Complex-ion equilibria

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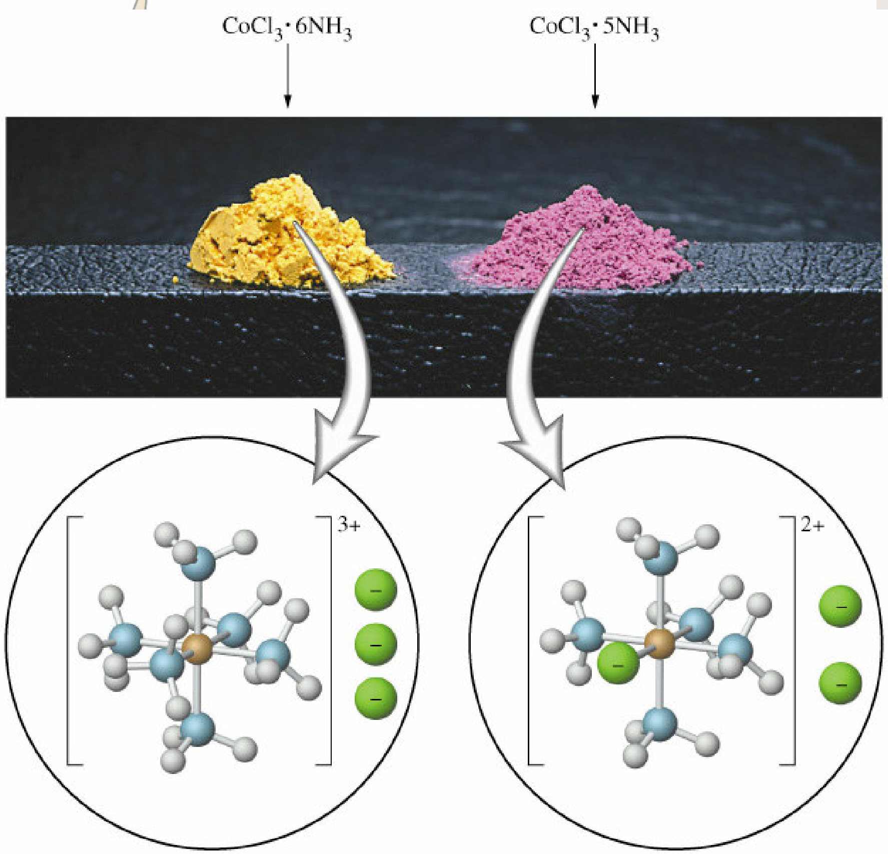
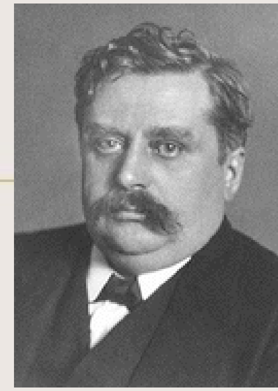
Alfred Werner

$$[Co(NH_3)_6]Cl_3(s) \xrightarrow{H_2O(l)} [Co(NH_3)_6]^{3+}(aq) + 3\,Cl^-(aq)$$

Golden orange

$$[CoCl(NH_3)_5]Cl_2(s) \xrightarrow{H_2O(l)} [CoCl(NH_3)_5]^{2+}(aq) + 2\,Cl^-(aq)$$





