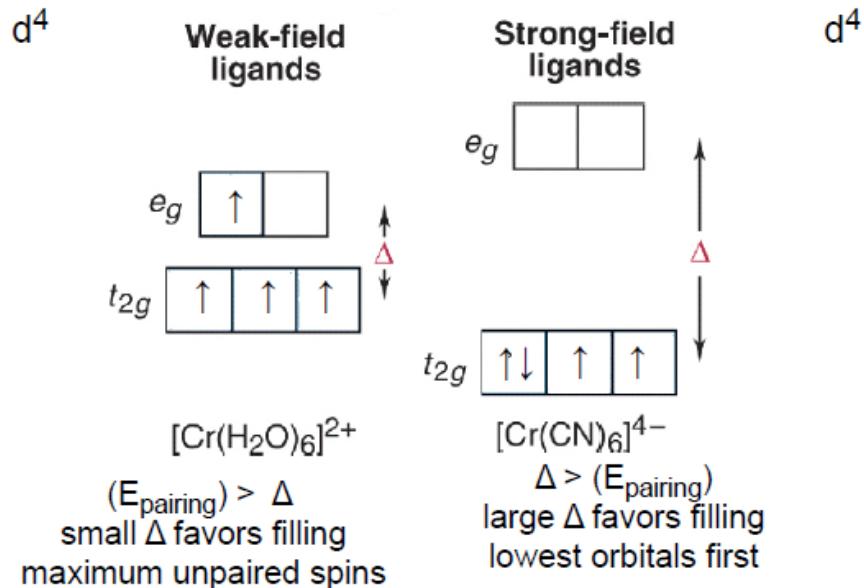
what happens to energies of *d*-orbitals when ligands bind to metal ion? (fig 23.18)



average ligand repulsion
for metal *d*-electrons

would each *d*-electron
be repelled the same?

strong and weak field ligands: lowest orbitals vs unpaired spins
 Δ vs (E_{pairing}) (Silberberg fig 23.18)



$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ vs $[\text{Cr}(\text{CN})_6]^{4-}$

- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, d^4 , weak-field \equiv high spin,
 4 unpaired electrons, paramagnetic
- $[\text{Cr}(\text{CN})_6]^{4-}$, d^4 , strong-field \equiv low spin,
 2 unpaired electrons, paramagnetic

other examples (do in section)

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, d^6 , weak field, 4 unpaired e's,
paramagnetic

$[\text{Fe}(\text{CN})_6]^{4-}$, d^6 , strong field, 0 unpaired e's,
diamagnetic

paramagnetism

- each electron behaves as tiny magnet \uparrow or \downarrow (Stern-Gerlach experiment)
- when electrons in a molecule have paired spins the individual magnets cancel one another $\uparrow\downarrow$
- when an atom or molecule has **unpaired** electrons there is a resulting “net-magnetic moment” $\uparrow\uparrow\uparrow$
- atoms with unpaired electrons are attracted by an [inhomogeneous] magnetic field
- atoms with unpaired electrons are **paramagnetic**