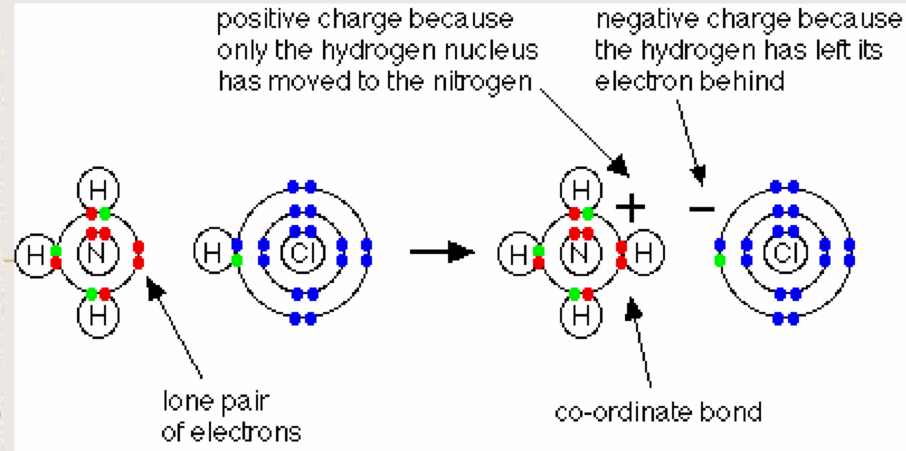
The concept of valence on which all modern chemical theory is based had been found unable to deal with a large and important group of mainly inorganic molecular compounds, because it was unable to provide a satisfactory explanation of their internal structure.

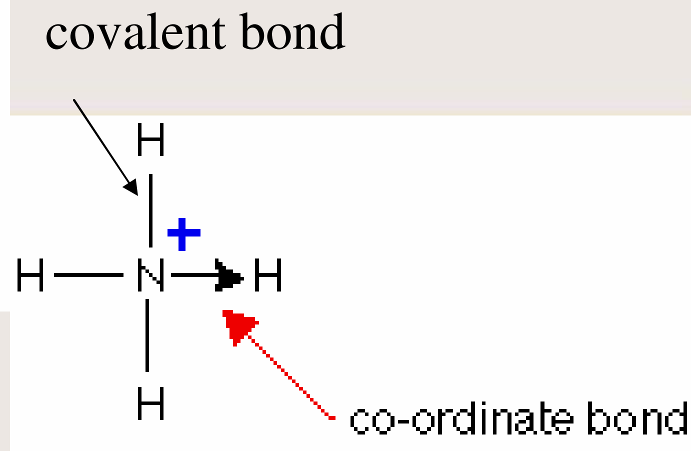
Werner developed his theory of coordination chemistry at the age of 26, received the 1913 Nobel Prize for chemistry and in 25 years supervised 200 PhD students and published syntheses for in excess of 8000 complexes.

CO-ORDINATE (DATIVE COVALENT) BONDING

- A covalent bond is formed by two atoms, sharing **a pair of electrons**. The atoms are held together because the electron pair is attracted by both of the nuclei.
- In the formation of a simple covalent bond, **each atom supplies one electron to the bond.**

- A co-ordinate bond (also called a dative covalent bond is a covalent bond (a shared pair of electrons) in which **both electrons come from the same atom.**



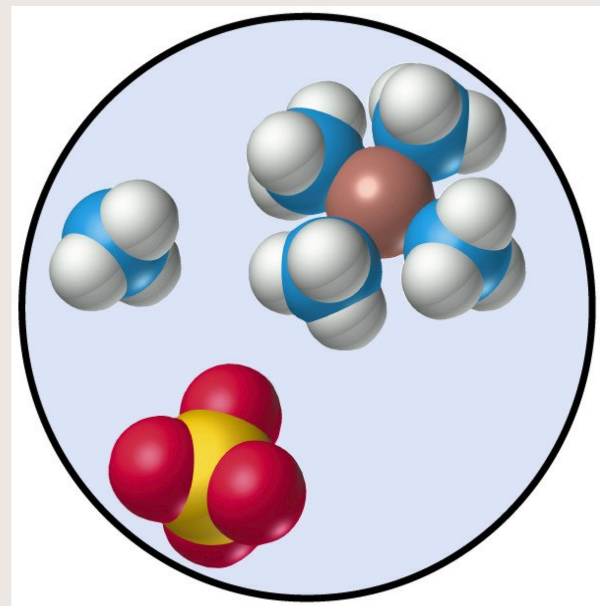


When the ammonium ion, NH_4^+, is formed **the 4th hydrogen is attached by a dative covalent bond**, because only the hydrogen's nucleus is transferred from the chlorine to the nitrogen. Once the ammonium ion has been formed it is impossible to tell any difference between the dative covalent and the ordinary covalent bonds. Although the electrons are shown differently in the diagram, there is no difference between them in reality. In simple diagrams a co-ordinate bond is shown by an arrow. **The arrow points from the atom donating the lone pair to the atom accepting it**.

Complexes

Most transition metals ions react with electron-pair donors to form coordination compounds or complexes

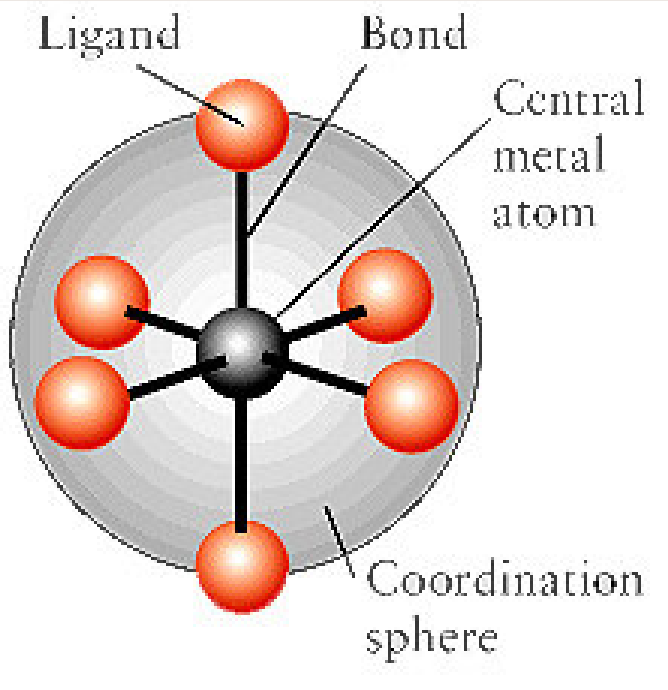
- **Complexes**.
  - A polyatomic cation, anion or neutral compound composed of:
    - **A central metal ion**.
    - **Ligands-donors of e pairs**
- **Coordination compounds**.
  - Substances which contain complex ions.



The molecules or ions surrounding the central metal ion are called **ligands.** They form **coordination sphere.**

Ligand is derived from Latin verb 'ligare' meaning 'to bind'.

- **Atoms in coordination sphere are directly bonded to central atom.**
- The **complex ion behaves like a polyatomic ion**: the ligands and central metal ion remain attached.



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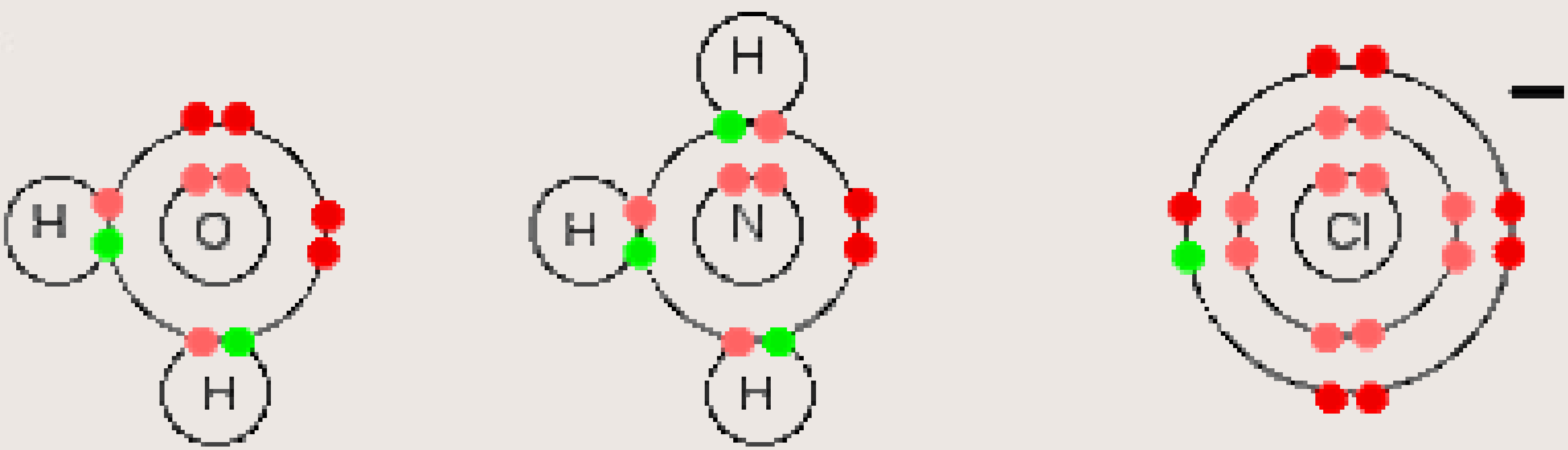
Simple ligands include water, ammonia and chloride ions. What all these have got **in common is active lone pairs of electrons in the outer energy level.** These are used to form co-ordinate bonds with the metal ion.

•Common feature: All ligands are lone pair donors. In other words, metals (**central atoms**) behave as **Lewis acids** all **ligands** function as **Lewis bases**.



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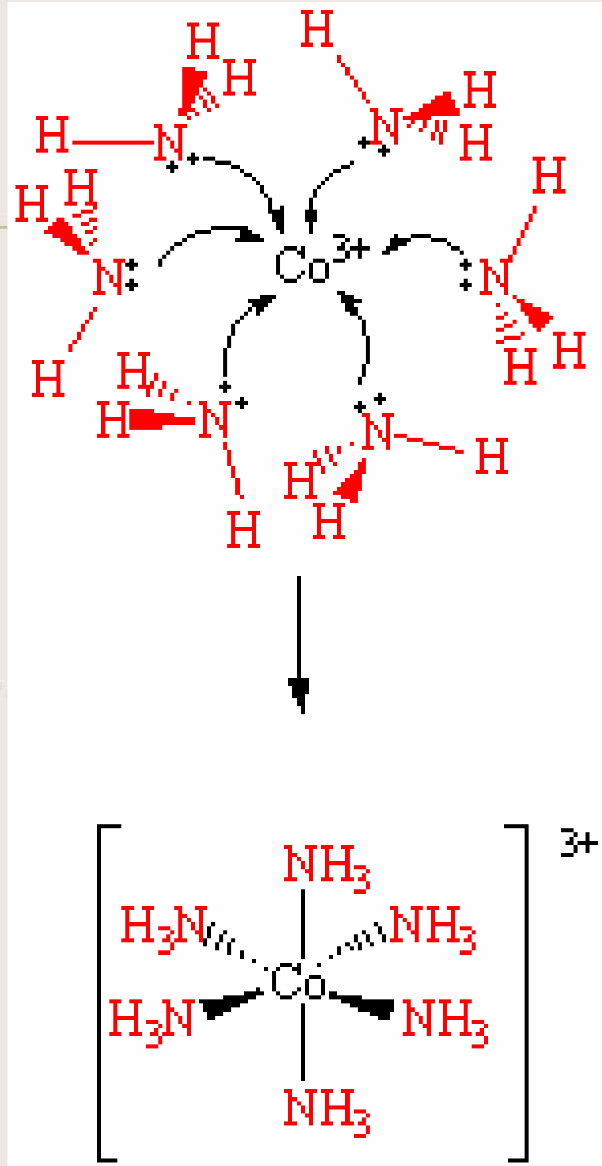


A bond like that seen in $[Co(NH_3)_6]^{3+}$ is a "coordinate-bond" or "dative-bond".

Co $3d^7 4s^2$

A covalent bond undergoes homolytic cleavage and a dative bond undergoes heterolytic cleavage

Six is the maximum number of ligands it is possible to fit around an metal ion (and most other metal ions). By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.

The coordination number is the number of covalent bonds that the metal cation tends to form with the electron donor

(**CN**- Number of ligand atoms bonded directly to the central metal ion.).

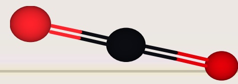
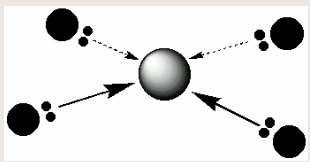
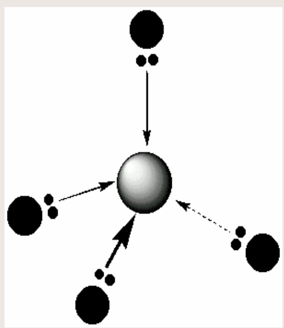
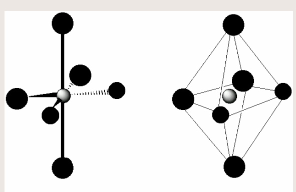
•For example, copper (II) has coordination number of 4. The species formed from such coordination or complexing, can be electrically positive, neutral or negative.

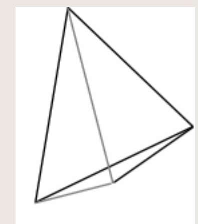
•Copper when complexed with ammonia results in a cationic complex, $Cu(NH_3)_4^{2+}$

•when complexed with glycine, a neutral complex, $Cu(NH_2CH_2COO)_2$,

•and when complexed with chloride, an anionic complex, $CuCl_4^{2-}$.

Complexes and Coordination Number

Coordination Number		Shape	Example
2		Linear	$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
3		Square Planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$ $[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4		Tetrahedral	$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$ ($[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6		Octahedral	$[Cu(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cu(NH_3)_4Cl_2]^+$, $[Co(en)_3]^{3+}$

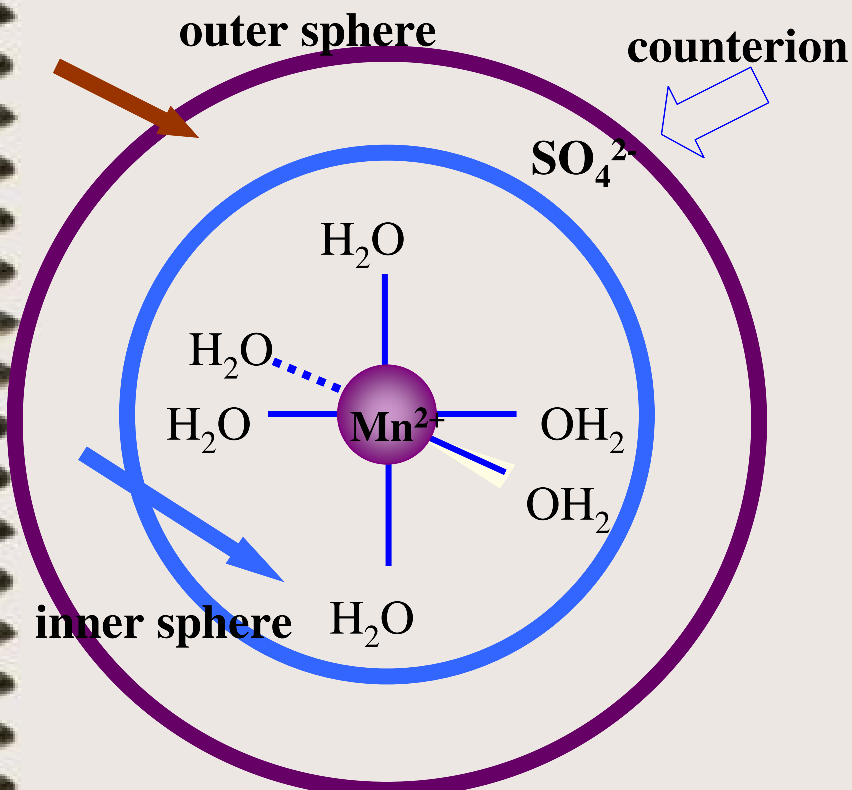


The shape of the complex depends on splitting of the d-orbitals of transition metal during complex formation

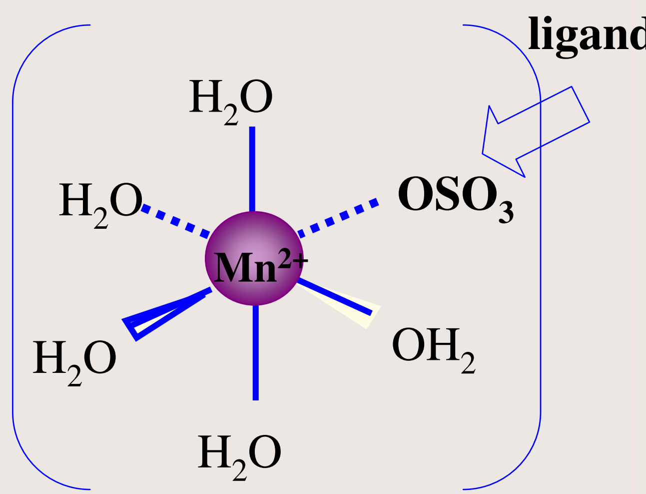
Inner and outer sphere complexes

Inner coordination sphere = ligands **directly** bonded to the metal ion

Outer coordination sphere =ions associated with the complex but not directly bonded to the metal centre



$[Mn(OH_2)_5(SO_4)_5]$: inner sphere complex



$[Mn(OH_2)_6]SO_4$: outer sphere complex-ion pair

Metal- Ligand compounds

- **[ML_n] i.e., [$Ag(NH_3)_2$]$^+$ -cationic complex or [$Co(NH_3)_6$] Cl_3-coordination compound**

[ ] **denote atoms bonded to each other through covalent bonds. These atoms are contained in the inner** coordination sphere**.**

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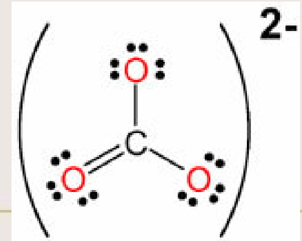
Denticity

Many ligands (H_2O, NH_3, CN^- occupy only one site in the coordination sphere and are called monodentate ligands.

- **Denticity – the number of atoms, which donate electron pair to central atom and through which a ligand coordinates to a metal ion.**
- Dentate – (Latin) having tooth-like projections **Monodentate** – ligand posses one donor atom (ammonia).
  - **Bidentate** – ligand posses two donor atoms (Glycine- 2 groups available for covalent bonding: the carbonyl oxygen and the amino nitrogen, NH_2CH_2COO).
  - **Polydentate** – ligand posses more than one donor atom

Typical Monodentate Ligands

F^-	fluoro
Br^-	bromo
I^-	iodo
CO_3^{2-}	carbonato
NO_3^-	nitrato
SO_3^{2-}	sulfito
$S_2O_3^{2-}$	thiosulfito
SO_4^{2-}	sulfato
CO	carbonyl
Cl^-	chloro
O^{2-}	oxo
O_2^{2-}	peroxo
OH^-	hydroxo
NH_2^-	amido
CN^-	cyano
SCN^-	thiocyano
NO_2^-	nitro

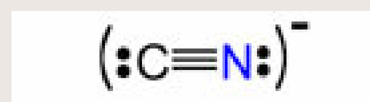


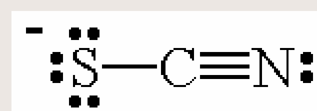
Can be bidentate

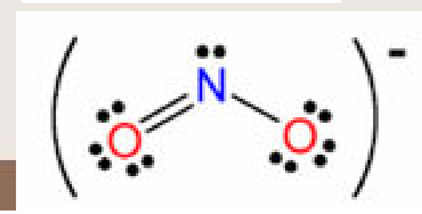
Common bridging ligands.

Common bridging ligands. That are also ambidentate.

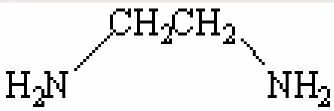
H_2O	aqua
NH_3	ammine
CH_3NH_2	methylamine
$P(C_6H_5)_3$	triphenylphosphine
$As(C_6H_5)_3$	Triphenyl arsine
N_2	dinitrogen
O_2	dioxygen
NO	nitrosyl
C_2H_4	ethylene
C_5H_5N	pyridine



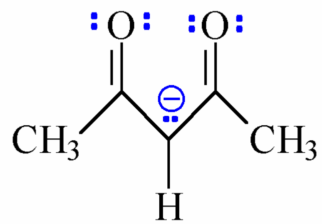




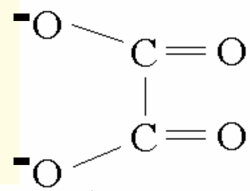
Typical multidentate ligands



ethylenediamine (en)



acetoacetonato (acac)

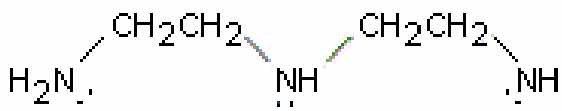


oxalato (ox)

$NH_2CH_2COO^-$

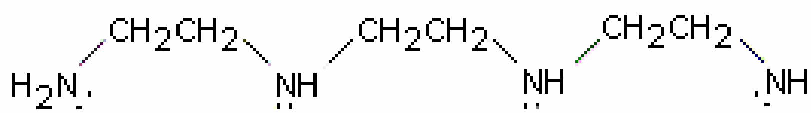
glycinato (gly)

Tridentate Ligand:



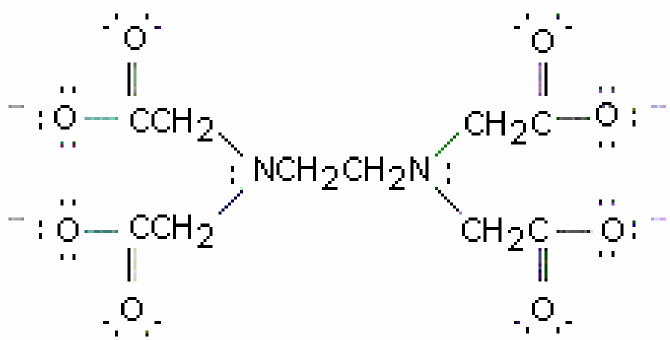
diethylenetriamine (dien)

Tetradentate Ligand:



triethylenetetraamine (trien)

Hexadentate Ligand:



ethylenediaminetetraacetate (EDTA)

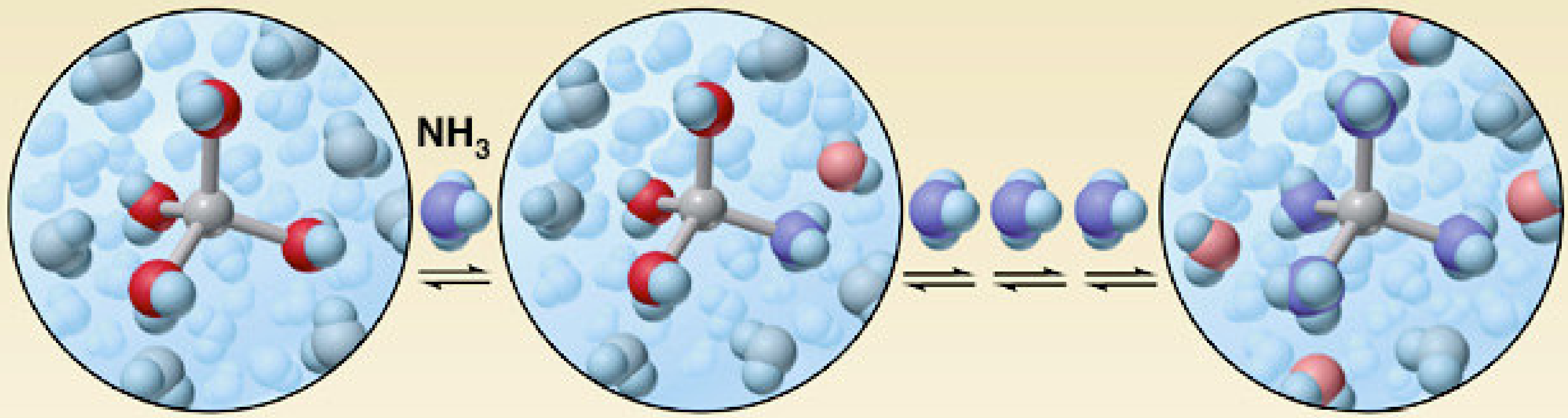
Thermodynamics and Complex Formation

- Highly charged ions have more negative values of $\Delta_{hyd}S^0$ because they impose more order on H_2O molecules in the environment of the ion.
- So, when a complex forms the entropy change is significantly positive.
  - The ligands cancel or reduce the charge density causing less order to be imposed on the surrounding waters.
- The enthalpy change when a complex forms is very negative because bonds are being made.

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

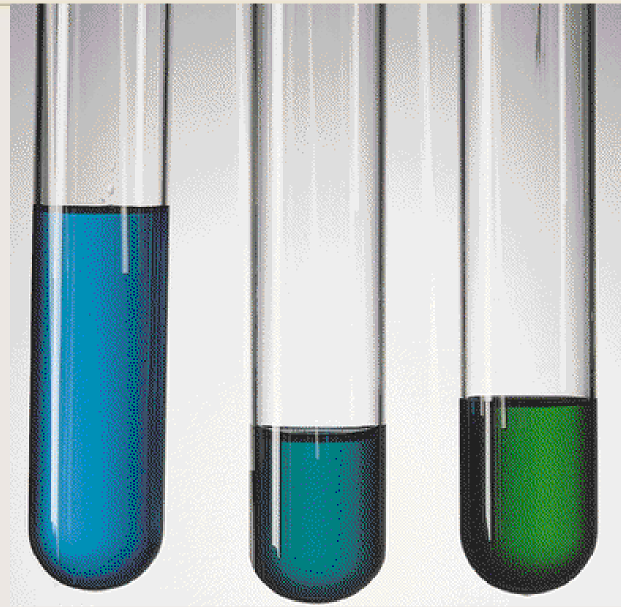
- Therefore, ΔG^0 **is substantially negative** and complexes are very stable.

The Stepwise Exchange of H_2O for NH_3 in $M(H_2O)_4^{2+}$



$$M(H_2O)_4^{2+}(aq) + NH_3(aq) \rightleftharpoons M(H_2O)_3(NH_3)^{2+}(aq) \xrightleftharpoons[\text{3 more steps}]{3NH_3} M(NH_3)_4^{2+}(aq) + 4H_2O(l)$$

Adding or Removing a Reactant or Product



- Addition of H_2O Addition of HCl
- $Cu(H_2O)_4^{+2}{}_{(aq)} + 4\ Cl^{-1}{}_{(aq)} \rightleftharpoons CuCl_4^{-2}{}_{(aq)} + 4\ H_2O_{(l)}$

  blue green